Single molecule fluorescence decay rate statistics in disordered media

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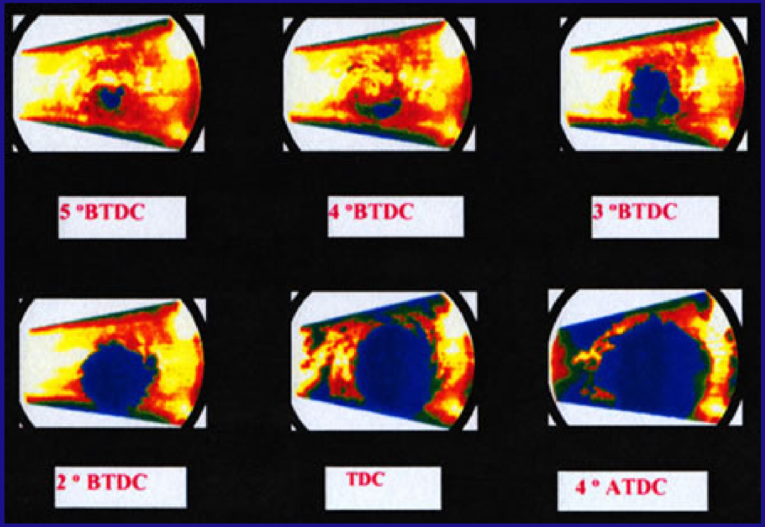
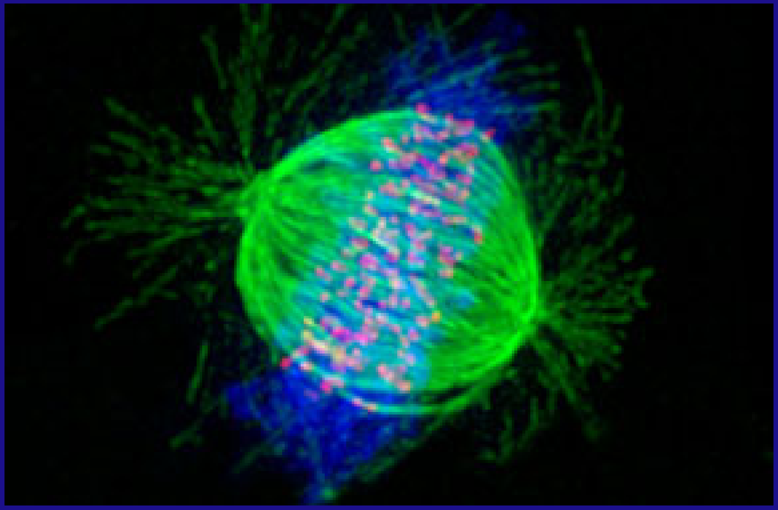
Applications of fluorescence: Imaging

- Molecular level
- Different modes of operation
  - Intensity signal
  - Fluorescence lifetime

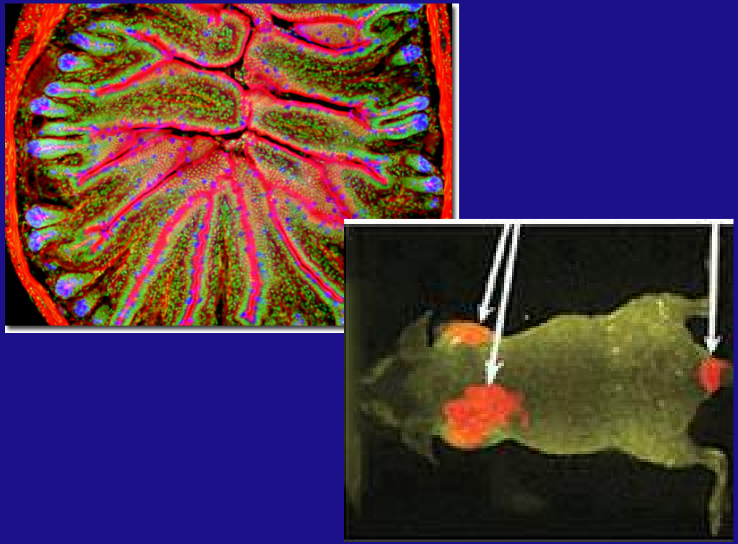
Combustion



Cell imaging

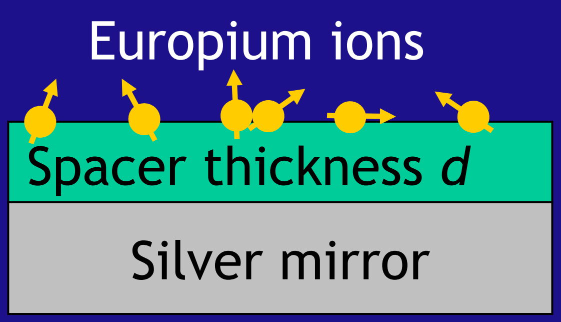


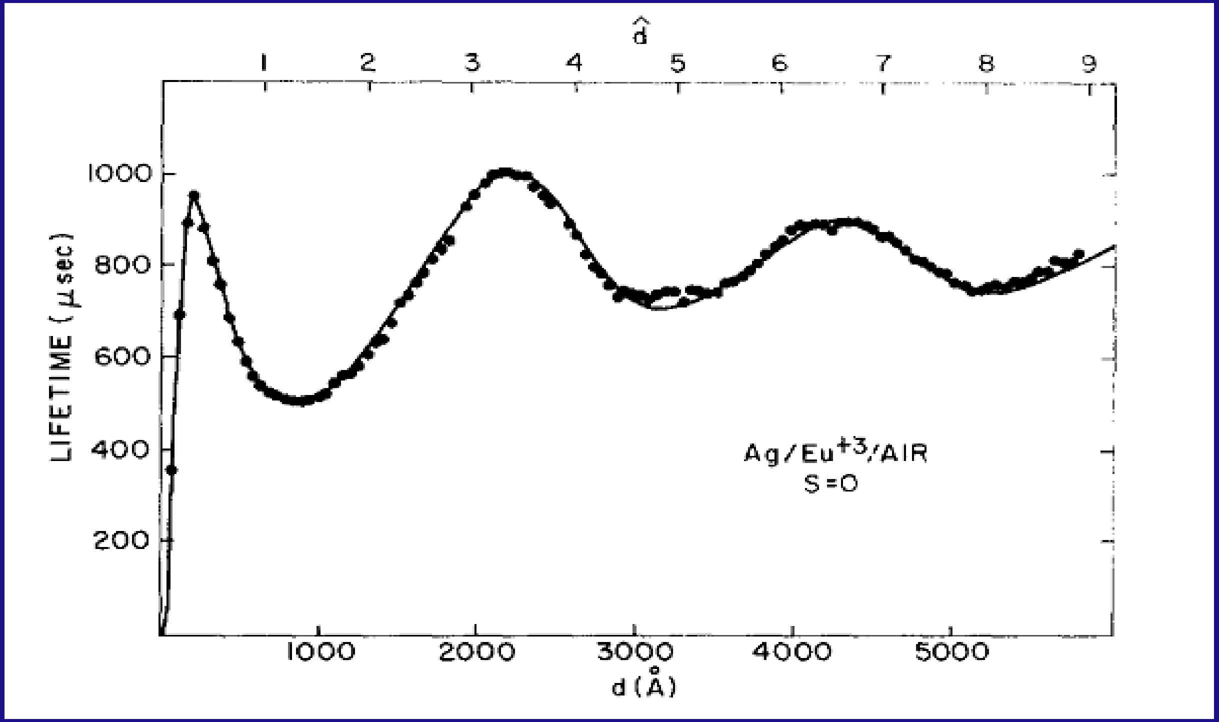
Whole organ imaging



Lifetime depends on the environment

Emission in front of a mirror

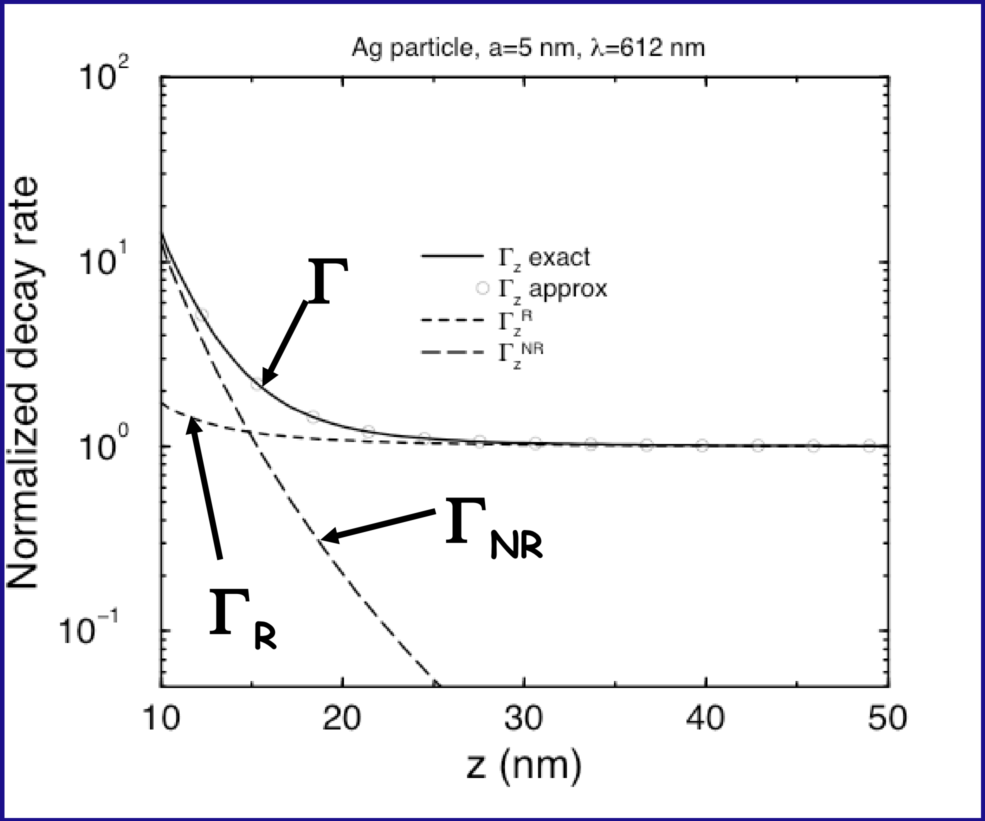




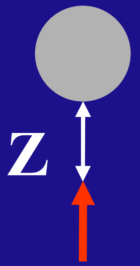
Drexhage (1966): fluorescence lifetime of Europium ions depends on source position relative to a silver mirror *(l=612 nm)*

