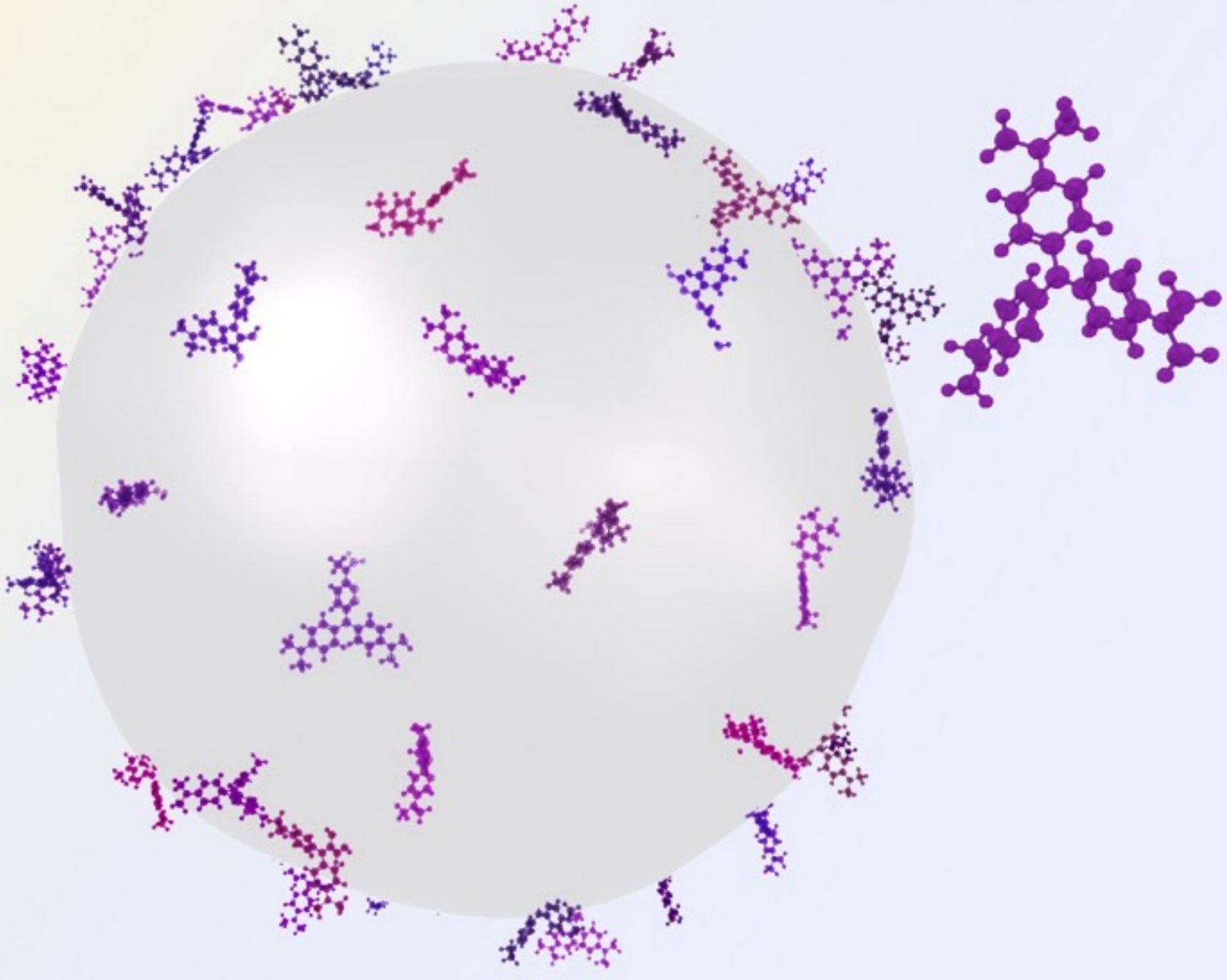
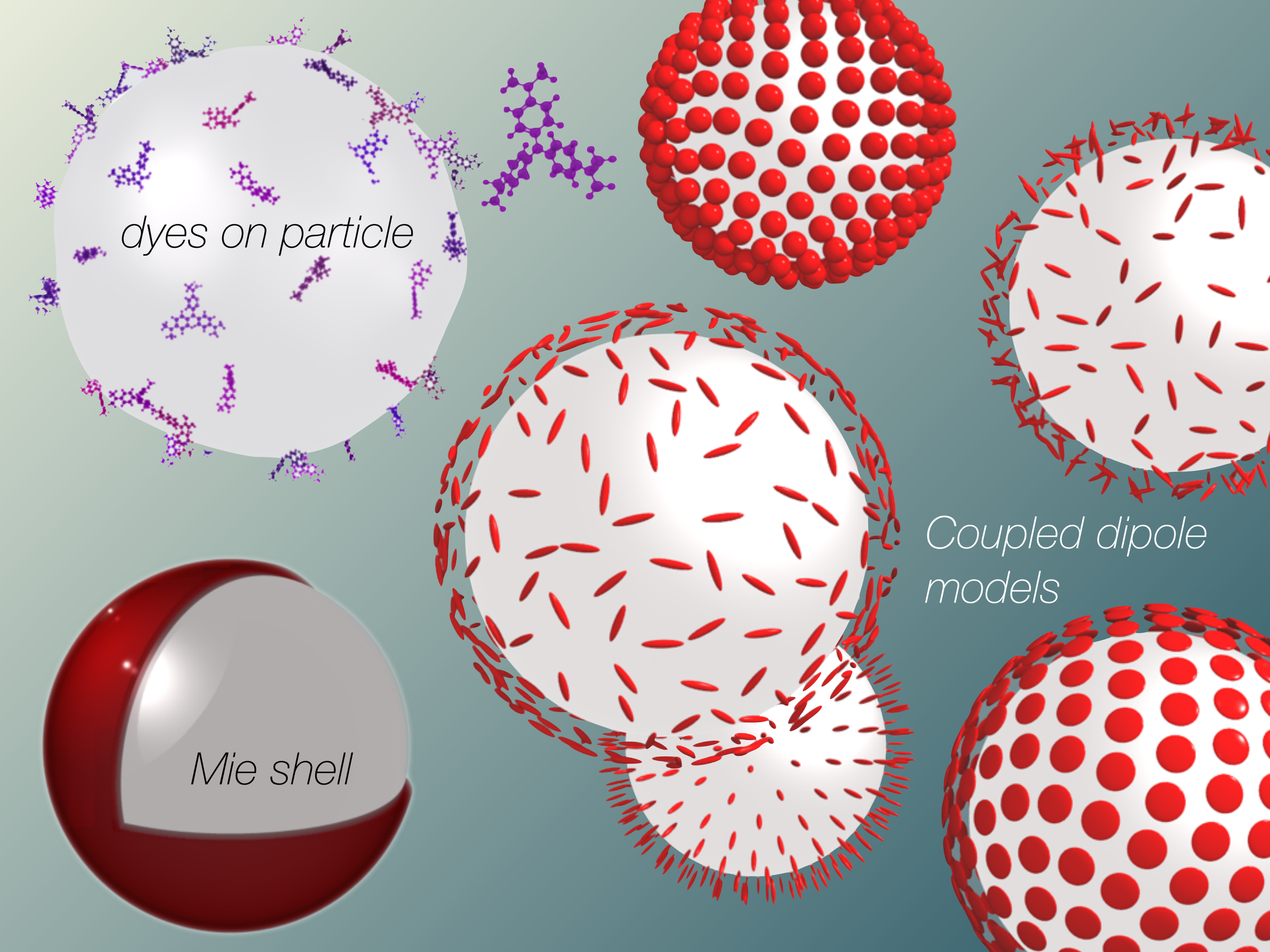
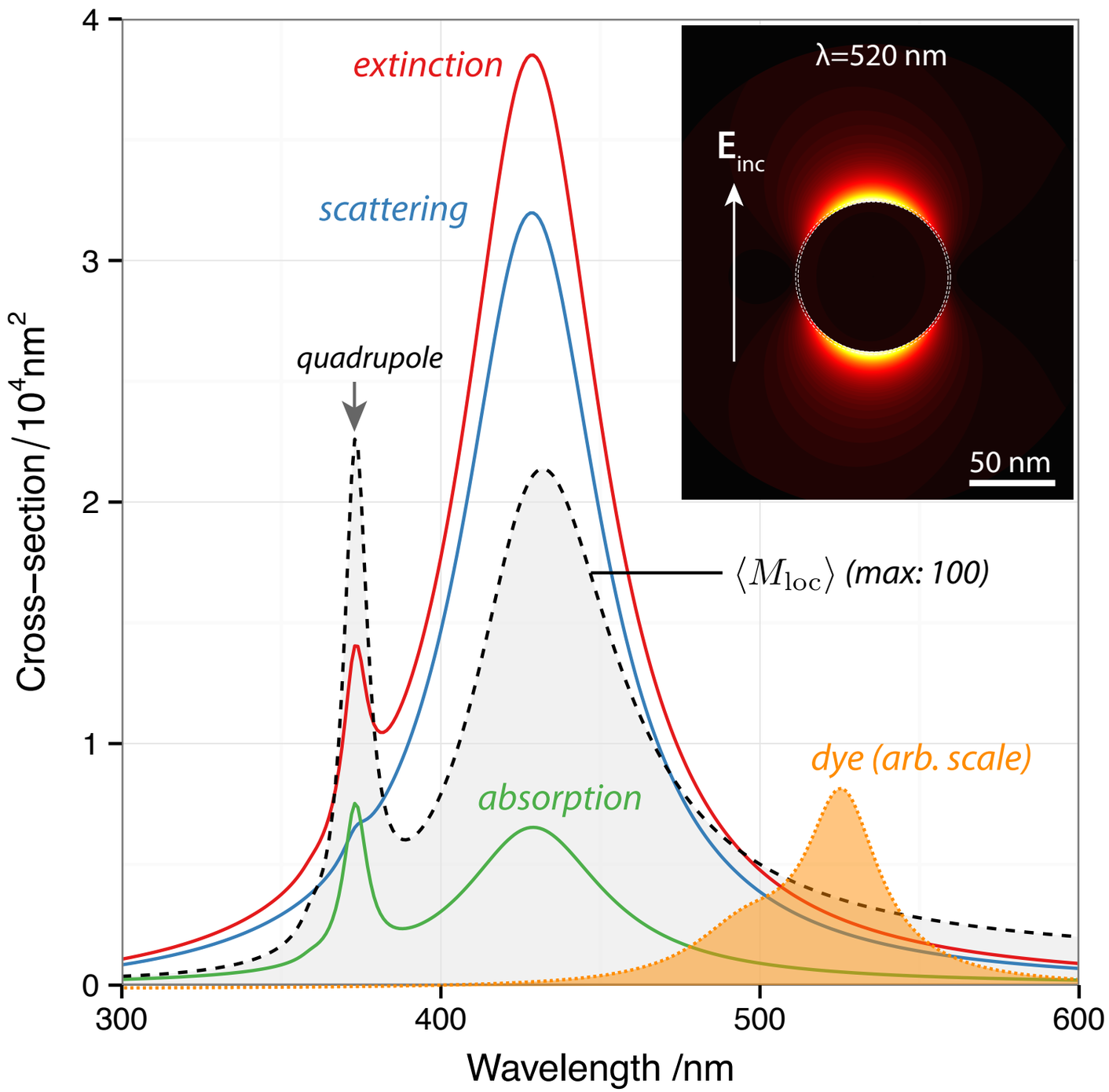


