Light in complex dielectrics

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CHAPTER 3

Spontaneous emission of impurity atoms in homogeneous dielectrics

The spontaneous emission rate of an impurity atom in an otherwise homogeneous dielectric is calculated using the Onsager-Böttcher approach. By identifying substitutional and interstitial impurities, the well-known empty-cavity and Lorentz local-field factors are obtained, respectively. For fluids, the substitutional case is predicted to occur prevalently.

3.1 Introduction

In 1917, Einstein demonstrated that spontaneous emission must occur if matter and radiation are to achieve thermal equilibrium [44]. This picture is so fundamental, that spontaneous emission rates are often believed to be an inherent property of the atom. However, the spontaneous emission rate can be modified by changing the environment, as was noticed by Purcell [45]. In the early 1970s, Drexhage carried out pioneering experiments on the modification of the luminescence decay rate of Europium complexes in front of a metallic mirror [46]. Later, many theoretical [47] and experimental [48] investigations have been devoted to the enhancement and inhibition of spontaneous emission of atoms in resonant cavities, in which case larger modifications are possible.

Modifications of the spontaneous emission rate can also be induced by placing the radiator inside a spatially inhomogeneous dielectric. For example, the case of emission near a dielectric interface has been studied both experimentally [46, 49] and theoretically [50]. More recently, spontaneous emission rates were predicted to alter in photonic crystals [8], materials in which the dielectric constant is periodically modulated on length scales of the wavelength of light. As a result, light in a certain frequency range cannot propagate in the crystal because of multiple Bragg reflections. At this so-called full photonic band gap, the radiative density of states (RDOS) is zero and, therefore, spontaneous emission of excited atoms embedded
in these materials is expected to be inhibited at those frequencies, since then coupling to propagating modes is absent. At other frequencies, it has been shown that spontaneous emission can be either enhanced or reduced [8]. Note that the atoms in question are different from the ones constituting the dielectric; in the rest of this chapter such atoms will be referred to as impurity atoms or, equivalently, impurity dipoles.

In this chapter, the most simple and fundamental problem is treated: the spontaneous emission rate of an impurity dipole in a macroscopically homogeneous dielectric. As will be shown, merely placing a dipole in a dielectric medium already modifies its spontaneous emission rate.

### 3.2 Which local-field correction applies to spontaneous emission?

The spontaneous emission rate $\Gamma(\varepsilon)$ of an impurity dipole inside a homogeneous medium with dielectric constant $\varepsilon$ is predicted by Nienhuis and Alkemade [10] to follow the $\sqrt{\varepsilon}$ dependence of the RDOS, and is thus given by

$$
\Gamma(\varepsilon) = \sqrt{\varepsilon} \Gamma_0,
$$

(3.1)

where $\Gamma_0$ is radiative decay rate of the dipole in vacuum. This dependence of $\Gamma(\varepsilon)$ is exactly identical to Eq. 2.60, which describes the radiation damping rate, the classical analog of spontaneous emission, of the dynamic polarizability of a dipole inside a dielectric that fulfills the optical theorem. However, Nienhuis and Alkemade arrived at Eq. 3.1 by quantizing the macroscopic Maxwell’s equations, while in principle the dipole couples to the microscopic vacuum fluctuations. The microscopic, or local, electric field felt by a dipole is usually different from the macroscopic field, and hence deviations from Eq. 3.1 are expected.

The concept of the local field was already explained in detail in the previous chapter. There it was shown that for highly symmetric, completely homogeneous dielectrics, i.e. fluids and cubic lattices, the ratio of the local to the macroscopic field is given by the Lorentz local-field factor

$$
L_{\text{Lor}} = \frac{\varepsilon + 2}{3},
$$

(3.2)

which is the same for all dipoles that constitute the dielectric, see also Eq. 2.45. Indeed, in experiments [51] involving only pure systems, i.e. only one kind of atom or molecule is present, the observed local-field effects agree very well with this Lorentz description. However, in the case of an impurity dipole, it is not at all clear whether Eq. 3.2 should apply.

The Onsager-Böttcher local-field approach, see section 2.4.5, allows an impurity dipole to be treated: an impurity dipole with polarizability $\alpha_1$ is placed at the
center of a spherical cavity with volume $\Omega$ in an otherwise homogeneous medium with dielectric constant $\varepsilon$. The local-field correction pertaining to the field in the cavity is

$$L_{OB}(\alpha_l/\Omega) = \frac{3\varepsilon}{2\varepsilon + 1 - \frac{2\alpha_l}{3\Omega}(\varepsilon - 1)},$$

(3.3)

see Eq. 2.49. As already explained, the Lorentz result [Eq. 3.2] is regained when the polarizability $\alpha_l$ of the impurity dipole is identical to the polarizability $\alpha$ of the dipoles that form the dielectric, and the inverse volume $\Omega^{-1}$ of the cavity equals the density $\rho$ of dipoles in the medium.