Lifetime depends on the environment

Emission in front of a nanoparticle



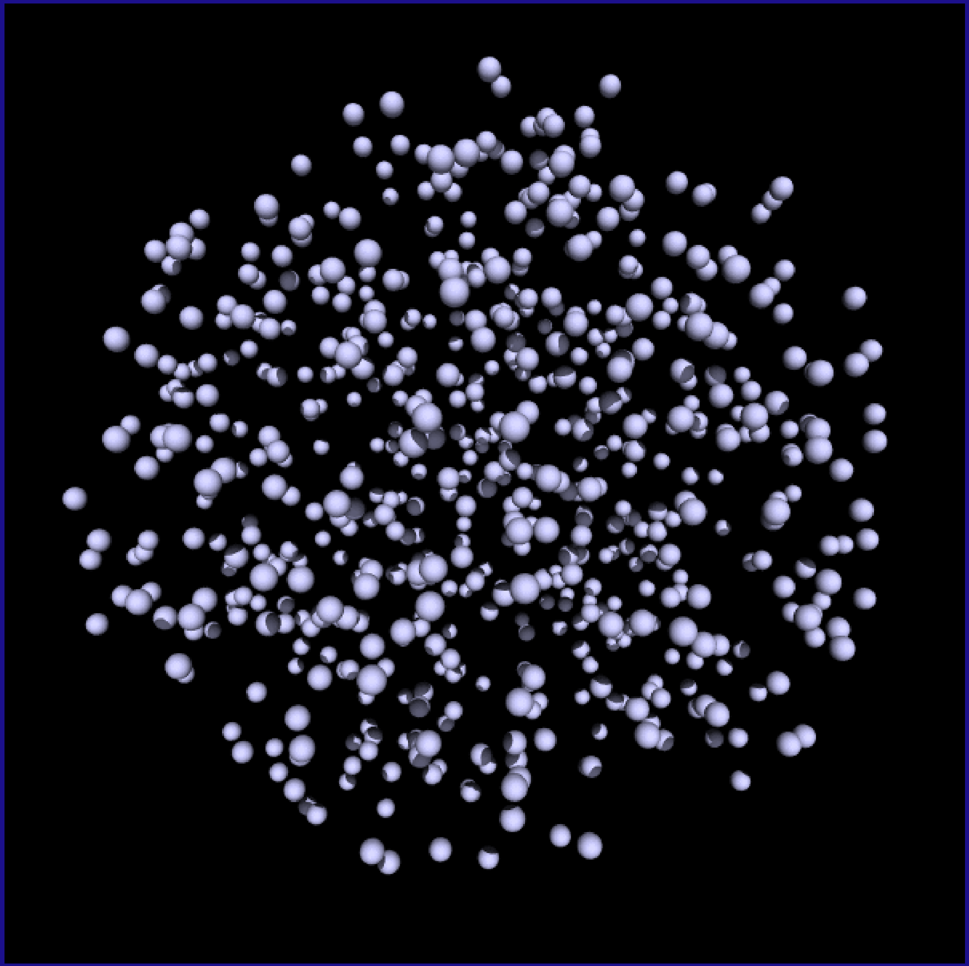
Silver nanoparticle, diameter 10 nm



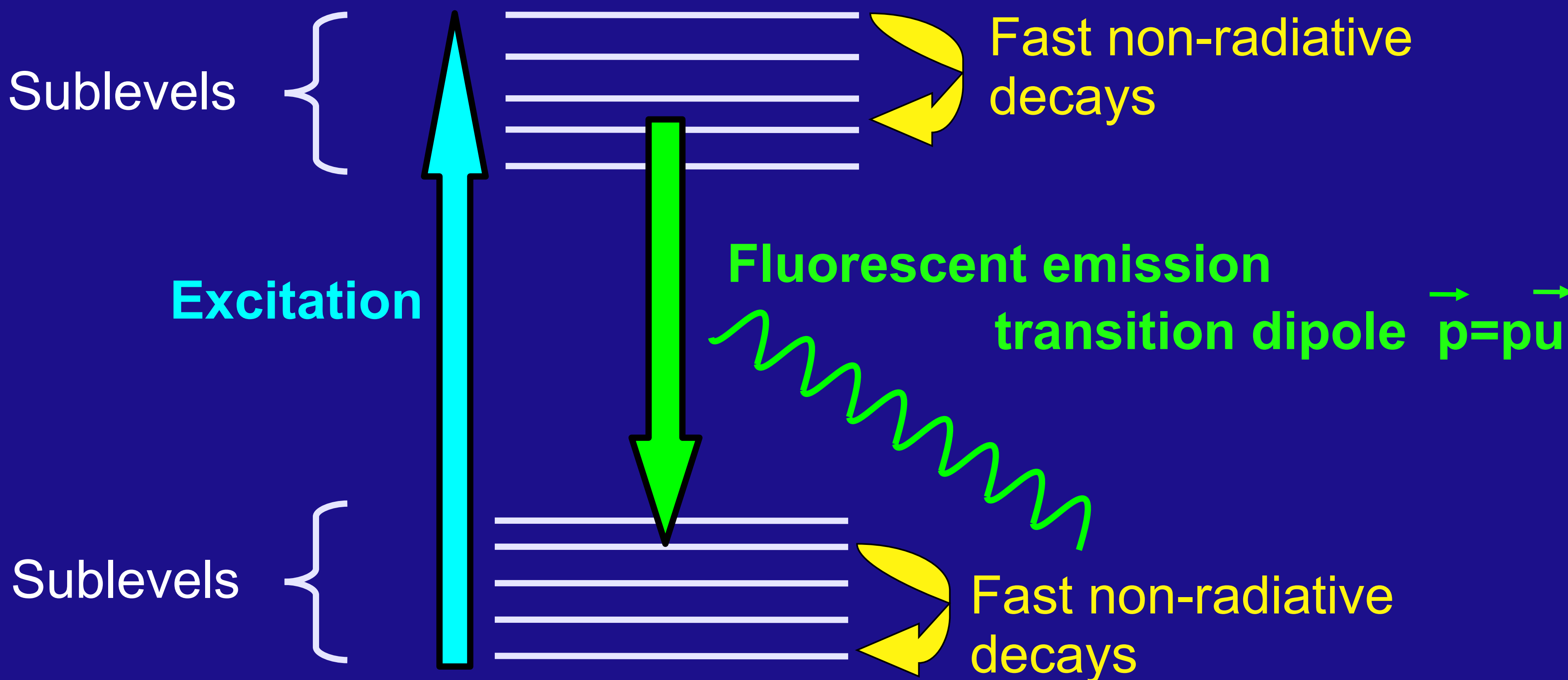
Carminati, Henkel, Greffet, Vigoureux, Opt. Commun. **261**, 368 (2006)

Lifetime depends on the environment

What happens when the environment is disordered?



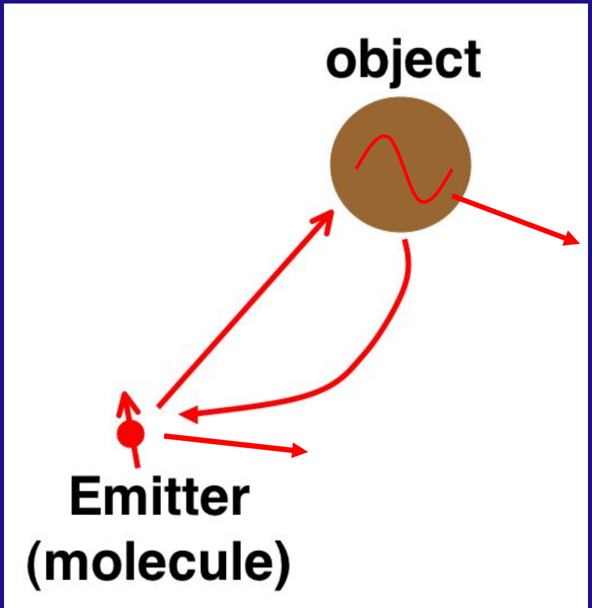
Fluorescence: spontaneous decay



Probability of spontaneous decay $P(t) \propto \exp(-t\Gamma)$

Γ= decay rate

Decay rates



Total decay rate

$$\Gamma = \frac{2p^2}{\hbar}\frac{\omega^3}{c^3\varepsilon_0}\Im\left\{\hat{\mathbf{u}}\mathbb{G}\left(\mathbf{r},\mathbf{r},\omega\right)\hat{\mathbf{u}}\right\}$$

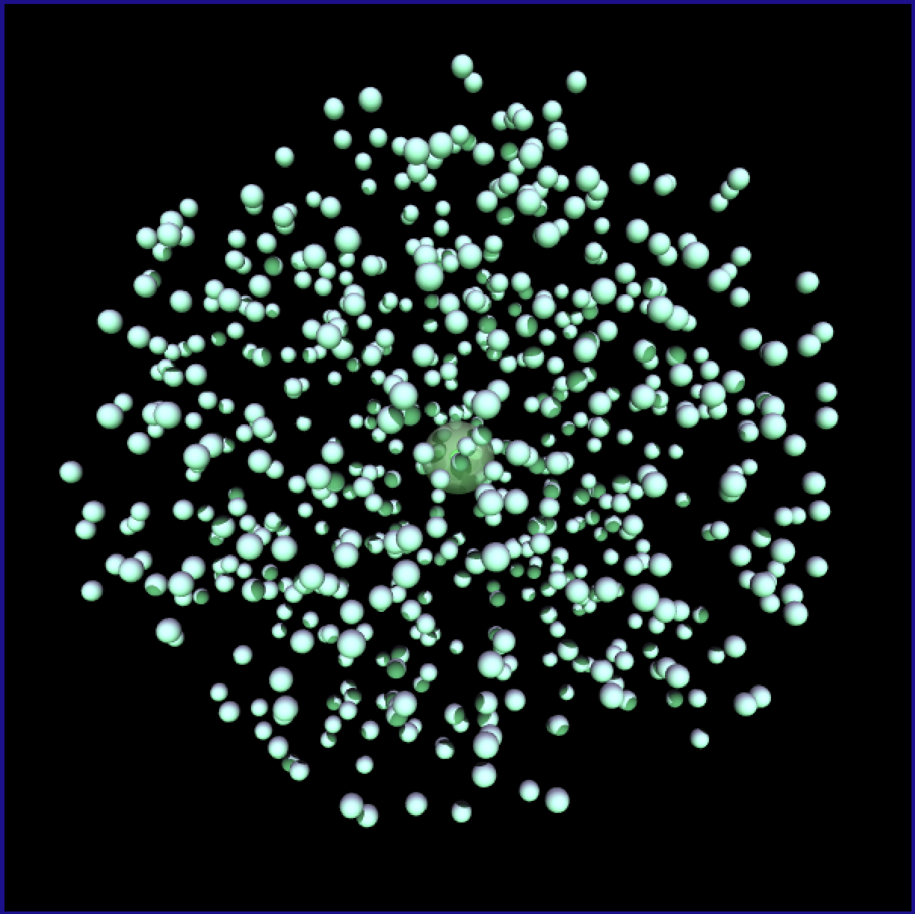
The emitted light can be either **radiated** out of the system or **absorbed**

- Power (classical) $P = P_R + P_{NR}$
- Decay rate (quantum) $\Gamma = \Gamma_R + \Gamma_{NR}$

In this talk

Disordered clusters of nanoparticles: statistical properties

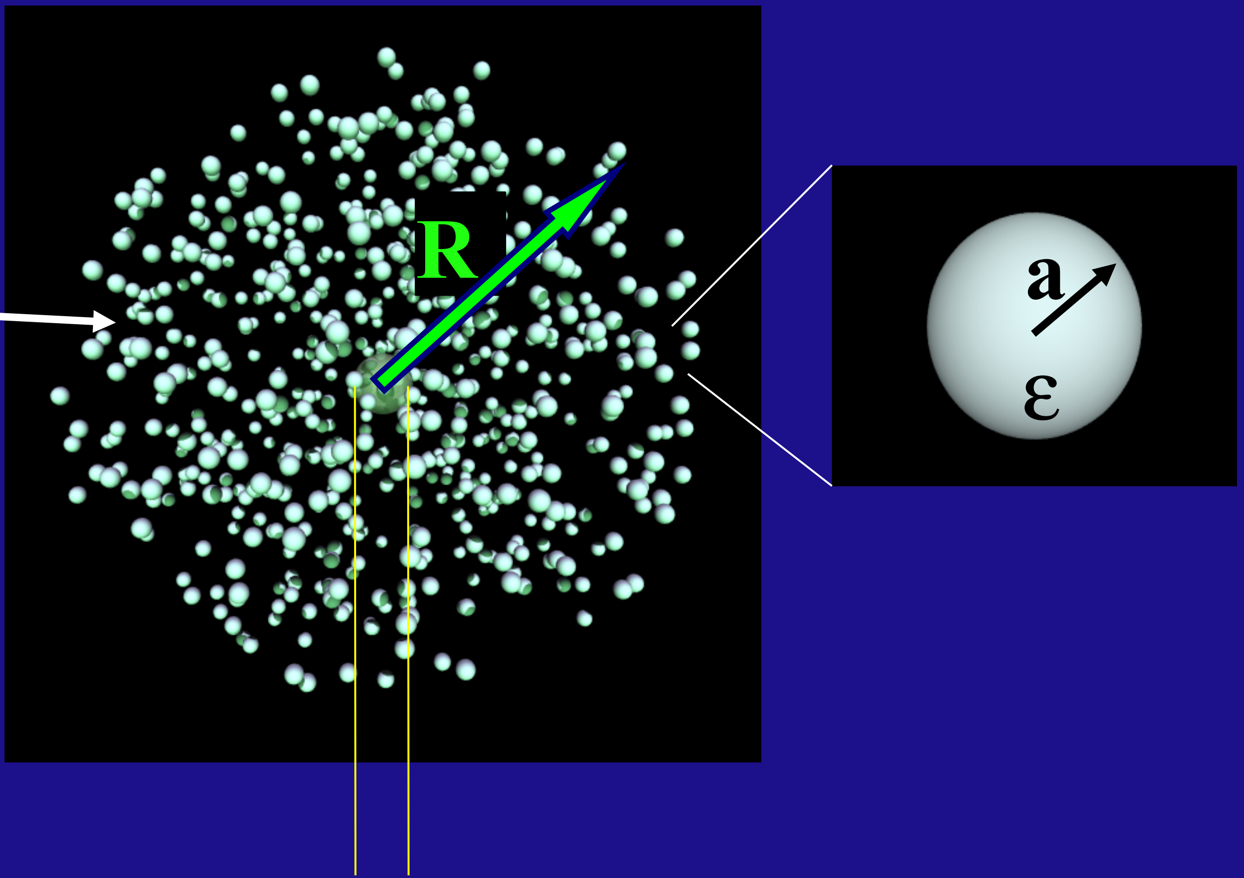
- Geometry of the system
- Statistics of the emitter
- Numerical results
- An analytical approach:
  - Averaged values
  - **Fluctuations**