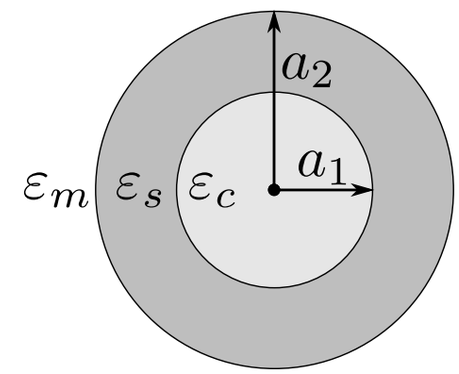
Dipole-dipole coupling & plasmonics

Otago University workshop
September 2015


dyes on particle
Coupled dipole models
Mie shell

Mie theory





$$\mathbf{E}_{\text{Inc}} = E_0 \sum_{l,m} a_{lm} \mathbf{M}_{lm}^{(1)}(k\mathbf{r}) + b_{lm} \mathbf{N}_{lm}^{(1)}(k\mathbf{r})$$

$$\mathbf{E}_{\text{Sca}} = E_0 \sum_{l,m} c_{lm} \mathbf{M}_{lm}^{(3)}(k\mathbf{r}) + d_{lm} \mathbf{N}_{lm}^{(3)}(k\mathbf{r})$$

$$c_l = \frac{s\psi_l(x)\psi_l'(sx) - \psi_l(sx)\psi_l'(x)}{\psi_l(sx)\xi_l'(x) - s\psi_l'(sx)\xi_l'(x)} a_l$$

