Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental information for

Rotational diffusion and alignment of short gold nanorods in an external electric field

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1 UV-VIS spectra

Gold nanorods were synthesized using seed-mediated wet-chemical synthesis in the presence of silver [1]. By varying the concentration of silver ions and seeds in the growth solution, we obtained three different samples with different volumes but similar aspect ratios. All samples exhibited a longitudinal SPR around 650 nm, close to the wavelength of our probe laser (671 nm). The UV-VIS extinction spectra (measured with a Shimadzu UV1701 spectrometer) of the three samples employed in this study are shown in Fig. S1. The curves are normalized to a path-length of 400 μm to reflect the OD in the sample cell.

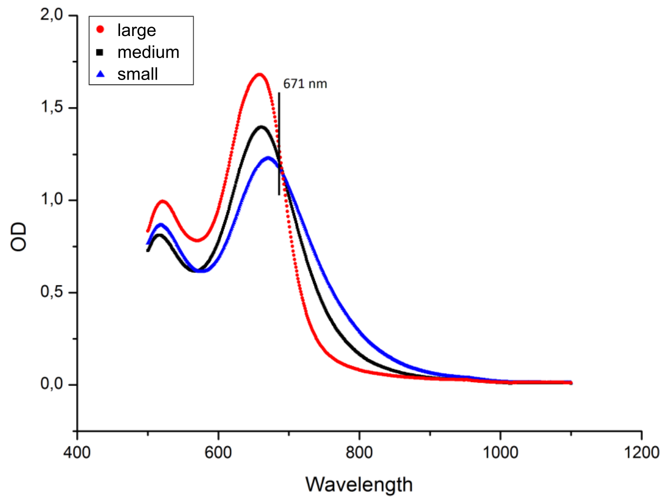

Figure S1 Extinction profiles of the three samples employed in this study. The curves are normalized to a pathlength of 400 μm to reflect the OD in the sample cell. The probe laser wavelength employed for the polarized extinction measurements is indicated at 671 nm.

2 Zeta-potential

The surface charge (zeta-potential) of the CTAB-stabilized particles was measured using a Malvern zeta-sizer. The zeta-potential is determined by applying an electric field E across the dispersion of nanoparticles [2]. Charged particles migrate towards the electrode of opposite charge (electrophoresis), with a velocity that is proportional to the zeta-potential. A laser Doppler anemometer determines the velocity of the particles by measuring the frequency- or phase-shift of a laser beam. This velocity v is related to the electrophoretic mobility μ_e through $\mu_e = v/E$. We measure μ_e=3.45×10^{-8} m^{2}V^{-1}s^{-1}, which can be related to the zeta-potential ζ through the Smoluchowski equation $\mu_e = \epsilon_r \epsilon_0 \zeta / \eta$, where ϵ_r is the static dielectric constant of the medium (water), ϵ_0 is the permittivity of free space, and η is the dynamic viscosity of the medium [2]. Note that this simple relation is only valid for a thin double layer, i.e. for particle radii much greater than the Debye length. This yields a mean zeta-potential of ∼44 mV at neutral pH, as expected for CTAB stabilized particles. The complete zeta-potential distribution of a typical sample in CTAB solution ([CTAB] ≈ 2 mM) is shown in Fig. S2.

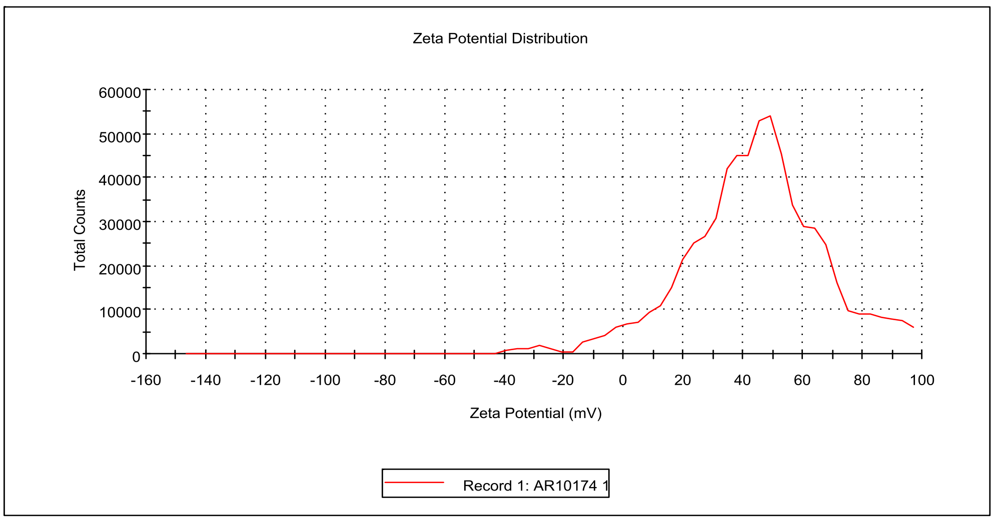

Figure S2 Zeta-potential distribution of an aqueous solution of gold nanorods stabilized by CTAB at neutral pH.