Geometry of the system: disordered spherical clusters

There is a **minimum distance** between particles

uncorrelated positions if low filling fraction (f)

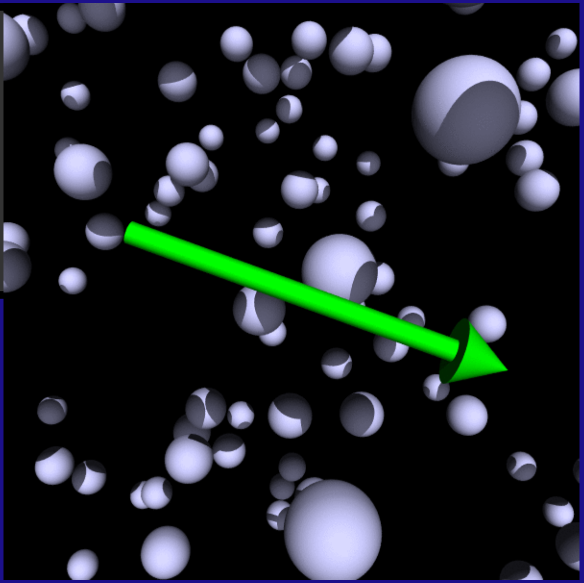


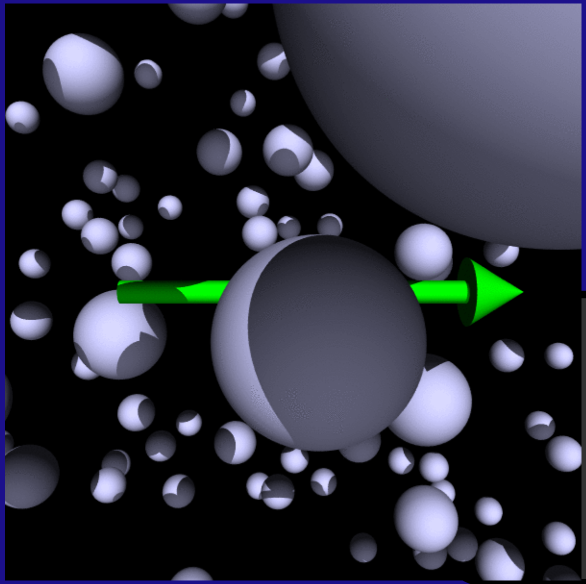
$2R_0$ Excluded Volume

The emitter

Orientation dynamics FASTER than medium dynamics:

Γ averaged in all directions



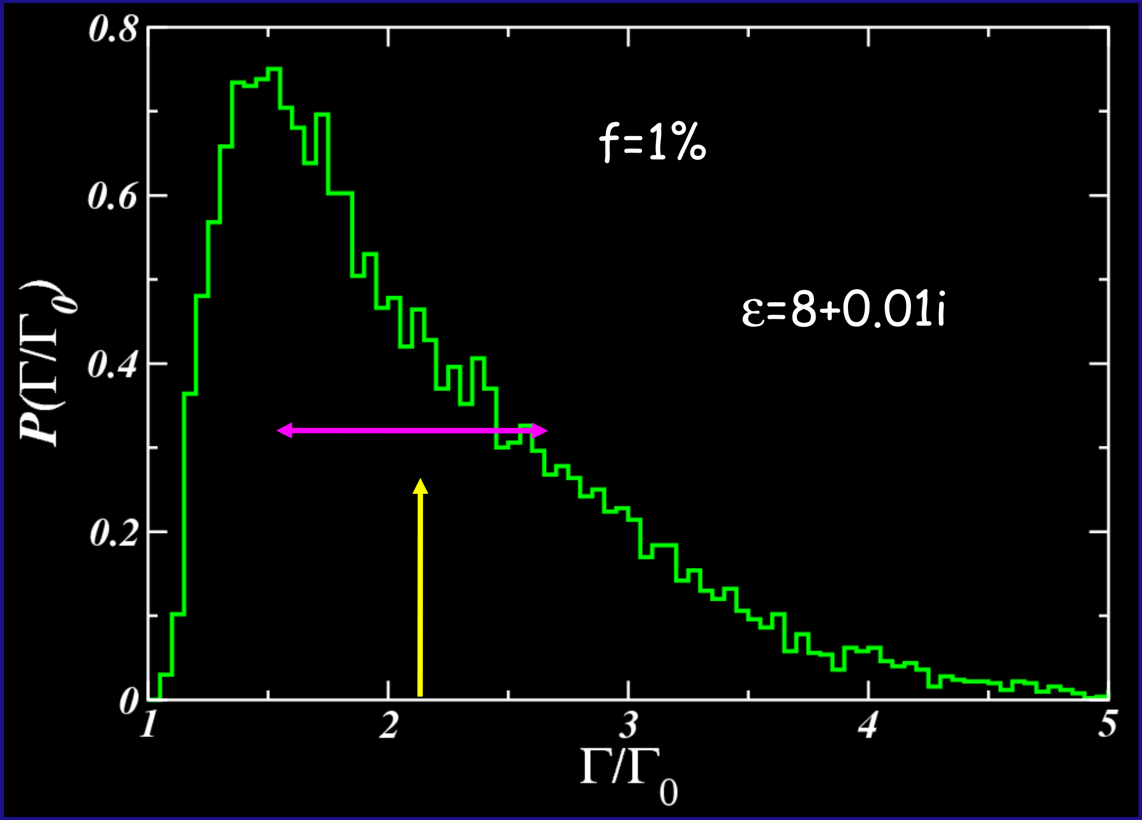


Orientation dynamics SLOWER than medium dynamics:

Γ taken along one direction

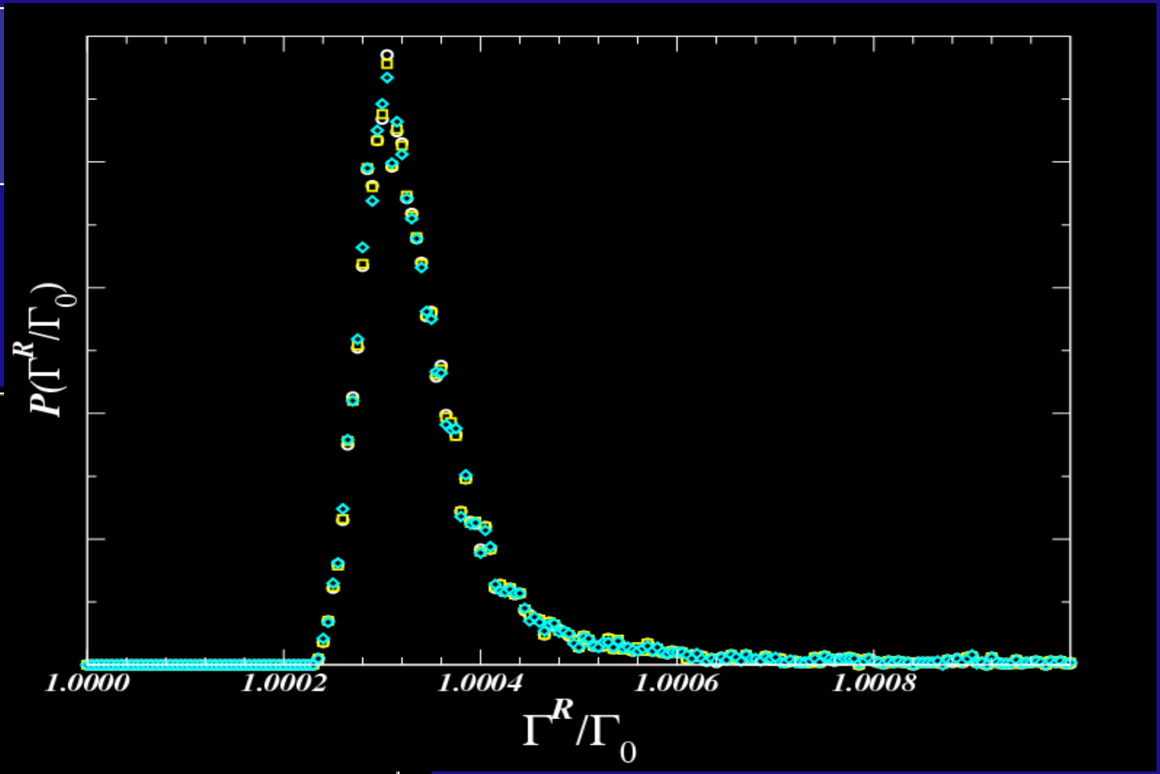
Emission rates in disordered systems: numerical results

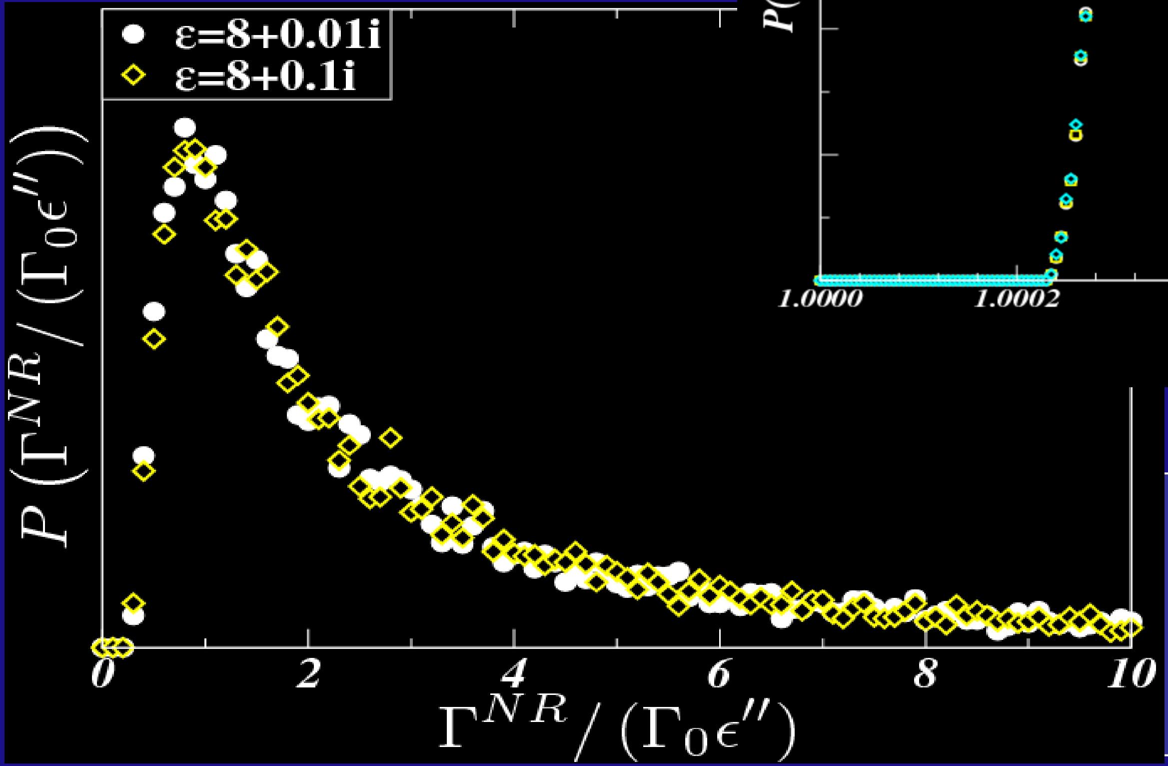
- Broad distributions.
- Strong dependence on absorption level.
- Strong dependence on orientation statistics.



Emission rates in disordered systems: numerical results

Radiative contribution does not depend on absorption.

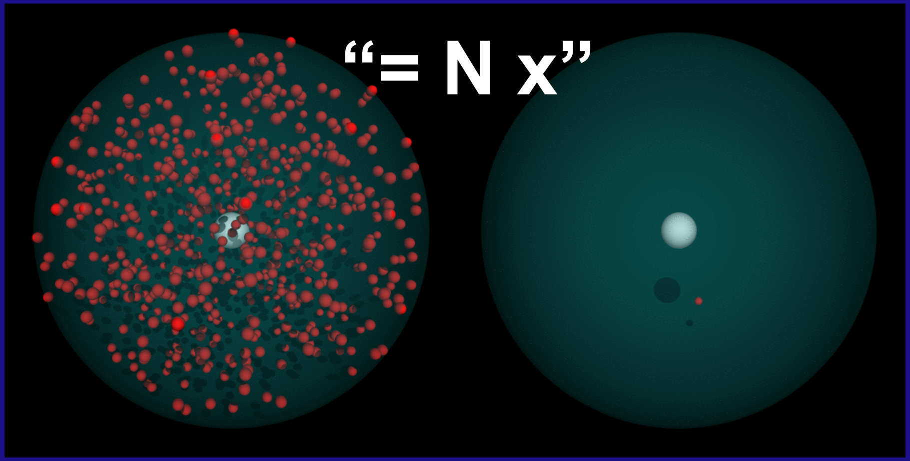




Non-Radiative contribution increases almost linearly with absorption. Dominating the statistical properties of emission rates.