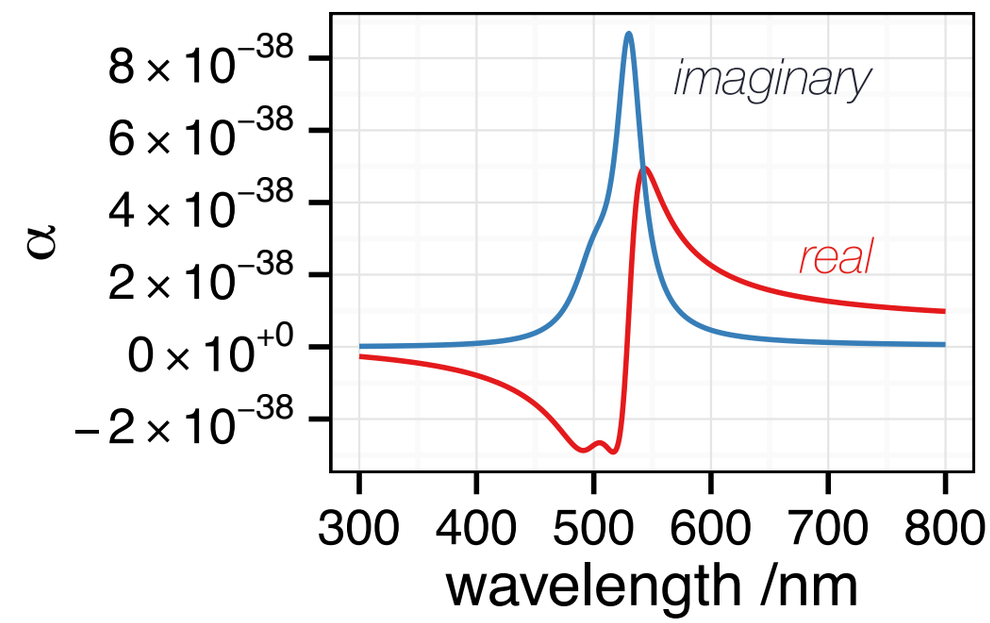
$$d_l = \frac{\psi_l(x)\psi_l'(sx) - s\psi_l(sx)\psi_l'(x)}{s\psi_l(sx)\xi_l'(x) - \psi_l'(sx)\xi_l'(x)} b_l$$

Shell model: effective medium

Bare dye in water

$$\sigma_{\text{abs}}(\omega) = \frac{(\epsilon_M + 2)^2}{9\sqrt{\epsilon_M}} \frac{\omega}{\varepsilon_0 c} \text{Im}\left[\alpha_D(\omega)\right]$$

$$\alpha(\lambda) = \alpha_{\text{static}} + \sum_{n=0,1} \frac{\alpha_n \lambda_n}{\mu_n} \left[\frac{1}{1 - \frac{\lambda_n^2}{\lambda} - i\frac{\lambda_n^2}{\lambda \mu_n}} - 1 \right]$$