Considering the case of an impurity dipole inside the cavity, one sometimes neglects the response of the dielectric on $\alpha_l$, i.e. the reaction field is neglected. Equation 3.3 then simplifies to the so-called empty-cavity factor

$$L_{\text{emp}} = \frac{3\varepsilon}{2\varepsilon + 1},$$

(3.4)

identical as for the field inside a real empty cavity, see Eq. 2.23. It has been proposed theoretically [13, 16, 52, 53] that one of the factors, $L_{\text{Lor}}$ or $L_{\text{emp}}$, should be included in a description of $\Gamma(\varepsilon)$ of impurity dipoles inside dielectrics, that is $\Gamma(\varepsilon) = \varepsilon L_{\text{Lor}}^2 \Gamma_0$ or $\Gamma(\varepsilon) = \varepsilon L_{\text{emp}}^2 \Gamma_0$. The majority of the researchers in the field [53] favor the Lorentz factor. On the other hand, experimental results [54, 55] indicate that the empty-cavity factor [52] should be employed. Obviously, there is a controversy to be resolved.

Barnett et al. [13] indicated that part of the confusion arises from the choice of cavity that is used in the macroscopic derivation of the local-field correction. The virtual cavity, often employed in the derivation of the Lorentz-Lorenz equation [see section 2.4.4], would give rise to $L_{\text{Lor}}$. Contrary, $L_{\text{emp}}$ applies when the impurity dipole is considered inside a real empty cavity. They do not make a clear statement as to which type of cavity applies to impurity dipoles in a dielectric.

De Vries and Lagendijk [16] presented a full microscopic calculation of point dipoles on a cubic lattice, which form the dielectric, plus one impurity dipole, using Green’s function formalism [27]. The resonance width of the elastic impurity dipole is taken as the spontaneous emission rate. For substitutional impurity dipoles, that is a medium dipole is replaced by an impurity dipole (at a lattice position), the empty cavity result $L_{\text{emp}}$ is found to apply. For interstitials, that is the impurity dipole is placed in between lattice sites and no medium dipoles are removed, the Lorentz-cavity factor $L_{\text{Lor}}$ determines the modification of spontaneous emission. In this derivation, the polarizability of the impurity dipoles is required to obey the optical theorem, so that it captures spontaneous emission. In fact, the
optical theorem may be viewed as the microscopic analogon of Einstein's thermodynamic arguments [44] relating absorption, stimulated and spontaneous emission. A generalization to fluids is made and it is concluded that most often the substitutional result, that is $L_{\text{emp}}$, applies, in agreement with experimental observations [54, 55].

In the rest of this chapter, an alternative derivation of the results of De Vries and Lagendijk [16] will be presented, using the Onsager-Böttcher approach to model both substitutional and interstitial impurity dipoles.

### 3.3 Substitutional impurity dipoles

In the case of the substitutional impurity dipole, just the standard Onsager-Böttcher approach is considered. The impurity dipole in the cavity replaces the medium dipole, which would have been there in the case of a homogeneous dielectric. So indeed, the impurity dipole substitutes a dipole of the dielectric. In the far field, the total static polarizability for the substitutional case is then given by [see Eq. 2.50]

$$
\alpha_{\text{sub}} = \alpha_l L_{\text{emp}} L_{\text{OB}} \left( \frac{\omega_l}{\omega_0} \right) + (1 - \varepsilon) L_{\text{emp}} \Omega,
$$

where the first term is the contribution of the impurity dipole $\alpha_l$, and the second corresponds to the polarizability of the empty cavity with volume $\Omega$. Note that for $\alpha_l = 0$, the total static polarizability $\alpha_{\text{sub}}$ is not zero; the polarizability of the empty cavity is still remnant. The polarizability of the impurity dipole itself determines the spontaneous emission rate, and therefore only the first term of Eq. 3.5 is considered.