Analytical model

·Single scattering
·Uncorrelated disorder



$$\left\langle \Gamma^{(N)} - \Gamma_0 \right\rangle = N \times \left\langle \Gamma^{(1)} - \Gamma_0 \right\rangle$$

$$\sigma^2 \left(\Gamma^{(N)} \right) = N \sigma^2 \left(\Gamma^{(1)} \right)$$

Valid for clusters of nanoparticles

- Small polarizability
- Low filling fraction

Averaged decay rates

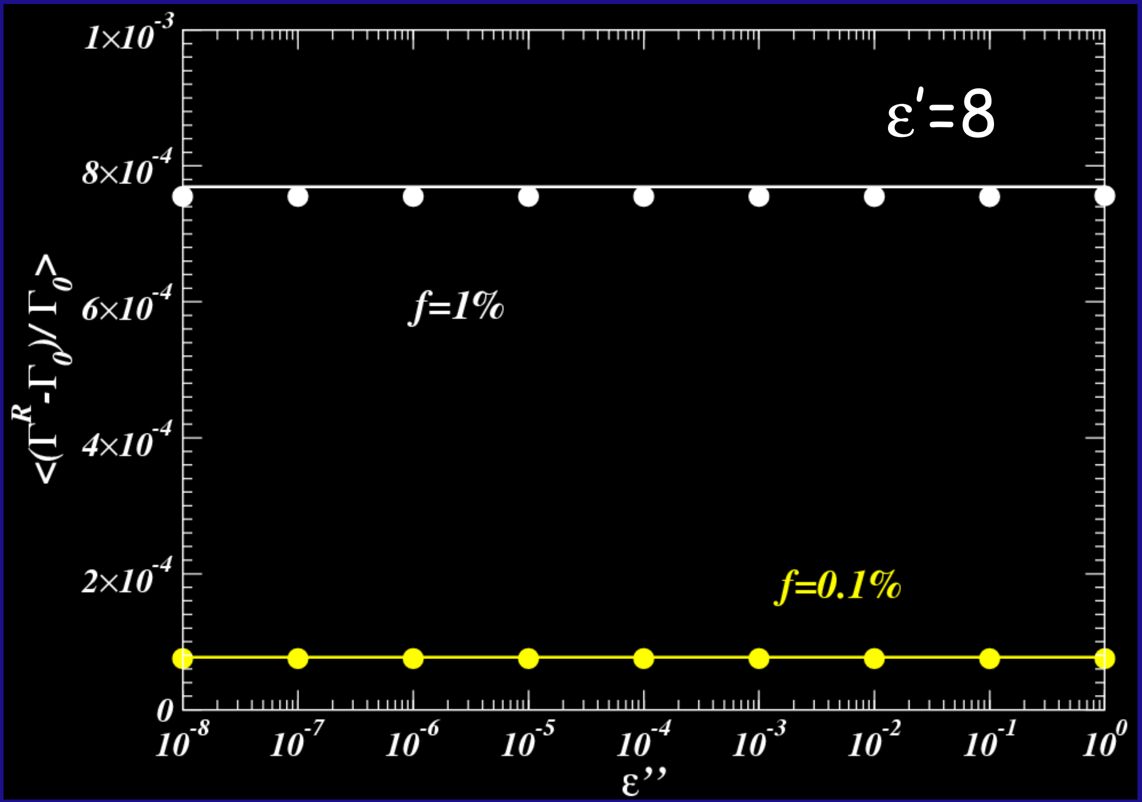
Radiative contribution

$$\left\langle \frac{\Gamma^R - \Gamma_0}{\Gamma_0} \right\rangle \simeq \frac{11}{5} f \Re(\beta) (kR)^2 + 2f |\beta|^2 \left(\frac{a}{R_0} \right)^3$$

$$\beta = \frac{\epsilon - 1}{\epsilon + 2}$$

·First order term in powers of filling fraction f (single scattering)

·Almost independent on absorption level



Averaged decay rates

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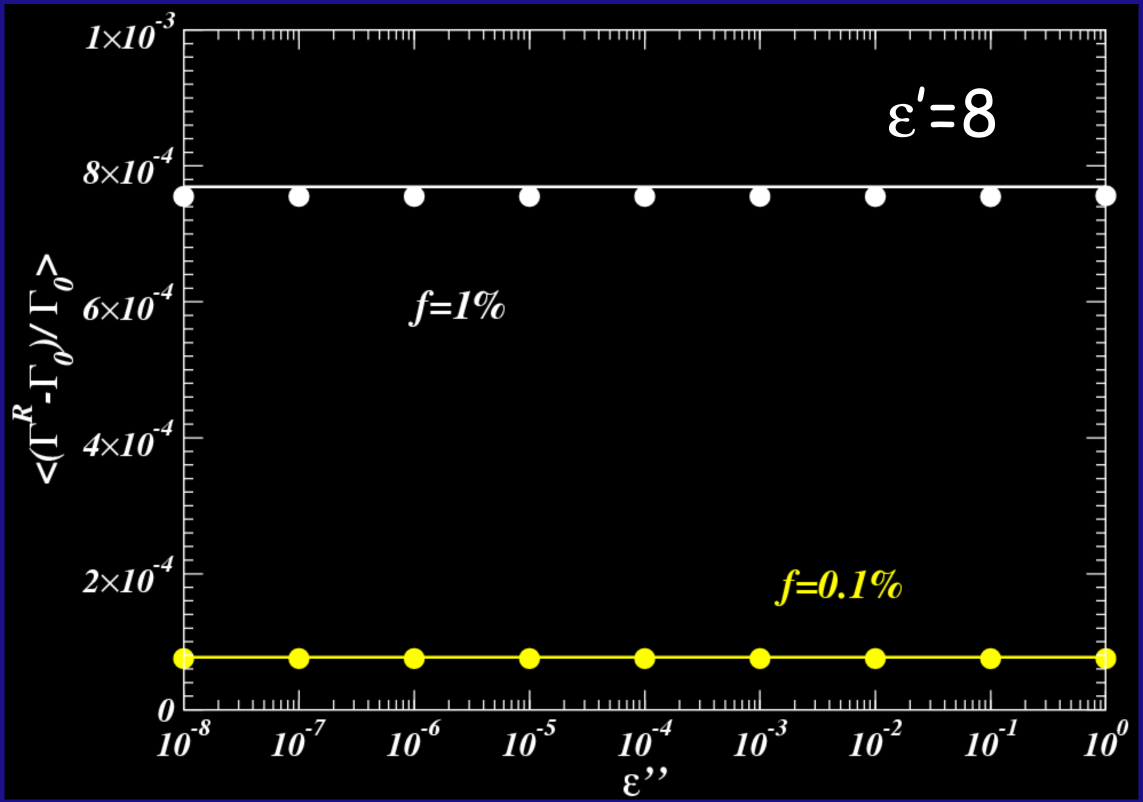
$$\left\langle \frac{\Gamma^R - \Gamma_0}{\Gamma_0} \right\rangle \simeq \frac{11}{5} f \Re(\beta)(kR)^2 + 2f|\beta|^2 \left(\frac{a}{R_0}\right)^3$$

Averaged radiated field

Explicit separation of terms:

- averaged field
- fluctuations



Averaged decay rates

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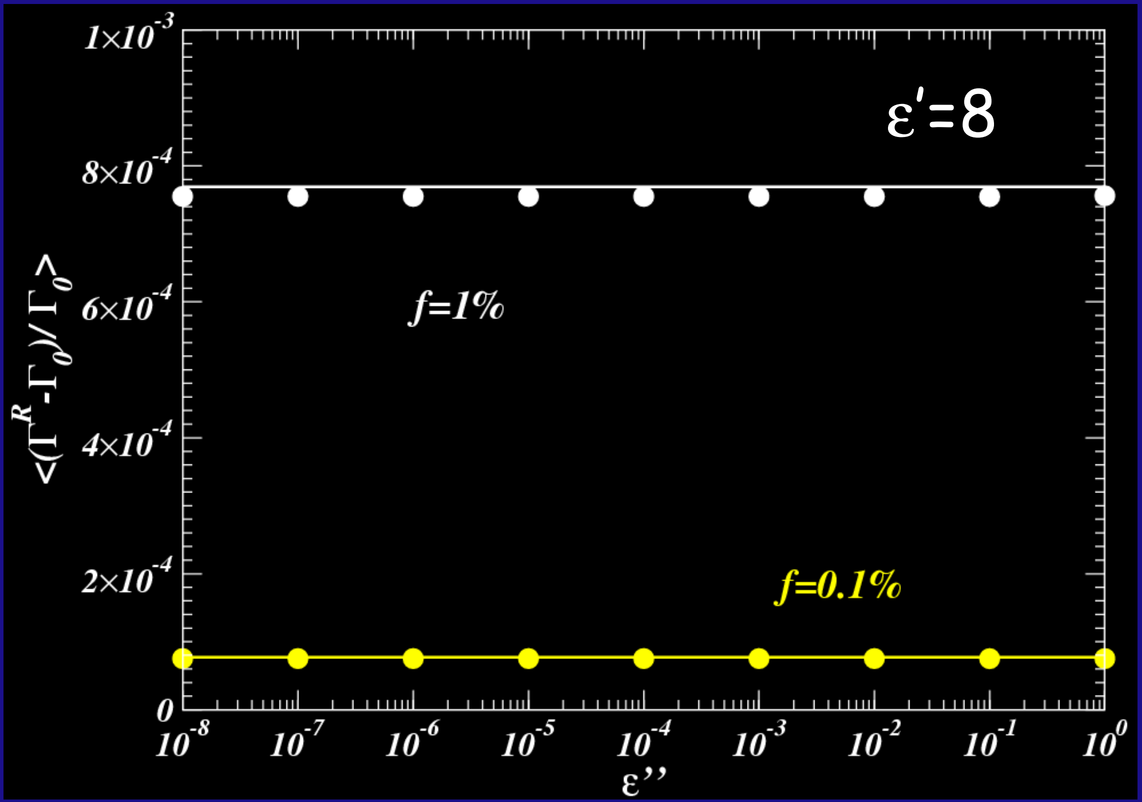
Averaged radiated field

Fluctuations far field

Explicit separation of terms:

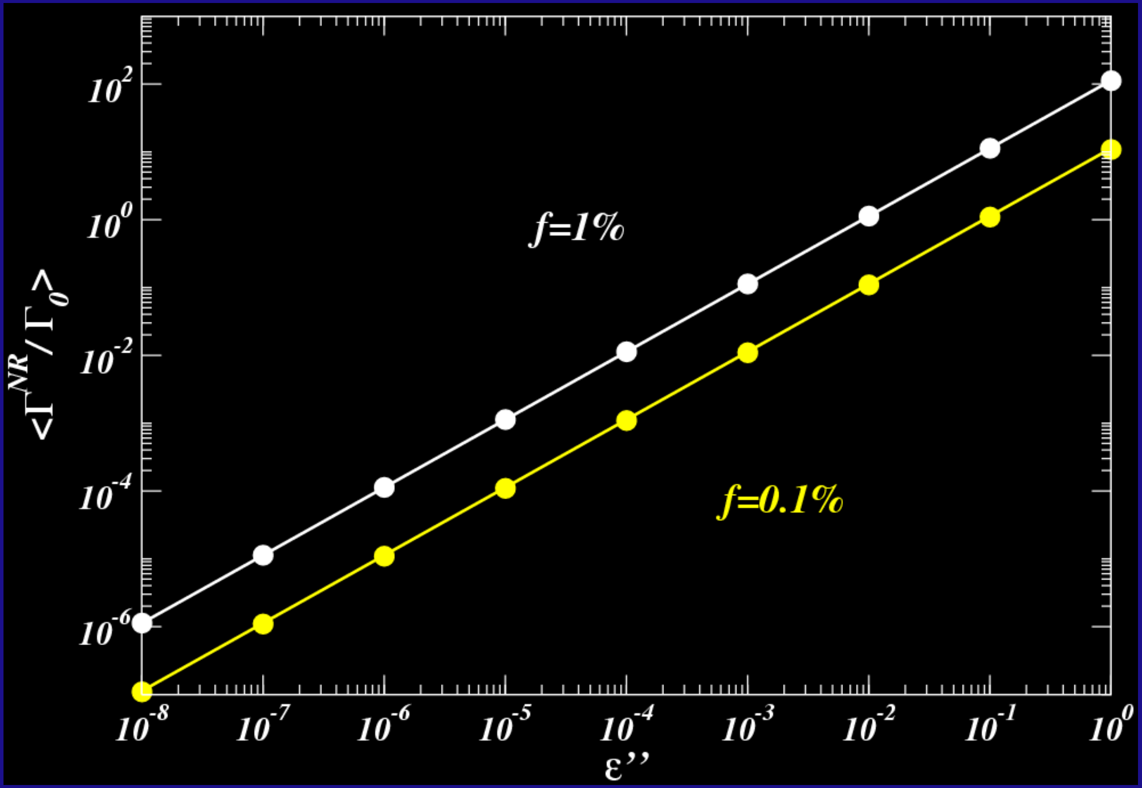
- averaged field
- fluctuations



Averaged decay rates

Non-Radiative contribution

$$\left\langle \frac{\Gamma^{NR}}{\Gamma_0} \right\rangle \simeq 9f \frac{\Im(\epsilon)}{|\epsilon+2|^2} \frac{1}{(kR_0)^3}$$