3 Blank: CTAB only

To verify that the observed ΔOD/OD is caused by the presence of the nanorods in the cell we measured the polarized extinction of a sample containing an aqueous solution of 1 mM CTAB. The results are shown in Fig. S3, and are plotted on the same scale as Fig. 2 in the main text. Because we cannot define ΔOD/OD due to the transparency of the CTAB solution, we have plotted the normalized lock-in voltage instead. In the full range of field-strengths we observe a constant lock-in voltage equal to the noise level of the measurement. This confirms that the lock-in signal observed in our measurements is caused by the orientation of gold nanorods in the external field.

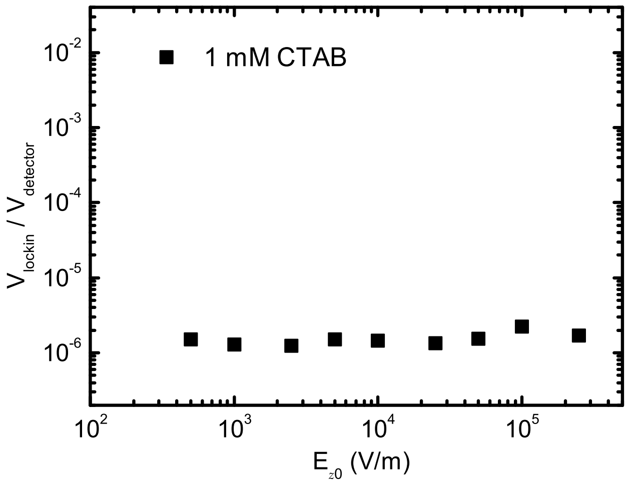

Figure S3 Lock-in voltage as a function of electric field strength for a sample containing an aqueous solution of 1 mM CTAB. The experimental parameters are identical to the ones used for the measurements of the nanorods (i.e. 400 μm spacing between electrodes, $\Omega/2\pi$=2.1 kHz.)

4 Theory

We discuss the frequency dependence of the amplitude and phase of the optical density (OD) of a solution of gold nanorods in a weak amplitude-modulated alternating-current electric field. The optical density is probed by a laser beam traveling in the $\hat{z}$ direction with linear polarization along the $\hat{x}$ direction. The applied electric field is given by

$$\vec{E}(t) = E_z(t)\,\hat{z} = \tfrac{1}{2}E_{z0}\left(1+\cos\left(\Omega t+\Phi\right)\right)\cos\left(\omega t+\phi\right)\hat{z}, \tag{S1}$$

where ω is the carrier frequency and Ω the modulation frequency. Because the period of the carrier wave is much shorter than the rotational diffusion time ($\omega \gg D_{\mathrm{rot}}$) the nanorods will not be able to follow the field and we can average over the high frequency components such that the squared electric field becomes

$$\vec{E}^2(t) = \frac{1}{4}E_{z0}^2\left\{\frac{3}{4}+\cos\left(\Omega t+\Phi\right)+\frac{1}{4}\cos\left[2\left(\Omega t+\Phi\right)\right]\right\}\hat{z} \tag{S2}$$

The polarizability tensor of a gold nanorod can be written as $\overline{\alpha}_0 = \alpha_{\|,0}\hat{1}\hat{1}^{\mathrm{T}} + \alpha_{\perp,0}\left(\hat{2}\hat{2}^{\mathrm{T}}+\hat{3}\hat{3}^{\mathrm{T}}\right)$, where

$$\begin{aligned}
\hat{1} &= \sin(\theta)\cos(\varphi)\,\hat{x} + \sin(\theta)\sin(\varphi)\,\hat{y} + \cos(\theta)\,\hat{z},\\
\hat{2} &= \cos(\theta)\cos(\varphi)\,\hat{x} + \cos(\theta)\sin(\varphi)\,\hat{y} - \sin(\theta)\,\hat{z}, \text{ and}\\
\hat{3} &= -\sin(\varphi)\,\hat{x} + \cos(\varphi)\,\hat{y},
\end{aligned} \tag{S3}$$