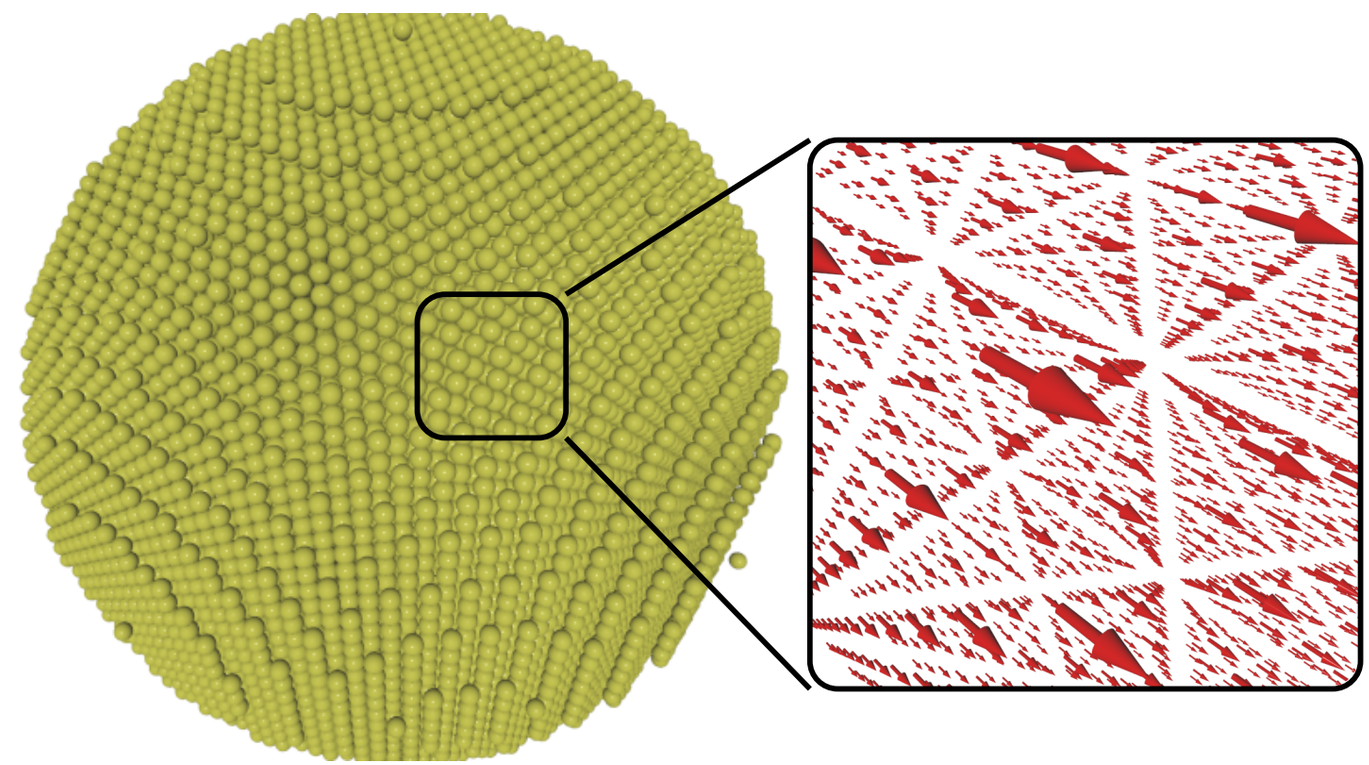


Clausius-Mossotti relation

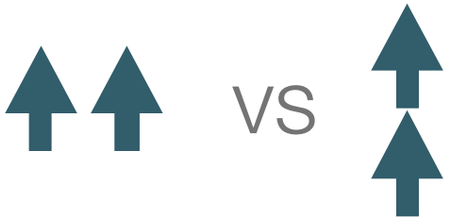
$$\varepsilon_{\text{dye}} = \frac{1 + \frac{2}{3}(\tilde{\alpha}_M + \tilde{\alpha}_D)}{1 - \frac{1}{3}(\tilde{\alpha}_M + \tilde{\alpha}_D)}$$

concentration-dependence:

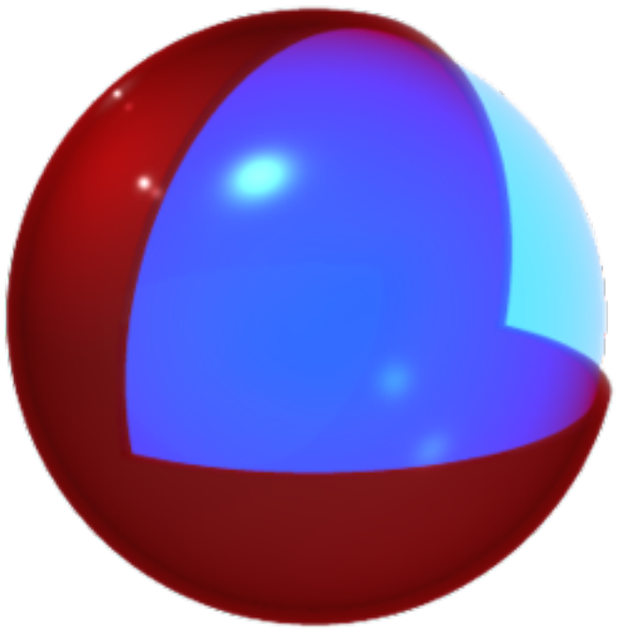
$$\tilde{\alpha}_D(\omega) = c_D \frac{\alpha_D}{\varepsilon_0}$$



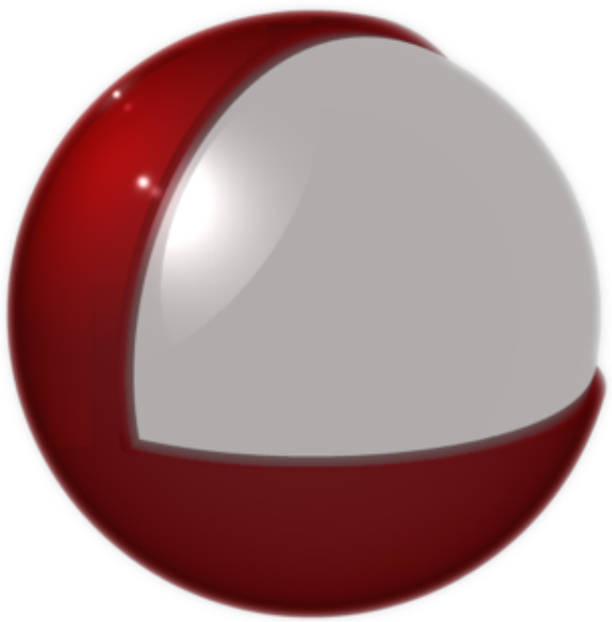
Geometry

- Orientation with respect to incident field 

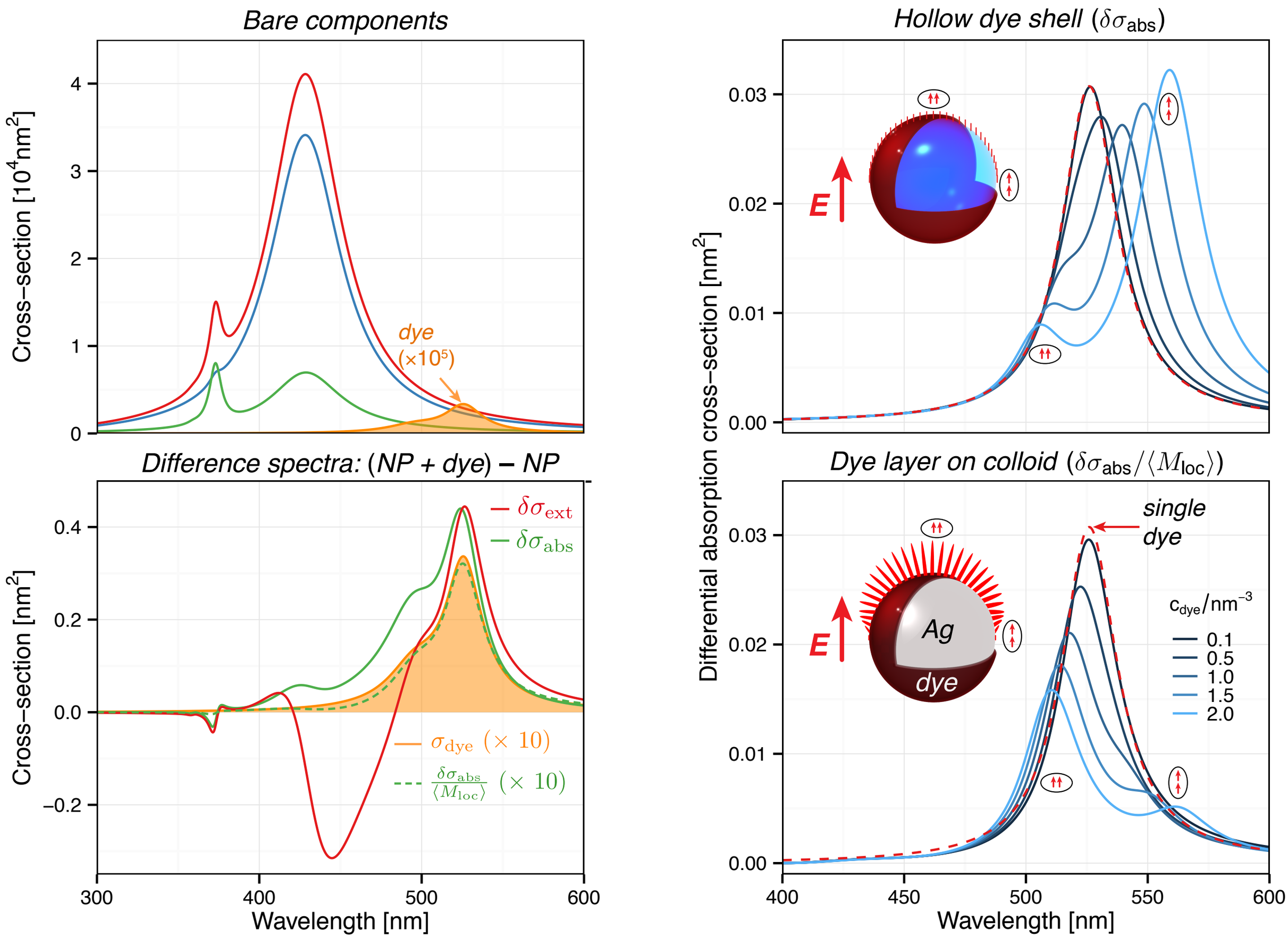
- Field enhancement (metal)

