

## Control of stability/flocculation and rheology of concentrated suspensions

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**Abstract.** The various interaction forces that govern the stability/flocculation of concentrated suspensions are briefly described. Combination of these interactions result in three main energy-distance curves which determine the final state of the suspension. This ranges from colloidally stable to strongly flocculated (coagulated) suspensions. A schematic representation of the various states of suspensions is given. These states are reflected in the rheology of the suspension which can be investigated using steady state, constant stress (creep) or oscillatory measurements. Examples are given to illustrate the rheology of various systems: (i) those based on hard sphere interaction; (ii) those based on double layer repulsion; (iii) sterically stabilised systems; (iv) flocculated systems either weakly or strongly.

### INTRODUCTION

Concentrated solid/liquid dispersions (suspensions) occur in many industrial applications, of which we mention paints, dyestuffs, paper coatings, printing inks, ceramics, cosmetics, pharmaceuticals and agrochemicals. These suspensions can be aqueous or non-aqueous and the disperse phase may be organic or inorganic. They also cover a wide range of particle sizes, ranging from the colloid limit (1 nm - 1  $\mu$ m) to coarse suspensions that exceed 1  $\mu$ m and may reach tens of  $\mu$ ms. The control of the properties of suspensions is crucial in their preparation and subsequent application. This requires control of the interaction forces between the particles which will also control the flow characteristics (rheology) of the system. The formation of three dimensional structures in these systems is also governed by the interaction forces between the particles. In concentrated suspensions, the particles interact with many body collisions and the translational motion is restricted. These systems show time dependent spatial and temporal correlations and they are generally viscoelastic.

In this short review, I will briefly summarise the interaction forces between the particles and their various combinations. The form of the energy-distance curve may be used to describe the three dimensional structures that may be produced in the system. The rheology of the suspension can also be described in terms of the various interactions between the particles. Four systems may be distinguished: those where the interaction is of the hard sphere type; those containing double layers (electrostatic or soft interaction); those containing adsorbed or grafted polymer layers; and those where the net interaction is attractive. A brief description of these four different systems will be given. For more detail the reader may refer to recent articles by the author (ref. 1-5).

### INTERACTION FORCES BETWEEN PARTICLES AND THEIR COMBINATIONS

Four main types of interaction forces may be distinguished. The first is represented by hard sphere type, in which no interaction is felt till the centre-centre distance of separation between the particles approach the hard sphere diameter in which case the interaction rises steeply with further reduction in separation distance. The second type of interaction is that encountered with charged particles surrounded by an electrical

double layer. In this case the repulsive energy increases rapidly at a separation distance whereby the double layers begin to overlap. The third type of interaction, referred to as steric, shows a rapid increase in energy with reduction of distance of separation between the particles, as soon as the adsorbed or grafted layers begin to overlap. The fourth type of interaction, that is universal, is the van der Waals attraction, which increases rapidly with decrease of interparticle separation, beyond the so called capture distance.

Several combinations of the above interactions have been made. One of the earliest of such combinations is the double layer repulsion and van der Waals attraction, in the well known theory of stability of lyophobic colloids by Deryaguin, Landau, Verwey and Overbeek (ref. 6). This is illustrated in Fig. 1a. The energy-distance curve shows two minima and one maximum. A secondary minimum occurs at relatively large distance of separation, whose depth depends on particle size and shape, electrolyte concentration and Hamaker constant.

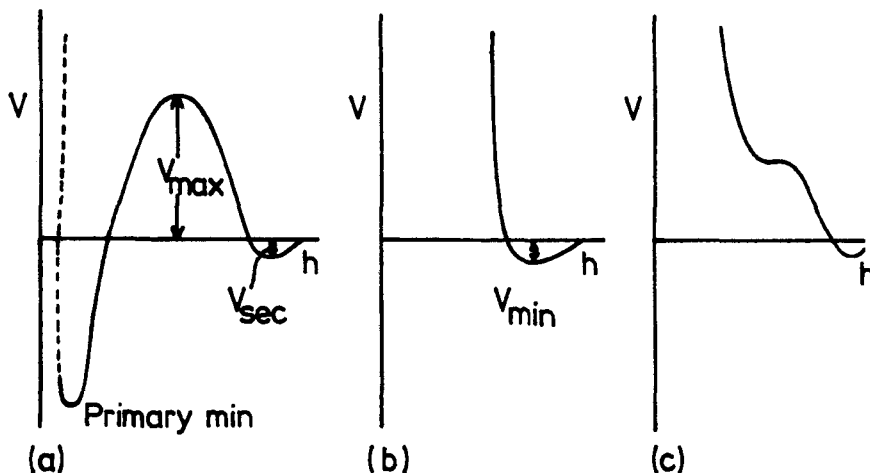


Fig. 1 Energy-distance curves for three types of stabilisation mechanisms: (a) Electrostatic; (b) Steric; (c) Electrosteric.

