

Fundamental aspects of suspension stabilisation and some of their applications

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This paper reviews the mechanisms by which the solid particles interact among themselves and with the medium in a suspension and the theories of stabilisation of suspensions based on the combination of these interactions. This is followed by a qualitative description of the structural units that can be produced in a suspension in terms of the energy-distance curves between particles. The sedimentation of suspensions on storage and the methods to prevent it are discussed. Finally examples of the application of these principles to industrial systems are given.

Suspensions occur in many industrial applications, e.g. paints, dyestuffs, paper coatings, printing inks, ceramics, cosmetics and personal care, detergents, pharmaceuticals, agrochemicals and coal-water slurries. The solid particles may be organic or inorganic and the continuous medium can be aqueous or non-aqueous. These preparations cover wide particle size ranges. Suspensions that cover the size range 1 nm-1 μ m are referred to as colloidal systems. However, many suspensions consist of particles that are outside this range ($>1 \mu$ m) and in some cases, particle sizes reaching hundreds of micrometers are encountered, e.g. coal-water suspensions.

The control of the properties of suspensions is crucial in their preparation and subsequent application [1]. For this purpose it is necessary to control the properties of the interfacial region at the solid/liquid boundary. If the particles of the suspension contain surface ionogenic groups (e.g. oxides), charge separation occurs as a result of the dissociation of these groups with the result that an electrical double layer is formed. The main parameters that need to be controlled in this case are the surface (or zeta) potential and electrolyte concentration and valency. The latter controls the extension of the double layer and hence the double layer repulsion between the particles (see below). An electrical double layer may also be produced as a result of adsorption of ionic surfactants or polyelectrolytes. In all these cases,

the stability of the suspension is controlled by the double layer repulsion. However, this is not the only stabilisation mechanism, since many stable suspensions can be prepared using nonionic surfactants or polymers (macromolecular surfactants), whereby the contribution from charge stabilisation is relatively less important. The interfacial region in this case consists of an adsorbed (or grafted) surfactant or polymer chain, whose conformation and interaction with the solvent are important in the control of stability of the suspension. This is usually referred to as steric stabilisation (see below). In this overview we will describe the various interaction forces between particles in a suspension. This is followed by the theories of stabilisation of suspensions that are based on the combination of these interaction forces. A qualitative description of the various structural units that are produced in suspensions is given. Such units can be described in terms of the total energy-distance curves between particles in a suspension. This is followed by a section on the problem of sedimentation of suspensions and the methods that may be applied to prevent it. Some examples will be given to illustrate the application of these principles in some industrial systems.

Interparticle interactions and their combinations

Types of interparticle interactions

Four different types of interparticle interactions may be considered and these are summarised below.

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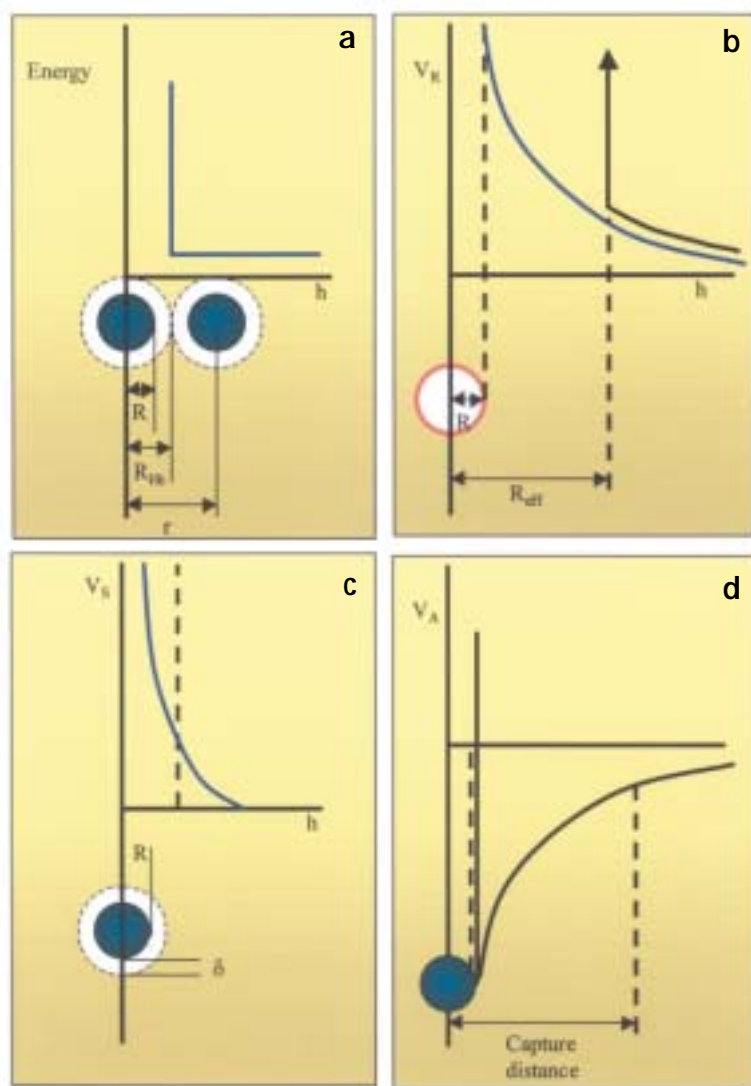


