

Gel transition of depletion flocculated emulsions

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Abstract

The gel transition of depletion flocculated oil-in-water emulsions is analyzed as a function of the strength of the droplet–droplet interaction. The critical volume fraction for gelation has been found to decrease exponentially with the magnitude of the interaction energy at contact, in agreement with recent proposals for aggregating colloids. The viscosity modeling of these emulsions had been discussed in a previous work (Colloids Surf. A 203 (2002) 11). The results reported here show the interplay between phase behavior and rheology of flocculated emulsions.

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1. Introduction

It is well known that colloidal interactions determine the phase behavior and rheology of colloidal dispersions. In a recent paper [1], we discussed the shear flow behavior of oil-in-water emulsions in relation to droplet–droplet interactions. These emulsions were prepared using sodium caseinate as emulsifier. The oil volume fraction was $\phi = 0.30$ and the oil droplets presented a narrow size distribution with mean radius $a = 190$ nm. The excess sodium caseinate in the aqueous phase forms sub-micelles, which yields

reversible droplet–droplet aggregation by the mechanism of depletion. The aggregation increases the effective volume fraction of the disperse phase, hence the low shear viscosity η_0 increases significantly with protein concentration (Table 1). For higher shear rates, strong shear-thinning was observed due to the gradual breakup of droplet aggregates induced by shear [1]. The interaction energy between droplets was evaluated as the superposition of DLVO and depletion interactions. The last was described by the Asakura–Oosawa exclusion volume theory. Physicochemical parameters characterizing the protein-covered oil droplets dispersed in water were used in calculations [1]. Fig. 1 shows typical curves of the pair potential U normalized with the thermal energy $k_B T$ (k_B is the Boltzmann constant and T is the

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Table 1

Low shear viscosity (relative to the suspending fluid viscosity) and depth of the potential well (relative to the thermal energy) of oil-in-water emulsions ($\phi = 0.3$, $T = 20^\circ\text{C}$) for different concentrations of protein and electrolyte [1]

C (g kg ⁻¹)	As prepared		12.5 mM NaCl added	
	η_0/η_F	$U_{\min}/k_B T$	η_0/η_F	$U_{\min}/k_B T$
20	7.9	–	5.9	–
30	15.3	–	7.6	–
40	87.1	0.95	42.1	0.03
50	2.2×10^3	2.53	667	0.52
60	7.8×10^3	4.05	17×10^3	1.39

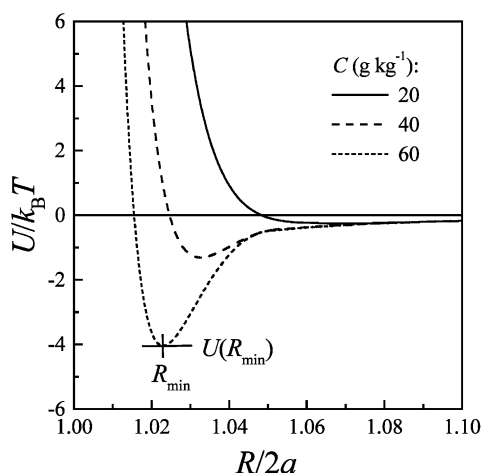


Fig. 1. Dimensionless pair potential, as a function of the relative center-to-center distance between particles, predicted by the superposition of DLVO and depletion interactions. Data for numerical calculations correspond to protein-covered oil droplets dispersed in water at 20°C [1].

absolute temperature) as a function of the relative interparticle distance $R/2a$. It can be observed that depletion attraction leads to a secondary minimum in the potential curves. The depth of the potential well, $U_{\min} = |U(R_{\min})|$, is an increasing function of protein concentration. In these calculations, the exclusion distance was included as $L = r_{\text{sm}} + b\kappa^{-1}$, where r_{sm} is the mean sub-micelles radius and κ^{-1} is the Debye length [1]. Values of b of order unity were required to predict potential wells in agreement with rheometric data (the size ratio $\xi = L/a$ ranged 0.034–0.066 in the samples studied). In

