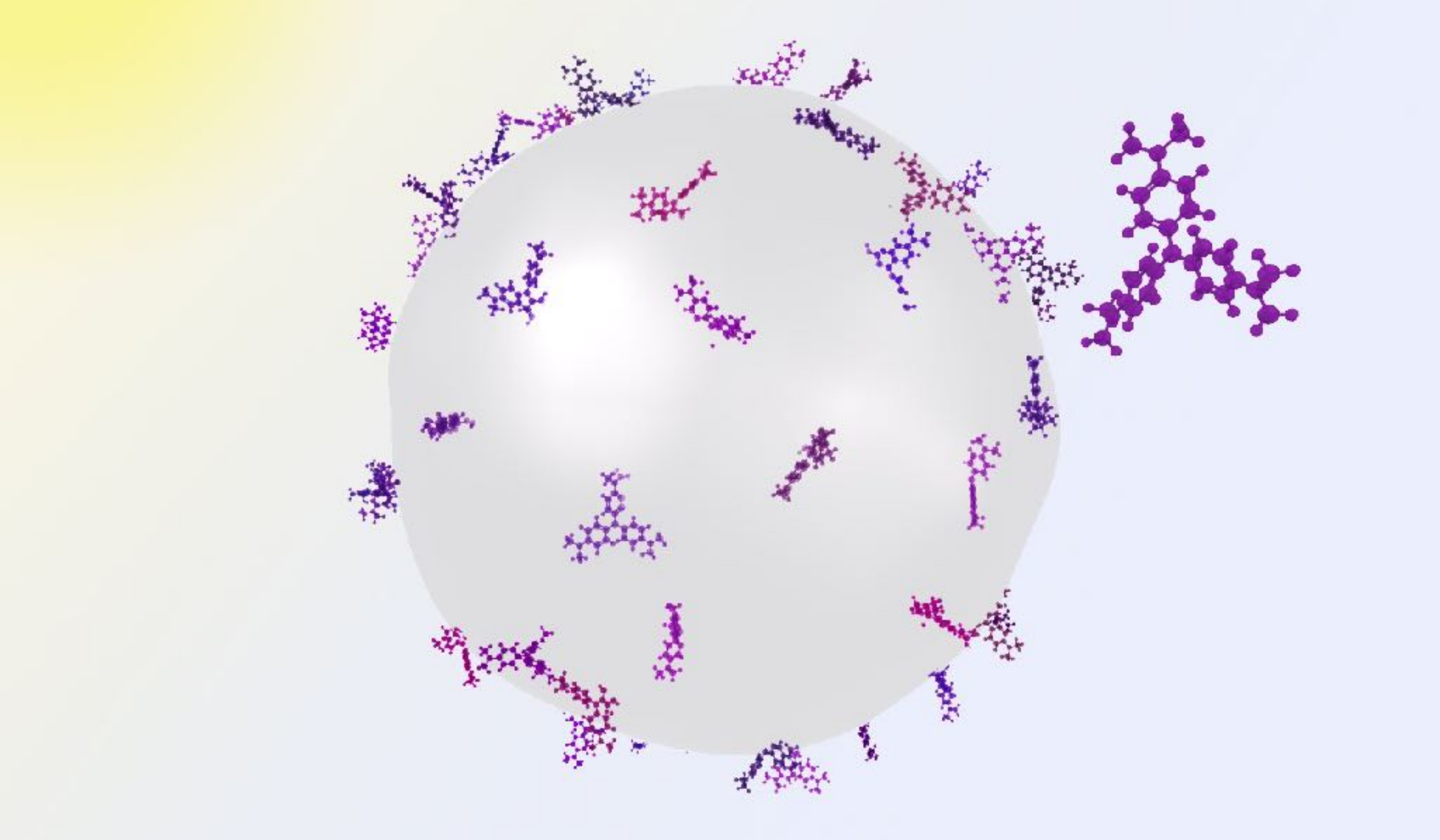
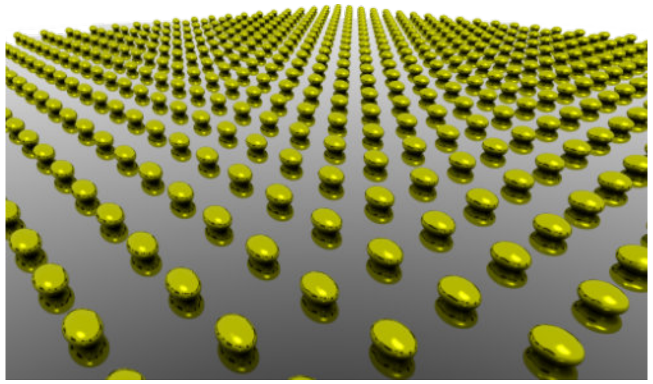


Coupled dipole simulations of light scattering by molecules & nanoparticles

Baptiste Auguié, Eric Le Ru
Victoria University of Wellington, NZ
Thanks: Brendan Darby, Matthias Meyer

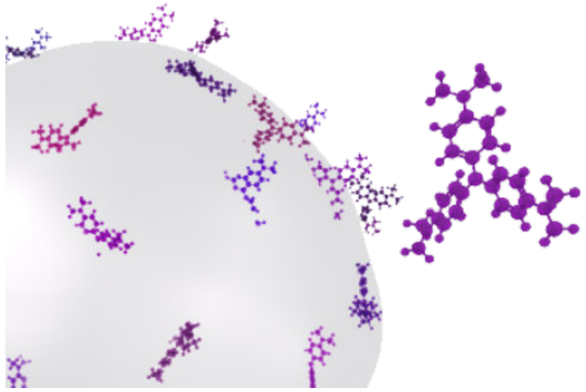
Coupled dipoles in nano-optics: selected topics

