Estimation of bivariate probability distributions of nanoparticle characteristics, based on univariate measurements

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1 Calculation of hydrodynamic properties of nanorods

The hydrodynamic properties of real particles are heavily influenced by their ligand shell with height \( h \) (see Figure SI1). This has to be taken into account when hydrodynamic properties are to be investigated. More precisely, while the core particle has an aspect ratio \( \nu \) and a volume \( V \), the ligand shell leads to a modified aspect ratio \( \nu_s \) and volume \( V_s \) for the hemispherical end capped nanorods which are given by

\[
\nu_s = \frac{\ell + 2h}{d + 2h},
\]

\[
V_s = (d + 2h)^3 \pi \left( \frac{\nu_s}{4} - \frac{1}{12} \right).
\]

Additionally, the mass \( m \) and density \( \rho_{\text{eff}} \) of the integral particle are given by

\[
m = (V_s - V) \rho_{\text{shell}} + V \rho_{\text{core}},
\]

\[
\rho_{\text{eff}} = \frac{m}{V_s},
\]

with core density \( \rho_{\text{core}} \) and shell density \( \rho_{\text{shell}} \), where the latter is given by the average of the densities \( \rho_{\text{ligand}} \), \( \rho_{\text{solvent}} \) of the ligand and solvent, i.e., \( \rho_{\text{shell}} = 0.5(\rho_{\text{ligand}} + \rho_{\text{solvent}}) \). The volume-equivalent diameter \( x_V \) is calculated in the conventional manner, i.e.,

\[
x_V = \frac{3}{\pi} \sqrt[3]{6 \pi V_s}.
\]

Finally, the frictional ratio \( \frac{f_f}{f_0} \) has to be determined. In Hansen (2004) it was shown that the frictional ratio is solely a function of the aspect ratio \( \nu_s \) for a huge range of aspect ratios for cylinders. The functional relationship is given...
by

\[
\frac{f}{f_0} = 1.0304 + 0.0193 \ln (\nu_s) + 0.06229 (\ln (\nu_s))^2 + 0.00476 (\ln (\nu_s))^3 \\
+ 0.00166 (\ln (\nu_s))^4 + 2.66 \cdot 10^{-6} (\ln (\nu_s))^7.
\]

Figure SI1: Schematic representation of a nanorod. The core has hemispherical end caps and its shape is characterized by its length \(\ell\) and diameter \(d\). The depicted nanorod has a ligand shell height of \(h\).

2 Calculation of optical properties of gold nanorods

The Gans theory up to first order gives the scattering and absorption cross sections \(\sigma_{sca}\) and \(\sigma_{abs}\) (Olson et al., 2015):

\[
\sigma_{sca} = \frac{2\pi V(\ell, d)\varepsilon_m^2}{3\lambda} \sum_{j=1}^{3} \frac{1}{P_j} \varepsilon_2 \left( \varepsilon_1 + \left[ \frac{1 - P_j}{P_j} \right] \varepsilon_m \right)^2 + \epsilon_2^2,
\]

\[
\sigma_{abs} = \frac{8\pi V^2(\ell, d)\varepsilon_m^2}{9\lambda^4} \sum_{j=1}^{3} \frac{1}{P_j} \left( \varepsilon_1 - \varepsilon_m \right)^2 + \epsilon_2^2,
\]

where \(\lambda\) is the wavelength of the light, \(V(\ell, d) = \frac{4}{3} \pi \left( \frac{\ell}{12} \right) \) is the volume of the particle core with length \(\ell\) and diameter \(d\), and \(\varepsilon_m\) denotes the wavelength dependent dielectric function of the medium. The functions \(\varepsilon_1\) and \(\varepsilon_2\) are defined through the complex dielectric function of gold, given by \(\varepsilon_{Au}(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda)\). The shape factors \(P_j\) in (1) and (2) are given by

\[
P_1(\ell, d) = \frac{1 - \delta^2(\ell, d)}{\delta^2(\ell, d)} \left[ \frac{1}{2\delta(\ell, d)} \ln \left( \frac{1 + \delta(\ell, d)}{1 - \delta(\ell, d)} \right) - 1 \right],
\]

\[
P_2(\ell, d) = P_3(\ell, d) = \frac{1 - P_1(\ell, d)}{2},
\]

\[
\delta(\ell, d) = \sqrt{1 - \left( \frac{1}{\nu(\ell, d)} \right)^2},
\]

where the aspect ratio \(\nu\) is defined as the ratio of length to diameter, i.e., \(\nu(\ell, d) = \ell/d\).
References