A primary deep minimum occurs at very short distances of separation, whose magnitude may reach several hundreds of  $kT$  units (where  $k$  is the Boltzmann constant and  $T$  the absolute temperature). At intermediate distances of separation an energy maximum exists whose height depends on electrolyte concentration, zeta potential and particle size. When the height of this maximum is significantly larger than the thermal energy (usually one quotes a maximum height that is larger than  $25 kT$ ), a colloiddally stable suspension is produced. This stability is kinetic in origin, since with time some flocculation may occur as a result of some particles overcoming the energy barrier during a Brownian encounter. However, the rate of flocculation becomes so small with high energy barriers that, within a practical time scale, no flocculation is detected. The second type of combination, illustrated in Fig. 1b, is steric and van der Waals attraction (ref.7). In this case the energy-distance curve shows only one minimum at separation distances  $h$  comparable to twice the adsorbed layer thickness. The depth of this minimum depends on the adsorbed layer thickness  $\delta$ , particle size  $a$  and the Hamaker constant. Provided that  $\delta$  is sufficiently large ( $>5$  nm) and  $a$  is small, steric stabilisation may approach thermodynamic stability as a result of the steep rise of repulsion when  $h < 2\delta$ . The third type, illustrated in Fig. 1c, shows a combination of double layer repulsion, steric repulsion and van der Waals attraction. This occurs when using polyelectrolytes as dispersants.

#### DESCRIPTION OF STATES OF SUSPENSIONS USING ENERGY-DISTANCE CURVES

Several states may be reached on standing and these are schematically represented in Fig. 2. The first three states represent the case of systems that are stable in the colloid sense. State (a) represents the case of a suspension with sufficiently small particles, such that the Brownian motion overcomes any gravitational sedimentation. When the particles are coarse and uniform in size, one may reach the condition represented by (b)

in which case the suspension forms a compact sediment (dilatant) leaving a clear supernatant. If the suspension has a size distribution, the larger particles may sediment faster leaving the very small particles suspended in the top layer of the continuous medium (Fig. 2c). States (d) - (f) represent coagulated suspensions, whereby strong attraction between the particles occur, e.g., in the primary minimum. State (d) shows chain aggregates, which may be produced in a relatively dilute suspension at constant temperature and in the absence of stirring. If the suspension is stirred during

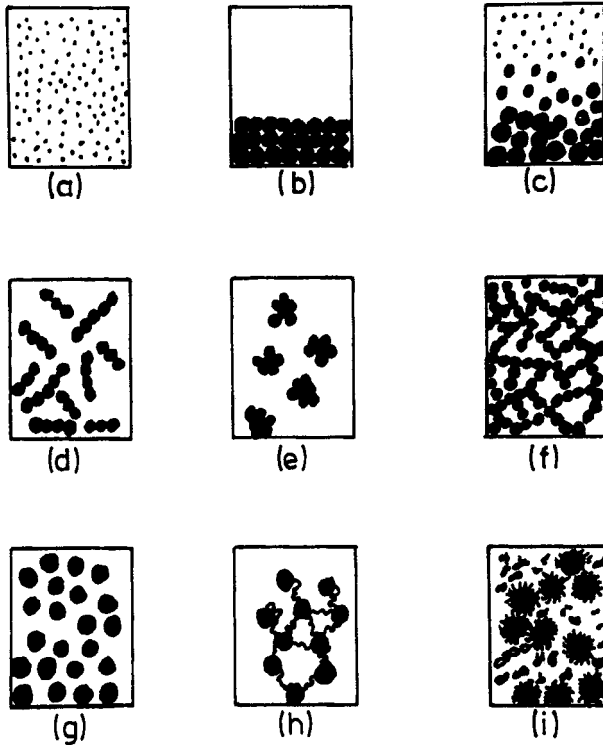


Fig. 2 Schematic representation of the various states of suspensions : (a) Stable colloidal suspension; (b) Stable coarse suspension with uniform size; (c) Stable coarse suspension with size distribution; (d) Coagulated suspension forming chain aggregates; (e) Coagulated suspension forming compact clusters; (f) Coagulated suspension with a continuous network; (g) Weakly flocculated suspension; (h) Bridging flocculation; (i) Depletion flocculation.

