Online supplementary material.

We estimate the spring constant κ_s for stretching the bond between two neighboring particles from the interaction potential, $U(r)$. This potential includes contributions from both the depletion attraction and the electrostatic repulsion: $U(r) = U_d(r) + (u_e /r)\exp[-(r - 2a)/l_D]$. The second term describes the electrostatic repulsion using the Poisson-Boltzmann theory. The parameters of U_d are known, but there are two fit parameters from the electrostatic repulsion: u_e is related to the charge on the particle surface and l_D is the Debye screening length, which varies depending on sample details. These two parameters are roughly estimated from the gelation time by assuming that the increase over that expected from purely diffusion-limited cluster aggregation reflects the contribution of an electrostatic repulsive barrier. Specifically, the repulsion increases the gelation time, τ_g, by a factor equal to the Fuchs stability ratio, $W(U(r))$ [1]. Thus the estimated gelation time is $\tau_g = W\tau_d\phi^{-d_f/(3-d_f)}$, where τ_d is the Smoluchowski doubling time, $\tau_d = a^2/(6\phi D)$, with D being the diffusion coefficient of a single colloidal particle [1]. For samples with ϕ = 0.04, we estimate that $\tau_d \approx 8$ s. The values of τ_g were estimated using microscopy to estimate the time at which a system-spanning network appeared. We found τ_g values of approximately 1 h (R_p = 35 nm), 50 ± 30 h (R_p = 25 nm), and 300 ± 100 h (R_p = 6 nm). The barrier is more pronounced in samples with short-range depletion attraction owing to the long range of the repulsion. Using the experimental value of d_f = 2.1, we find the best agreement with u_e= 19 ± 2 $k_BT\cdot\mu$m and l_D = 60 ± 15 nm, which leads to calculated τ_g values of 1.0 ± 0.5, 10 ± 4, and 200 ± 100 h respectively.

Using the equipartition theorem, we assign ½ k_BT to each normal mode, and thus obtain $\kappa_s = k_B T \Big/ \left\langle \left(r - \langle r \rangle \right)^2 \right\rangle$. This is the method used in analyzing the experimental data. Here, the averaged quantities are calculated by weighting according to the Boltzmann distribution; thus, $\langle r \rangle = \int dr r e^{-U(r)/k_B T} \Big/ \int dr e^{-U(r)/k_B T}$. Table 1 lists the predicted values of κ_s for each of the samples that were analyzed in detail.

$U_d(r{=}2a)$, c_p^{eff}	R_p/a, ϕ	Measured κ_0 ($k_BT/\mu m^2$)	Calculated κ_s ($k_BT/\mu m^2$)
-44 k_BT, 22.3 mg/mL	6/750 nm, 0.04	of order 10^3	5×10^7
-20 k_BT, 9.3 mg/mL	22/750 nm, 0.04	$(3.0 \pm 0.6)\times10^3$	$(330 \pm 50)\times10^3$
-16 k_BT, 7.2 mg/mL	25/750 nm, 0.04	$(2.0 \pm 0.5)\times10^3$	$(100 \pm 30)\times10^3$
-16 k_BT, 7.1 mg/mL	33/750 nm, 0.04	140 ± 20	$(30 \pm 10)\times10^3$
-11 k_BT, 4.6 mg/mL	35/750 nm, 0.05	650 ± 150	$(3.5 \pm 1)\times10^3$

Table 1: List of parameters for the samples presented in detail. The measured spring constant κ_0 is obtained by extrapolation of the measured $\kappa(r)$ to $r = 2a$. The predicted two-particle bond-stretching spring constants κ_s are computed from the interaction potential.

Reference:

1. W. B. Russel, *et al.*, *Colloidal Dispersions* (Cambridge U. Press, 1989).