In order to obtain spontaneous emission rates, the dynamic polarizability is considered. The impurity dipole has to obey the optical theorem, as to describe spontaneous emission, and hence the dynamic polarizability of the dipole in vacuum is

$$
\alpha_l(\omega) = \alpha_l(0) \times \frac{\omega_0^2}{\omega_0^2 - \omega^2 - i(\Gamma_0\omega^3/\omega_0^3)},
$$

identical to Eq. 2.6. For completeness, here $\alpha_l(0)$ is the static polarizability, $\omega_0$ the resonance frequency, and $\Gamma_0$ the vacuum spontaneous emission rate. Implementing this polarizability $\alpha_l(\omega)$ in Eq. 3.5 readily gives the dynamic polarizability $\alpha_{\text{sub,l}}(\omega)$ of a substitutional impurity

$$
\alpha_{\text{sub,l}}(\omega) = \alpha_l(\omega) L_{\text{emp}}^2 \left[ 1 - \frac{2\alpha_l(\omega)(\varepsilon - 1)L_{\text{emp}}}{9\varepsilon\Omega} \right]^{-1}.
$$
where $L_{OB}(\alpha_{l}(\omega)/\Omega)$ is explicitly written in terms of $L_{emp}$. The polarizability of this "dressed" impurity near resonance has a Lorentzian structure analogous to Eq. 3.6:

$$\alpha_{sub,1}(\omega) = \alpha_{sub,1}(0) \times \frac{\omega_{0}^{2}(\varepsilon)}{\omega_{0}^{2}(\varepsilon) - \omega^{2} - i(\Gamma(\varepsilon)\omega^{2}/\omega_{0}^{2}(\varepsilon))},$$

with parameters given by

$$\frac{\alpha_{0}^{2}(\varepsilon)}{\omega_{0}^{2}} = \left[ 1 - \frac{2\alpha_{l}(0)(\varepsilon - 1)L_{emp}}{9\varepsilon\Omega} \right],$$

$$\alpha_{sub,1}(0) = L_{emp}^{2} \frac{\omega_{0}^{2}}{\omega_{0}^{2}(\varepsilon)} \alpha_{l}(0),$$

$$\frac{\Gamma(\varepsilon)}{\Gamma_{0}} = \sqrt{\varepsilon} L_{emp}^{2} \frac{\omega_{0}^{2}(\varepsilon)}{\omega_{0}^{2}}.$$

Here the spontaneous emission rate $\Gamma(\varepsilon)$ of the substitutional impurity follows from the polarizability $\alpha_{sub,1}(0)$ and the resonance frequency $\omega_{0}(\varepsilon)$ by use of the optical theorem, see Eqs. 2.5 and 2.60. Note that in vacuum, $\varepsilon = 1$, the original results are regained, that is $\omega_{0}(1) = \omega_{0}$, $\alpha_{sub,1}(0) = \alpha_{l}(0)$, and $\Gamma(1) = \Gamma_{0}$. The resonance frequency is red shifted and the line width behaves in accordance with the empty-cavity description, identical to the results of De Vries and Lagendijk [16].

### 3.4 Interstitial impurity dipoles

The case of the interstitial impurity dipole is modeled by placing an extra impurity dipole in the cavity without removing the medium dipole; there are two dipoles in the cavity, but for convenience of calculation it is positioned at the center of the cavity, on top of the medium dipole. In principle, the impurity dipole can be placed anywhere in the cavity, but for convenience of calculation it is positioned at the center of the cavity, on top of the medium dipole. It might seem unjustified to place the impurity at a point of high symmetry. However, a randomly positioned impurity is on average indeed located at the center. Furthermore, even if the impurity is not placed at the exact center of the cavity, but reasonably close, the results found by assuming a centered impurity dipole are in first approximation correct, see pages 150-153 of [14]. This indicates that choosing a point of high symmetry for the position of the impurity does not determine the outcome of the derivation.

By symmetry, it follows that the impurity and medium dipole have the same orientation. As a result, analogous to Eq. 3.5, the total static polarizability for the interstitial case reads

$$\alpha_{int} = (\alpha_{l} + \alpha) L_{emp} L_{OB}((\alpha_{l} + \alpha)/\Omega) + (1 - \varepsilon) L_{emp} \Omega,$$
where $\alpha$ is the polarizability of the dipoles that form the dielectric. The three different contributions (impurity dipole, medium dipole, and empty cavity) are clearly identified. Contrary to the substitutional case, the total polarizability $\alpha_{\text{int}} = 0$ for $\alpha_i = 0$, as then the medium is homogeneous, and hence the polarizabilities of the medium dipole and the empty cavity exactly cancel. In fact, $\alpha_{\text{int}}$ represents the effective polarizability $\alpha_{\text{int}1}(\omega)$ of the interstitial impurity dipole embedded in the dielectric, that is $\alpha_{\text{int}} = \alpha_{\text{int}1}(0)$. The polarizability $\alpha$ of the medium dipole can be eliminated from Eq. 3.12 by recognizing that $\alpha/\Omega = \rho a = 3(\epsilon - 1)/(\epsilon + 2)$ [Eq. 2.51], where $\rho$ is of course the density of the dipoles in the dielectric. The dynamic polarizability of the interstitial impurity then resides to