fact, the values of U_{\min} presented in Table 1 were estimated by using a viscosity model for colloidal dispersions. The interaction potential enters this model through the relaxation time associated to the attractive force field. It is assumed that after a shear deformation, the structure of flocculated emulsions is rapidly restored due to interparticle forces. The characteristic time of this process was estimated to be $\tau \sim \eta_F a^3 / U_{\min}$, where η_F is the suspending fluid viscosity (a detailed description of this modeling is given in [2]). Therefore, the concentrations of both protein and electrolyte ions in the aqueous phase were related to the characteristics of the viscosity curves [1]. In the present work, we wish to add some insights into the phase behavior of these emulsions, in particular, the gel transition after droplet flocculation.

2. Theoretical concepts

Colloidal particles interacting through potentials with an attractive minimum form roughly spherical clusters of effective radius, R_{eff} . At low particle concentrations, these clusters move freely through the medium and the suspension remains liquid-like. As the particle concentration increases, the clusters overlap. Eventually, the gelation threshold is reached and the system becomes solid-like. In suspensions of hard spheres, this fluid-to-solid transition occurs when the particle volume fraction ϕ reaches the glass transition volume fraction, $\phi_G \approx 0.58$ [3,4]. At this concentration, particles are trapped in transient cages formed by their nearest neighbors and diffusion is no longer possible. Similarly, it has been recently suggested [5,6] that the gelation of aggregating colloids occurs when clusters become crowded. The idea is pictured in Fig. 2. The critical concentration at which the system reaches the gel transition is $\phi_c \approx \phi(\phi_G/\phi_{\text{eff}})$, where ϕ_{eff} is the effective volume fraction of the disperse phase. This volume fraction includes not only the volume occupied by the particles, but also the volume of solvent immobilized hydrodynamically in the flocs. Therefore, $\phi_{\text{eff}} > \phi$ and hence $\phi_c < \phi_G$, i.e. the crowding of clusters may occur at relatively

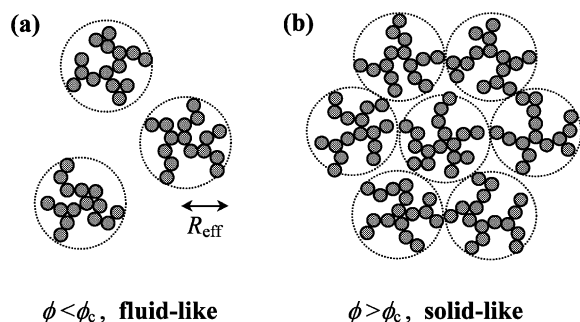


Fig. 2. Schematic representation of clusters of aggregated particles for concentrations below (a) and above (b) the critical one.

low particle concentrations. The effect is readily seen by assuming that the cluster structure is self-similar, thus $\phi_{\text{eff}} \approx \phi (R_{\text{eff}}/a)^{3-f}$, where the fractal dimension f accounts for the cluster compactness. The unifying view of gelation and the glass transition has gained consensus in the recent literature [7,8]. In fact, both phenomena are due to the kinetic arrest of structural relaxations [5,9]. Nevertheless, it is worth noting that, while the glass transition involves the caging of hard spheres, gelation is due to the crowding of particle clusters, which are formed by particle–particle ‘bonds’.

Another interesting feature of flocculated suspensions is that the value of ϕ_c depends on the strength the attractive interaction [10–14]: the higher the interaction, the lower the critical concentration for gelation. These results can be understood as follows: strong attraction yields loosely packed clusters. Consequently, the gelation threshold is reached at low particle concentrations. In contrast, when the magnitude of the attraction is of the order of the thermal energy $k_B T$, the particle–particle ‘bonds’ are easily broken and the flocs reorganize to form compact clusters. This leads to low values of ϕ_{eff} and relatively high values of ϕ_c . Further, ϕ_c has been reported to decrease exponentially with the magnitude of the interaction at contact [5,6]. In this context, we discuss our results for the rheology of the depletion flocculated emulsions.