flocculation, one usually obtains more compact aggregates as illustrated in Fig. 2e. At sufficiently high volume fraction of the suspension the aggregation process produces chains and cross chains that may extend through the whole suspension (sometimes referred to as one floc structure) as shown in Fig. 2f. The state represented in Fig. 2g is that of a weakly flocculated structure, e.g., secondary minimum flocculation. Since the energy of attraction in this case is relatively weak (usually less than 5 kT), the flocculated structure may be destroyed by shaking, resulting in a dispersed state. On standing, the particles undergo weak flocculation forming a gel network. This sol  $\rightarrow$  gel process leads to thixotropy and could find application in many systems, e.g., paints. State (h) represents bridging flocculation that may be produced by high molecular weight materials under conditions of incomplete coverage. State (i) represents the case of weak flocculation that may be produced by the addition of a "free" (non-adsorbing) polymer. At a critical concentration of the "free" polymer, flocculation of the suspension may occur as a result of depletion of the chains from the zone between the particles. The solvent chemical potential in the zone between the particles is, therefore, higher than that in bulk solution containing the polymer chains. This difference in chemical potential (or osmotic pressure) results in weak attraction between the particles, a phenomenon that is referred to as depletion flocculation.

## CONTROL OF RHEOLOGY OF SUSPENSIONS

The rheology of concentrated suspensions (or its viscoelasticity) is determined by the balance of three forces : Brownian diffusion, hydrodynamic interaction and interparticle forces. All these interactions are determined by their range, which is determined by the volume fraction  $\phi$  and the particle size  $a$ . The total energy of interaction  $G_T$  is the sum of the various energies involved : electrostatic, steric and van der Waals. Various viscoelastic responses may be obtained depending on the time scale of the experiment,  $t_e$ , relative to the relaxation time of the system,  $t_r$ . The ratio ( $t_r/t_e$ ) is referred to as the Deborah number  $D_e$ . If  $D_e \gg 1$ , one obtains elastic response whereas if  $D_e \ll 1$  one obtains viscous response, and if  $D_e \sim 1$  mixed viscous and elastic (viscoelastic) response is produced. The latter is the most common response obtained with concentrated suspensions since the time scale of most rheological experiments cover a range that is comparable to the relaxation time of the system. Four different types of systems may be distinguished, whose rheology is summarised below.

### Rheology of hard sphere dispersions

These are systems where both attraction and repulsion are screened. Examples of these systems (monodisperse polystyrene latex) were prepared by Krieger and coworkers (ref.8) who screened the double layer repulsion either by addition of electrolyte or replacing water with a less polar medium like benzyl alcohol. When the relative viscosity,  $\eta_r$ , of the suspensions, at a given volume fraction, was plotted versus the reduced shear stress or shear rate (the reduced shear rate is simply the product of the translational diffusion time and the reciprocal shear rate), all results for the various particle sizes fell on the same curve. The latter showed two Newtonian regions in the low and high shear rate regime with a shear thinning region at intermediate shear rates. The first (low shear) Newtonian region with a high relative viscosity results from the presence of a random arrangement of particles, whereby the Brownian diffusion predominates over any hydrodynamic interaction. As the shear rate is increased beyond a certain limit, the particles arrange themselves in layers coincident with the plane of shear and the viscosity decreases with further increase of the applied shear rate (shear thinning region). In the high shear rate regime, the hydrodynamic flow predominates over any Brownian diffusion and the suspension shows a second Newtonian region but with much lower relative viscosity, than the value obtained in the low shear rate region. A plot of the Newtonian relative viscosity, in the low or the high shear rate region, versus  $\phi$  showed an initial gradual increase in  $\eta_r$  with increase of  $\phi$ , followed by a much more rapid increase in  $\eta_r$  with increase in  $\phi$ , when the latter exceeds 0.5. Indeed when  $\phi$  reached a value of  $\sim 0.6$ ,  $\eta_r$  showed a very rapid increase and any increase of  $\phi$  beyond this limit produced a near solid suspension with infinite viscosity. The change of  $\eta_r$  with  $\phi$  for hard sphere suspensions could be represented by the following equation,

$$\eta_r = [1 - (\phi/\phi_p)]^{-[\eta]\phi_p} \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity and  $\phi_p$  is the maximum packing fraction which for most suspensions is  $\sim 0.6$ . Bachelor (ref.9) derived an expression for the relative viscosity of hard sphere dispersions by taking into account the balance between Brownian diffusion and hydrodynamic interaction,

$$\eta_r = 1 + 2.5 \phi + 6.2 \phi^2 \quad (2)$$

The term in  $\phi^2$  accounts for hydrodynamic interaction at higher volume fractions. Equation (2) applies at  $\phi$  values  $< 0.2$ .