Figure 1 - Types of interparticle interactions in suspensions: (a) hard-sphere interactions; (b) electrostatic ("soft") interactions; (c) steric interactions; (d) van der Waals attraction

Hard-sphere interactions

This is the simplest type to consider where both repulsion and attractive forces are screened, i.e. corresponding to the so-called neutral stability. Examples of hard-sphere suspensions are those where water is replaced by a less polar medium such as benzyl alcohol or suspensions containing sufficient electrolyte to compress the double layers. In this case, the particles may be considered to be hard-spheres with a radius R_{hs} that is only slightly larger than the actual radius R (the core radius) of the particles.

When the particles approach each other reaching a centre-to-centre separation h which is smaller than the hard-sphere diameter ($2 R_{hs}$), strong repulsion occurs and the interaction rises very steeply [2, 3].

This is shown in Figure 1a. In this case the suspension changes from "dilute" to "solid" over a narrow range of volume fraction ϕ . As soon as ϕ exceeds the maximum hard-sphere volume fraction ($\cong 0.6$ for random packing), the repulsive interaction increases very sharply and the viscosity of the suspension increases very much with further increase in the volume fraction.

Electrostatic ("Soft") interaction

This occurs with systems containing extended double layers (i.e. at low electrolyte concentration). The double layer extension is given by the reciprocal of the Debye-Huckel parameter ($1/\kappa$) which depends on the electrolyte concentration C and valency Z as given by the equation:

$$\frac{1}{\kappa} = \left(\frac{\epsilon_r \epsilon_0 kT}{2Z^2 e^2 N_A C} \right)^{1/2} \quad (1)$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of free space, k is the Boltzmann constant, T is the absolute temperature, e is the electronic charge and N_A is the Avogadro's constant.

$(1/\kappa)$ is basically the distance from the surface at which the surface potential ψ_0 is reduced to ψ_0/e (where e is the exponential term, i.e. 2.72).

For a 1:1 electrolyte, $(1/\kappa)$ is 100 nm in 10^{-5} mol dm^{-3} , 10 nm in 10^{-3} mol dm^{-3} and 1 nm in 10^{-1} mol dm^{-3} . The repulsive force V_R between two particles at a centre-to-centre separation h is given (for small values of ψ_0) by [4]:

$$V_R = 4\pi\epsilon_r\epsilon_0 R^2 \Psi_o^2 \exp[-\kappa(h-2R)]/h \quad (2)$$

Thus V_R decays exponentially with h and the rate of such decay depends on the value of $(1/\kappa)$. At low electrolyte concentration ($<10^{-3}$ mol dm^{-3}), $(1/\kappa)$ is relatively large and V_R decays slowly with h . In this case strong repulsion due to double layer overlap occurs at relatively large h values as illustrated in Figure 1b. An effective radius R_{eff} may be defined to include this double layer interaction. R_{eff} is simply R plus the double layer thickness $(1/\kappa)$.

With small particles and low electrolyte concentration R_{eff} can be much larger than R . The interparticle interaction that occurs at large distances of separation between the particles (long-range interaction) is sometimes referred to as "soft" interaction. In this case the interaction becomes strong at relatively low actual (core) particle volume fraction.

Steric interactions

This is the case when the particles contain layers of surfactants and/or macromolecules. Interaction occurs as soon as the adsorbed or grafted layers begin to overlap [5]. This is illustrated in Figure 1c. It is convenient to divide the interaction into two main contributions: mixing (or osmotic) interaction G_{mix} resulting from the free energy obtained in mixing two surfactant or polymer layers and elastic (volume restriction or entropic) interaction G_{el} resulting from the loss in configurational entropy of the chains on the approach of a second particle. The mixing interaction, G_{mix} can be calculated from a consideration of the free energy of mixing of polymer solutions as given by the Flory-Krigbaum theory [6]. When two particles containing layers with thickness δ approach to a distance of separation h that is smaller than twice the layer thickness 2δ , repulsion occurs as a result of the unfavourable mixing of the chains (when these are in good solvent conditions). G_{mix} is given by the following expression:

$$\frac{G_{mix}}{kT} = \frac{4\pi V_2^2}{V_1} v_2 (1/2 - \chi) \left(\delta - \frac{h}{2}\right)^2 (3R + 2\delta + \frac{h}{2}) \quad (3)$$

where V_2 is the molar volume of the polymer, V_1 is the molar volume of the solvent, v_2 is the number of chains per unit area and χ is the chain-solvent (Flory-Huggins) interaction parameter.