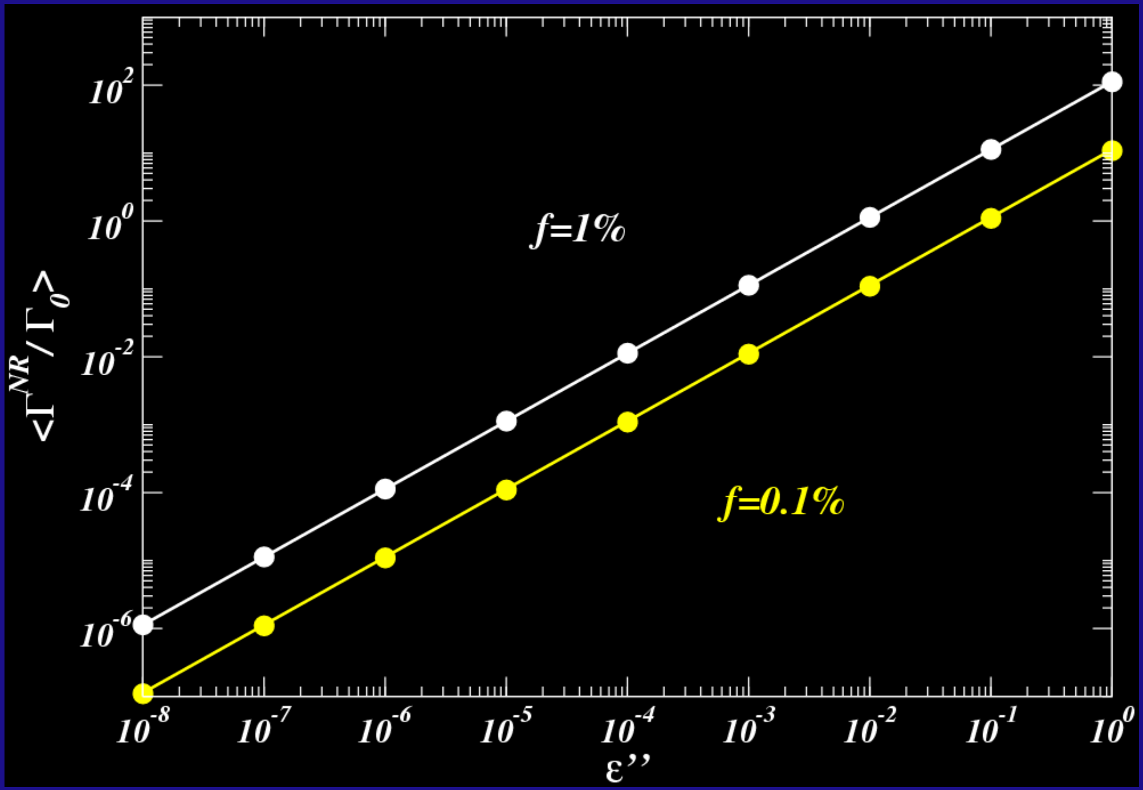


Averaged decay rates

Non-Radiative contribution

$$\left\langle \frac{\Gamma^{NR}}{\Gamma_0} \right\rangle \simeq 9f \frac{\Im(\epsilon)}{|\epsilon+2|^2} \frac{1}{(kR_0)^3}$$

Linear with Im(ε)



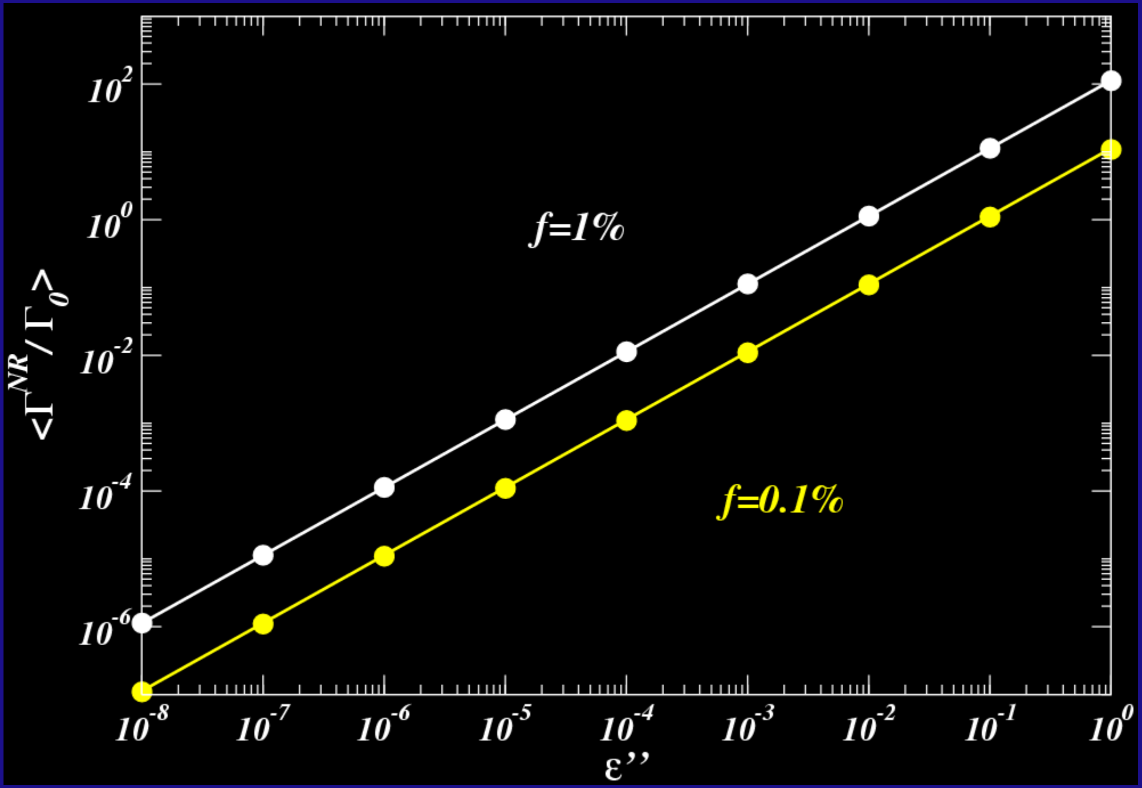
Averaged decay rates

Non-Radiative contribution

$$\left\langle \frac{\Gamma^{NR}}{\Gamma_0} \right\rangle \simeq 9f \frac{\Im(\epsilon)}{|\epsilon+2|^2} \frac{1}{(kR_0)^3}$$

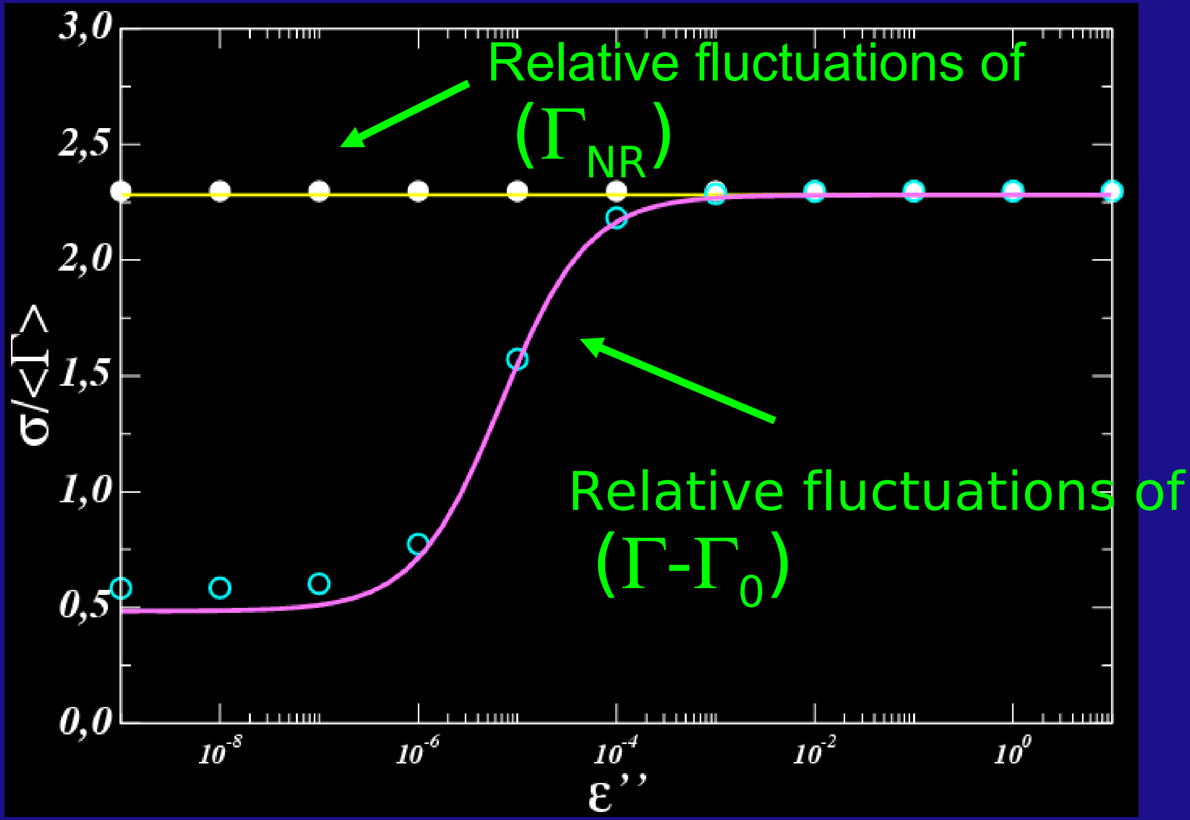
Strong local field effects

Linear with Im(ε)



Fluctuations of decay rates:

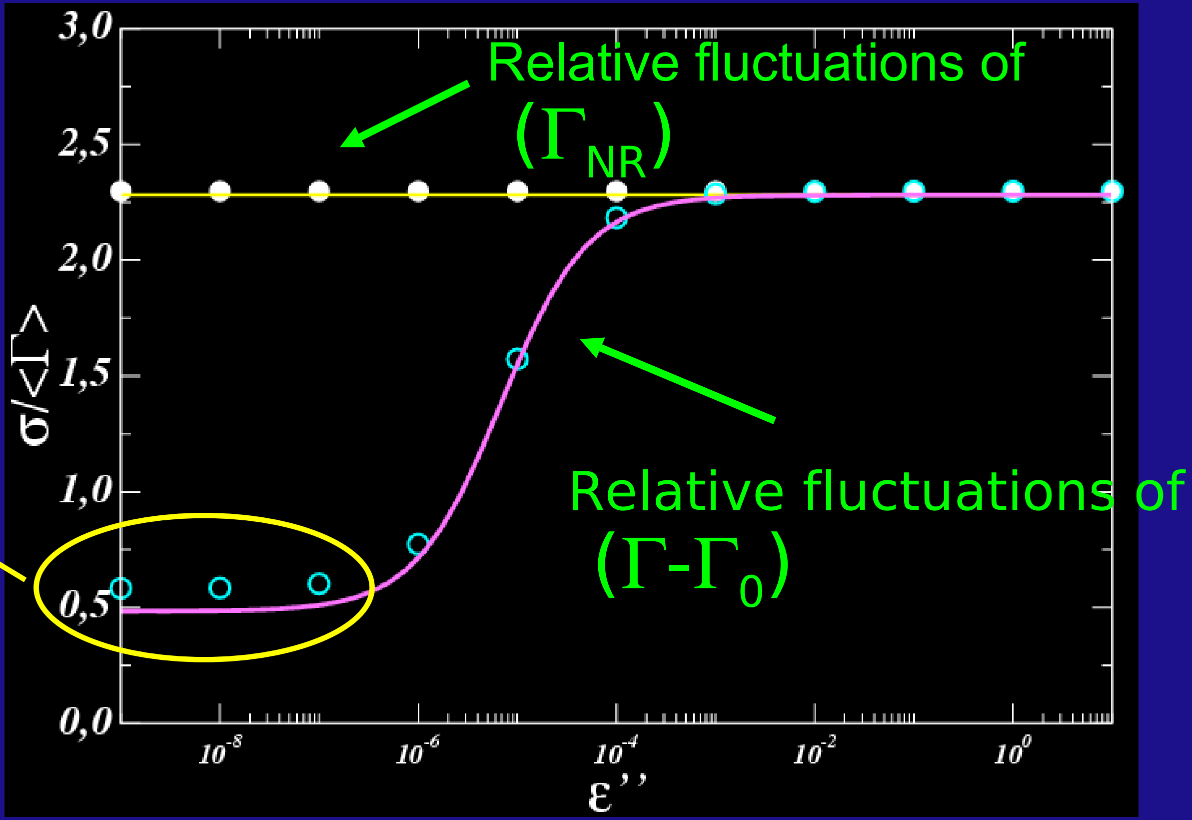
can be explicitly obtained within this model