Particle arrays

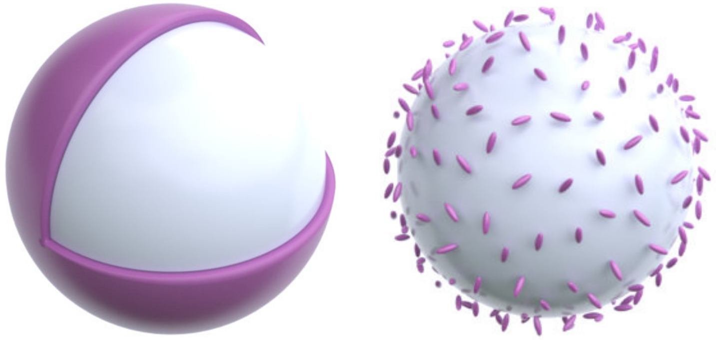


Chiral nano-clusters

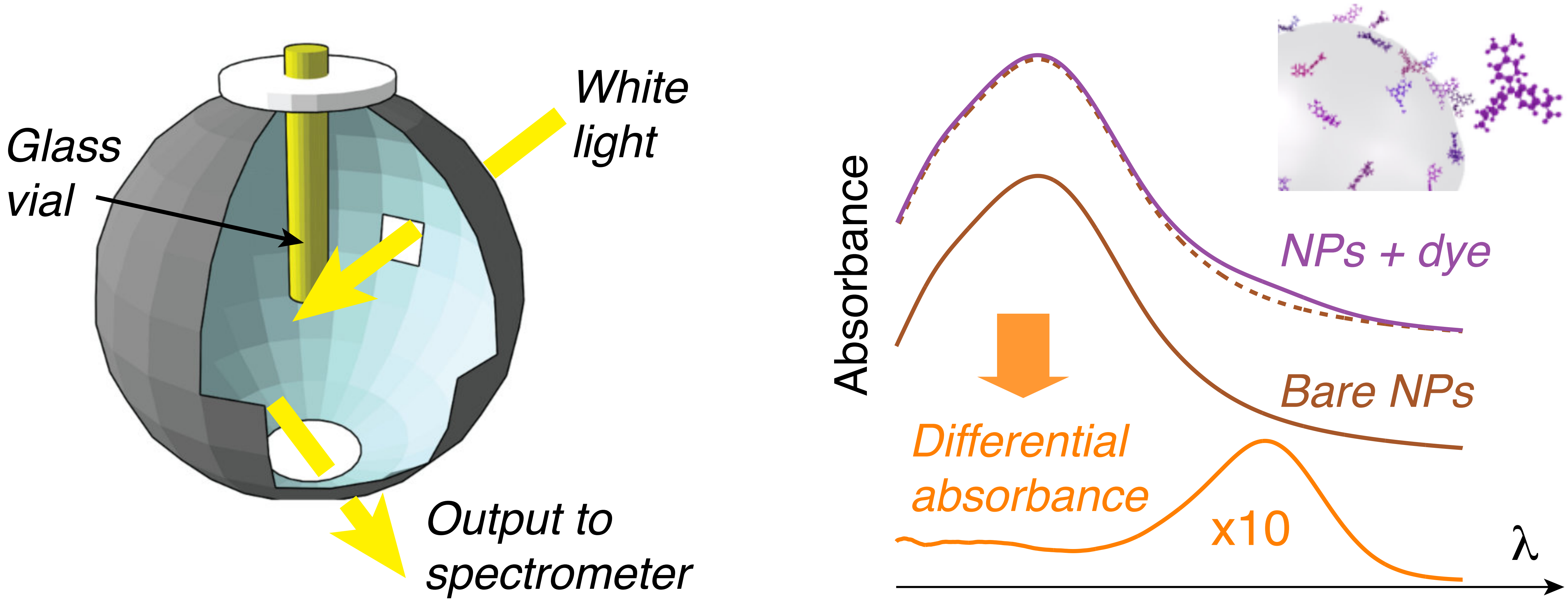
Molecules on colloids



Core-shells of interacting dyes

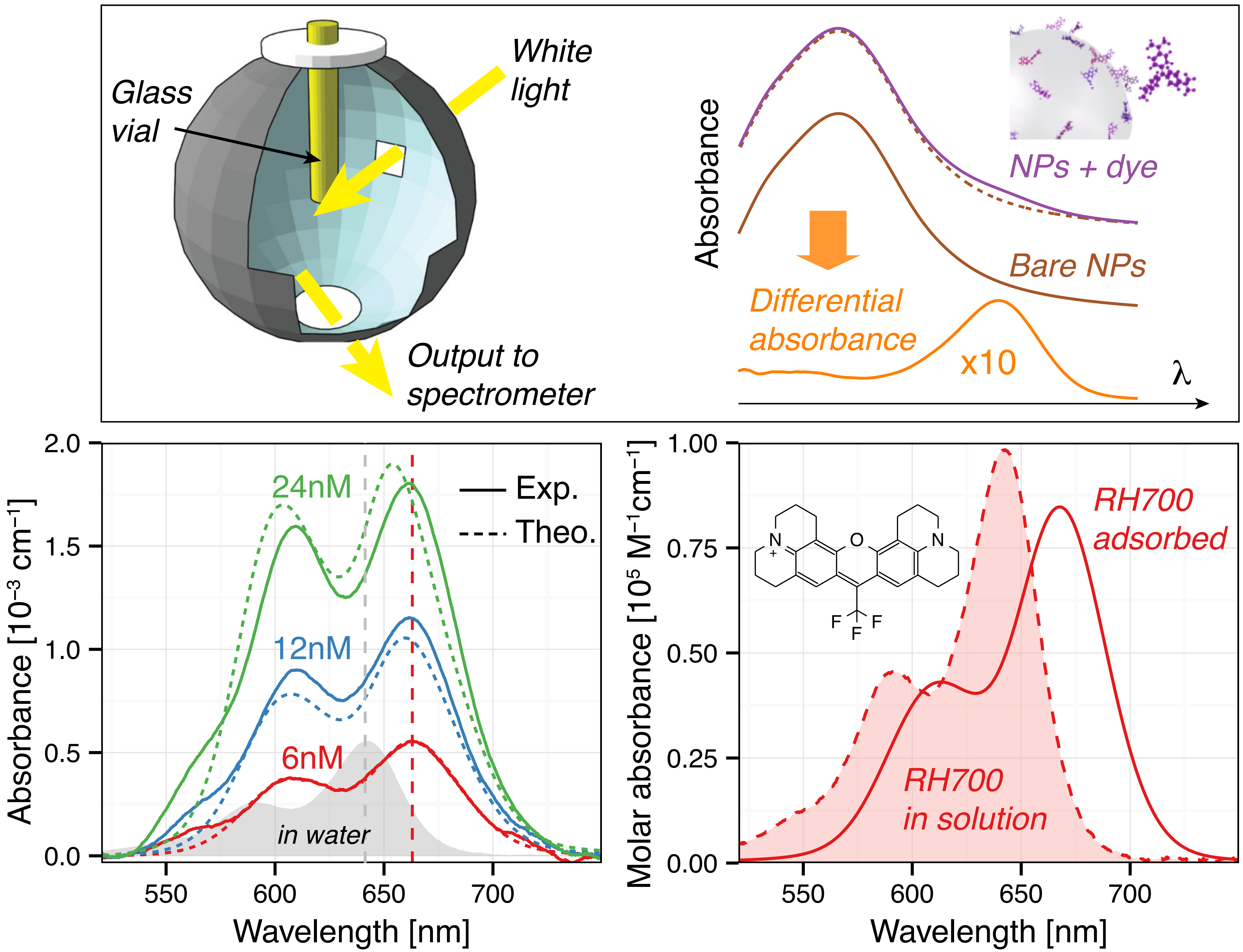


Integrating sphere for absorption measurements

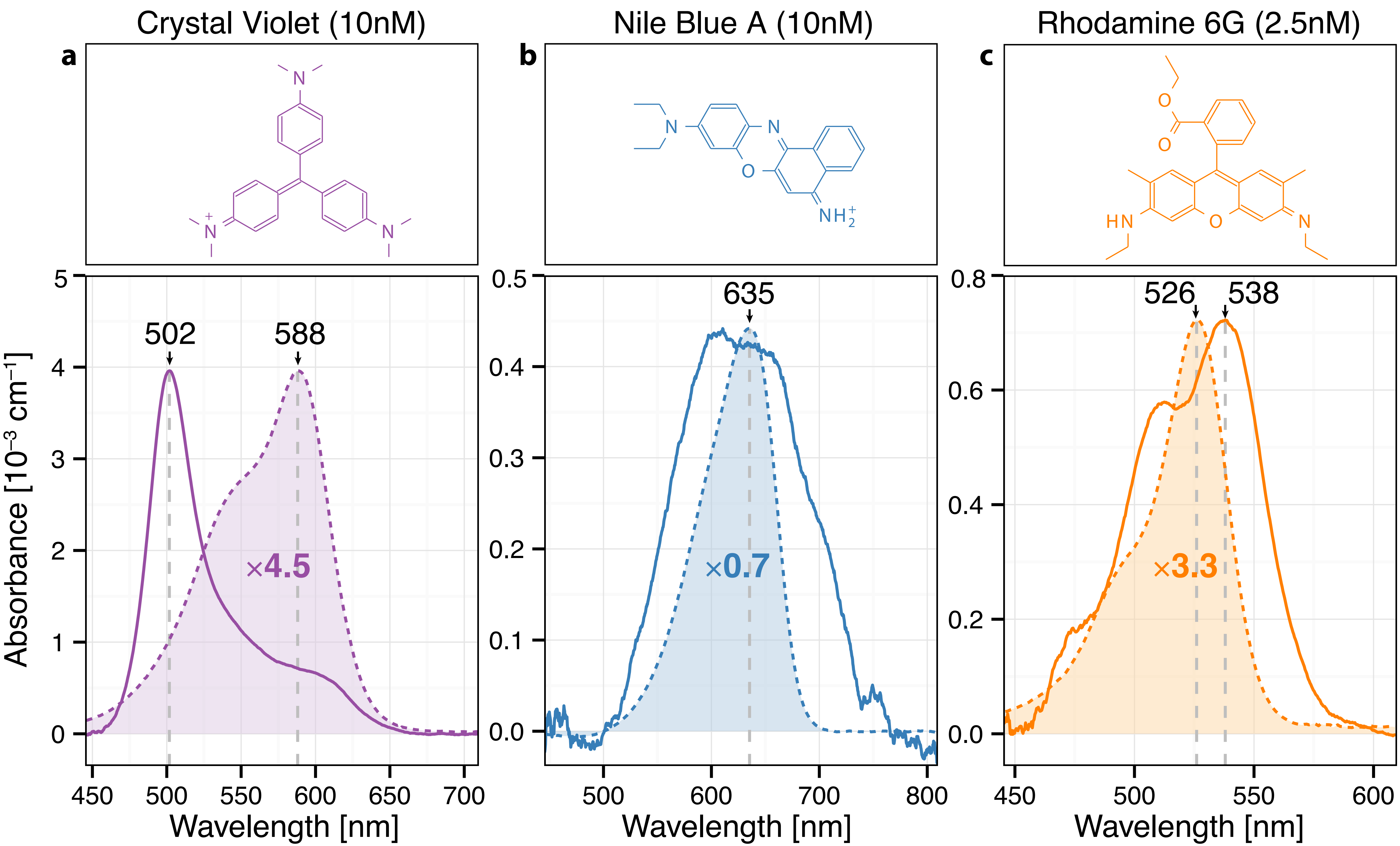


B. L. Darby, B. Auguié, M. Meyer, A. E. Pantoja, and E. C. Le Ru
Nat. Photonics **10**.1 (2016), pp. 40–45

ABSORPTION OF DYES ON METAL COLLOIDS



DIFFERENT MOLECULES



What we want to know

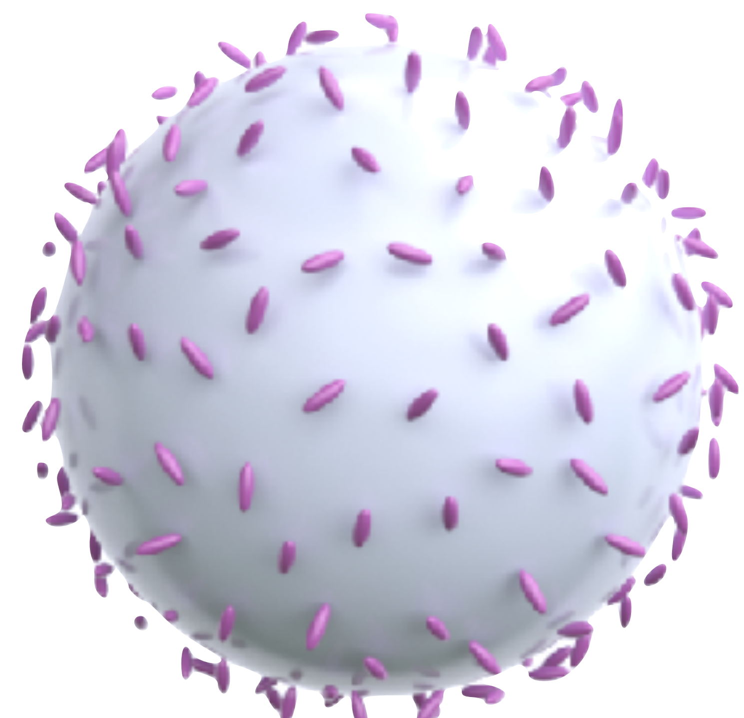
