Criticality for shear-induced gelation of charge-stabilized colloids

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Electronic supplementary information

Part 1: The typical liquid-like and solid-like states of the colloidal systems after passing through the z-MC.

Note that the solid-like sample is of cylindrical shape, which results from the shape of the outlet tube after passing through the z-MC.
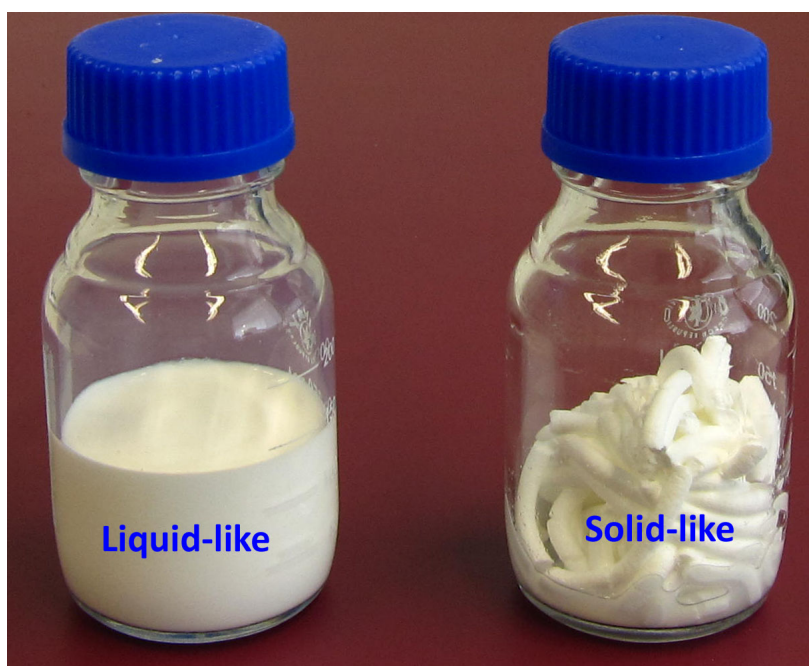
Part 2: Estimation of the interaction barrier U_{max} and the bonding strength h

In the frame of classical DLVO theory, accounting for the short-range Born repulsion, the colloidal interaction energy can be computed as the sum of three contributions, the van der Waals attractive interaction, U_A, the electrostatic repulsive interaction, U_R, and the Born repulsion, U_{Born}, as follows:

$$U = U_A + U_R + U_{Born} \tag{S1}$$

To compute U_A, the well-known Hamaker relation is used:

$$U_A = -\frac{A_H}{6}\left\{\frac{2}{l^2-4} + \frac{2}{l^2} + \ln\left[1-\frac{4}{l^2}\right]\right\} \tag{S2}$$

where A_H is the Hamaker constant, and $l=r/R_p$ with r the interparticle center-to-center distance. A value of $A_H=1.3\times10^{-20}$ J for polystyrene[1] is used in this work. For U_R, we use the modified Hogg-Healy-Fuersteneau expression derived by Sader et al.,[2]

$$U_R = \frac{4\pi\varepsilon_r\varepsilon_o R_p\psi^2}{l}\ln\left[1 + \exp(-\kappa R_p(l-2))\right] \tag{S3}$$

which can be applied for both small and large values of $\kappa R_p(l-2)$, where ε_r is the relative dielectric constant of the dispersion medium, ε_o the permittivity of vacuum, ψ the surface potential and κ the reciprocal Debye length, defined as

$$\kappa \equiv \left(N_A e^2 \sum_i C_i z_i^2 / \varepsilon_r\varepsilon_0 kT\right)^{1/2} \tag{S4}$$

where N_A is the Avogadro constant, and C_i and z_i are the bulk concentration and charge valency of the i-th ion, respectively. For U_{Born}, we use the expression made by Feke et al.,[3]

$$U_{Born} = N_{12}\frac{1}{l}\left[\frac{l^2-14l+54}{(l-2)^7} + \frac{-2l^2+60}{l^7} + \frac{l^2+14l+54}{(l+2)^7}\right] \tag{S5}$$

where N_{12} is a parameter expressing the strength of the van der Waals attraction relative to the Born repulsion, which should be in the range of 10^{-18} to 10^{-23} for most colloidal systems.

For the present systems, we use a value of $N_{12}=1\times10^{-21}$.

It is seen that the most important quantity for computing the colloidal interactions at the criticality for solid-like transition is the surface potential, ψ. To estimate it, we first assume that at $\phi=5.0\times10^{-4}$, where the zeta-potential was measured, the surface potential, ψ, is equal to the zeta-potential. Then, based on the following usual linear approximation, we can estimate the surface charge density, σ,

$$\sigma = \varepsilon_r\varepsilon_0\kappa\psi \qquad\qquad (S6)$$

Since all the colloidal systems used in this work have been cleaned by the resins, the ionic strength arises mainly from dissociation of the counterions (K^+) from the surface charge groups. Moreover, at the very low particle volume fraction of $\phi=5.0\times10^{-4}$, where the zeta-potential was measured, the K^+ concentration is very low (even completely dissociated), and the ions in the systems are dominated by H^+ and OH^- from dissociation of water. In fact, the measured conductivity in this case is basically equal to that of pure water. Therefore, at $\phi=5.0\times10^{-4}$, the $1/\kappa$ value was estimated from the H^+ and OH^- concentrations and equal to 9.62×10^{-7} m, with which the estimated values for the charge density σ from eqn (S6) are listed in Table 1.