3. Results and discussions

The low shear viscosity of concentrated dispersions is related to the particle volume fraction by $\eta/\eta_F = (1 - \phi/\phi_0)^{-2}$, where ϕ_0 is the maximum packing fraction [15]. According to this equation, the viscosity diverges when ϕ reaches ϕ_0 . Thus, the critical volume fraction of the emulsions can be estimated using: $\phi_0/\phi \approx \phi_0/\phi = [1 - (\eta_0/\eta_F)^{-1/2}]^{-1}$, from viscosity on the low shear plateau where the microstructure is intact (see also [4]). Values of η_0 reported in Table 1 are used for this purpose. As discussed above, the values of U_{min} corresponding to the same emulsions are also available (Table 1). By analyzing these data we found that the critical concentration and the interaction energy are well correlated through $\phi_c = \phi + (\phi_c^* - \phi) \exp(-\alpha U_{\text{min}}/k_B T)$, where α is a dimensionless parameter of order unity and ϕ_c^* represents a critical concentration for the suspension of fully dispersed droplets. The exponential decay has been reported previously in the literature [5,6], nevertheless, it should be noted that the relation proposed here satisfies: $U_{\text{min}}/k_B T \rightarrow \infty, \phi_c \rightarrow \phi$ and $U_{\text{min}}/k_B T \rightarrow 0, \phi_c \rightarrow \phi_c^*$ for the limits of very high and very low attractive interaction, respectively.

Results are plotted in Fig. 3, where data involves different concentrations of proteins and electrolyte in the aqueous phase. It is observed that, for weak depletion interaction, high particle volume fractions are required to reach the gelation threshold. On the other hand, for low particle volume fractions, a pronounced well depth is required to reach a particle network spanning throughout the sample. In fact, Fig. 3 represents a phase diagram for depletion flocculated emulsions, where the data mark the boundary between the fluid and the solid. Also the phase line in Fig. 3 shows clearly that the critical volume fraction for gelation decreases as protein concentration increases. It is worth noting that the rheological response of the emulsion changes likewise [1]: both the low shear viscosity and the degree of shear-thinning increase with protein concentration. Finally, it must be mentioned that the gelation transition may be affected by gravitational stress [5,16]. Conversely, depletion flocculation greatly influences the

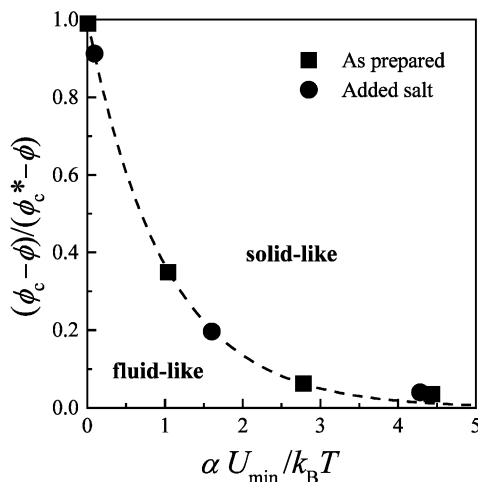


Fig. 3. Phase diagram of oil-in-water emulsions ($\phi = 0.3$, $T = 20^\circ\text{C}$) with different concentrations of protein and electrolyte [1]. The parameter values are: (■) $\alpha = 1.09$, $\phi_c^* = 0.40$; (●) $\alpha = 3.08$, $\phi_c^* = 0.36$. The dotted line is the exponential function, $\exp(-\alpha U_{\min}/k_B T)$.

creaming of oil-in-water emulsions [17–19]. The interplay between these phenomena and rheology deserves further investigation.

4. Concluding remarks

The critical concentration at which the gel transition occurs in depletion flocculated emulsions is correlated quantitatively with the strength of the interaction energy between droplets. Thus, one may control the phase behavior and rheology of emulsions by changing the magnitude of the inter-droplet attraction, besides the droplet volume fraction. The results are in full agreement with recent proposals [6] concerning the phase diagram of colloidal dispersions of attractive particles.

The values of both ϕ_c and U_{\min} were obtained from rheometric data by using a model that provides a relationship between the interparticle potential and the macroscopic viscosity [1,2]. In this sense, the results discussed above also help to

show the relationship between flocculation, gelation and rheology of aggregating colloids.

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