1
General Introduction

Several types of disperse system may be defined, depending on the nature of the disperse phase and medium; these are summarized in Table 1.1.

The present book deals with the rheology of three main disperse systems, namely solid in liquid (suspensions), liquid in liquid (emulsions), and liquid in solid (gels). It is essential to define the dimensions of the particles or droplets of the internal phase. Systems where such dimensions fall within 1 nm to 1000 nm (1 μm) are classified as "colloidal systems," whereas those which contain particles or droplets larger than 1 μm are outside the colloid range. However, in both cases, the property of the system is determined by the nature of the interface which separates the internal phase from the medium in which it is dispersed. Clearly, with colloidal systems the interfacial region presents a significant proportion of the whole system. The structure of the interfacial region determines the properties of the system, and in particular the tendency of the particles to form aggregate units or to remain as individual particles.

Two main types of interfacial structure may be distinguished. The first type occurs with charged interfaces, whereby a double layer develops as a result of the presence of a surface charge which is compensated near the interface by unequal distribution of counter-ions and co-ions. At the interface, there will be an excess of counter-ions and a deficiency of co-ions. This picture of the double layer has been introduced by Gouy and Chapman [1, 2], and is referred to as "the diffuse double layer." Later, Stern [3] introduced a modified picture whereby the first layer of the counter-ions is regarded to be fixed (due to specific adsorption) and the rest of the double is diffuse in nature. In this way, Stern defined a potential ψ_d at the center of the first fixed layer; this potential may be close to the measurable electrokinetic or zeta potential. A modification of the Stern picture was later introduced by Grahame [4, 5], who considered two planes: an inner Helmholtz plane (IHP) at the center of the counter-ions that lose their hydration shell (chemisorbed counter ions); and an outer Helmholtz plane (OHP) at the center of the physically adsorbed counter-ions with their hydration shell. As will be seen in Chapter 2, the extension of the double layer depends on the concentration of counter-ions and co-ions, as well as their valency. At low electrolyte concentrations ($<10^{-2}$ mol dm^{-3} for 1 : 1 electrolyte and ($<10^{-3}$ mol dm^{-3} for 2 : 2 electrolyte), the double layer is sufficiently extended.

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Table 1.1 Types of disperse systems.

Disperse phase	Disperse medium	Type
Solid	Liquid	Suspension
Liquid	Liquid	Emulsion
Liquid	Solid	Gel
Liquid	Gas	Aerosol
Gas	Liquid	Foam
Solid	Solid	Composite

As will be discussed in detail in Chapter 2, when two particles or droplets with their extended double layers (at low electrolyte concentration) approach each other to a distance of separation at which the diffuse parts of the double layers begin to overlap, a strong repulsion occurs as the double layers can no longer develop unrestrictedly. This repulsion decreases exponentially with the decrease in the distance of separation h between the particles or droplets. The magnitude of the repulsive energy, G_{el}, at any separation distance h increases with a decrease in electrolyte concentration and a decrease in the valency of the electrolyte.

In addition to the repulsive energy described above, the particles or droplets in a dispersion have an attractive energy, sometimes referred to as van der Waals attraction, G_A, which is universal to all disperse systems. The main contribution to the van der Waals attraction is the *London dispersion energy*, and expressions have been derived by Hamaker [6] for G_A (as will be discussed in detail in Chapter 2).

The combination of G_{el} and G_A results in the well-known theory due to Derjaguin–Landau–Verwey–Overbeek (DLVO [7, 8]; this is discussed in detail in Chapter 2). The DLVO theory predicts the presence of an energy barrier at intermediate distances of separation between the particles that prevents flocculation of the dispersion. The height of the barrier depends on the surface or zeta potential, the electrolyte concentration, and the particle radius.

The second type of interfacial structure arises when surfactants and/or macromolecules are adsorbed at the particle surface. With surfactant molecules consisting of few units, adsorption simply occurs with one part of the molecule being preferentially attached to the particle surface. For example, with ionic surfactants adsorbed onto charged surfaces, an electrostatic attraction occurs between the charged head groups of the surfactant molecule and the charged sites on the surface. The surfactant molecules may adopt either horizontal or vertical orientations. With nonionic surfactants, such as alcohol or alkyl phenol ethoxylates, the alkyl or alkyl phenyl chain may become adsorbed onto a hydrophobic surface, leaving the poly(ethylene oxide) (PEO) chain dangling in solution.