- "Chemical enhancement" / EM ("image dipole") effect?
- Implications for Raman and fluorescence
- What concentration is low enough to avoid interactions?
- Surface dimerisation?
- Orientation effects

(Naïve) effective-medium shell model

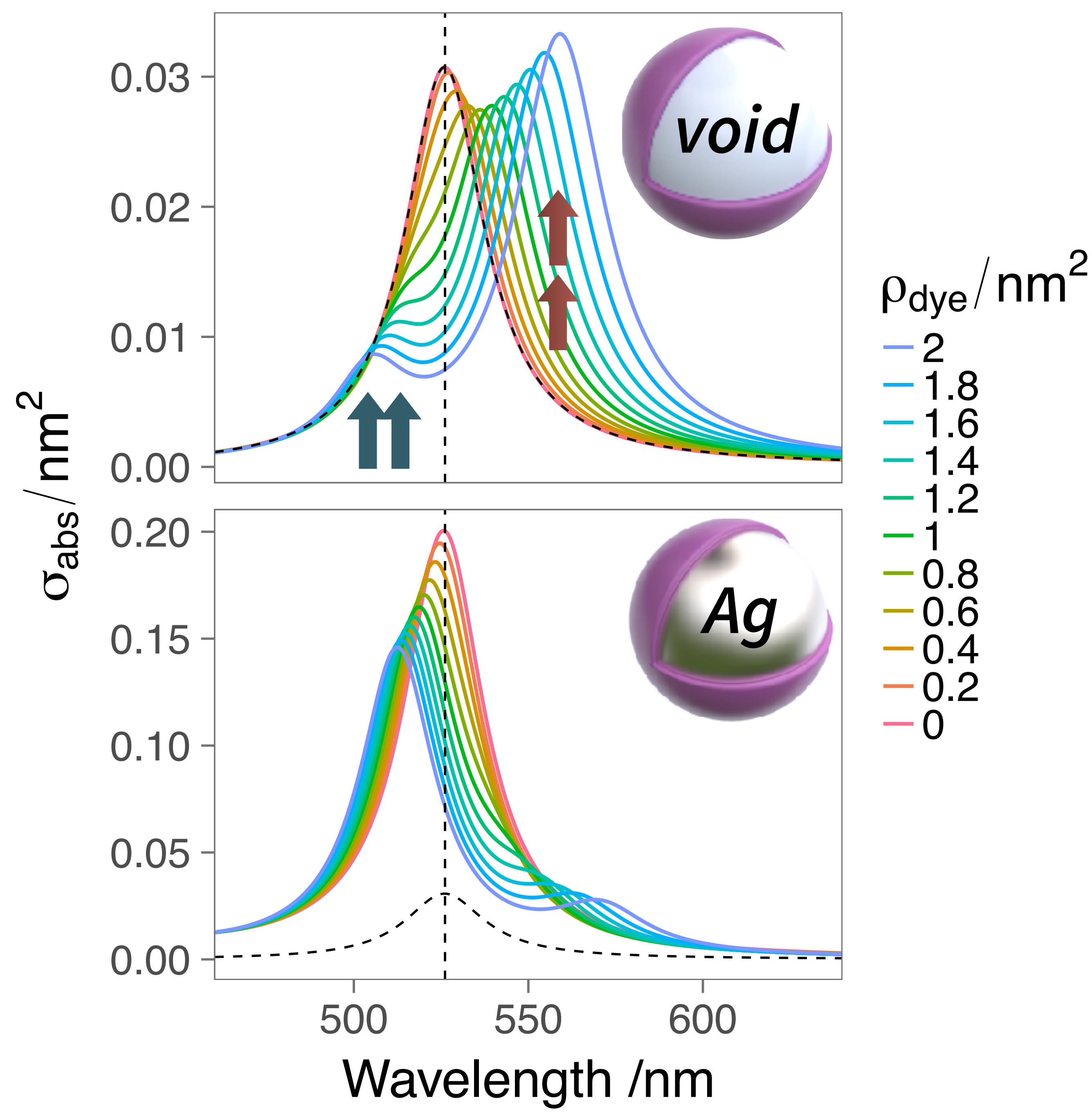
- Clausius–Mossotti $\alpha \rightsquigarrow \varepsilon$
- Concentration dependence
- Local field enhancement

Challenges & limitations

- CM for bulk, not for 2D shell…
- Anisotropy, orientation
- Inhomogeneities
  (~*100 dyes/colloid @1nM*)
- Dipole image?