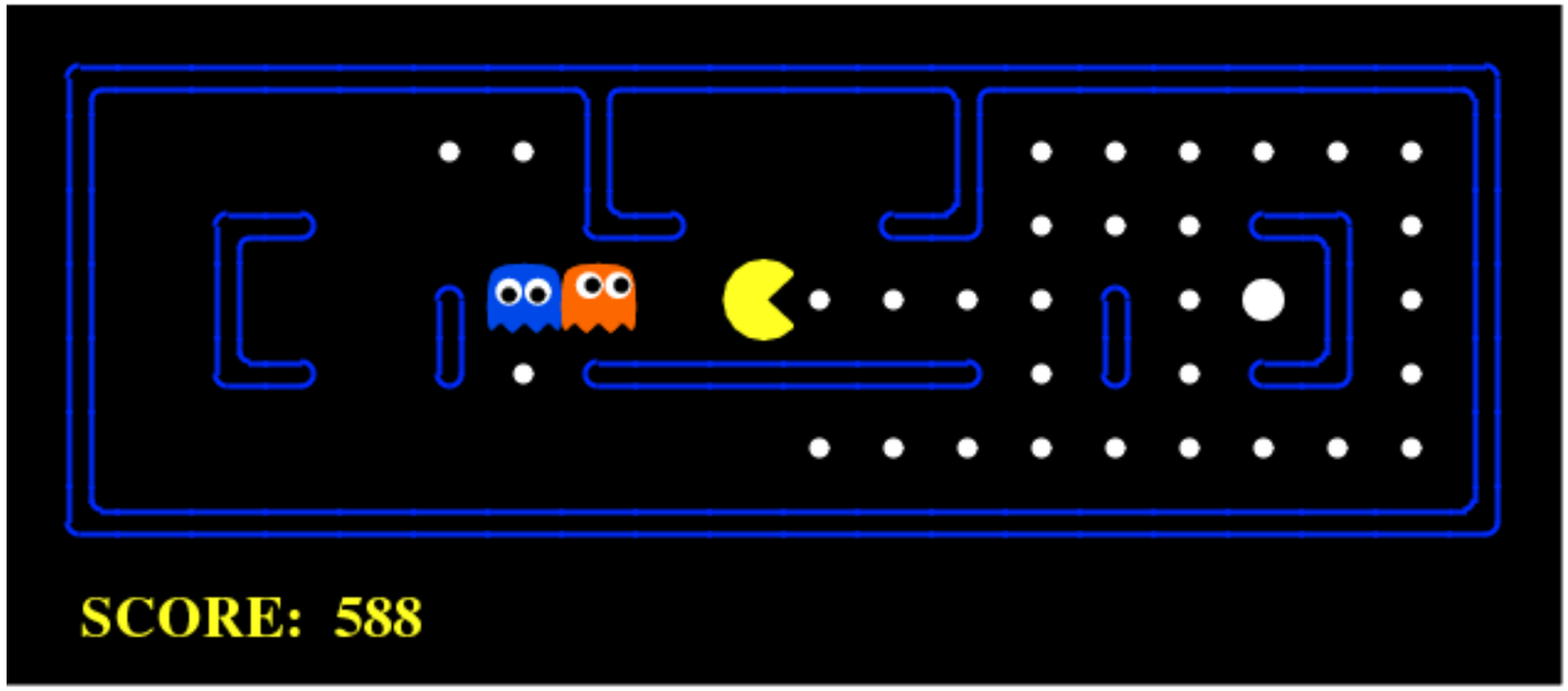


Toy model
(dye in water)

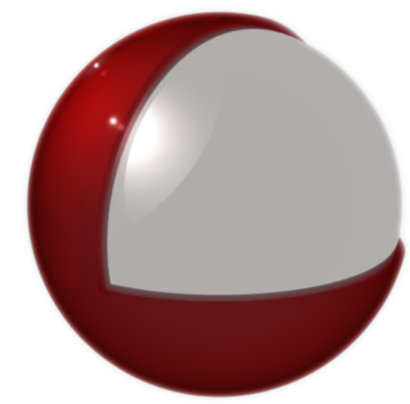


Ag core
(dye on particle)