It can be seen that if $\chi < 0.5$, i.e. the chains are in good solvent condition, G_{mix} is positive and the interaction is repulsive. In contrast, if $\chi > 0.5$, i.e. the chains are in poor solvent conditions, G_{mix} is negative and the interaction is attractive (i.e. mixing of the chains is favourable). The point $\chi = 0.5$ is referred to as the theta condition which denotes the start of change of repulsion to attraction. G_{el} results from the loss in configurational entropy of the chain on the approach of a second particle and this is given by the following expression:

$$\frac{G_{el}}{kT} = 2v_2 \ln \frac{\Omega(h)}{\Omega(\infty)} \quad (4)$$

where $\Omega(h)$ is the number of configurations of the chain at a separation distance h and $\Omega(\infty)$ is the value at infinite separation. Note that G_{el} is always positive and hence repulsive. The steric interaction G_s is the sum of G_{mix} and G_{el} and if both terms are positive, this interaction is very large at separation distances smaller than 2δ , as is illustrated in Figure 1c.

Van der Waals attraction

Three main types of interaction may be distinguished, namely dipole-dipole (Keesom), dipole-induced-dipole (Debye) and dispersion (London) interaction. The last is the most important since it operates with polar and non-polar molecules. It arises from charge fluctuations within an atom or a molecule associated with the motion of their electrons. Although, the London force between two molecules is short range (being inversely proportional to the seventh power of their separation), the net force (or energy) between two particles is of much longer range and its magnitude depends on the particle radius R and the nature of atoms or molecules in the particles.

Hamaker [7] obtained an expression for the London-van der Waals interaction by summing all contributions from the atoms or molecules in each particle. For two identical particles with equal radius R , the Van der Waals attraction is given by the simple expression:

$$V_A = -\frac{AR}{12h_o} \quad (5)$$

where A is the effective Hamaker constant that sums the contribution from the London dispersion force of all atoms and molecules within the particles A_{11} and the corresponding value for the medium A_{22} :

$$A = (A_{11}^{1/2} - A_{22}^{1/2})^2 \quad (6)$$

The Hamaker constant of any material is given by the product of the number density of atoms or molecules q and the London dispersion constant β :

$$A = \pi q^2 \beta \quad (7)$$

Equation (6) shows that V_A increases with decrease of h_o and it can reach very large values at small distances. This is illustrated in Figure 1d which shows a capture distance that can be significantly larger than R . As we will see later, the contribution of V_A to the total interaction depends on the magnitude of the repulsive force at any given distance of separation.

Combination of interparticle interactions: theories of colloid stability

Electrostatic stabilisation

Theory of stability of lyophobic collids by Derjaguin, Landau, Verwey and Overbeek [8, 9] (DLVO theory). These authors combined V_R and V_A at various interparticle distances to obtain the total energy-distance curve, i.e.:

$$V_T = V_R + V_A \quad (8)$$

The general form of the energy-distance curve is shown in Figure 2a. The curve clearly shows two minima at short and large distances of separation (referred to as primary and secondary minimum respectively).

The reason for this arises from the way by which V_R and V_A change with distance of separation h_o . V_R shows an exponential decay with h_o whereas V_A decreases with increase of h_o as an inverse power. At very short distances, the increase in V_A is much larger than the exponential increase in V_R and hence V_A increases much faster with decrease of h_o . This results in a deep primary minimum at very short distances of separation. On the other hand, at relatively large distances of separation, V_R decays much faster with increase of h than V_A . This means that at large distances of separation there will be a residual attraction, resulting in a secondary minimum in the energy-distance curve.

At intermediate distance of separation between the particles, V_R is larger than V_A resulting in an energy maximum V_{max} . The relative magnitudes of $V_{primary}$, V_{sec} and V_{max} depend on the parameters of the system such as surface potential ψ_o (or zeta potential ζ), particle radius, electrolyte concentration and the magnitude of the effective Hamaker constant A . V_{max} increases with increase of ζ , and decrease of electrolyte concentration (and valency). At low electrolyte concentrations, V_{max} can reach several hundreds of kT units thus preventing coagulation of the particles (into the primary minimum) and this gives the basis of colloid stability.

At intermediate electrolyte concentrations, and with large (and asymmetric) particles, V_{sec} can reach several kT units and this can induce weak flocculation in the suspension. This phenomenon is very important in several applications, whereby a weakly flocculated structure (that produces a kind of a gel network in the suspension) offers some advantages, e.g. in thixotropic paints). By application of shear on this weakly flocculated structure, the weak gel is broken (producing a sol) and when the shear force is removed, the gel structure rebuilds in a controlled manner. Weak flocculation can also be applied for prevention of settling and formation of dilatant sediments which are undesirable in many systems (this will be discussed below).

Steric stabilisation

The combination of steric repulsion and van der Waals attraction forms the basis of the theory of steric stabilisation.