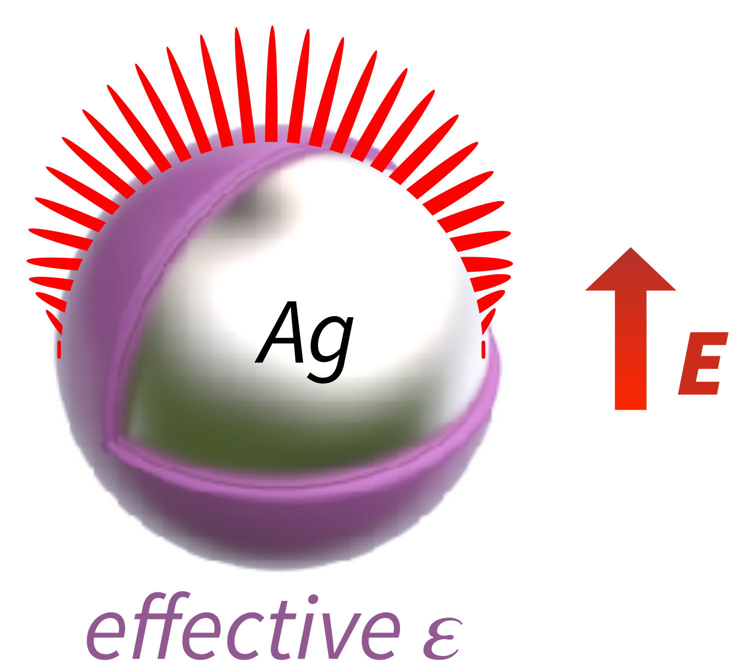


(Naïve) effective-medium shell model



First insights:

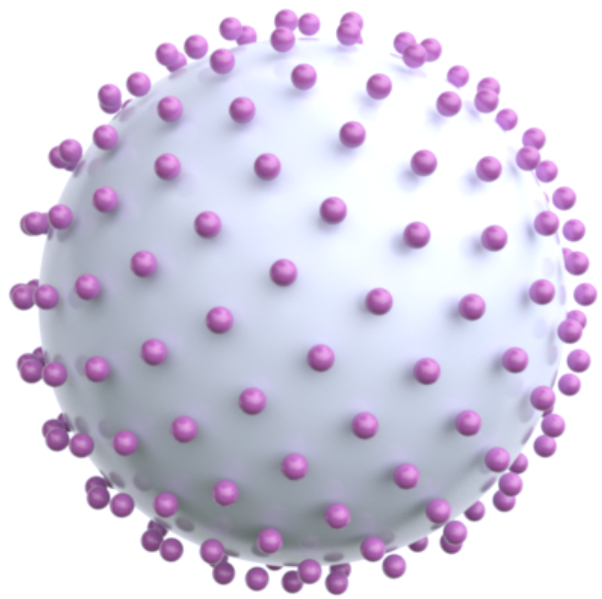
- Shifts & splitting
- Local field: *enhancement or "quenching"*



