Supporting Information for: Tumbling of Quantum Dots: Rheo-optics

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Numerical solution of the Smoluchowski equation

The time-dependent orientation angle χ is determined by the time evolution of the probability distribution function $P(\hat{\mathbf{u}}, t)$ of the orientation $\hat{\mathbf{u}}$ as given in eq. 4 of the paper. For the case of Rayleigh scatterers, Frattini and Fuller[1] employed the following expression for χ in terms of spherical coordinates (θ,ϕ)

$$\tan 2\chi = \frac{\left\langle \sin^2\theta \sin 2\phi \right\rangle}{\left\langle \sin^2\theta \cos 2\phi \right\rangle}. \tag{1}$$

This expression provides numerical predictions in good agreement with experimental results.[1,2] The average $\langle \mathrm{A} \rangle$ is calculated according to

$$\langle \mathrm{A} \rangle = \int_0^{\pi}\int_0^{2\pi} \mathrm{A}(\theta,\phi)\, P(\theta,\phi;t) d\theta d\phi \quad , \tag{2}$$

where a monodisperse suspension is considered. In order to calculate the time evolution of the orientation angle χ, the time dependence of $P(\theta,\phi;t)$ has to be accounted for. The Smoluchowski equation can be expressed in spherical coordinates as

$$\begin{aligned} \frac{\partial P}{\partial \tau} = \quad & \frac{1}{Pe}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial \theta}\right) + \frac{1}{\sin\theta^2}\frac{\partial^2 P}{\partial \phi^2}\right] \\ - \quad & \frac{p^2-1}{p^2+1}\left[\frac{\sin\phi\cos\phi}{\sin\theta}\frac{\partial}{\partial\theta}\left(P\sin^2\theta\cos\theta\right) - \frac{\partial}{\partial\phi}(P\sin^2\phi)\right] \\ - \quad & \frac{1}{p^2+1}\left(\frac{1}{2}\frac{\partial P}{\partial \phi}\right), \end{aligned} \tag{3}$$

where $\tau = \dot{\gamma}t$ is the strain, or dimensionless time. For the boundary condition at the two poles, $\theta = 0$ and $\theta = \pi$, the probability density function is given by:

$$P|_{\theta=0} = \left[\sum_1^{N_\theta}\left(4P\left(1,j_\theta\right) - P(2,j_\theta)\right)/3\right]\Big/ N_\theta \tag{4}$$

$$P|_{\theta=\pi} = \left[\sum_1^{N_\theta}\left(4P\left(N_\theta-1,j_\theta\right) - P(N_\theta-2,j_\theta)\right)/3\right]\Big/ N_\theta \tag{5}$$

where $P(i_\theta,j_\phi)$ is the value of probability density function at the grid point (i_θ,j_ϕ). The probability density function is also continuous, so that the periodic condition applies in the azimuthal direction ϕ.

The equation for the averages is here numerically solved for each fixed value of the aspect ratio p, and Peclet number Pe. We use a finite difference method, in which the time term is discretized by a 3$^{\mathrm{rd}}$ order TVD (total variation diminishing) Runge-Kutta, while the space terms are discretised by a central difference scheme on a grid domain with N intervals for the θ variable with $(0 \leq \theta \leq \pi)$, and $2N$ intervals for the ϕ variable with $(0 \leq \phi \leq 2\pi)$. The central difference scheme is 2nd order, which, however, gives rise to large spurious numerical oscillations for high values of Pe and large time steps when it is used in the convection term. Therefore, in order to guarantee numerical stability and accuracy of the method, we tested different grids. The grid sensitivity analysis reveals that an accurate solution is obtained by grid systems with $N = 40$ for values from $Pe = 0.1$ to 10^3; grids with $N = 60$ for $Pe = 10^3$ to 10^5; and grids with $N = 150$ for $Pe \geq 10^5$. The integration is here performed by discretizing each of the three terms in eq. 3, since splitting the second term into smaller terms leads to undesired divergences.

In order to consider the effect of polydispersity, the orientation angle includes an additional averaging with respect to the aspect ratio

$$\langle \mathrm{A} \rangle = \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \mathrm{A}(\theta, \phi)\, P(\theta, \phi; t) m(p) d\theta d\phi dp \quad , \tag{6}$$

where both A and P are implicitly p-dependent. The distribution of aspect ratios $m(p)$ can be approximated by a log-normal distribution

$$m(p) = \frac{1}{p(2\pi)^{1/2} s} \exp\left[\frac{-(\ln p - \mu)^2}{2s^2}\right], \qquad p > 0. \tag{7}$$

where μ is the location parameter and s the scale parameter, respectively. The average aspect ratio $\bar{p}$ and the polydispersity σ are then given by

$$\bar{p} = \mathrm{e}^{\mu + s^2/2} \tag{8}$$

$$\sigma^2 = \mathrm{e}^{2\mu + s^2}(\mathrm{e}^{s^2} - 1). \tag{9}$$

The continuous distribution of aspect ratios is discretized into $N_\sigma = 30$ discrete values, which proves to be sufficient to obtain accurate results. The program calculates $\chi(\dot{\gamma}t)$, for various input values, namely the physical parameters (Pe, p, σ), and the integrating parameters (N, N_σ).

References

(1) Frattini, P. L.; Fuller, G. G. The dynamics of dilute colloidal suspensions subject to time-dependent flow-fields by conservative dichroism. *J. Colloid Interface Sci.* **1984**, *2*, 506.

(2) Frattini, P. L.; Fuller, G. G. Conservative dichroism of a sheared suspension in the Rayleigh-Gans light-scattering approximation. *J. Colloid Interface Sci.* **1987**, *119*, 335.