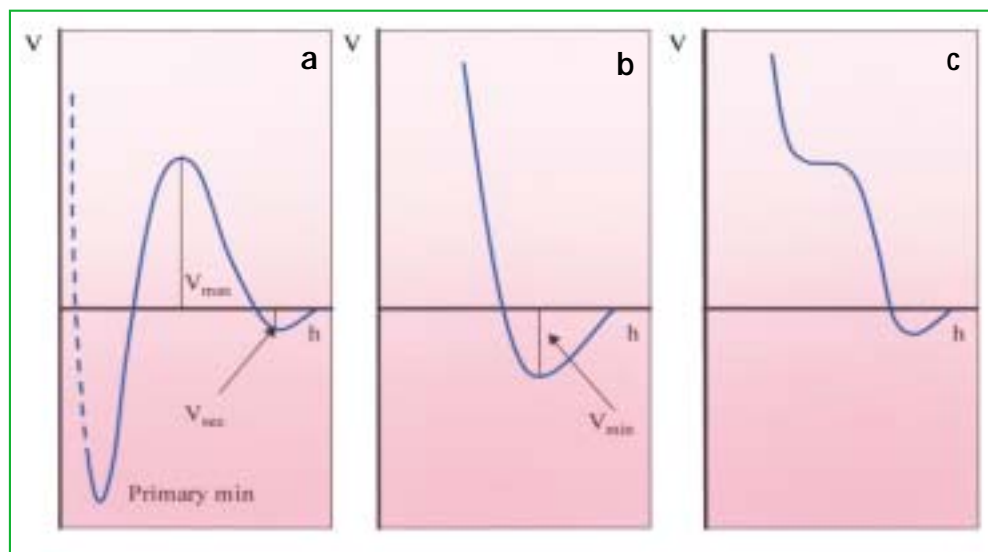


Figure 2 - Total energy of interaction-distance curves for three different stabilisation mechanisms: (a) electrostatic; (b) steric; (c) electrosteric

tion as for example given by Hesselink, Vrij and Overbeek [10]. Representing the interactions as free energies:

$$G_T = G_S + G_A = G_{MIX} + G_{el} + G_A \quad (9)$$

The form of the energy-distance curve is shown in Figure 2b. Unlike the DLVO energy-distance curve, steric interaction results in only one minimum at separation distance comparable to twice the adsorbed (or grafted) layer thickness 2δ . As h is reduced below 2δ , the interaction rises very rapidly, thus screening the van der Waals attraction. The small minimum (G_{min}) at large distances has a depth that is determined by 2δ , particle radius and Hamaker constant. It seldom exceeds few kT units, unless the particles are relatively large and the adsorbed layer thickness is small. With small particles and thick layers, G_{min} can be very small and may approach thermodynamic stability.

Electrosteric stabilisation

This is the case with charged particles containing adsorbed nonionic surfactants or polymers, whereby the contribution from electrostatic repulsion is significant. The same applies to particles stabilised by polyelectrolytes which produce a significant electrostatic contribution. In this case, the total energy of interaction is given by:

$$G_T = G_S + G_R + G_A \quad (10)$$

The form of the energy-distance curve is shown in Figure 2c. It is characterised by a shallow minimum at large separation, an ill-defined maximum arising from the double layer repulsion and a steep increase at shorter distance of separation due to steric repulsion.

Schematic representation of the structural units formed as a result of interparticle interaction

Several three dimensional structural units may be distinguished as a result of interparticle interaction. These units

are schematically shown in Figure 3 and they can be classified into three main classes.

Cases (a)-(c)

These represent suspensions that are stable in the colloid sense, i.e. the net interaction is repulsive, e.g. a high energy maximum with electrostatically stabilised suspensions or strong steric repulsion.

In this case, the particles remain as individual units with strong repulsive potential.

However, the state of the suspension on standing depends on the balance between the Brownian diffusion ($\sim kT$) and the gravity force (that is equal to $4/3 \pi R^3 \Delta \rho g L$, where $\Delta \rho$ is the buoyancy that is the difference

in density between the particles and the medium, ($\rho_p - \rho_o$). With very small particles (case a), the Brownian diffusion can overcome the gravity force and in this case no settling occurs (the suspension remains homogeneous). This situation is seldom achieved in practice, unless the particle radius is very small (below say $0.1 \mu m$) and $\Delta \rho$ is very small.

State (b) represents the case of a coarse suspension of uniform particles. In this situation, the particles will settle under gravity and they produce a "hard" sediment (technically referred to as "clay" or "cake"). As a result of the small distances between the particles in such a sediment, redispersion becomes extremely difficult. The "clay" or "cake" is dilatant, i.e. shear thickening. The same situation arises with a polydisperse suspension as represented in (c). However, in this case the smaller particles may remain suspended and the whole system may visually appear homogeneous, although one can detect the "clay" or "cake", for example by inserting a glass rod in the suspension.