Bare components
Cross–section [10^4nm^2]
dye
(×10^5)
Difference spectra: (NP + dye) – NP
Cross–section [nm^2]
$\delta\sigma_{\rm ext}$
$\delta\sigma_{\rm abs}$
$\sigma_{\rm dye}$ (× 10)
$\frac{\delta\sigma_{\rm abs}}{\langle M_{\rm loc}\rangle}$ (× 10)
Wavelength [nm]
Hollow dye shell ($\delta\sigma_{\rm abs}$)
Differential absorption cross–section [nm^2]
E
Dye layer on colloid ($\delta\sigma_{\rm abs}/\langle M_{\rm loc}\rangle$)
single
dye
Ag
dye
$c_{\rm dye}$/nm^{-3}
0.1
0.5
1.0
1.5
2.0
Wavelength [nm]



Shell model: results & limitations

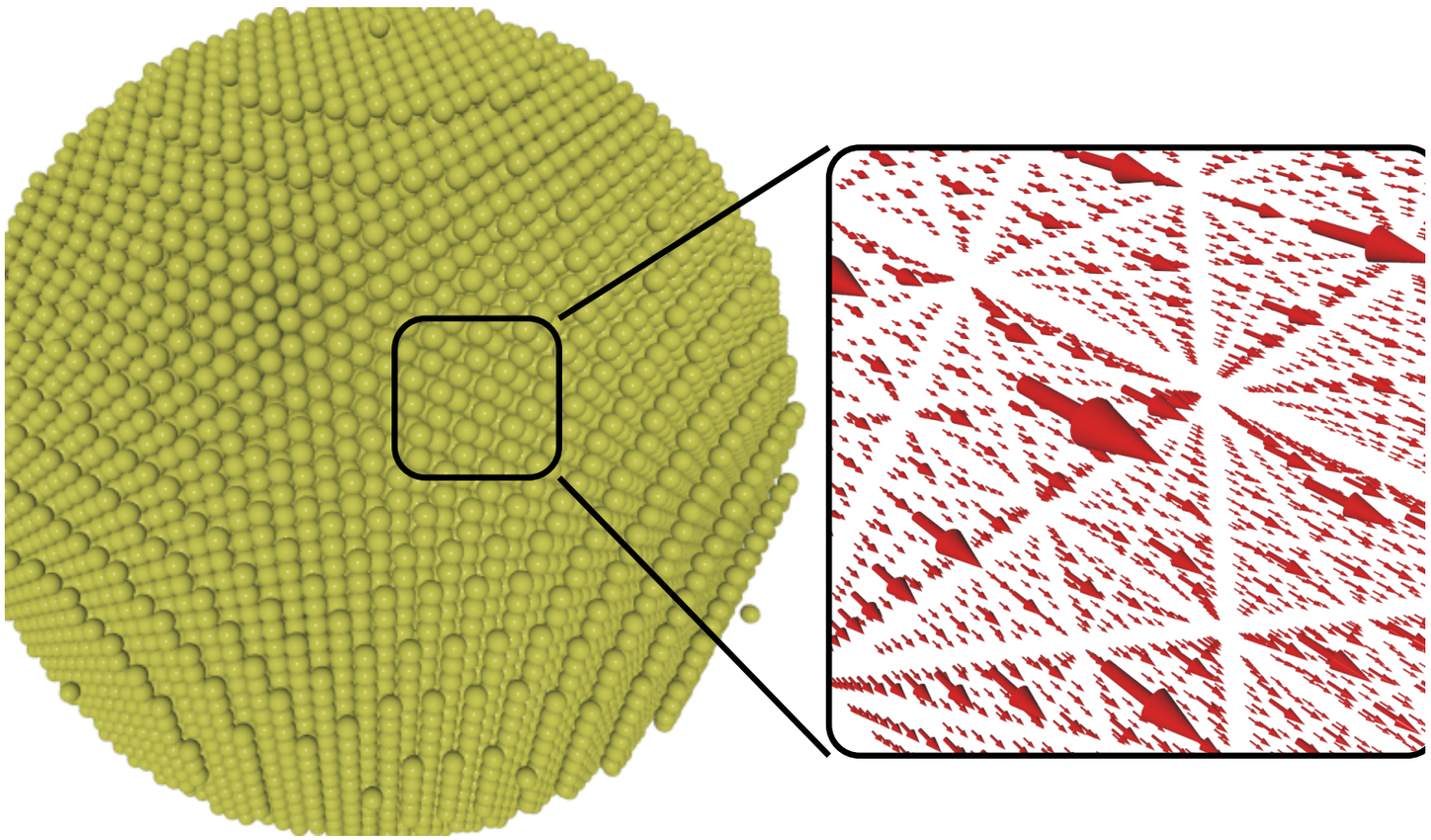


- predicts concentration-dependent spectral changes
- physical picture: near-neighbour coupling & enhancement factors

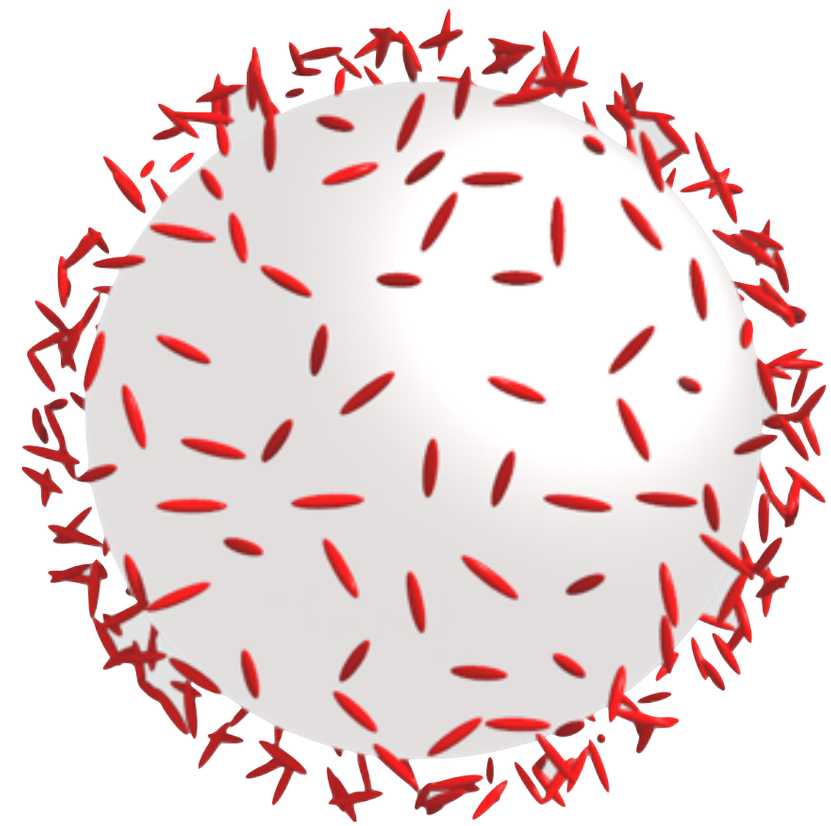
BUT

- **orientation effects** unaccounted for
- real coverage is inherently **discrete**: missing fluctuation effects
- rigorous theory should consider **image dipole** and **local field** beyond Clausius-Mossotti

