Supplementary material

Yielding of weakly attractive nanoparticle networks

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- *Calculation of the potential energy between interacting particles*

In the model system investigated here, the total potential energy between a pair of interacting particles (U_T) is the sum of the repulsive steric energy U_S and the attractive van der Waals energy U_A.

The repulsive energy arising from the steric layer is caused by a local increase in osmotic pressure and by the elastic compression of the surface adsorbed molecular chains as the particles approach one another. Estimates of the steric repulsive energy (U_S) taking into account the osmotic ($U_{S,Osm}$) and elastic effects ($U_{S,El}$) were obtained using the following equations: [35]

$$U_S = U_{S,Osm} + U_{S,El}, \tag{S1}$$

where:

$$U_{S,Osm} = \frac{4\pi akT}{v}\phi_p^2\left(\frac{1}{2}-\chi\right)\left(\delta-\frac{D}{2}\right)^2, \qquad \text{for } \delta \leq D < 2\delta \tag{S1a}$$

$$U_{S,Osm} = \frac{4\pi akT}{v}\phi_p^2\left(\frac{1}{2}-\chi\right)\delta^2\left(\frac{D}{2\delta}-\frac{1}{4}-\ln\left(\frac{D}{\delta}\right)\right), \qquad \text{for } D < \delta \tag{S1b}$$

$$U_{S,El} = \frac{2\pi akT\delta^2\rho\phi_p}{M_w}\left\{\frac{D}{\delta}\ln\left[\frac{D}{\delta}\left(\frac{3-(D/\delta)}{2}\right)^2\right]-6\ln\left[\frac{3-(D/\delta)}{2}\right]+3\left(1-\left(\frac{D}{\delta}\right)\right)\right\} \qquad \text{for } D < \delta, \tag{S1c}$$

where a is the particle radius, D is the distance between particle surfaces, k is the Boltzmann constant, T is the temperature, v is the volume of one solvent molecule, ϕ_p is the volume fraction of ligand molecules within the steric layer, χ is the Flory-Huggins solvency parameter, ρ is the ligand surface density and M_w is the ligand molar mass. The exact values of these parameters for this model colloidal system can be found in reference 29.

In addition to the repulsive energy imparted by the ligand steric layer, dipolar interactions between the interacting particles lead to an attractive van der Waals energy that can be estimated as follows:

$$U_A = -\frac{A}{6}\left(\frac{2a^2}{D(4a+D)}+\frac{2a^2}{(2a+D)^2}+\ln\frac{D(4a+D)}{(2a+D)^2}\right), \tag{S2}$$

where A is the Hamaker constant. An A value of 2.11×10^{-20} J, obtained from the Hamaker constants of alumina and toluene in vacuum, was used in the calculations. [29, 36]