These cases (b) and (c) are described as being physically unstable (although they are colloiddally stable). Settling and formation of these dilatant sediments must be prevented by the addition of an antissettling agent (sometimes referred to as suspending agent) which is usually a high molecular weight polymer as will be shown below.

Cases (d)-(f)

These states represent suspensions where the net interaction is attractive and the suspensions are strongly flocculated (coagulated). State (d) represents the case of formation of chain aggregates, which may be produced with an unstirred suspension. These chain aggregates will settle under gravity forming an open structure that is strongly held by van der Waals forces.

State (e) represents the formation of compact aggregates, which can be produced when stirring coagulated suspension. These compact clusters will also settle but the final sediment volume will be lower than that obtained with (d) at the same volume fraction of suspension. State (f) is the case of a coagulated suspension with a large particle volume fraction. In this case, the particles form a continuous

strongly held "gel" network, which may undergo some compression on storage leaving a clear layer of the supernatant liquid, a phenomenon referred to as syneresis.

Cases (g)-(i)

These states represent the case of weakly flocculated suspensions. In this case the net interaction is attractive, but the energies involved are much smaller than those encountered with states (d)-(f). Case (g) is a weakly flocculated structure produced by attraction in the secondary minimum (see Figure 2). The energy of attraction in this case is few kT units and the gel produced is relatively weak and hence it can be fluidised by application of shear, e.g. by shaking the container or application of shear in painting. When the shear forces are removed, the system will revert to the gel state. This process of sol-gel transformation produce thixotropy which can be very vital for some applications, e.g. in paints. State (h) is the case of a flocculated structure produced by polymer bridging (where in this case only few attachments are produced). Again the structure may be broken under shear and the system reverts to its gel state on removal of the shear forces. State (i) is a weakly flocculated suspension produced by the addition of a "free" (non-adsorbing) polymer. When the concentration of the free polymer reaches critical concentration, the polymer chains are "squeezed" out from between the particles. As a result the osmotic pressure outside the particle surfaces becomes larger than that in between the particles (which are free from polymer chains). This osmotic force produces weak flocculation between the particles and that phenomenon may be used to control the rheology of the suspension, e.g. in paint application. It should be mentioned that the above states produced are determined by several factors such as particle size and shape distribution, the net interaction between the particles as well as the various ingredients that are added to the suspension formulation, such as surfactants and polymers, thickeners, etc. The states produced affect the bulk properties of the suspensions, e.g. their settling characteristics and rheology. The latter in particular is very important to control both during the preparation of a suspension and during its application. Control of rheology is very important for controlling the long term physical stability of the suspension, in particular under external conditions, such as temperature fluctuations, transport, etc. Control of rheology is important for application of many suspensions in paints, agrochemicals and personal care products. Thus, studying the flow characteristics of suspension formulation is very important in all industrial applications.

Settling of suspensions and prevention of formation of sediments

Settling of suspensions is the result of gravity. With most practical suspensions, the gravity

force exceeds the Brownian diffusion. As a result the particles tend to settle to the bottom of the container forming dilatant sediments. This is particularly the case with colloidal stable suspensions. With flocculated suspensions, settling also occurs but in this case the equilibrium sediment volume is larger than that obtained with colloidal stable suspensions (at the same particle volume fraction). With weakly flocculated suspensions, the sediments may be re-dispersed by shaking the container since the interactions involved are relatively weak. This is not the case with strongly flocculated suspensions, where the sediments cannot be redispersed.

It is perhaps convenient to summarise the process of sedimentation by considering three cases: very dilute suspensions (with a volume fraction <0.01), moderately concentrated suspensions (with a volume fraction <0.2) and highly concentrated suspensions (with a volume fraction >0.4).