$$\alpha_{\text{int}1}(\omega) = \alpha_1(\omega) L_{\text{Lor}}^2 \left[ 1 - \frac{2\alpha_1(\omega)(\epsilon - 1)L_{\text{Lor}}}{9\epsilon\Omega} \right]^{-1},$$

where $\alpha_1(\omega)$ is given by Eq. 3.6. Note that for $\alpha_1(\omega) = 0$, indeed $\alpha_{\text{int}1}(\omega) = 0$. The structure of Eqs. 3.7 and 3.13 is identical, only $L_{\text{emp}}$ in Eq. 3.7 is replaced by $L_{\text{Lor}}$ in Eq. 3.13. Similar as in the substitutional case, the polarizability of the “dressed” interstitial impurity has a Lorentzian line shape given by Eq. 3.8. The parameters for the interstitial case are

$$\frac{\omega_0^2(\epsilon)}{\omega_0^2} = \left[ 1 - \frac{2\alpha_1(0)(\epsilon - 1)L_{\text{Lor}}}{9\epsilon\Omega} \right]^{-1},$$

$$\alpha_{\text{int}1}(0) = L_{\text{Lor}}^2 \frac{\omega_0^2}{\omega_0^2(\epsilon)} \alpha_1(0),$$

$$\Gamma(\epsilon) = \sqrt{\epsilon} \frac{\omega_0^2(\epsilon)}{\omega_0^2} L_{\text{Lor}}^2.$$

Again the resonance frequency is red shifted, although with a different functional dependence on $\epsilon$. The Lorentz local-field factor is found to determine the modification of the spontaneous emission rate, in agreement with Ref. [16].

### 3.5 Discussion

The obtained results for both the substitutional and interstitial impurity still depend on the volume of the cavity $\Omega$. For the case of the interstitials the volume is fixed: $\Omega = \rho^{-1}$. For substitutionals, $\Omega$ is free and generally taken to be the real volume of the impurity atom or molecule. For small impurity volumes, $\Omega < \rho^{-1}$, only one dipole of the dielectric is expelled from the cavity. If the impurity is large, $\Omega \gg \rho^{-1}$,
many dipoles of the dielectric are removed, and the impurity is a true macroscopic cavity.

The resonance frequency of the impurity slightly shifts to the red, see Fig. 3.1. This shift is a direct consequence of the reaction field produced by the polarization in the medium, which is induced by the impurity dipole. For small impurity polarization densities \( \alpha_{1}(0)/\Omega \ll 1 \), the reaction field disappears, and thus the resonance frequency shift can be neglected \( \omega_{0}^{2}(\varepsilon) = \omega_{0} \). In experiments, this is nearly always the case, except for extremely polarizable atoms like Na, Li, Rb, so that a shift of the resonance frequency is difficult to observe.

The spontaneous emission rate increases upon placing the impurity dipole in a dielectric, see Fig. 3.2. The volume \( \Omega \) of the cavity is irrelevant, if the impurity polarization density is small \( \alpha_{1}(0)/\Omega \ll 1 \). The relatively large differences between the models should allow for a clear distinction in experiment.

Two different classes of common host media can be distinguished: crystalline and disordered materials. In crystalline materials, which are necessarily solid, both substitutional and interstitial impurities occur. The substitutionals are positioned at
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Figure 3.2  The relative spontaneous emission rate of substitutional (dashed line, Eq. 3.11) and interstitial (dotted line, Eq. 3.16) impurities for zero resonance frequency shift, that is $\omega_0^2(\varepsilon)/\omega_0^2 = 1$. The solid line comes from Eq. 3.1. Large deviations from the vacuum spontaneous emission rate $\Gamma_0$ are predicted to occur in dielectrics.

lattice sites, the interstitials somewhere in between. In the case of disordered materials, like fluids and glasses, this distinction is not so clear. For such host media, it is essential to consider the local environment in order to distinguish between substitutional and interstitial [16]. Interstitial behavior occurs when impurities do not influence the positions of the particles that form the dielectric. So the volume of the impurity has to be much smaller than the voids in between the medium dipoles. On the other hand, if the size of the impurity is comparable, or larger, than the size of the medium particles, the substitutional result applies. As, in that case, the impurity forms a real excluded volume for the dipoles of the dielectric. At very low densities, the distinction between the two types of impurities is not relevant, since any distinct feature of positional correlation of the medium dipoles will disappear, and $L_{\text{Lor}} \approx L_{\text{emp}}$ to first order in $\Omega^{-1}$. In the case of fluids, only substitutional behavior is expected to occur, as the sizeable dimensions of the impurities present a real excluded volume for the surrounding dielectric.