where θ is the angle between the symmetry axis of the nanorod and the z-axis, ϕ is the angle between the x-axis and the projection of the symmetry axis onto the xy-plane,[1] $\alpha_{\|,0}$ is the longitudinal polarizability along the symmetry axis $\hat{1}$ of the nanorod and $\alpha_{\perp,0}$ is the transverse polarizability along the axes perpendicular to the symmetry axis of the nanorod ($\hat{2}$ and $\hat{3}$). The subscript zero is used to indicate the low frequency limit of the polarizability. The torque exerted on a nanorod by the electric field is given by [3]

$$\vec{\mathcal{T}}\left(\left(\theta,\varphi\right),t\right) = \left(\overline{\alpha}_0\vec{E}(t)\right)\times\vec{E}(t) = -\Delta\alpha_0\cos(\theta)\sin(\theta)\,E_z^2(t)\,\hat{3}, \tag{S4}$$

where $\Delta\alpha_0 = \alpha_{\|,0} - \alpha_{\perp,0}$ is the difference between the longitudinal- and transverse polarizability.

The time-evolution of the probability distribution $p\left(\left(\theta,\phi\right),t\right)$ for the orientation of the nanorods is given by the Fokker-Planck (FP) or Smoluchowski equation and can be expressed as

$$\frac{\partial p\left(\left(\theta,\phi\right),t\right)}{\partial t} = D_{\mathrm{rot}}\left\{\nabla_{\mathrm{S}}^2 p\left(\left(\theta,\phi\right),t\right) + \frac{1}{k_{\mathrm{B}}T}\nabla_{\mathrm{S}}\cdot\left(p\left(\left(\theta,\phi\right),t\right)\left(\hat{1}\times\vec{\mathcal{T}}\left(\left(\theta,\phi\right),t\right)\right)\right)\right\}, \tag{S5}$$

where ∇_{S} denotes the gradient operator restricted to the surface of a unit sphere and D_{rot} denotes the rotational diffusion coefficient for rotations perpendicular to the symmetry axis. The FP equation can be written in terms of a Smoluchowski operator $\hat{\mathcal{S}}$: $\partial p/\partial t = \hat{S}p$. Assuming the electric field to be weak ($\Delta\alpha_0 E_{z0}^2/\left(k_{\mathrm{B}}T\right) \ll 1$) we can consider the electric field as perturbation to the

[1] A third Euler angle ψ describing rotations about the $\hat{1}$ axis is ignored.

freely diffusing nanorods, and the Smoluchowski operator can be written as $\hat{\mathcal{S}} = \hat{\mathcal{S}}_0 + \hat{\mathcal{S}}'$. The zeroth order Smoluchowski operator is $\hat{\mathcal{S}}_0 = D_{\mathrm{rot}} \nabla_{\mathrm{S}}^2$. The eigenfunctions of the zero-field Smoluchowski equation are the spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$ with eigenvalues $-\kappa_\ell = -D_{\mathrm{rot}} \ell (\ell + 1)$ [4, 5, 6]. As $t \to \infty$ the probability distribution approaches the steady-state solution:

$$p((\theta, \phi), t) \to \frac{1}{\sqrt{4\pi}} Y_0^0(\theta, \phi) = \frac{1}{4\pi} \qquad \text{as} \qquad t \to \infty. \tag{S6}$$

Following Eq. S5 the perturbation to the Smoluchowski operator is given by

$$\hat{\mathcal{S}}' \ldots = D_{\mathrm{rot}} (\nabla_{\mathrm{S}} \ldots) \cdot \left(\hat{1} \times \vec{\mathcal{T}} \right) + D_{\mathrm{rot}} \ldots \nabla_{\mathrm{S}} \cdot \left(\hat{1} \times \vec{\mathcal{T}} \right). \tag{S7}$$