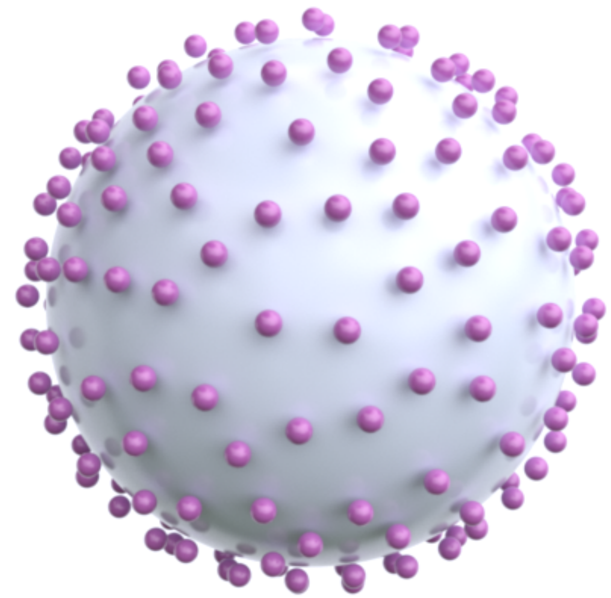
BEYOND HOMOGENEOUS ISOTROPIC SHELLS

- Position

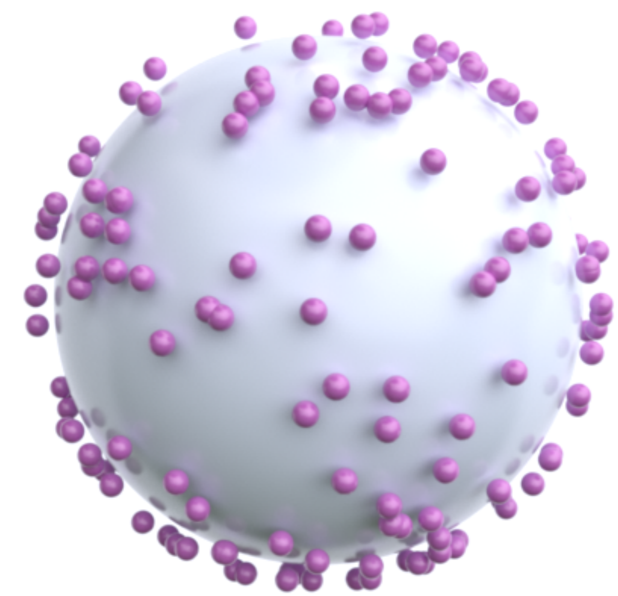
homogeneous



exclusion distance

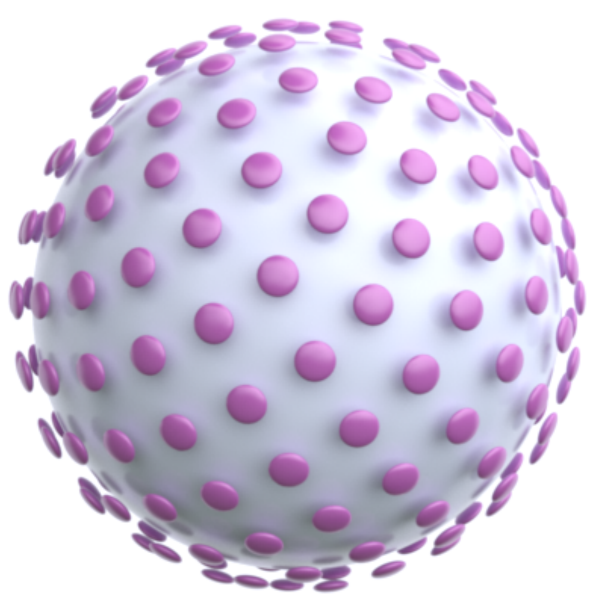


random

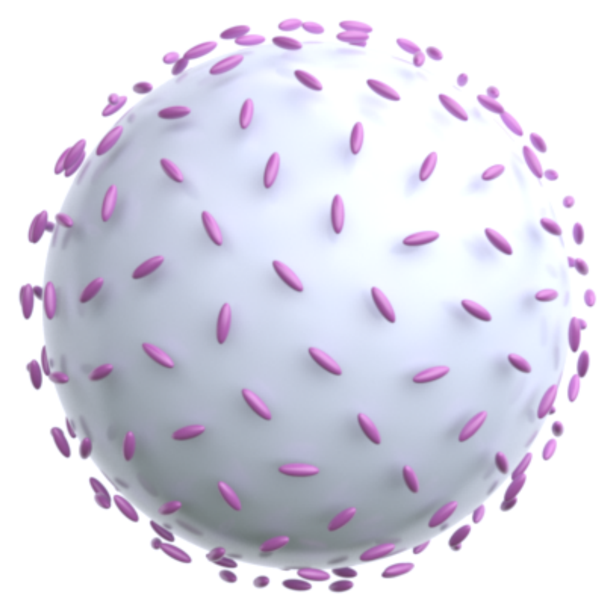


- Orientation

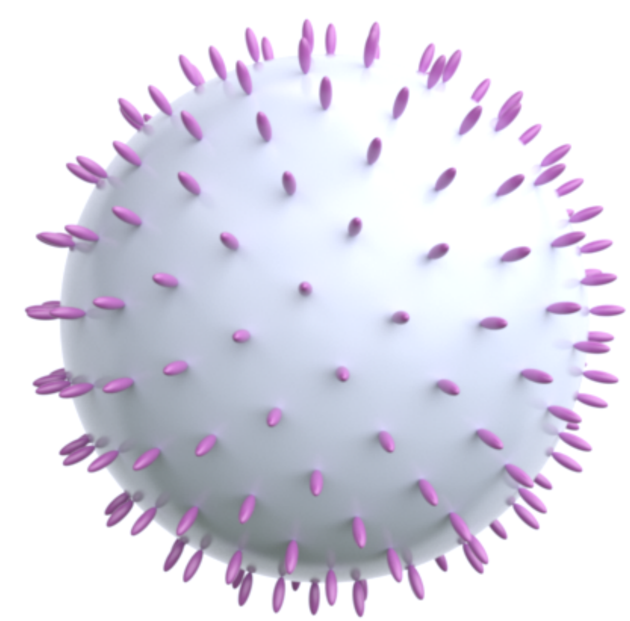