Fluctuations of decay rates:

can be explicitly obtained within this model

Dominated by scattering in the near field



Fluctuations of decay rates:

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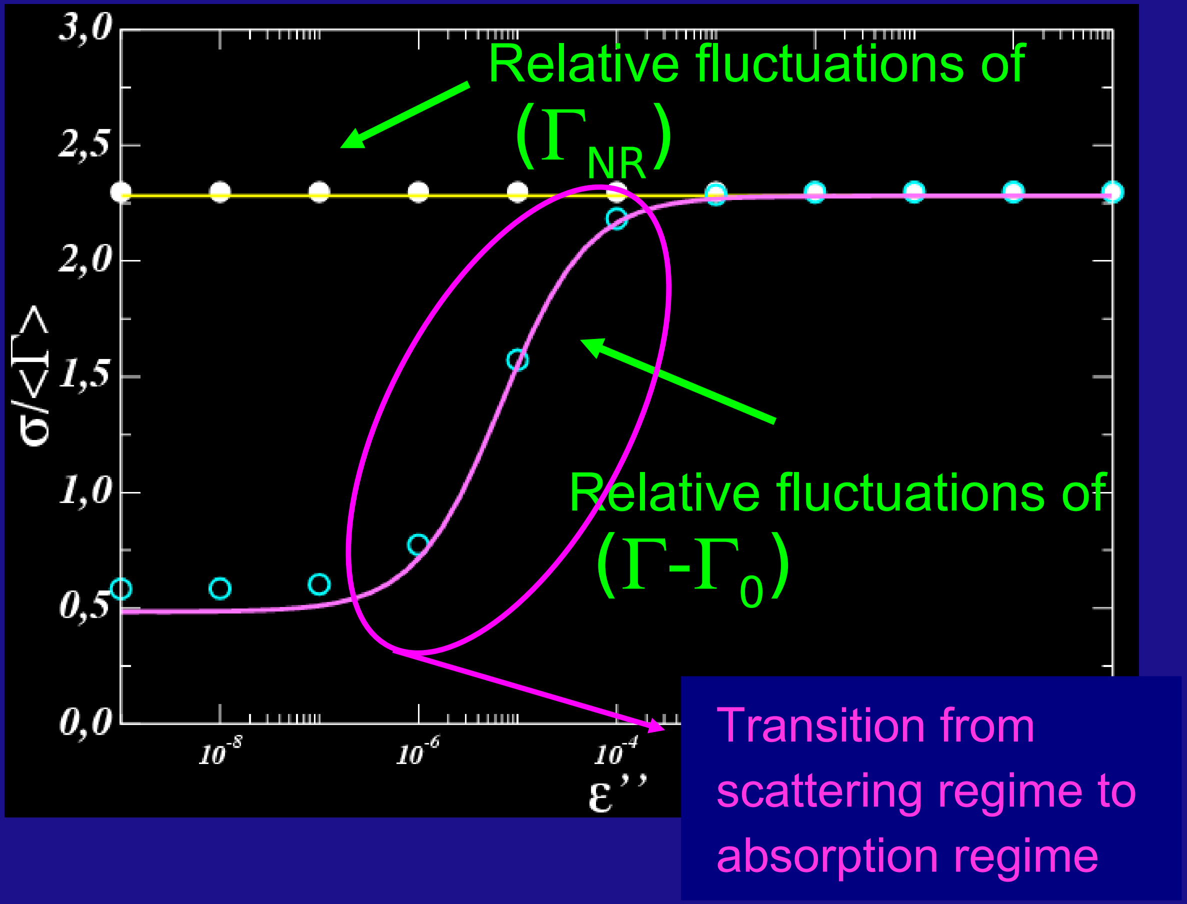
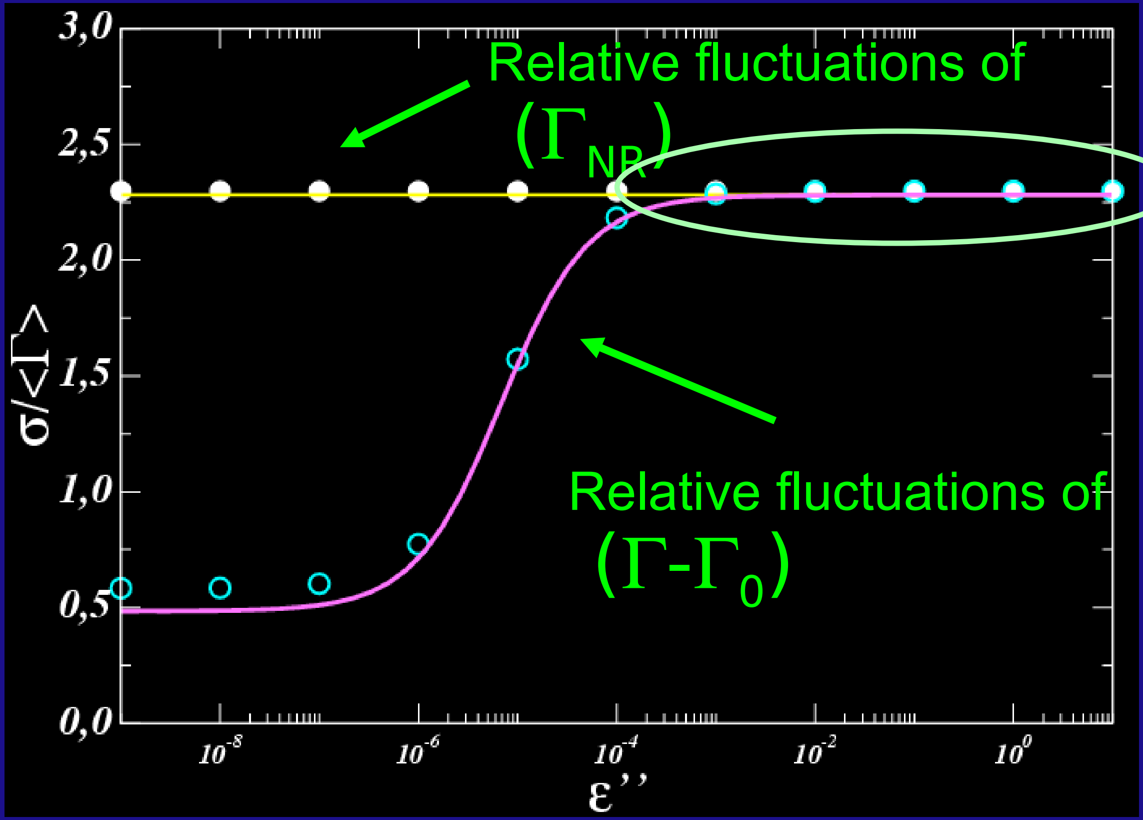


Fluctuations of decay rates:

can be explicitly obtained within this model

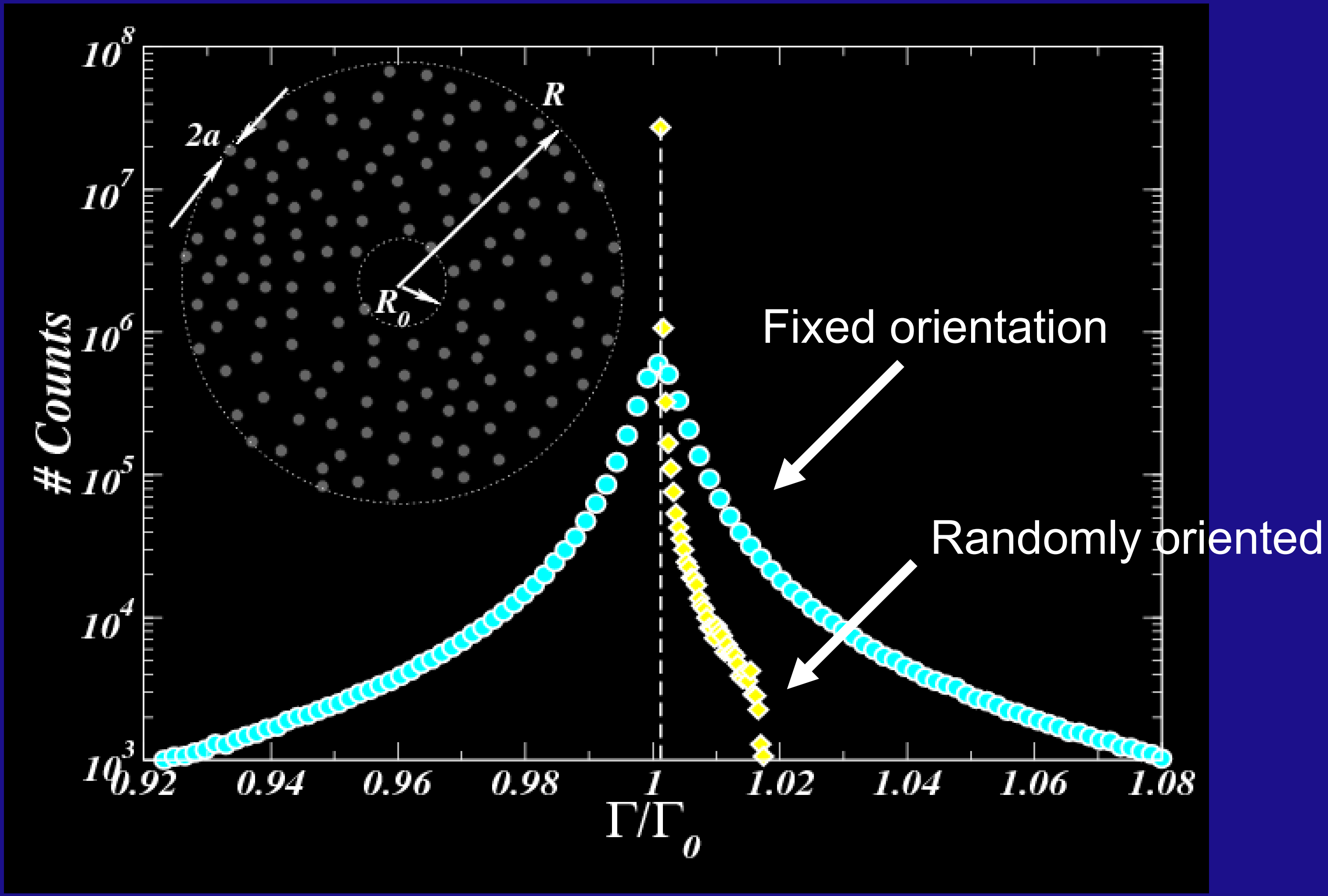


Dominated by Non-Radiative coupling

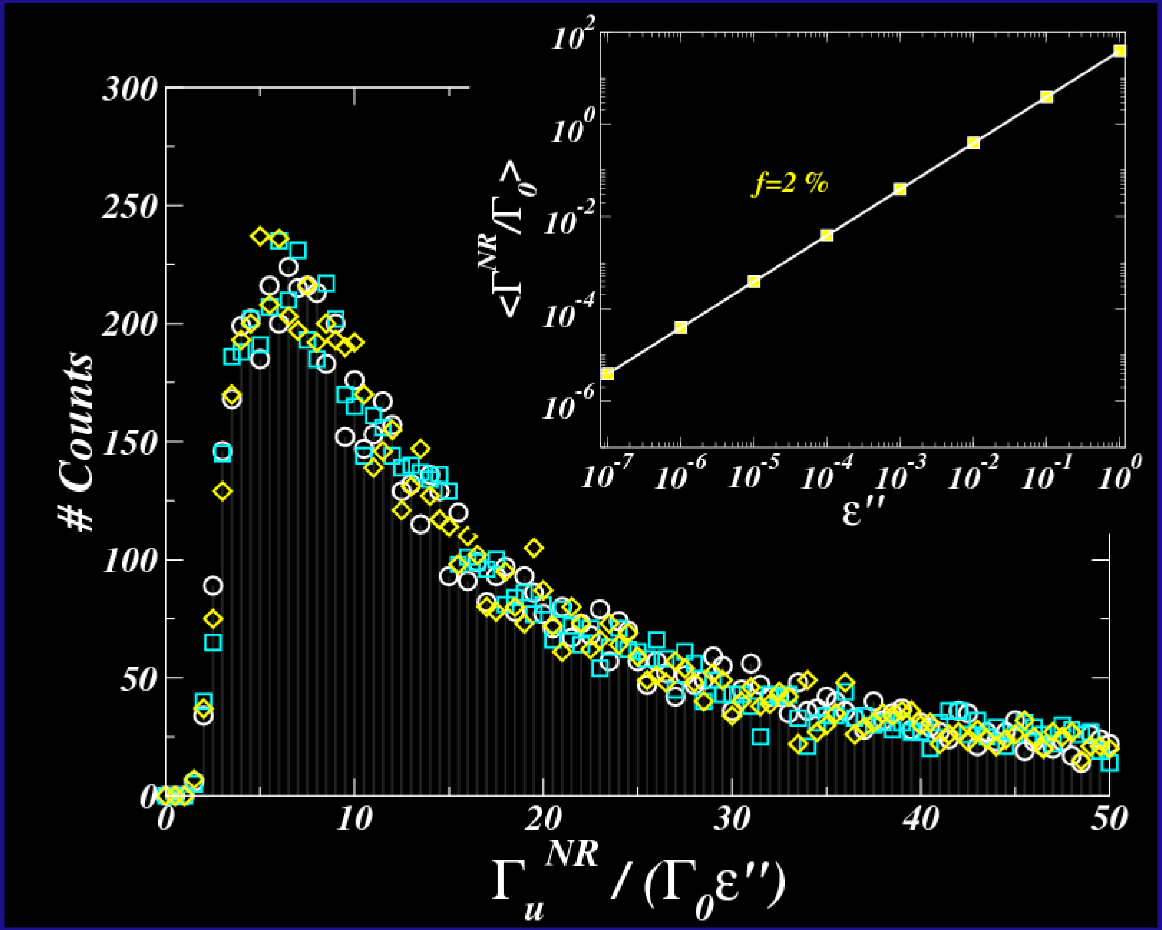
$$\sigma\left(\Gamma-\Gamma_0\right)/\left\langle\Gamma-\Gamma_0\right\rangle \simeq \sigma\left(\Gamma^{NR}\right)/\left\langle\Gamma^{NR}\right\rangle \simeq \left(a/R_0\right)^{3/2}\sqrt{3/f}$$

local field effects

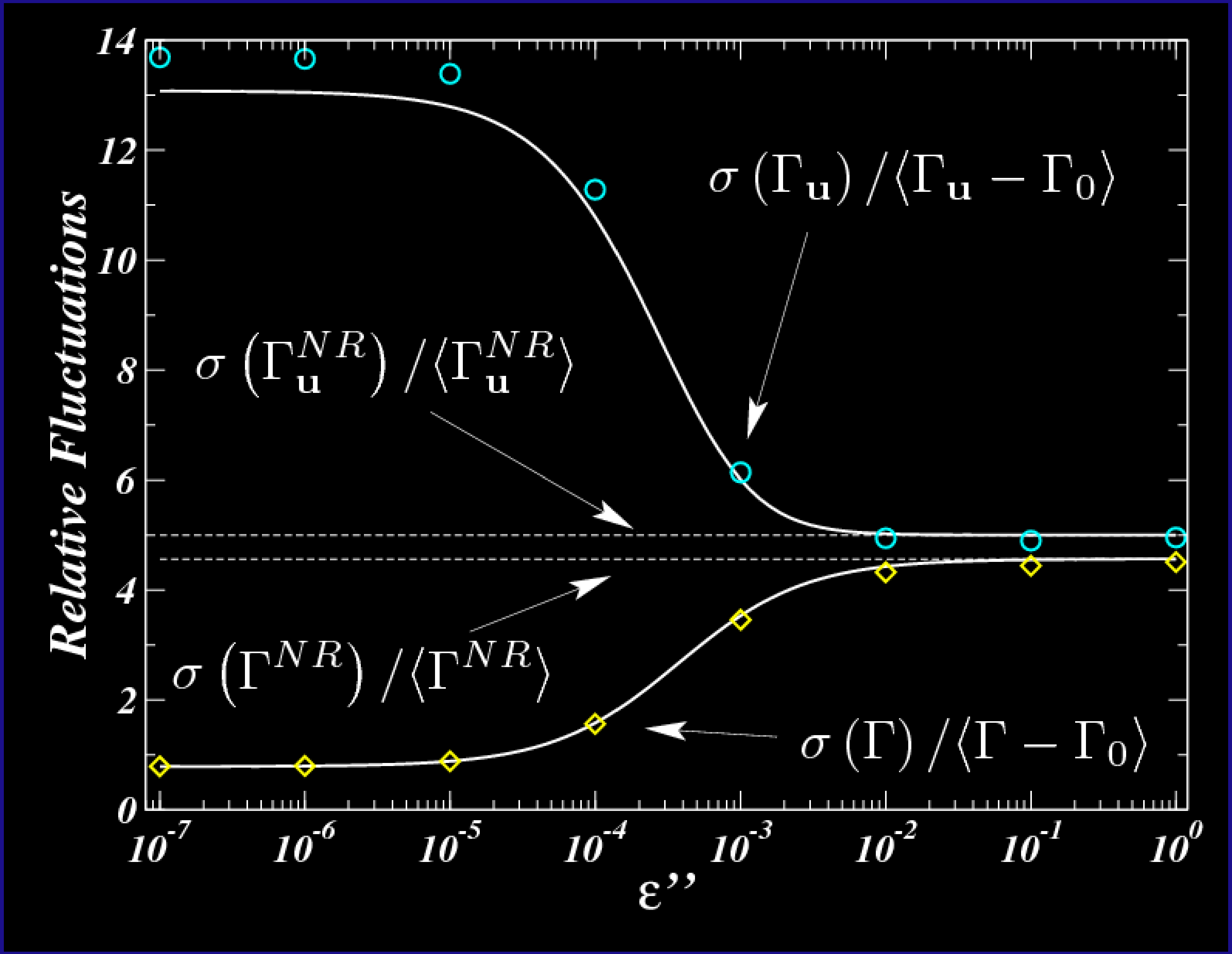
Fixed dipole orientation: statistical distributions



Fixed dipole orientation: non radiative Γ also linear with Im(ε)



Fixed dipole orientation:
Different fluctuations, different behavior



Conclusions

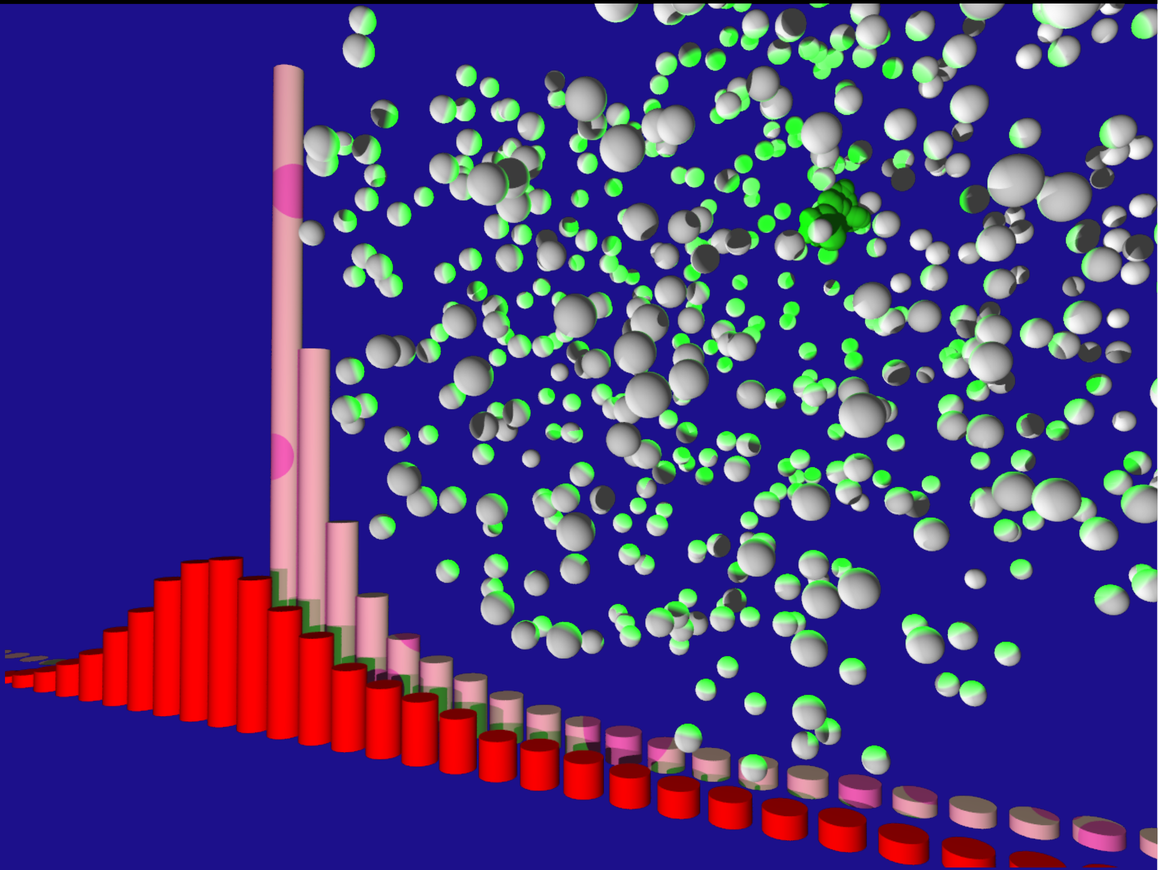
<u>Clusters of small particles</u>

✓Extensive statistical numerical study.
✓Simple analytical expressions for small clusters
✓Role of near-field scattering.
✓Role Non-Radiative coupling.
✓Strong dependence on the statistics of the orientation of the emitter
✓Strong deppendence on the miscroscopic (subwave-length) environment of the emitter

More Info:

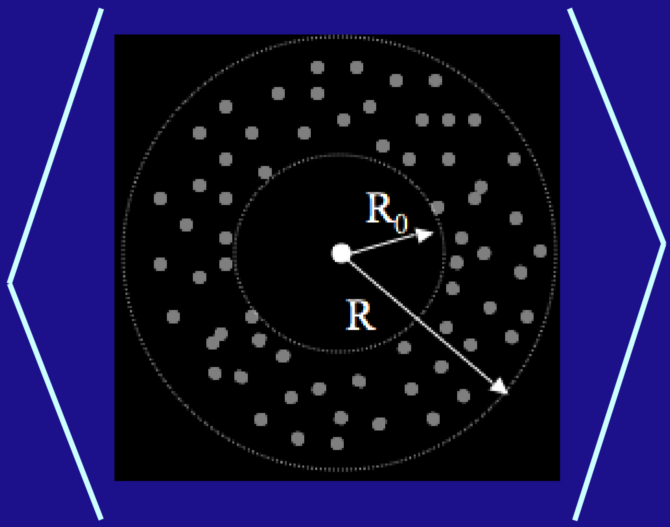
•L. S. Froufe-Pérez, R. Carminati, and J. J. Sáenz
Phys. Rev. A 76, 013835 (2007)
•L. S. Froufe-Pérez and R. Carminati
Phys. Stat. Sol. a, in press (2008)

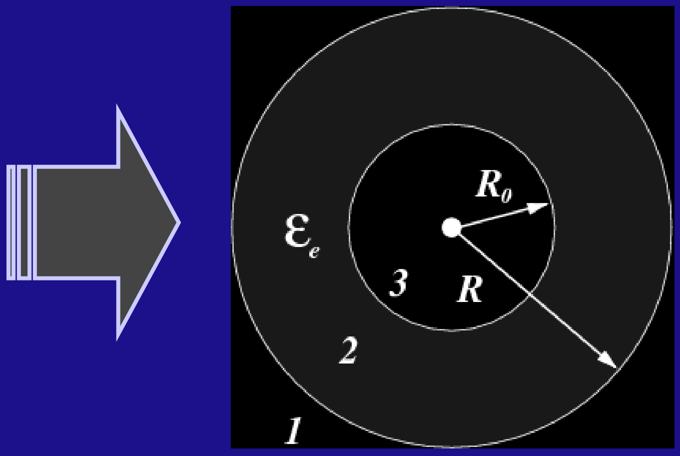
Additional information



Comparison with effective continuous model

Using an **effective dielectric constant**, we compute the decay rate from the Green function for a spherical crust (spherical cavity inside a sphere)





$$\epsilon_{eff} = 1 + \delta\epsilon$$

Maxwell-Garnett: $\delta\epsilon = n\alpha_s$

$$\delta\epsilon \simeq 3f\beta\left(1 + \frac{2}{3}i\,(ka)^3\,\beta^*\right)$$

See for instance P. Mallet, C.A. Guérin and A. Sentenac, PRB **72**, 014205 (2005)

