Electronic Supplementary Material: Optical Properties of Ordered Self-assembled Nanoparticle Arrays at Interfaces

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Model Outline

The effective medium dipole theory presented is an extension of that published in Refs. 1-4 here we present a derivation of this type of effective medium theory. When light is incident on an NP near a dielectric interface the NP is assumed to act as a dipole scatterer, with the total electric field at each NP being the sum of the external field $\vec{E}_0$ and the field due to all other oscillating dipoles $\vec{E}_{dip}$, the dipole moment on each sphere in terms of the polarisability of the average NP $\hat{\alpha}$ is:[1–4]

$$\vec{p} = \hat{\alpha}(\vec{E}_0 + \vec{E}_{dip}) \tag{A1}$$

If the dielectric properties of the materials composing the NP are described by a tensor with no off-diagonal components then the fields are decoupled into two parallel and one perpendicular component,[2] by decoupling the components and using $\vec{E}_{dip} = \hat{U}[-zp_z+\frac{1}{2}(xp_x+yp_y)]$ the parallel and perpendicular components of the dipole moment can be expressed as

$$p_{\parallel} = \frac{E_{0,\parallel}\alpha_{\parallel}}{1-\frac{1}{2}\alpha_{\parallel}U_{\parallel}} \tag{A2}$$

$$p_{\perp} = \frac{E_{0,\perp}\alpha_{\perp}}{1+\alpha_{\perp}U_{\perp}} \tag{A3}$$

Suppose that the NPs form a layer with some effective dielectric properties $\varepsilon_{\perp,\parallel}$ then the normal component of the displacement field and tangential component of the electric field must be continuous across the interface between the NP layer and the medium from which the light is incident.

$$E^0_{\parallel} = E_{\parallel} \tag{A4}$$

$$D^0_{\perp} = D_{\perp} \tag{A5}$$

The fields denoted by a superscript 0 are the external fields in Layer 0 of Fig. 1 of the main text, including both the incident and reflected fields. The right handside of Eqns. A4 & A5 are the macroscopic fields present in the NP layer. The effective dielectric properties of the NP layer can be calculated using the macroscopic fields and boundary conditions:

$$D_{\parallel} = (E_{\parallel} + 4\pi P_2) + 4\pi\frac{p_{\parallel}}{a^2 d} = \varepsilon_2 E_{\parallel} + 4\pi\frac{p_{\parallel}}{a^2 d} = \varepsilon_{\parallel} E_{\parallel} \tag{A6}$$

the dipole moment per unit volume $\frac{p_{\parallel,\perp}}{a^2 d}$ is defined by the lattice constant a and a characteristic dimension d. Similarly,

$$D_{\perp} = \varepsilon_{\perp} E_{\perp} = (E_{\perp} + 4\pi P_2) + 4\pi\frac{p_{\perp}}{a^2 d} = \varepsilon_2 E_{\perp} + 4\pi\frac{p_{\perp}}{a^2 d} \tag{A7}$$

Using Eqns. A4, A5, A6 & A7 and the fact that $D^0_{\perp} = \varepsilon_2 E^0_{\perp}$ we calculate $\varepsilon_{\parallel,\perp}$ as,

$$\varepsilon_{\parallel} = \varepsilon_1 + 4\pi\frac{\alpha^0_{\parallel}}{a^2 d} \tag{A8}$$

$$\varepsilon_{\perp} = \frac{\varepsilon_1^2 a^2 d}{\varepsilon_1 a^2 d - 4\pi\alpha^0_{\perp}} \tag{A9}$$

where,

$$\alpha^0_{\parallel} = \frac{\alpha_{\parallel}}{1 - \frac{\alpha_{\parallel}}{2}U_{\parallel}} \tag{A10}$$

$$\alpha^0_{\perp} = \frac{\alpha_{\perp}}{1 + \alpha_{\perp}U_{\perp}} \tag{A11}$$

Other than the NP lattice parameters the only terms left for calculation are now $\alpha_{\parallel,\perp}$ which depends on the level of order of the lattice as discussed in the main text and $U_{\parallel,\perp}$. The $U_{\parallel,\perp}$ are calcuated by considering at point charge located at a position z' on the z axis, the method of images can then be used to solve the potential for this charge,

$$\nabla\phi_1 = 0 \tag{A12}$$

$$\nabla\phi_3 = 0 \tag{A13}$$

$$\nabla\phi_4 = \frac{q}{4\pi\varepsilon_4}\delta(z-z')\delta(\vec{R}) \tag{A14}$$

This system of equations can be sovled using a Fourier-Bessel transform $\phi_i(R,z;z') = \frac{1}{2\pi}\int_0^\infty \mathrm{d}Q\ QJ_o(QR)\tilde{\phi}(Q,z;z')$ and the standard electrostatic boundary conditions to give,

$$\begin{aligned}\phi(R,z;z') =& \frac{q}{\varepsilon_3}\Bigg(\frac{1}{\sqrt{|z-z'|^2+R^2}} + \gamma_{43}\sqrt{|z+z'-D|^2+R^2})- \\ & ...\eta_{34}\eta_{43}\gamma_{13}\sum_{n=0}^{\infty}\frac{(\gamma_{13}\gamma_{43})^n}{\sqrt{(D(1+2n)+z+z')^2+R^2}}\Bigg)\end{aligned} \tag{A15}$$

The dipole potential can then be expressed through the dipole moment, $p_{\parallel,\perp}$, by considering two point charges located either parallel or perpendicular to each other separated by a distance, b. The dipole approximation here relies on point dipoles and thus the expression for $U_{\parallel,\perp}$ is calculated by expanding the dipole potentials about $b = 0$ to give Eqn. 3 of the main text for $U_\parallel$ and $U_\perp$ as,

$$\begin{aligned}U_\perp =& \sum_j \Bigg[\frac{1}{a^3|r_j|^{\frac{3}{2}}} + \gamma_{43}\left(\frac{1}{a^3(\frac{4h^2}{a^2}+|r_j|^2)^{\frac{3}{2}}} - \frac{12h^2}{a^5(\frac{4h^2}{a^2}+|r_j|^2)^{\frac{5}{2}}}\right) \\ & -\eta_{34}\eta_{43}\gamma_{13}\sum_{n=0}^{\infty}(\gamma_{13}\gamma_{43})^n\left(\frac{1}{a^3(\frac{4(h+D(n+1))^2}{a^2}+|r_j|^2)^{\frac{3}{2}}} - \frac{12(h+D(n+1))^2}{a^5(\frac{4(h+D(n+1))^2}{a^2}+|r_j|^2)^{\frac{5}{2}}}\right)\Bigg] \\ & + \frac{1}{2}U_\perp(|r_j|=0).\end{aligned} \tag{A16}$$

References

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