average flat



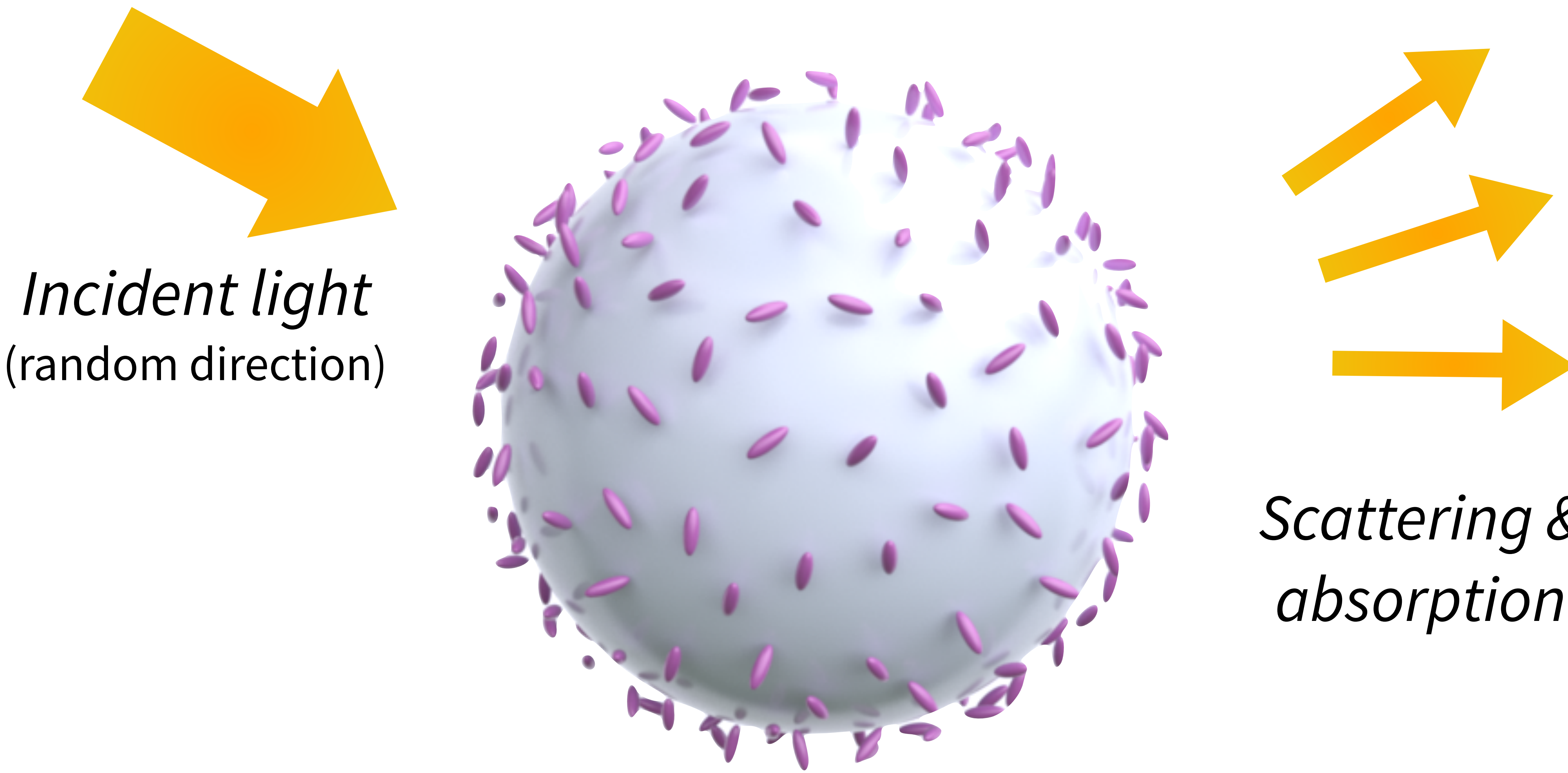
random flat



radial

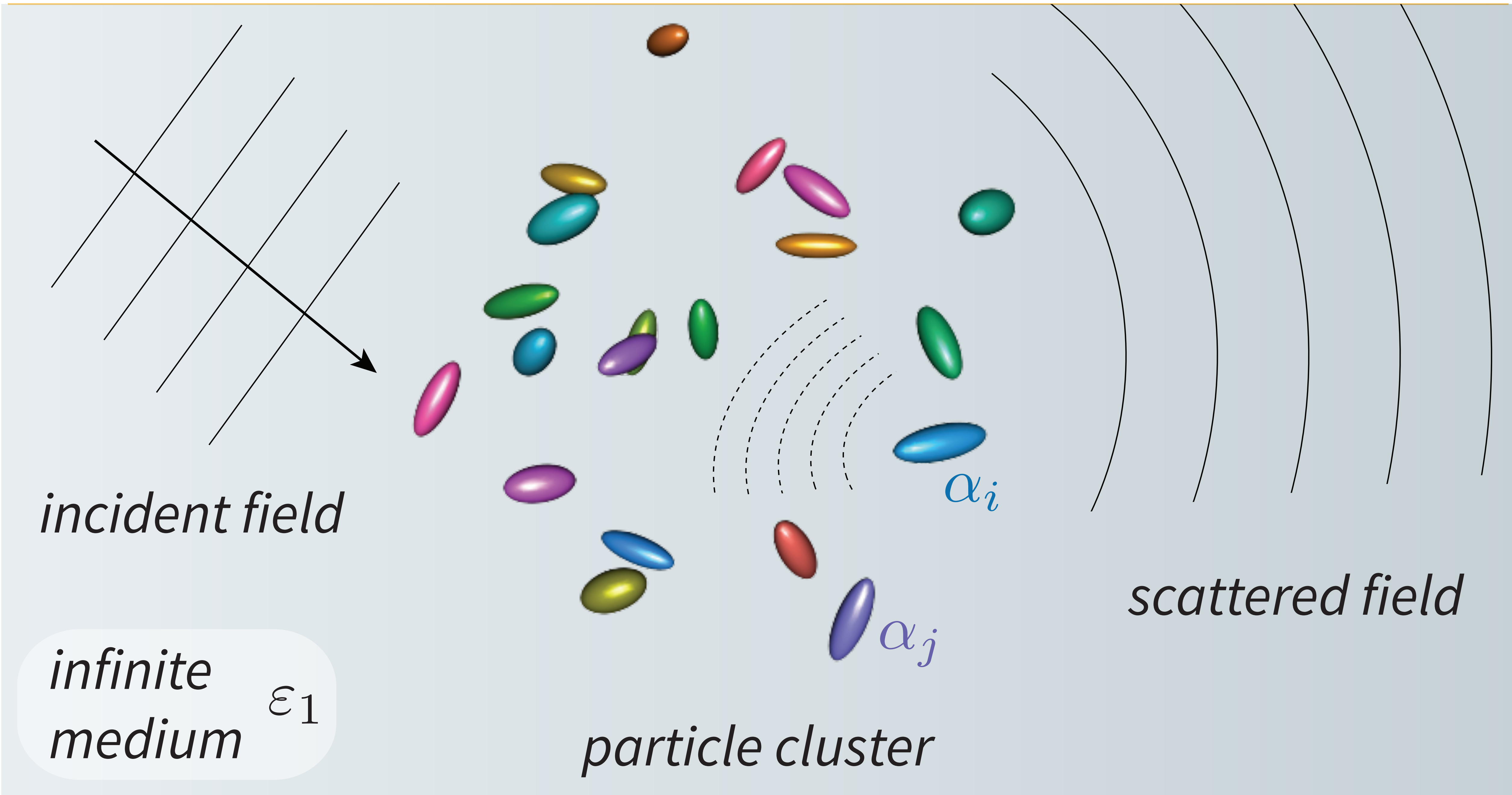


LIGHT SCATTERING PROBLEM



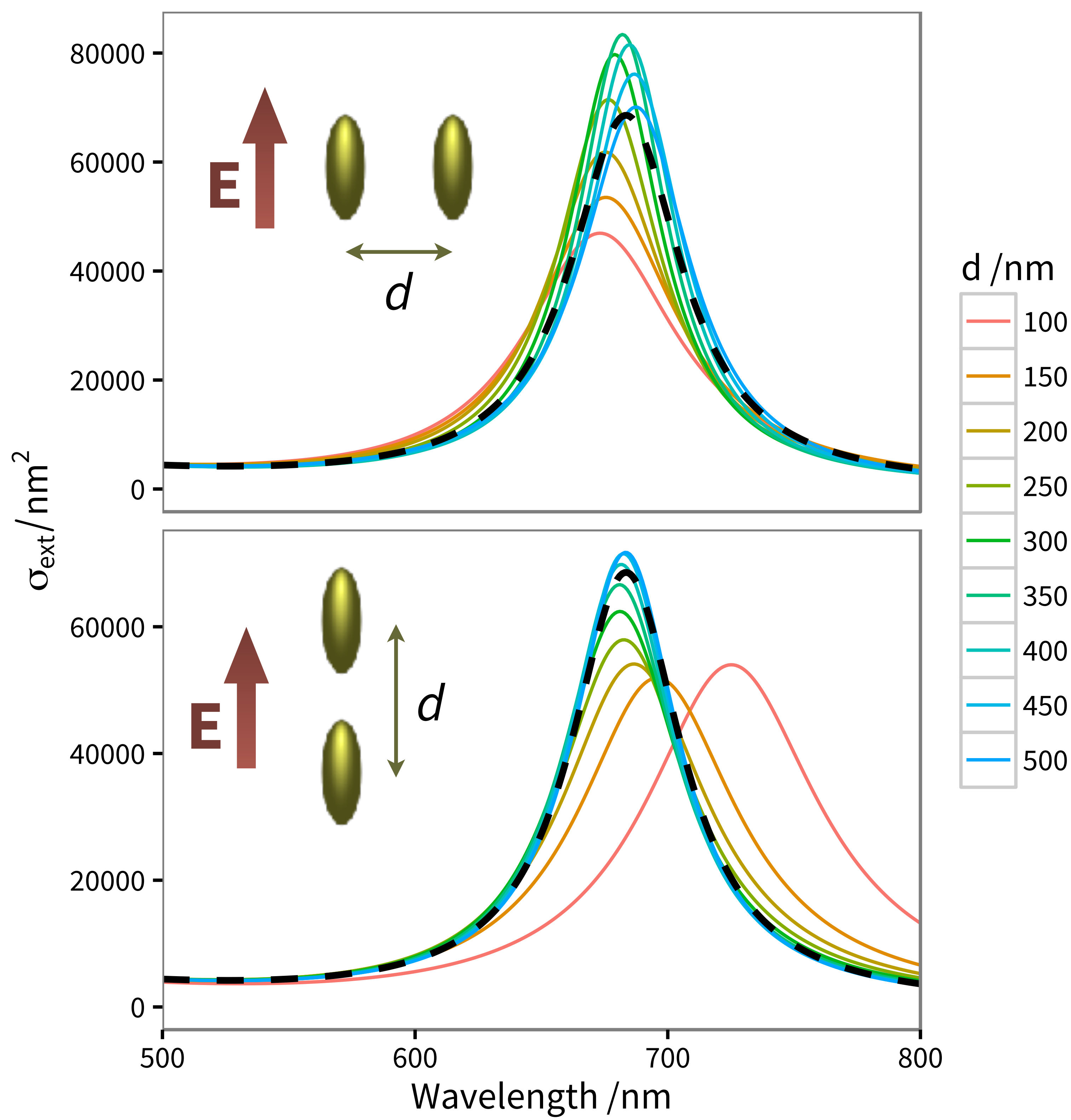
dipole-dipole and dipole-sphere interactions

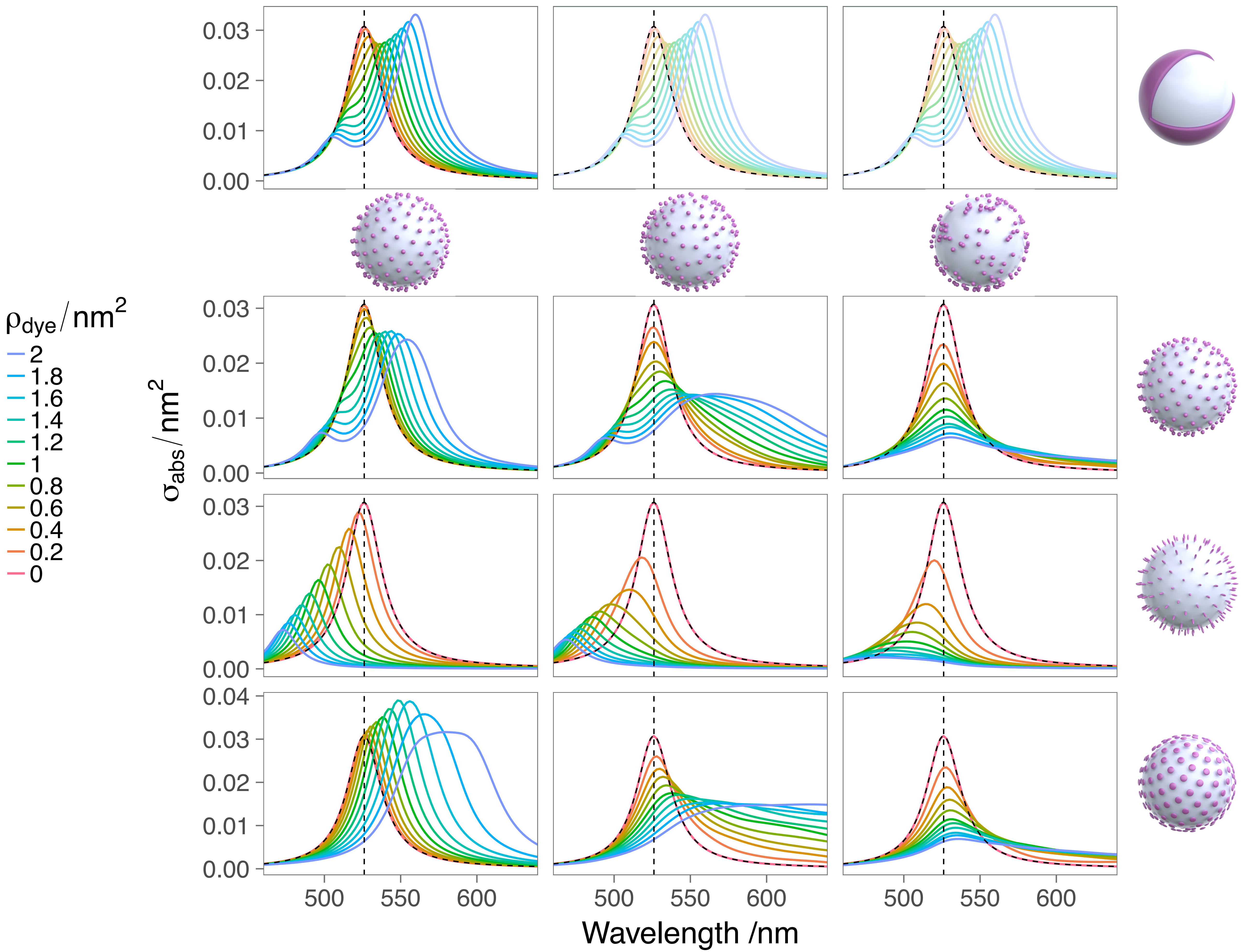
COUPLED DIPOLE EQUATIONS (NO SPHERE)