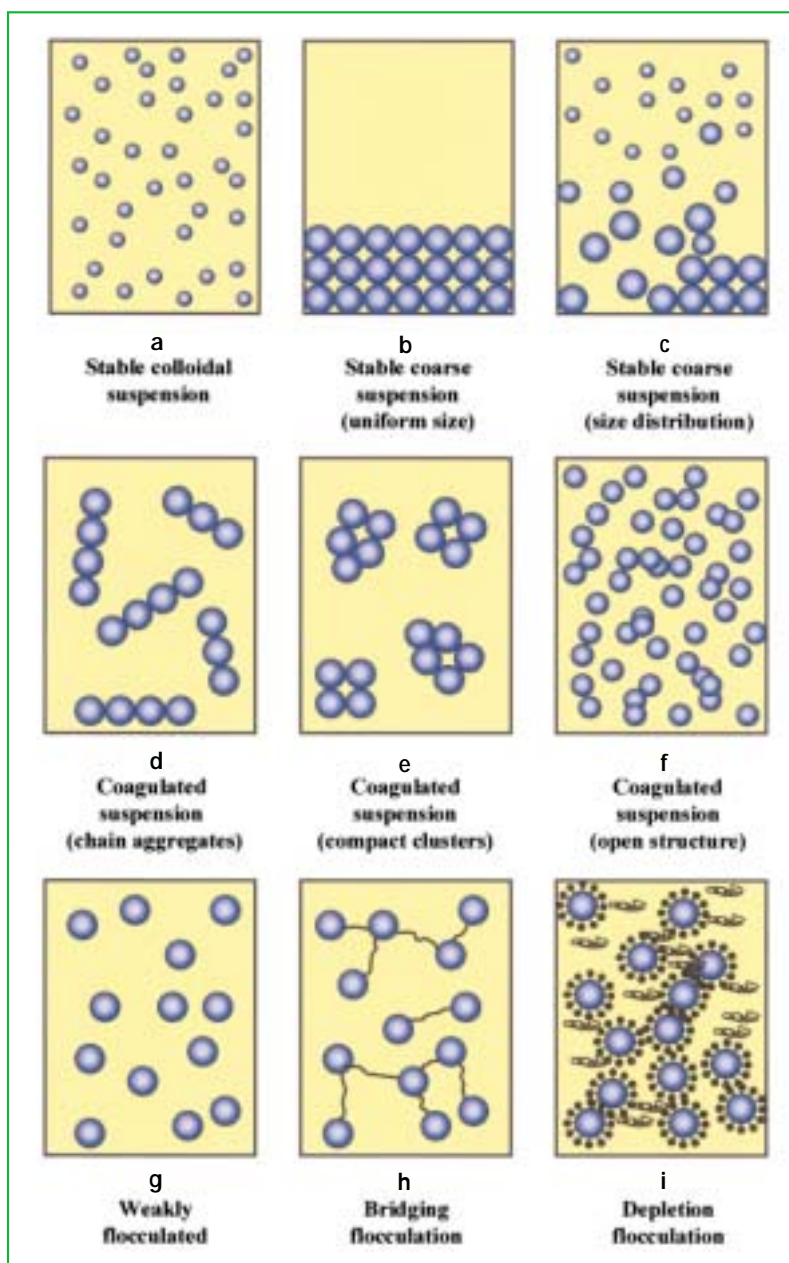


Figure 3 - Various structural units in suspension

Settling of very dilute suspensions

The settling velocity v_o of very dilute non-interacting hard-sphere suspensions may be described by Stokes' law:

$$v_o = \frac{2R^2 \Delta \rho g}{9\eta} \quad (11)$$

For particles with a density of 2 g cm^{-3} in water, the settling velocity is $\sim 2 \times 10^{-4} \text{ ms}^{-1}$ for $10 \text{ }\mu\text{m}$ particles and $\sim 2 \times 10^{-6} \text{ ms}^{-1}$ for $1 \text{ }\mu\text{m}$ particles.

Thus, the $10 \text{ }\mu\text{m}$ particles will settle to the bottom of a 0.1 m container in about 10 minutes, whereas the $1 \text{ }\mu\text{m}$ particles will take 1000 minutes (~ 16 hours).

Settling of moderately concentrated suspensions ($\phi < 0.2$)

The settling velocity of a suspension decreases with increase in the volume fraction of the particles. This is the result of hydrodynamic interaction between the particles, which no longer settle independent of each other. For a moderately concentrated suspension ($\phi < 0.2$), the settling velocity v is related to the Stokes' velocity v_o (the value for an infinitely dilute suspension) by the following expression:

$$v = v_o (1 + k\phi) \quad (12)$$

where k is a constant that is of the order of 5-6. Thus, for a suspension with a volume fraction of 0.1, the settling velocity is about 50% that of the Stokes' value.

Settling of highly concentrated suspension ($\phi > 0.2$)

The settling velocity of more concentrated suspensions becomes a complex function of the volume fraction of the particles. As ϕ increases v decreases exponentially and when $\phi > 0.4$, one reaches the hindered settling regime, whereby the sediment volume decreases very slowly with time and the rate of settling becomes independent of particle size [11]. With further increase of the volume fraction v decreases reaching almost zero when a critical volume fraction ϕ_p is reached. This critical volume fraction is the maximum pack-

ing fraction which is of the order of 0.6 for random packing. This reduction in v with increase of ϕ is accompanied by an exponential increase of the suspension viscosity η with increase in ϕ reaching an asymptote at ϕ_p . This is illustrated in Figure 4 which shows the variation of v and η with ϕ .

Reduction of settling and prevention of formation of "clays"

Several methods may be applied to reduce settling and prevent the formation of hard sediments ("clays" or "cakes") and these are summarised below.

Balance of density of particles with that of the medium

As is clear from equation (11), if $\Delta\rho=0$, $v=0$. Thus, if an inert substance (e.g. sugar or salt) is dissolved in the continuous phase, its density may reach that of the particles (which are not much larger than that of the medium). This method has only limited application and it can only be applied for suspensions with particle density not far from that of the medium. It can also be applied at one temperature, since the change of density with temperature is different for the particles and the medium.