Comparison with effective continuous model

Total decay rate

We obtain the same expression as the one given by the statistical model.

$$\frac{\Gamma - \Gamma_0}{\Gamma_0} = \frac{11}{5} f \Re(\beta) (kR)^2 + 2f |\beta|^2 \left(\frac{a}{R_0}\right)^3 + 3f \Im(\beta) \frac{1}{(kR_0)^3}$$

Averaged radiated field

Fluctuations of the radiated field

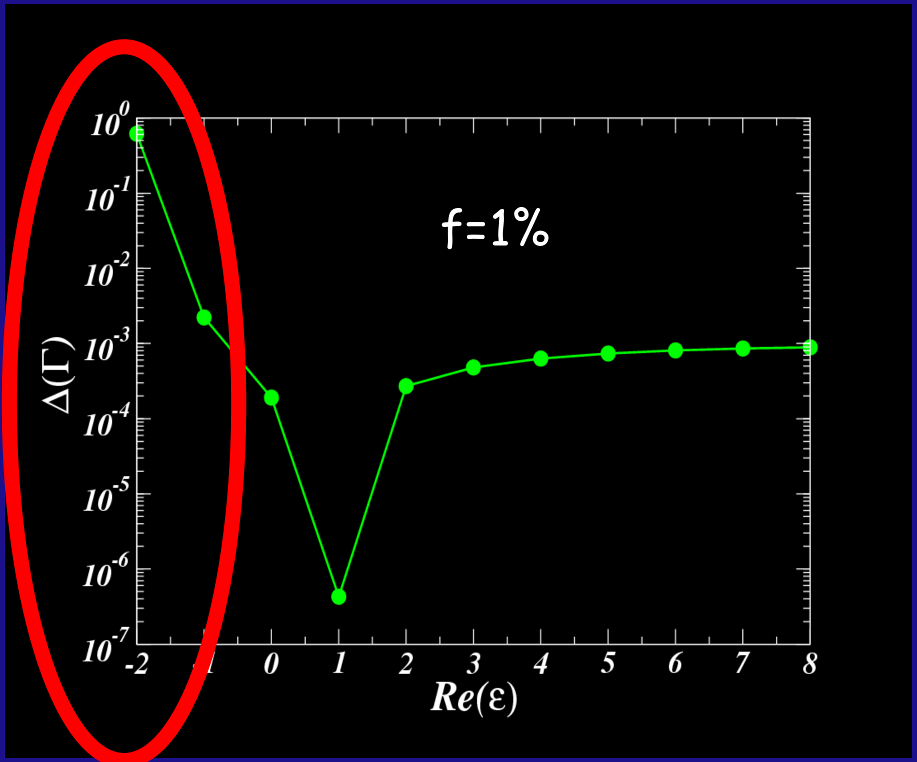
Absorption

Single Scattering statistical model

Instead of solving the exact problem, we can use a **single scattering** approach:
The field exciting any dipole only comes from the source.

- Small polarizability.
- Low filling fraction.

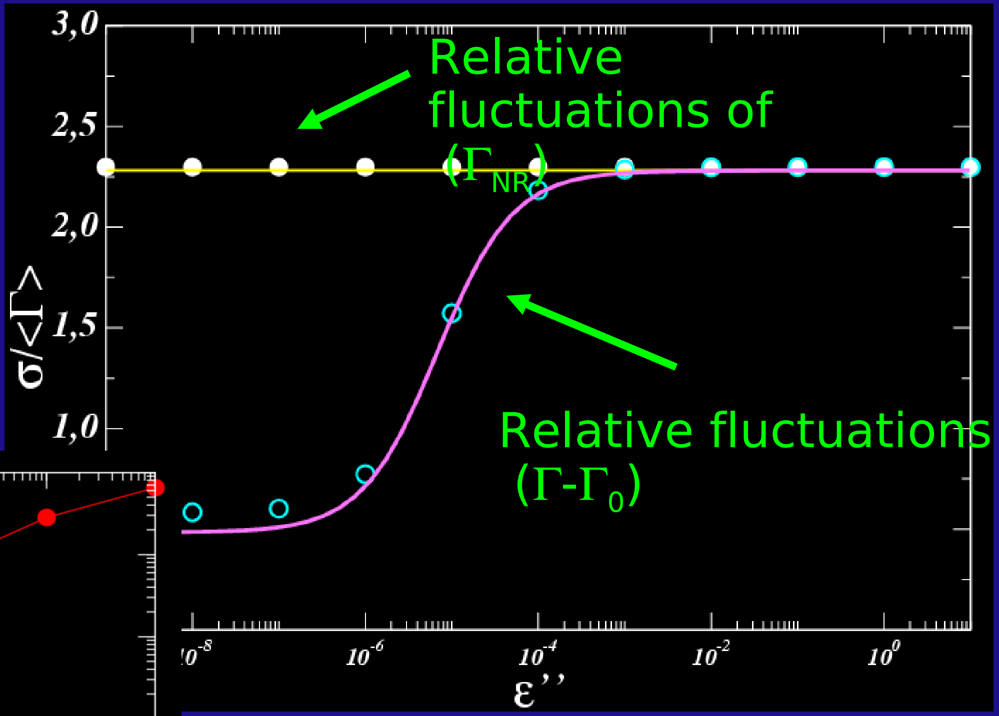
Close to the resonance, the polarizability is large. **The single scattering approach fails**

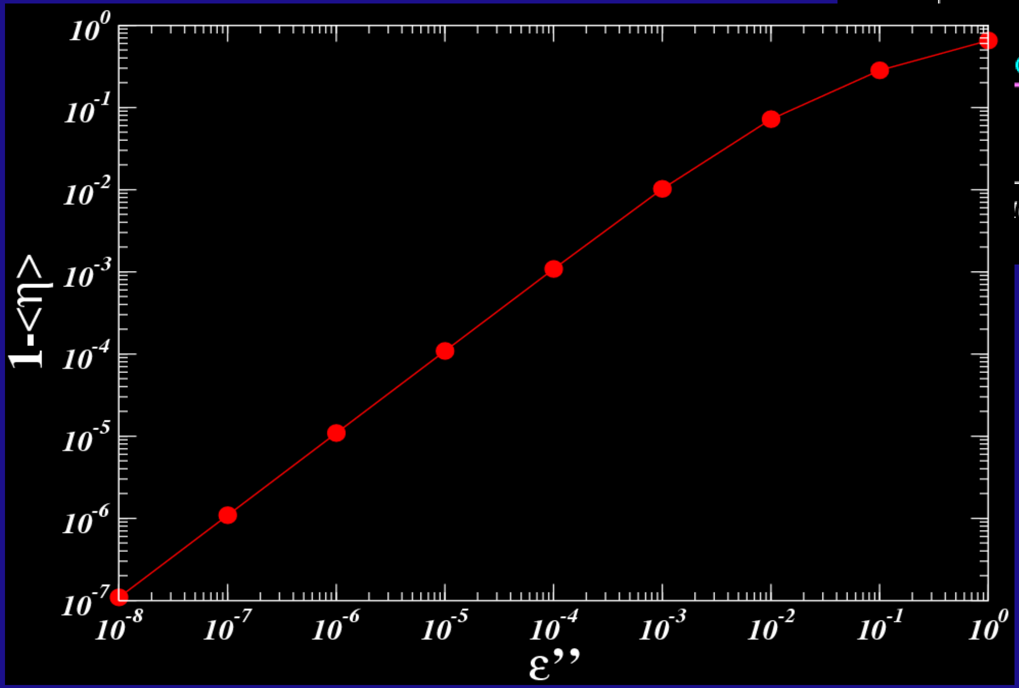


valid for clusters of nanoparticles

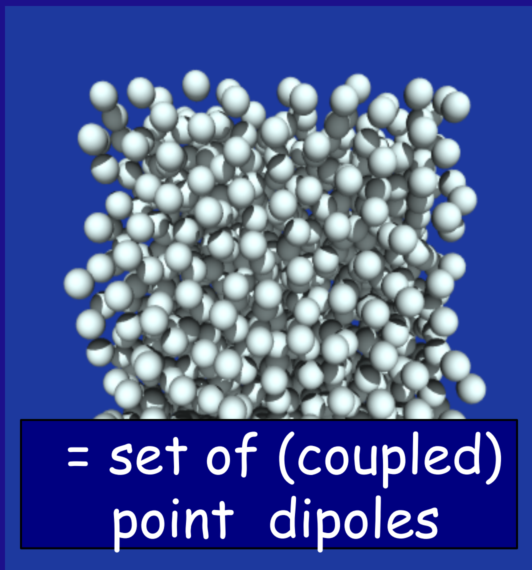
Averaged Quantum Yield

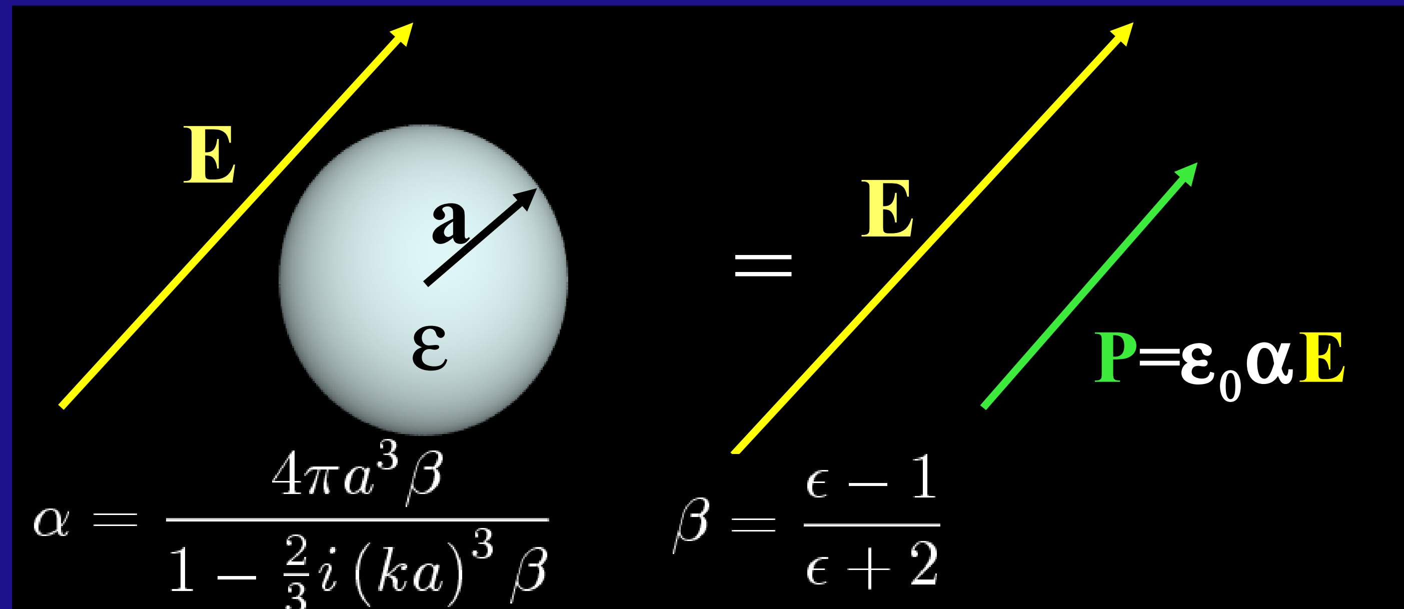
Even in the absorption regime, averaged quantum yield is high enough to obtain a measurable signal





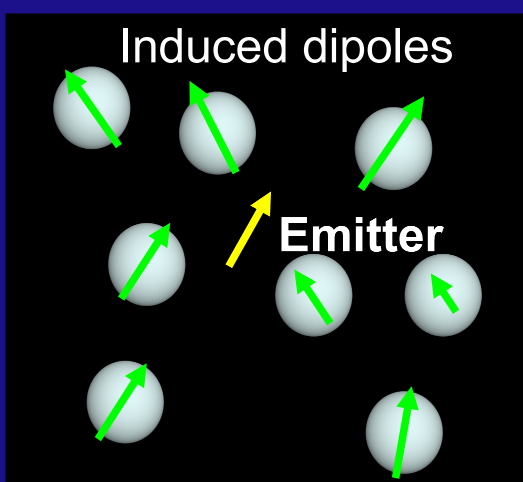
One approach to the problem: Coupled dipole model





$$\alpha = \frac{4\pi a^3 \beta}{1 - \frac{2}{3} i \left(ka\right)^3 \beta} \qquad \beta = \frac{\epsilon - 1}{\epsilon + 2}$$

$$P = \varepsilon_0 \alpha E$$



The exciting field of each dipole is created by the source and the remaining dipoles.

Coupled dipole system... Once solved:

The Green tensor of the system is obtained **exactly**