$$\mathbf{E}^i = \mathbf{E}^i_{\text{inc}} + \sum_{j\neq i} \mathbb{G}_{ij}\alpha_j \mathbf{E}^j$$

EXAMPLE • PLASMON HYBRIDISATION





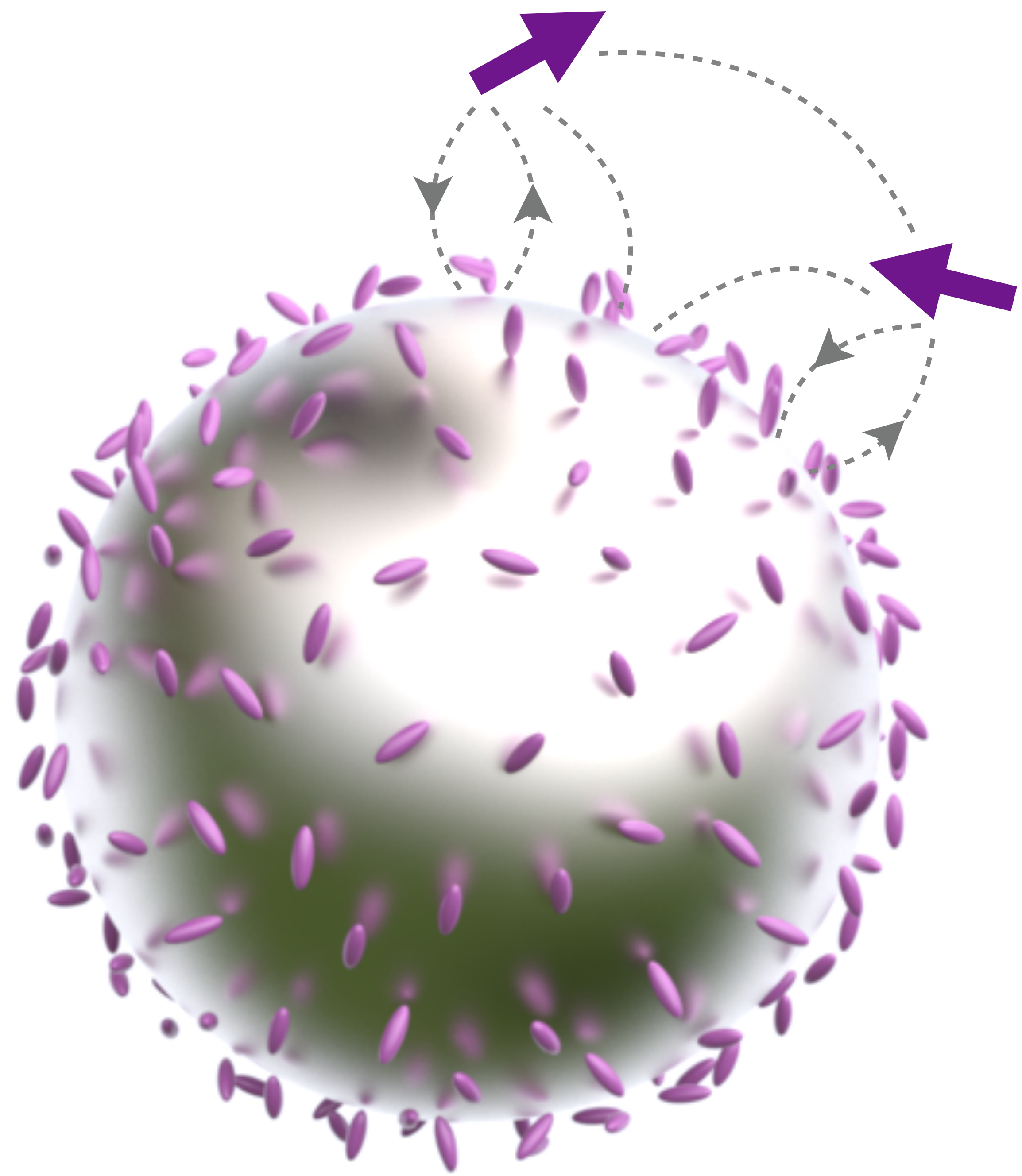
ρ_{dye}/nm^2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
σ_{abs}/nm^2
0.00
0.01
0.02
0.03
0.04
500
550
600
Wavelength /nm

Dipole–sphere interaction

- Sphere-mediated coupling
- Self-reaction (“image” dipole)
- Additional excitation from sphere-scattered field

Challenges:

- Slow convergence of series*
- Easier when source along z-axis:
  ➡ *many rotations!*



* M. Majić, B. Auguié, E. Le Ru • Phys. Rev. E **95**, 033307 (2017)

