Single molecule fluorescence decay rate statistics in disordered media

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1. Introduction

Several powerful optical imaging techniques are based on molecular fluorescence. Single emitters are also key elements in nanophotonics devices. Since the pioneering work of Purcell [1], it has been known that the spontaneous decay rate of a dipolar emitter (atom, molecule, Qdot) is dramatically affected by its environment. When a fluorescent molecule is placed in a complex environment (e.g., cluster, biological system), measurement of *statistical* properties can provide relevant information. This issue has been partially addressed in the literature [2]. In nanoscopic systems (e.g. clusters of nanoparticles) two important contributions are expected: (1) local field effects due to near-field interaction between the emitter and its environment; (2) absorption, which can substantially modify the statistics of the decay rate. In particular, the statistics of the radiative and non-radiative rates are expected to behave differently in the presence of absorption [3].

2. Discussion

In this work [4,5], we study the fluorescence rate statistics in a finite size (nanoscopic) random medium (cluster), made of small spherical particles (see the inset in Fig. 1 a). For a given configuration of the system, we calculate numerically the Green tensor of the system. We deduce the spontaneous decay rate Γ, as well the radiative and the non-radiative contributions. Repeating the calculation for the configuration distribution and performing ensemble averages allows to compute the full statistics (probability density, average value, standard deviation). These numerical experiments are used as a basis for a physical discussion.

We focus on the regime in which the statistics is determined by near-field interactions, with negligible multiple scattering. The decay rate statistics is influenced by the local environment of the emitter (i.e. the interaction with the surrounding particles).

In Fig. 1a we show the statistical distribution of the normalized spontaneous decay rate Γ/Γ_0 obtained from numerical simulations, for a cluster of $Ti0_2$ (Rutile) nanoparticles at an emission wavelength λ=700nm. At low filling fraction the correlations among particle positions are negligible. It can be seen that, although the average value is close to the one in free-space, the distribution is broad and present a long tail. This is a consequence of the large fluctuations of the local field at the emitter position.

In Fig. 1b we show the distributions functions of the non-radiative decay rate. As can be seen, for different levels of absorption (determined by the imaginary part of the dielectric constant of the particles), the shape of the distributions remains invariant when the non-radiative decay rate is scaled by the imaginary part of the dielectric constant. Hence, the average value (inset Fig. 1b) and fluctuations of Γ^{NR} scales linearly with ε'' .

In the case of small clusters compared to the emission wavelength, and low filling fraction, a simple analytical model reproduces with great detail the numerical calculations. It can be shown that the standard deviation, normalized to the averaged modification of the decay rate (Fig. 2a) presents two well defined regimes. For low absorption level fluctuations are controlled by near-field scattering, while for higher degrees of absorption, fluctuations reach a regime controlled by non-radiative coupling, although the apparent quantum yield is still high

(Fig. 2b). Also fluctuations and angular correlations of the emitted intensity pattern can be obtained within this framework. It will be shown how statistical properties of the emitted light intensity and it emission rate strongly depend on the optical and structural properties of the close neighborhood of the emitter at the nanoscale. And, interestingly, the fluctuations of the decay rate depend dramatically on the statistical properties of the orientation of the emitter [5]. Hence we could take advantage of this behavior to obtain information of the local environment of the emitter at the nanoscale.

3. Conclusions

In summary, we have studied the statistics of the spontaneous decay rates in disordered nanoscopic clusters using both numerical simulations and a simple analytical model. Our results show that such statistics carry useful information about the local structure of the environment at the nanometer scale, even in the presence of absorption. This paves the way towards new imaging techniques in complex media at the nanometer scale.

4. References

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2. Figures

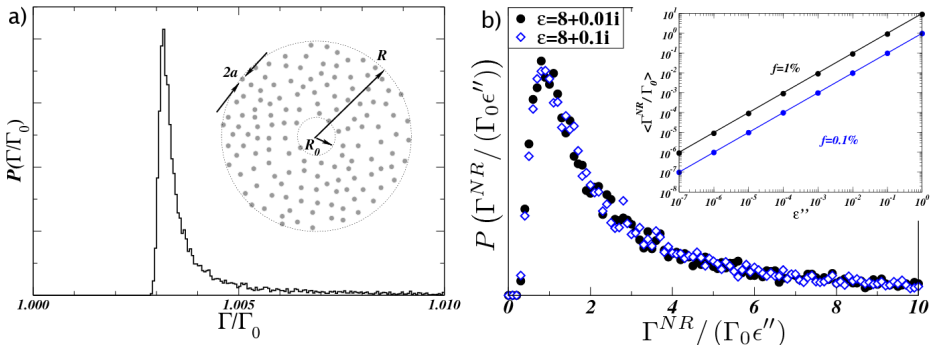

Fig.1. a) Statistical distribution of the normalized spontaneous decay rate Γ/Γ_0 for a cluster of non-absorbing nanoparticles. Particle radius a=2.5nm, dielectric constant ε=8, cluster radius R=54nm , volume fraction f=1%. Inset: geometry of the system. The emitter is placed at the center of the cluster, and is surrounded by a spherical exclusion volume of radius R_0=5nm. b). Statistical distribution of the non-radiative decay rate Γ^{NR} (normalized by $\varepsilon''\Gamma_0$) for a cluster of absorbing nanoparticles. The dielectric constant is $\varepsilon=8+i\varepsilon''$, with $\varepsilon''=10^{-2}$ (circles) and $\varepsilon''=10^{-1}$ (diamonds) . Inset: Averaged value of the normalized non-radiative decay rate $\langle\Gamma^{NR}/\Gamma_0\rangle$ versus the imaginary part of the dielectric constant of the particles, for f=0.1% and f=1%. Symbols: numerical calculation. Solid lines: analytical model.

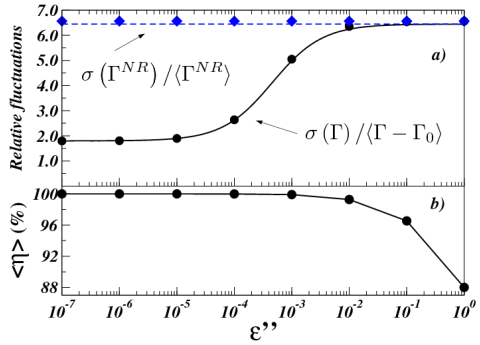

Fig. 2. a) Normalized standard deviation of the decay rate $\sigma(\Gamma)/\langle\Gamma-\Gamma_0\rangle$ versus the imaginary part of the dielectric constant of the particles. Symbols: numerical calculation. Solid line: analytical model. Dashed line: analytical model for the normalized standard deviation of the non-radiative rate $\sigma(\Gamma^{NR})/\langle\Gamma^{NR}\rangle$. b) averaged apparent quantum yield $\langle\eta\rangle$ (the intrinsic quantum yield of the emitter is assumed to be unity). f=0.1%, other parameters as in Fig. 1.