Use of "Thickeners"

These are the most commonly used materials to reduce settling and claying. Thickeners are high molecular weight polymers (natural or synthetic) which are dissolved in the continuous phase, e.g. hydroxyethylcellulose or xanthan gum. Above a certain polymer concentration (which depends on the molecular weight of the polymer and its structure) the chains begin to overlap and this produces a viscoelastic system that is non-Newtonian. The viscosity of this solution is very high particularly at low shear rates and it also shows a "yield stress" that overcomes the stresses exerted by the particles. Many inert inorganic finely divided particles such as fumed silica or swellable clays (e.g. sodium montmorillonite) can also be used to prevent settling of coarse suspensions. These systems produce three dimensional gel networks in the continuous medium which have sufficient yield values to overcome settling of the coarse particles. In many cases, mixtures of these finely divided particles with polymers (e.g. swellable clay with xanthan gum) are used to prevent settling, since these combinations produce synergetic effects thus reducing the amount required for prevention of settling. In addition such combinations show little change of their rheological characteristics within a reasonable temperature change.

Controlled flocculation

In some cases, weak flocculation of the suspension, e.g. in the secondary minimum, may be sufficient to prevent settling and claying of suspensions. The weak gel produced (self-structured system) may hold the

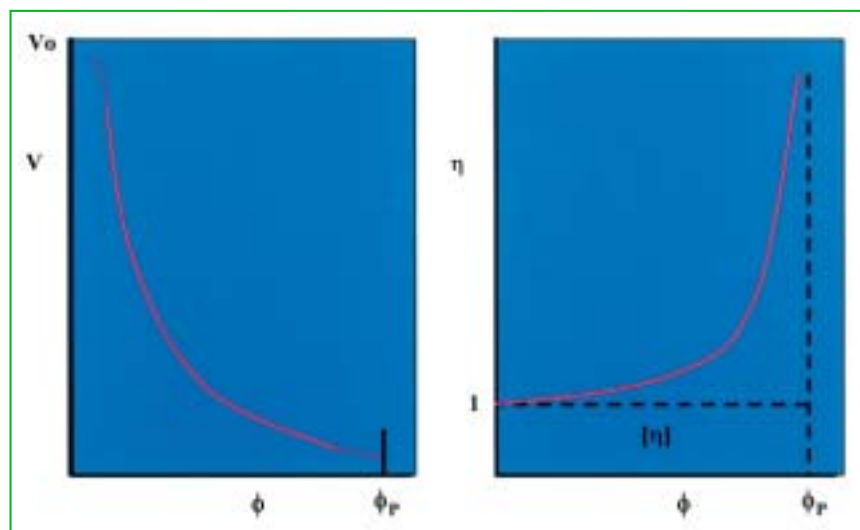


Figure 4 - Variation of settling velocity and viscosity with volume fraction

particles together thus preventing their rapid settling and the sediments produced are usually "soft" and can be redispersed by gentle shaking. However, the control of flocculation of suspensions is not easy in practice since one has to control the various parameters of the system such as particle size and shape, electrolyte concentration and the total interparticle interaction to produce a sufficiently deep secondary minimum.

Some applications of suspensions in industrial formulations

Agrochemical suspension concentrates

Many agrochemicals are formulated as aqueous suspension concentrates [12]. The agrochemical active ingredient (fungicide, herbicide or insecticide) which is insoluble in water and hydrophobic in nature is dispersed in water using a surfactant, polymer or polyelectrolyte. It is essential to wet the powder (which is formed from aggregates and agglomerates) into water using the dispersing agent. The latter reduces the surface tension of water and it helps wetting of the powder by reducing the solid/liquid interfacial tension (as a result of its adsorption on the particle surface). It is essential to wet both the external and internal surface of the powder. Dispersion of the powder in the aqueous solution of the dispersing agent is achieved using high speed stirrers which break-up all the aggregates and agglomerates. The dispersing agent should provide sufficient repulsion between the particles to prevent their reaggregation.

Once the powder is adequately dispersed in the continuous phase, the whole suspension is subjected to a wet milling process (referred to as comminution) to reduce the particle size distribution (particle sizes in the range 1-5 μm are usually produced). The resulting suspension, referred to as the mill base (which may contain 20-50 w/v% depending on application) should be fairly fluid and the particles must be adequately stabilised against any flocculation. For this purpose, powerful dispersing agents are used to prevent particle aggregation. In the early developments of agrochemical suspension concentrates, dispersing agents of the sulphonated naphthalene formaldehyde condensates or lignosulphonates were used. More recently macromolecular surfactants of the block and graft copolymer type (e.g. a graft copolymer of polymethylmethacrylate backbone with polyethylene oxide side chains) were used and this showed better dispersing ability than the conventional agents.