Terminology



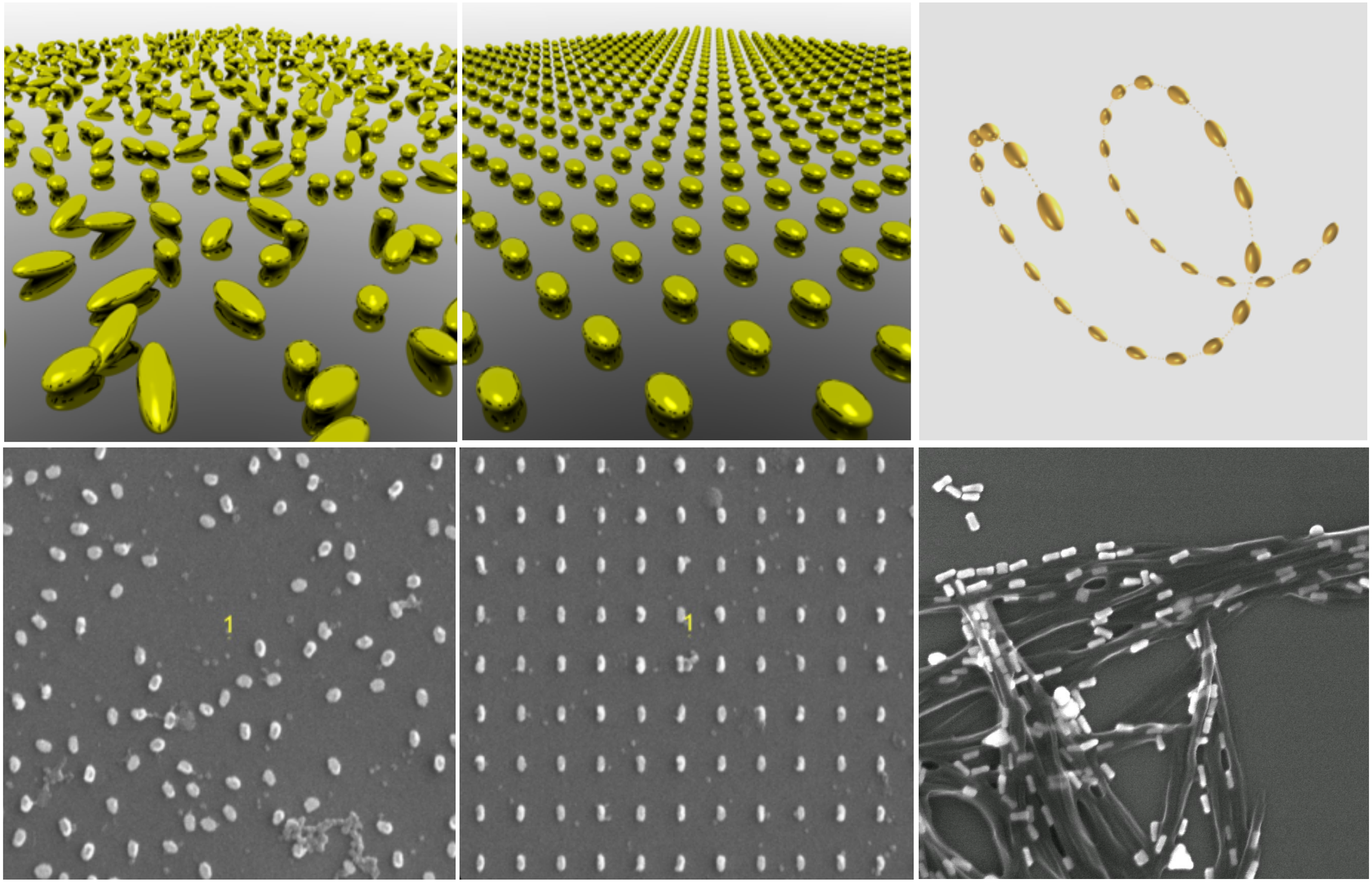
Discrete-Dipole Approx.



Coupled-Dipole Approx.

(and a sphere)

Other plasmonic applications



Coupled-dipole equations

$$\mathbf{E}^i = \mathbf{E}^{\mathrm{inc}} + \sum_{j \neq i} \mathbb{G}_{ij} \mathbf{P}^{\mathrm{j}} \qquad \mathbf{P}^{\mathrm{j}} = \alpha_j \mathbf{E}^{\mathrm{j}}$$

$$\mathbb{G}_{ij} = -\frac{e^{(ikr_{ij})}}{r_{ij}} \left\{ k^2 (\widehat{\mathbf{r}} \otimes \widehat{\mathbf{r}} - \mathbb{I}) + \frac{ikr_{ij} - 1}{r_{ij}^2} (3\widehat{\mathbf{r}} \otimes \widehat{\mathbf{r}} - \mathbb{I}) \right\}$$