Then, assuming that all the K^+ ions are dissociated from the surface charge groups, the K^+ concentrations at the criticality, $\phi=\phi_g$, can be computed from the σ values, and are used to estimate the $1/\kappa$ values at the criticality, which are given in Table 1. With the values of σ and $1/\kappa$, we can calculate the surface potentials, ψ at the criticality, again from eqn (S6), as reported in Table 1.

Now, we are ready to compute the total interaction energy from eqn (S1), with the values of all the parameters in Table 1. Figure S1 shows the computed total interaction energy, U, as a function of the interparticle surface-to-surface distance, $r-R_p$, for the three colloidal systems

of different particle radii, at the criticality for solid-like transition. It is seen that both the primary minimum, U_{min}, and the interaction barrier, U_{max}, increases as the particle radius increases. However, the difference, $U_b = U_{max} - U_{min} = hk_BT$, does not change very much with the particle radius, which can be clearly seen from the estimated h values in Table 1.

References

1   S. H. Maron, M. E. Elder and I. N. Ulevitch, *J. Colloid Sci.*, 1954, **9**, 89.

2   J. E. Sader, S. L. Carnie and D. Y. C. Chan, *J. Colloid Interface Sci.*, 1995, **171**, 46.

3   D. L. Feke, N. D. Prabhu and J. A. Mann, *J. Phys. Chem.*, 1984, **88**, 5735.

Table 1 Colloidal interaction parameters at the criticality for solid-like transition for the three colloidal systems of different particle sizes.

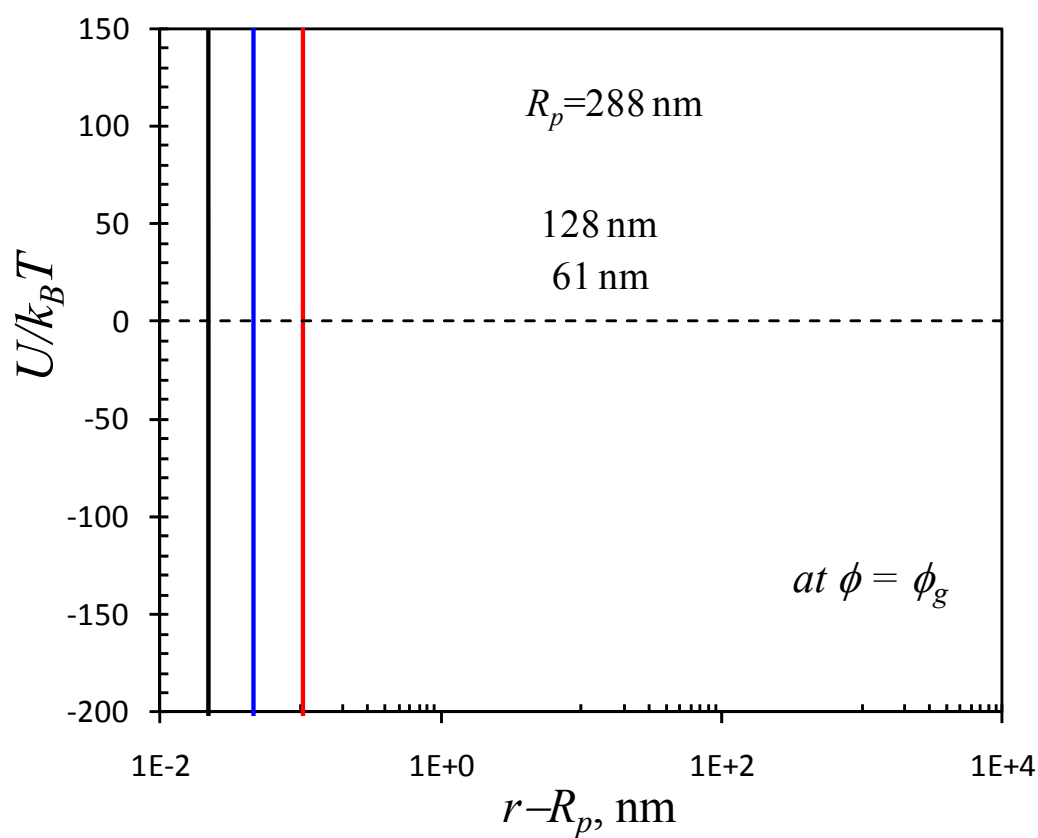| R_P (nm)	ϕ_g	σ (C/m^2)	$1/\kappa$ (m)	ψ (V)	A_H (J)	N_{12}	U_{max} (k_BT)	h
61	0.09	4.86×10^{-5}	2.76×10^{-7}	0.0193	1.3×10^{-20}	1×10^{-21}	14.3	211
128	0.15	4.83×10^{-5}	2.14×10^{-7}	0.0214	1.3×10^{-20}	1×10^{-21}	38.1	209
288	0.22	3.92×10^{-5}	2.28×10^{-7}	0.0228	1.3×10^{-20}	1×10^{-21}	100.7	204

Fig. S1 Interparticle interaction energy, U/k_BT, at the criticality for the liquid-like to solid-like transition, as a function of the surface-to-surface distance, $r-R_p$, for the three colloidal systems of different particle sizes. Parameters used for the calculations are listed in Table 1.