STATISTICAL PROPERTIES OF SINGLE MOLECULE FLUORESCENCE IN DISORDERED MEDIA

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1. Introduction

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 of either lifetime or fluorescence intensity 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. Fluorescence lifetime statistics

In the first part of this work [4], we study the fluorescence lifetime 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 Ginverse of the lifetime, 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).

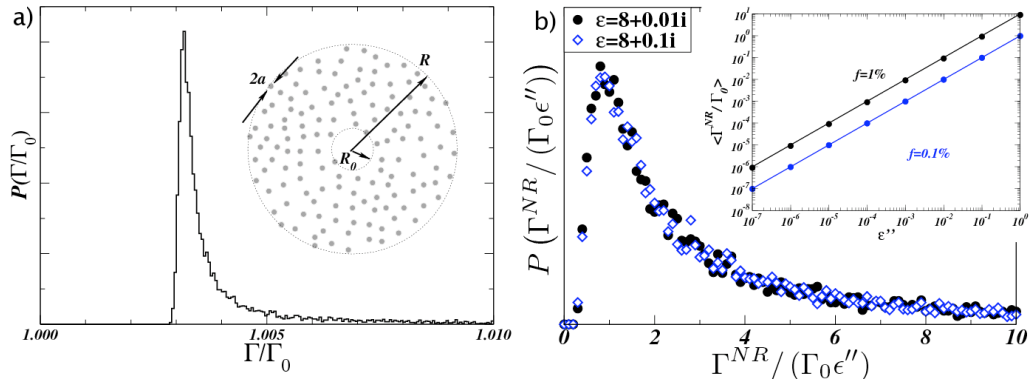

Fig.1. a) Statistical distribution of the normalized spontaneous decay rate G/G_0 for a cluster of non-absorbing nanoparticles. Particle radius a=2.5nm, dielectric constant e=8, cluster radius R=54nm , volume fraction f=1%. Inset: geometry of the system. The emitter is placed at the center of the cluster, and is surrounded by a spherical exclusion volume of radius R_0=5nm. b). Statistical distribution of the non-radiative decay rate G^{NR} (normalized by e''G_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 $\langle G^{NR}/G_0 \rangle$ 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.

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 l=700nm. At low filling fraction the correlations among particle positions is 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 G^{NR} scales linearly with ε''.

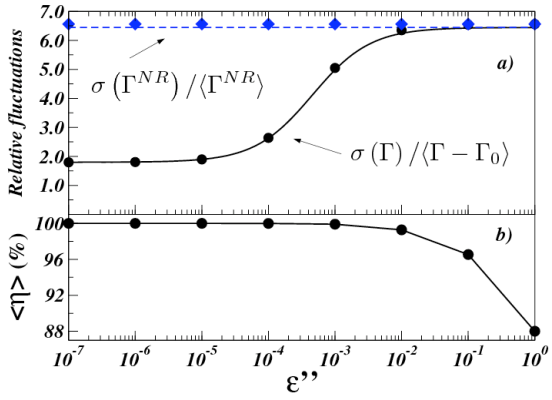

Fig. 2. a) Normalized standard deviation of the decay rate s(G)/<G-G_0> versus the imaginary part of the dielectric constant of the particles. Symbols: numerical calculation. Solid line: analytical model. Dashed line: analytical model for the normalized standard deviation of the non-radiative rate s(G^{NR})/<G^{NR}>. b) averaged apparent quantum yield <h> (the intrinsic quantum yield of the emitter is assumed to be unity). f=0.1%, other parameters as in Fig. 1.

In order to study quantitatively the fluctuations of decay rates, we have numerically calculated the standard deviation, normalized to the averaged modification of the decay rate. The results are shown in Fig. 2a. Two well defined regimes can be identified. 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. In both regimes, the apparent quantum yield remains high enough to permit practical measurements (Fig. 2b). In order to analyze numerical data, we have developed a simple analytical model based on the assumptions of small clusters and low filling fraction.

3. Statistical properties of the fluorescence signal

Another interesting quantity in fluorescence imaging is the fluorescence intensity that, in the non-saturated regime, is proportional to the intensity of the local field at the excitation wavelength. In a random system under coherent illumination, the spatial structure of the local intensity is a speckle pattern. When either the location of the emitter or the configuration of the system changes, the fluorescence intensity exhibits random fluctuations. In a non-absorbing system, the statistics of the fluorescence intensity will directly reflect the statistics of the speckle pattern. We will examine different regimes, involving near-field interaction and/or multiple scattering. In the presence of absorption the fluorescence intensity statistics is strongly affected by the fluctuation of the apparent quantum yield. Our results show that volume speckle pattern probing by fluorescence signals is a promising imaging technique in complex media.

References

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