To first order in time-dependent perturbation theory we can neglect the first term in equation S7 because $\nabla_{\mathrm{S}} Y_0^0 = 0$. The second term becomes

$$\hat{\mathcal{S}}' = \Delta\alpha_0 E_z^2(t) D_{\mathrm{rot}} 4 \sqrt{\frac{\pi}{5}} Y_2^0(\theta, \varphi) \tag{S8}$$

which gives rise to a term proportional to $Y_2^0(\theta, \phi)$ in the probability distribution. Assuming the perturbing electric field has been on for a long time and the steady-state has been reached, the solution to the FP equation is given by:

$$\begin{aligned} p((\theta, \varphi), t) = {} & \frac{1}{\sqrt{4\pi}} Y_0^0(\theta, \varphi) + \frac{1}{24\sqrt{5\pi}} \frac{\Delta\alpha_0 E_{z0}^2}{k_{\mathrm{B}} T} \left(\frac{3}{4} + \frac{\cos(\Omega t + \Phi - \Delta\Phi_\Omega)}{\sqrt{1 + (\Omega / (6 D_{\mathrm{rot}}))^2}} \right. \\ & \left. + \frac{1}{4} \frac{\cos(2\Omega t + 2\Phi - \Delta\Phi_{2\Omega})}{\sqrt{1 + (\Omega / (3 D_{\mathrm{rot}}))^2}} \right) Y_2^0(\theta, \varphi). \end{aligned} \tag{S9}$$

The phase differences $\Delta\Phi_\Omega$ and $\Delta\Phi_{2\Omega}$ are given by:

$$\tan \Delta\Phi_\Omega = \frac{\Omega}{6 D_{\mathrm{rot}}}, \text{ and} \tag{S10}$$

$$\tan \Delta\Phi_{2\Omega} = \frac{\Omega}{3 D_{\mathrm{rot}}}. \tag{S11}$$

We calculate the orientation-dependent extinction cross section $\sigma_{\mathrm{ext}}(\theta, \phi)$ for a particle in the Rayleigh regime in terms of its polarizability $\overline{\alpha}$ [7]. We use this together with equation S9 to obtain the time dependent ensemble average of the extinction cross section, probed along $\hat{x}$:

$$\begin{aligned} \langle \sigma_{\mathrm{ext}} \rangle (t) = {} & \frac{1}{3} \left(\frac{k \Im\{\alpha_\parallel\}}{\epsilon_m \varepsilon_0} + \frac{k^4 |\alpha_\parallel|^2}{6\pi (\epsilon_m \varepsilon_0)^2} \right) + \frac{2}{3} \left(\frac{k \Im\{\alpha_\perp\}}{\epsilon_m \varepsilon_0} + \frac{k^4 |\alpha_\perp|^2}{6\pi (\epsilon_m \varepsilon_0)^2} \right) \\ & - \frac{1}{180} \frac{\Delta\alpha_0 E_{z0}^2}{k_{\mathrm{B}} T} \left(\frac{3}{4} + \frac{\cos(\Omega t + \Phi - \Delta\Phi_\Omega)}{\sqrt{1 + (\Omega / (6 D_{\mathrm{rot}}))^2}} + \frac{1}{4} \frac{\cos(2\Omega t + 2\Phi - \Delta\Phi_{2\Omega})}{\sqrt{1 + (\Omega / (3 D_{\mathrm{rot}}))^2}} \right) \\ & \times \left(\frac{k}{\epsilon_m \varepsilon_0} \Im\{\alpha_\parallel - \alpha_\perp\} + \frac{k^4}{6\pi (\epsilon_m \varepsilon_0)^2} \left(|\alpha_\parallel|^2 - |\alpha_\perp|^2 \right) \right), \end{aligned} \tag{S12}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the longitudinal- and transverse polarizabilities at the frequency of the laser, ε_0 is the permittivity of the vacuum, ϵ_m is the relative permittivity of the medium surrounding the particle and k is the wavenumber in the medium surrounding the nanorods. The first line of Eq. S12 represents the extinction cross section for the zero-field case, whereas the second and third line provide the changes in the presence of the electric field (with contributions at Ω and 2Ω).

Because $\alpha_{\perp} \ll \alpha_{\parallel}$ at the wavelength of our probe laser (λ_{laser} =671 nm), the magnitude of the component of Eq. S12 at frequency Ω can be simplified to

$$\frac{\Delta\mathrm{OD}}{\mathrm{OD}} = -\frac{1}{60}\frac{1}{\sqrt{1+\left(\Omega/\left(6D_{\mathrm{rot}}\right)\right)^2}}\frac{\Delta\alpha_0 E_{z0}^2}{k_{\mathrm{B}}T}, \tag{S13}$$

where we have used the fact that the OD is proportional to $\langle\sigma_{\mathrm{ext}}\rangle$. The phase difference between the applied field and the induced alignment is then given by Eq. S10.

References

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