Using these macromolecular surfactants it was possible to produce highly concentrated suspensions (with concentrations greater than 60 w/v%) which remained very stable for long periods and at various temperatures. Once the mill base is produced, it is essential to add an antissettling (suspending) agent to prevent settling of the particles and formation of dilatant sediments. The most commonly used antissettling agents are those based on a swellable clay such as sodium montmorillonite (bentonite) and xanthan gum. The bentonite particles swell in water and produce thin platelets which form a "gel" as a result of double layer repulsion or edge-to-face flocculation (house of card structure) [13]. The xanthan gum (which is a high molecular weight polymer) can also form gels by interaction of the polymer chains when these overlap in bulk solution. The mixture of bentonite clay and xanthan

gum produces a cooperative effect whereby interaction between the clay platelets and xanthan gum may take place producing a coherent gel. The latter is viscoelastic and it gives very high viscosity at low shear rates and sufficient elastic modulus to prevent particle sedimentation and separation of the suspension. The long term physical stability of the suspension is evaluated using rheological measurements which may be carried out at various temperatures.

Coal-water suspensions

Suspensions of coal in water can be applied as fuel, as well as for transportation in pipe lines. It is necessary to have highly concentrated suspensions, that usually exceed 65 w/v%. The ground coal is first purified from sulphur compound as well as inorganic substances (such as clays and oxides). This is carried out by a flotation process, whereby agents are added to the coal-water slurry and the undesirable materials are selectively floated and separated from the suspension. The final coal slurry (which is very concentrated) is "fluidised" by the addition of a dispersing agent which breaks down the flocculated structure and produce mainly individual particles. This will cause a sharp reduction in the viscosity of the coal-water suspension, which can be pumped and atomised for burning as a fuel.

Several dispersing agents have been investigated to produce stable coal-water suspensions. Initially materials such as sulphonated naphthalene formaldehyde condensates, polyacrylates or lignosulphonates were used. These materials adsorb on the coal particles which acquire a high negative charge and the particles become stabilised by double layer repulsion. Unfortunately, such agents could not produce fluid highly concentrated suspensions and the sedimented particles produced "cakes" which could not be easily redispersed by stirring. More recently, nonionic polymeric surfactants of the block and graft type were used and these allowed one to produce more fluid suspensions with concentrations exceeding 65 w/v%. The suspensions could be stored in tanks with some agitation to prevent settling of the particles. In addition, some suspending agents such as xanthan gum are added to prevent the formation of any hard sediments during storage. The coal-water suspensions produced are usually shear thinning and when transported and atomised they become more fluid and hence they could be used as a fuel. In the formulation of coal-water suspensions one should ensure the absence of dilatancy (shear thickening) since on application the spray nozzles could be blocked. This could be achieved by controlling the interparticle interaction (by proper choice of the dispersing agent) as well as the added suspending agent.

Ceramics

Ceramic powders such as silicon nitride, silicon carbide and alumina are also formulated as highly concentrated aqueous suspensions (pastes) by the addition of a dispersing agent. Ionic as well as non-ionic agents could be used for this purpose, e.g. polyacrylates, block and graft copolymers, etc. It is essential to control the rheology of the suspension (sometimes referred to as the "green body") for adequate moulding of the paste. In addition, such agents should control the particle interaction in such a way that on sintering no cracks are produced.

Pigment dispersions

Many pigments (inorganic such as titania or organic such as synthetic dyes) are formulated as suspension both in aqueous and non-aqueous media. The dispersion of solids in aqueous media is widespread in many industrial process, e.g. in paints, dyestuffs, inks, etc. Water based emulsion paints containing fine latices of a variety of synthetic copolymers, pigments, thickeners and other additives are complex formulations that require good control of the surface properties of the pigment particles and this is achieved by the use of surface active agents. The use of surface active agents to facilitate the dispersion of pigments in non-aqueous media is not an easy task. One of the major difficulties in working with non-aqueous media is in finding a dispersing agent which is adsorbed on the surface of the pigment. A possible solution to this difficulty is to coat the pigment with the surface active compound before attempting to disperse it in the medium. This is particularly the case with polymeric surfactants that are used to coat the particles. ♦

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Aspetti fondamentali della stabilizzazione di una sospensione ed alcune loro applicazioni

In questo articolo vengono descritti i meccanismi di interazione di particelle solide, fra loro e con il mezzo disperdente, nelle sospensioni e le teorie che permettono di interpretare il fenomeno della stabilità delle sospensioni. Segue quindi una descrizione qualitativa delle possibili unità strutturali che si possono formare in una sospensione ponendole in relazione con le curve distanza-energia tra le particelle in sospensione. Viene poi esaminata la sedimentazione delle sospensioni sotto l'influenza della gravità ed il suo controllo. L'articolo si conclude con alcuni esempi dell'applicazione di questi principi a sistemi industriali.