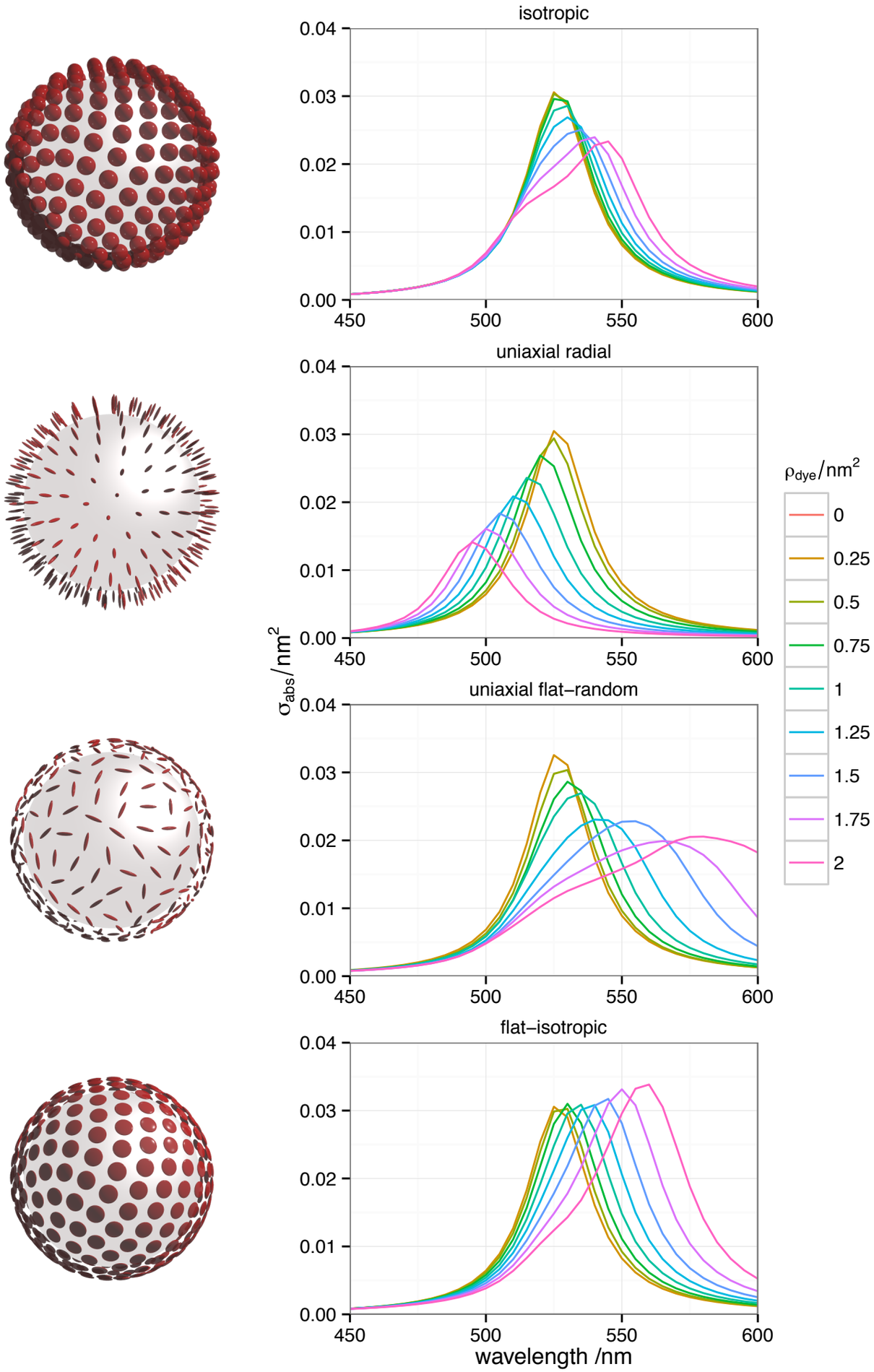
Linear system

$$\mathbb{A}\mathbf{E} = \mathbf{E}^{\mathrm{inc}}$$

Cross-sections

$$\sigma_{\mathrm{ext}} = 4\pi k \Im(\mathbf{E}_{\mathrm{inc}}{}^* \cdot \mathbf{P})$$

$$\sigma_{\mathrm{abs}} = 4\pi k \left[\Im(\mathbf{E}^* \cdot \mathbf{P}) - k^3 |\mathbf{P}|^2 \right]$$



Preliminary results

- Rich behaviour
- Orientation matters!
- No direct comparison with continuous model?

Including the sphere

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

Linear system (3x3 example)

$$\left[\begin{pmatrix} \mathbb{I} & \mathbb{O} & \mathbb{O} \\ \mathbb{O} & \mathbb{I} & \mathbb{O} \\ \mathbb{O} & \mathbb{O} & \mathbb{I} \end{pmatrix} - \begin{pmatrix} \mathbb{O} & \mathbb{G}_{12}\mathbb{\alpha}_2 & \mathbb{G}_{13}\mathbb{\alpha}_3 \\ \mathbb{G}_{21}\mathbb{\alpha}_1 & \mathbb{O} & \mathbb{G}_{23}\mathbb{\alpha}_3 \\ \mathbb{G}_{31}\mathbb{\alpha}_1 & \mathbb{G}_{32}\mathbb{\alpha}_2 & \mathbb{O} \end{pmatrix} - \begin{pmatrix} \mathbb{S}_{11}\mathbb{\alpha}_1 & \mathbb{S}_{12}\mathbb{\alpha}_2 & \mathbb{S}_{13}\mathbb{\alpha}_3 \\ \mathbb{S}_{21}\mathbb{\alpha}_1 & \mathbb{S}_{22}\mathbb{\alpha}_2 & \mathbb{S}_{23}\mathbb{\alpha}_3 \\ \mathbb{S}_{31}\mathbb{\alpha}_1 & \mathbb{S}_{32}\mathbb{\alpha}_2 & \mathbb{S}_{33}\mathbb{\alpha}_3 \end{pmatrix} \right] \begin{pmatrix} \mathbf{E}^1 \\ \mathbf{E}^2 \\ \mathbf{E}^3 \end{pmatrix} = \begin{pmatrix} \mathbf{E}^1_{\text{inc}} \\ \mathbf{E}^2_{\text{inc}} \\ \mathbf{E}^3_{\text{inc}} \end{pmatrix} + \begin{pmatrix} \mathbf{E}^1_{\text{sphere}} \\ \mathbf{E}^2_{\text{sphere}} \\ \mathbf{E}^3_{\text{sphere}} \end{pmatrix}$$

Steps:

- *Solve the Mie scattering problem for plane-wave (E_{sphere})*
- *Solve the Mie scattering problem for dipole source (S)*
- *Solve system*
- *Calculate cross-sections*

Wrap-up

- Semi-quantitative predictions

- Discrete model will allow study of *orientation effects*

Bigger picture:

- *Any observed shift/broadening/spectral modification* ***unaccounted for*** *will be attributed to:*

✤ "*chemical enhancement*"

✤ *more generally, physisorption or chemisorption effects*