### Rheology of electrostatically stabilised suspensions

These are systems with extended double layers, i.e., at low electrolyte concentrations. The viscoelastic properties of these systems are determined by the double layer extension, volume fraction and particle size. As an illustration Fig. 3 shows the variation of complex modulus  $G^*$ , elastic modulus  $G'$  and loss modulus  $G''$  ( at a frequency  $\omega = 1$  Hz) as a function of  $\phi$  for polystyrene latex suspensions ( $a = 700$  nm) at  $10^{-5}$  and  $10^{-3}$  mol dm $^{-3}$

NaCl. At the lowest electrolyte concentration, all rheological parameters increase very rapidly with increase in  $\phi$  within the range studied and  $G^* > G''$  over the whole  $\phi$  range. In contrast the results in  $10^{-3}$  mol dm $^{-3}$  NaCl show that  $G'$  is either very close to  $G''$  or even lower than it, within the  $\phi$  range studied. These results reflect the double layer interaction which, at any given  $\phi$ , is much stronger at the lower electrolyte concentration. In  $10^{-5}$  mol dm $^{-3}$  NaCl, the double layer thickness is 100 nm and at the

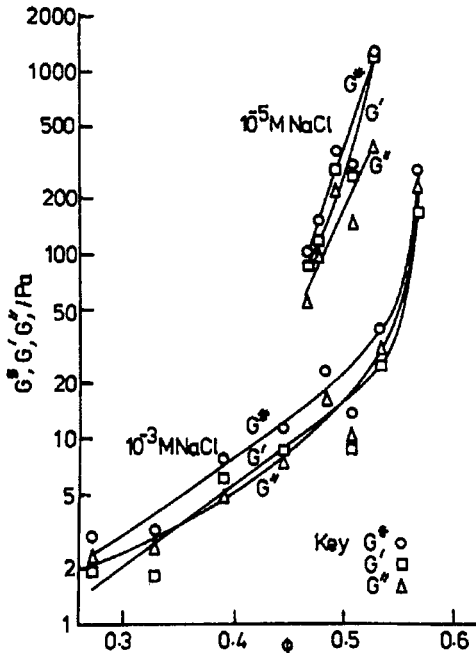


Fig. 3 Variation of  $G^*$ ,  $G'$ ,  $G''$  (at  $\omega=1$ Hz) for electrostatically stabilized suspensions.

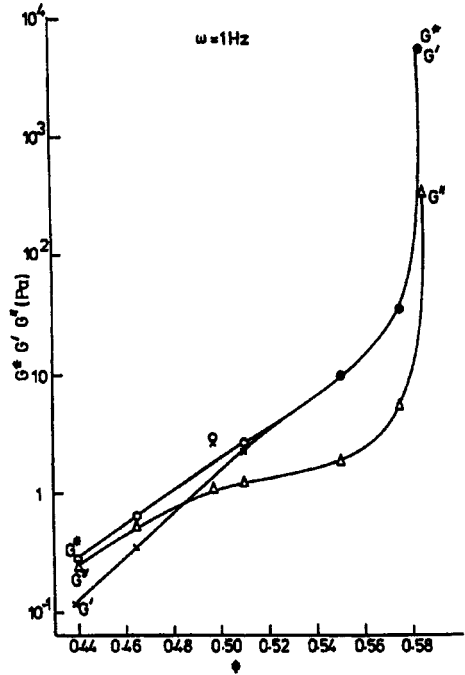


Fig. 4 Variation of  $G^*$ ,  $G'$ ,  $G''$  (at  $\omega=1$ Hz) for sterically stabilized suspensions.

lowest  $\phi$  value studied, namely 0.463, overlap of the double layers is significant leading to a predominantly elastic response. On the other hand, in  $10^{-3}$  mol dm $^{-3}$  NaCl the double layer extension is only 10 nm and double layer overlap is not significant up to the highest volume fraction studied, namely 0.566. In this case the elastic component of the modulus becomes comparable to the viscous component.

#### Rheology of sterically stabilised suspensions

These are systems with adsorbed or grafted polymer layers. As an illustration Fig. 4 shows the variation of  $G^*$ ,  $G'$  and  $G''$  (at  $\omega = 1$  Hz) as a function of  $\phi$  for polystyrene latex suspensions ( $a = 175$  nm) containing grafted polyethylene oxide (PEO) chains (ref.10) with a molecular weight of 2000. At  $\phi < 0.49$ ,  $G'' > G'$ , indicating weak interaction between the steric layers. At  $\phi > 0.49$ ,  $G' > G''$  and both  $G^*$  and  $G'$  show a rapid increase with further increase in  $\phi$ . This marks the onset of strong steric interaction when the grafted polymer layers are forced close to each other, thus undergoing some interpenetration and/or compression.

