

Supplementary Material

Quantifying the Reversible Association of Thermosensitive Nanoparticles

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Dynamic light scattering analysis

The quantity measured in the DLS experiments is the intensity autocorrelation function. This generates the field autocorrelation function, which in turn gives an estimate of the diffusion coefficient D averaged over all the colloidal particles (in our case, including dimers) present in the system. The cumulant method has been used in the determination of D [1]. From this, the average hydrodynamic radius r_h is extracted based on the well-known Stokes-Einstein equation: $D = k_B T / 6\pi\eta r_h$, where η is the viscosity of the solvent (water) at temperature T .

The effective association constant is extracted from the measurements of the time-evolution of the average hydrodynamic radius by applying the following equation

$$\frac{1}{r_{h,1}} \frac{dr_h(t)}{dt} = \frac{I_2(q)}{2I_1(q)} \left(1 - \frac{r_{h,1}}{r_{h,2}}\right) N K_{\text{eff}} \quad (1)$$

which gives access to the effective association constant K_{eff} of the experimental system. Here, $q = (4\pi/\lambda)\sin(\theta/2)$ is the wave-vector of the incident light, where $\lambda = 632.8\text{nm}$ is the wavelength of the laser beam and $\theta = 90^\circ$ is the scattering angle. The experimental values of the latter quantity are then fitted using

$$K_{\text{eff}} = \frac{16k_+^3 N^2}{[2k_- + 4k_+ N - k_- (I_2(q)/I_1(q))(r_{h,1}/r_{h,2})]^2} \quad (2)$$

where the only fitting parameter is k_- . The other parameters in the above equations are evaluated as follows. N is the total number density of colloidal particles in the system, which is known for any given concentration of the suspension. The hydrodynamic radius of the thermoresponsive nanoparticles used in the experiments is $r_{h,1} = 85\text{nm}$. This was evaluated by DLS before the onset of the association and is practically T -independent above 32°C . Hence the hydrodynamic radius of the dimers is given by $r_{h,2} = 1.38 \times 85\text{nm} = 117.3\text{nm}$ [2]. The ratio of the intensity of light scattered by dimers to the intensity of light scattered by monomers $I_2(q)/I_1(q)$ depends uniquely upon the scattering angle (which in our case is $\theta = 90^\circ$) through q , according to the Rayleigh-Debye-Gans theory of light scattering [2, 3]. For our calculation we used a value

FIG. 1: (color online). Time-evolution of the normalized average hydrodynamic radius of a $2.5 \cdot 10^{-3}$ wt% colloidal suspension measured at different scattering angles at 32.6°C .

$I_2(q)/I_1(q) \simeq 1.5$ at 90° estimated by using

$$\frac{I_2(q)}{2I_1(q)} = \left(1 - \frac{r_{h,1}}{r_{h,2}}\right) \left[\frac{\frac{1}{r_{h,1}} \frac{dr_h(t)}{dt}}{\frac{1}{I(q,0)} \frac{dI(q,t)}{dt}} - \left(1 - \frac{r_{h,1}}{r_{h,2}}\right) \right]^{-1} \quad (3)$$

based on experimentally measured quantities (see Fig. 1). This estimated value however, is not very different from the value $I_2(q)/I_1(q) \simeq 1.3$ that one obtains from RDG theory. If one would use the theoretical value instead of the one measured, the error on the kinetic constant would be within 14% of the estimated value.

Finally, for attractive colloidal nanoparticles, k_+ is given by the Smoluchowski diffusion-limited rate, $k_+ = (8/3)k_B T / \eta$, with η the water viscosity [2].

Parameter sensitivity in the kinetic model

We have checked that changing the range of the effective square-well potential δ from 10nm to 1nm leads a value of the depth of the attractive square-well V_{min} which is about $16.5k_B T$. This has to be compared with the value of $12k_B T$ which we obtain using the value of 10nm which follows from the assumption on the hydrophobic nature of the attraction [4]. It is clearly seen that changing the range of the potential by one order of magnitude leads to an almost negligible change in V_{min} , namely of just a few $k_B T$'s. This is so because $V_{\text{min}}/k_B T$ depends only logarithmically on the parameters: $V_{\text{min}}/k_B T = -\ln(k_- \delta^2 / D)$, so that an order of magnitude change in any of the parameters (in particular in δ), means a change of only a few $k_B T$'s in V_{min} . This demonstrates that our estimate of V_{min} is very robust and not significantly affected by the error in the estimate of potential range δ .

Reversible aggregation of thermosensitive nanoparticles upon varying T

In order to verify that the aggregation is reversible upon changing the temperature (T), dynamic light scattering was

FIG. 2: (color online). Time-evolution of the average hydrodynamic radius of the colloidal suspension measured by DLS upon varying the temperature.

used to measure the time evolution of the average hydrodynamic radius of the colloidal suspension, $r_h(t)$, at different temperatures. For this purpose we used a Zetasizer (Malvern model nanoZs), in which the sample could be quickly equilibrated due to a set of Peltier elements. The dilute suspension (2.5×10^{-3} wt% with 5×10^{-2} M KCl) was first maintained 10 min at 25°C , then heated first at 32°C , and afterwards at different temperatures in the range between 33°C and 35°C . The cooling process was then recorded first at 32°C and then at 25°C . As shown in Fig. 2 of this appendix, whereas the system is stable at 25°C and 32°C , it instead coagulates at 33°C .

The kinetics was found to increase with increasing temperature (as is visible from the increasing slopes in Fig. 2 upon increasing T) and the hydrodynamic radius varies between

150 nm and 400 nm within 10 min. Upon cooling down to 32°C the hydrodynamic radius sharply decreases and reaches the same value as before the coagulation occurred, which was also confirmed at 25°C . Note that the association is much slower than the dissolution process in the dilute regime as it is mostly limited to the diffusion of the particles. This experiment confirms the reversibility of the association and that the interaction potential can be tuned from repulsive (hard-sphere like) to attractive within a narrow temperature range.

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