INTERLUDE: HYBRID COUPLED-DIPOLE – MIE THEORY

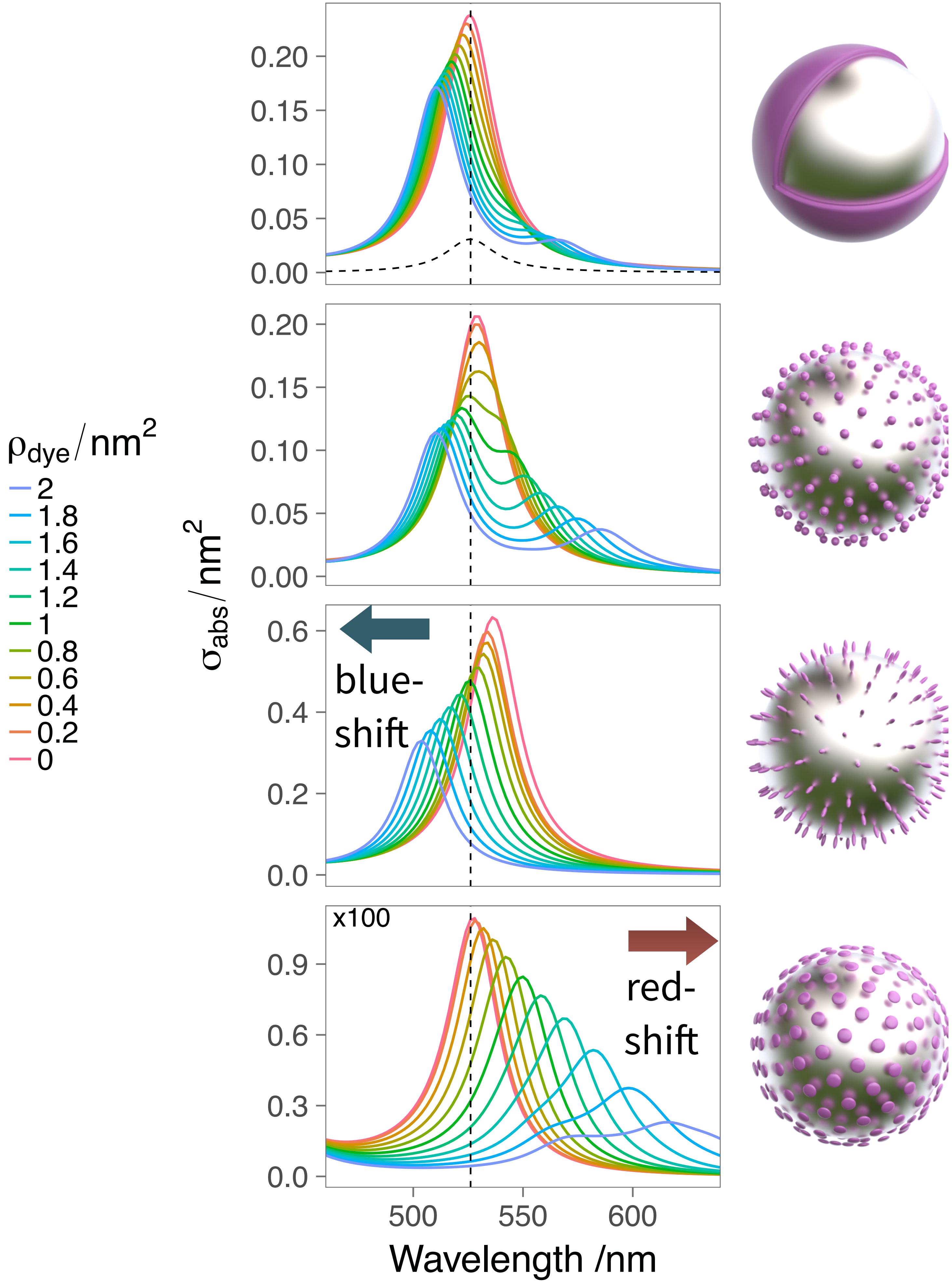
- Extended coupled-dipole system

$$\mathbf{E}^i = \mathbf{E}^i_{\text{inc}} + \mathbf{E}^i_{\text{SPH}} + \sum_{j\neq i} \mathbb{G}_{ij}\alpha_j \mathbf{E}^j + \sum_{\forall j} \mathbb{S}_{ij}\alpha_j \mathbf{E}^j$$

- Cross-sections: Mie theory with *N+1* sources

$$\begin{cases} \mathbf{E}_{\text{DIP}} = \displaystyle\sum_{n=1}^{\infty}\sum_{m=-n}^{n} a^{\text{DIP}}_{mn}\mathbf{M}^{(1)}(k_1,\mathbf{r}) + b^{\text{DIP}}_{mn}\mathbf{N}^{(1)}(k_1,\mathbf{r}), & r < r_{\text{dip}} \\ \mathbf{E}_{\text{DIP}} = \displaystyle\sum_{n=1}^{\infty}\sum_{m=-n}^{n} e^{\text{DIP}}_{mn}\mathbf{M}^{(3)}(k_1,\mathbf{r}) + f^{\text{DIP}}_{mn}\mathbf{N}^{(3)}(k_1,\mathbf{r}), & r > r_{\text{dip}} \end{cases}$$

- Orientation-averaging (multiple directions)

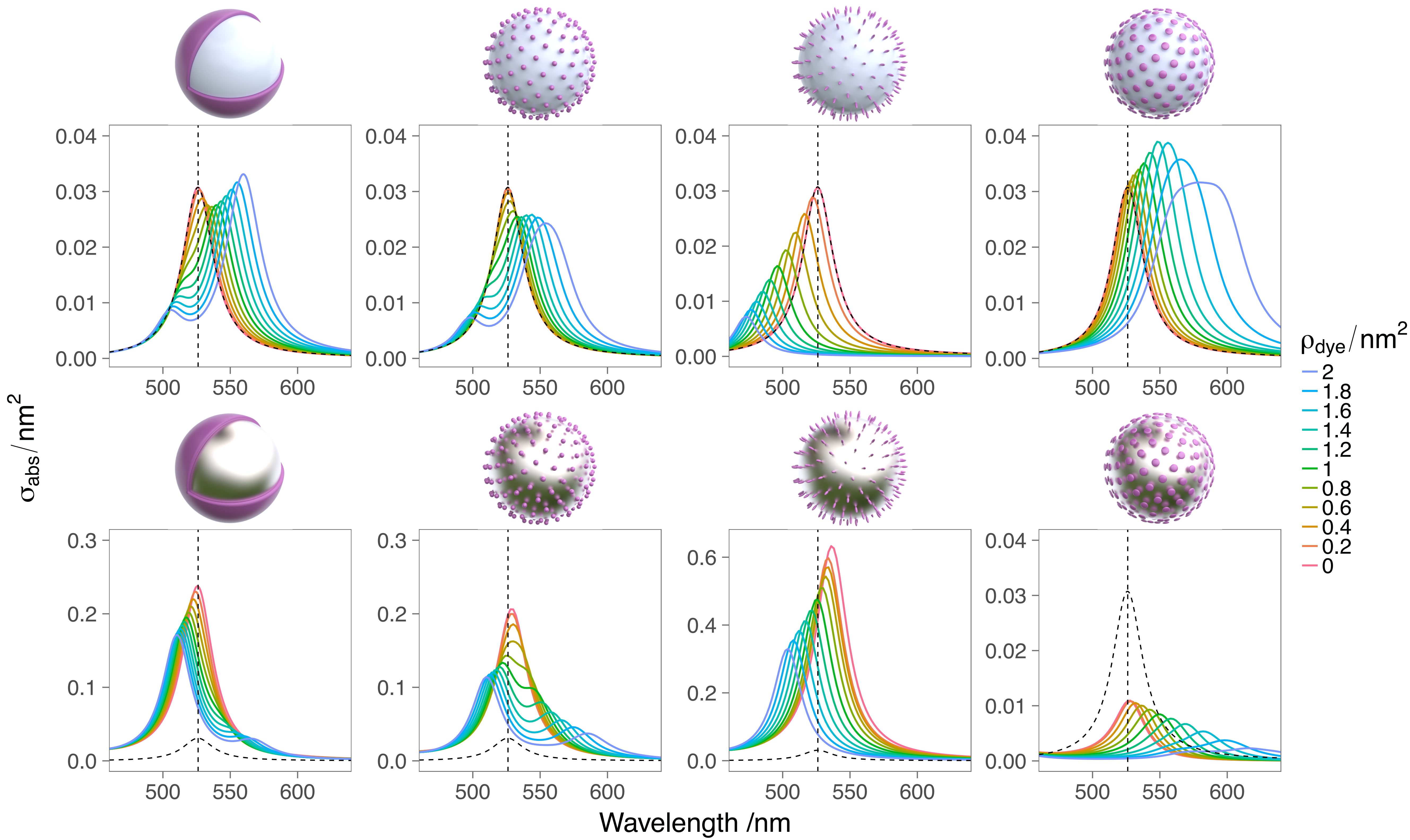


First insights:

- CM ≈ isotropic shell
- Blue-shift: radial
- Red-shift: flat
- Image dipole shift

Note: R-dependence
(here 15 nm radius)

EFFECT OF METAL CORE



PERSPECTIVES

☑ **Effect of orientation, density, inhomogeneities, dipole image**

☐ Comparison with anisotropic shell models

☐ Shell of finite thickness, unusual coverage (e.g. Janus)

☐ Surface dimerisation

☐ Implications for Raman and fluorescence

Less likely:

☒ *Chemical enhancement*, DFT predictions

☒ Super-radiance

☒ Non-spherical particles

Thank you!