#### Rheology of unstable suspensions

These systems show complex rheology as a result of the non-equilibrium structure. Any application of shear results in partial breakdown of the structure and the flocs may undergo rearrangement. This is reflected in the time dependence of rheology, e.g. thixotropy. It is perhaps convenient to classify unstable systems into "weakly" and "strongly" flocculated reflecting the magnitude of the attraction energies involved. One of the best examples of a weakly flocculated suspension is that produced by the addition of "free" (nonadsorbing) polymer. Above a critical volume fraction of the free polymer,  $\phi_p$ , the system shows significant non-Newtonian behaviour which increases in magnitude with

further increase of  $\phi_p$  (ref.11). It is possible to relate some of the rheological parameters to the energy of separation,  $E_{sep}$ , between particles in a flocculated suspension. For example  $E_{sep}$  may be calculated from the extrapolated yield value  $\tau_B$  by the equation,

$$\tau_B = \frac{3 \phi n E_{sep}}{8 \pi a^3} \quad (3)$$

where  $n$  is the average number of contacts between particles in a floc.  $n$  is probably in the range 4 (for an open floc) to 8 (for random arrangement of particles).  $E_{sep}$  may be compared with the free energy of depletion,  $G_{dep}$ , which may be calculated from the difference in chemical potential of the solvent in the presence of the free polymer and its value in the absence of the polymer. Several theories are available for calculating  $G_{dep}$  (ref.12,13) to which the reader should refer to. In some cases agreement between  $E_{sep}$  calculated from rheology and  $G_{dep}$  calculated from theory was obtained (ref.11). Strongly flocculated suspensions are exemplified by electrostatically stabilised systems coagulated by addition of electrolyte or sterically stabilised systems flocculated by reduction of solvency of the medium for the chains to worse than a theta solvent. Both systems were recently studied in our laboratory (ref.1-5) and various examples were given to illustrate the powerful use of viscoelastic measurements for investigating concentrated flocculated suspensions. For example, reduction of solvency for a sterically stabilised suspension showed an initial reduction in the moduli (as a result of collapse of the chains) followed by a rapid increase in moduli values at and above the critical flocculation point. With strongly flocculated suspensions, the elastic modulus could be related to the volume fraction using scaling laws, i.e.,  $G' \sim \phi^n$ . The exponent  $n$  may be related to the structure and strength of the flocculated structure.

#### REFERENCES

1. Th.F. Tadros, Prog. Colloid and Polymer Sci., **79**, 120-127 (1989).
2. Th.F. Tadros, "Rheology of Concentrated Stable and Flocculated Suspensions" in "Flocculation and Dewatering", B.M. Mougdil and B.J. Scheiner Editors, Engineering Foundation Publishers (1989) pp 43 - 87.
3. Th.F. Tadros, "Polymer Colloids as Models for Studying Interaction Forces in Concentrated Dispersions", in "Scientific Methods for the Study of Polymer Colloids and Their Applications", F. Candau and R.H. Ottewill Editors, C303 Kluwer Academic Publishers (1990) pp 338-441.
4. Th.F. Tadros, Langmuir, **6**, 28-35 (1990).
5. Th.F. Tadros and A. Hopkinson, Faraday Disc. Chem. Soc., **90**, 41-55 (1990).
6. E.J.W. Verwey and J.Th.G. Overbeek, "Theory of Stability of Lyophobic Colloids", Elsevier Publishing Co. Amsterdam (1948).
7. D.H. Napper "Polymeric Stabilisation of Colloidal Dispersions", Academic Press, London, N.Y. (1981).
8. I.M. Krieger, Adv. Colloid and Interface Sci., **3**, 111-136 (1972).
9. G.K. Bachelor, J. Fluid Mech., **83**, 97 (1977).
10. C. Prestidge and Th.F. Tadros, J. Colloid Interface Sci., **124**, 660-665 (1988).
11. C. Prestidge and Th.F. Tadros, Colloids and Surfaces, **31**, 325-346 (1988).
12. S. Asakura and F. Oosawa, J. Chem. Phys., **22**, 1255 (1954); J. Polym. Sci., **33**, 245 (1958).
13. G.J. Fleer, J.H.M.H. Scheutjens and B. Vincent, ACS Symp. Ser., **240**, 245 (1984).