With polymer molecules consisting of a large number of units, the adsorbed molecule adopts different configurations depending on the concentration, the molecular weight of the polymer, and its structure (e.g., flexibility, branching, etc). The most general configuration is that whereby a number of units become attached to the surface, in so-called “trains,” with loops in between and tails at the ends of the chain. However, with block copolymers of the A–B or A–B–A type (where B represents the “anchor” chain that is strongly attached to the surface by small loops and A is the stabilizing chain), the polymer can adopt a configuration whereby the B chain becomes strongly attached to the surface, leaving one or two A chains (which are strongly solvated by the molecules of the medium) that provide a strong steric repulsion; in this way, a very stable dispersion is produced.

When two particles or droplets which have a radius R and contain adsorbed layers with thickness δ approach each other to a surface-to-surface distance h that is less than 2δ, a strong repulsion will occur as a result of two main effects [9]. When the layers begin to overlap, the segment density in the overlap region becomes larger than the rest of the layer, and this results in an increase in the osmotic pressure in this region. Provided that the stabilizing chains are in good solvent conditions, this increase in osmotic pressure resists any overlap of the layers (unfavorable mixing of the stabilizing chains) and results in a strong repulsion that is given by G_{mix} (which has a positive sign). As a result, solvent diffuses to the overlap region, thus separating the particles or droplets. The second repulsive energy arises from the loss of configurational entropy of the chains on significant overlap; this is referred to as elastic interaction, G_{el}. A combination of G_{mix} and G_{el} gives the total steric interaction free energy which, when added to the van der Waals attraction, causes the energy–distance curve to show a shallow minimum at separation distances comparable to 2δ; moreover, when $h < 2\delta$ a strong repulsion will occur with a further decrease of h.

As mentioned above, the structure of the interfacial region determines the interaction between particles in a disperse system. For example, with systems containing double layers or adsorbed layers of surfactants or polymers, an interaction will lead to a repulsion as soon as the double layers or the adsorbed layers begin to overlap. This repulsion leads to a colloidally stable system. On the other hand, if the repulsive energy is not sufficiently large, then the van der Waals attraction will dominate the interaction and an aggregated system will result. These interactions determine the flow characteristics (rheology) of the disperse systems.

The main objective of this book is to describe the rheology of dispersions in terms of the various forces between the particles or droplets. The rheology of a dispersion is determined by the balance of three main forces [10–12]: Brownian diffusion; hydrodynamic interaction; and surface forces (repulsive or attractive). For this reason, Chapter 2 will be dedicated to describing these interaction forces, and how these can be controlled in practice. As will be seen, four different types of interaction must be considered:

- Hard-sphere interaction, whereby both the repulsive and attractive forces are screened (this is sometimes referred to as “neutral stability”). In this case, the rheology of the dispersion is determined by the balance between Brownian diffusion and hydrodynamic interaction. This simplifies the analysis and, as will be seen in Chapter 3, theories are available to describe the variation of relative viscosity η_r with the volume fraction ϕ of the dispersion.

- Systems with “soft” (electrostatic) interaction with extended double layers. As will be seen in Chapter 3, the rheology of the dispersion will be determined by the double-layer repulsion.
- Systems with steric interaction – that is, containing adsorbed surfactant or polymer layers. In this case, the rheology of the dispersion is determined by the steric repulsion.
- Systems where the net interaction is attractive; in this case, it is possible to distinguish between weak and strong flocculation, depending on the magnitude of the attraction.

Particular attention will be given to concentrated systems and the formation of three-dimensional (3-D) structural units that determine the rheology of dispersions. These structural units are the result of the balance between the various interaction forces. In addition, the effect of gravity must be considered, since the presence of dense particles with diameters larger than the colloid range may result in the settling and formation of hard sediments. The latter must be prevented when dealing with suspensions.

Investigations of the rheology of dispersions are very important in many industrial applications such as:

Paints: The rheological characteristics of any paint formulation is important, both for its long-term stability as well as on application.

Printing inks: The flow behavior of inks (e.g., ink jets) is crucial for its application.

Paper coatings: These mostly consist of suspensions which need to be applied at high shear rates. Shear thickening (dilatancy) must be prevented under these conditions.

Ceramics: These are suspensions with a high volume fraction (approaching maximum packing), and control of their rheology for molding and casting is crucial.

Cosmetics: Most cosmetic formulations consist of emulsions or suspensions and their mixtures. The control of their rheology is crucial for long-term stability and application (skinfeel).

Food industry: Most products used in the food industries, such as mayonnaise, salad creams, and desserts require an accurate control of their rheology for good texture and mouthfeel.

Pharmaceutical formulations: These include emulsions, suspensions, creams, and gels. The control of rheology is crucial for long-term physical stability and application, especially for injectables and topical applications.

Agrochemical formulations: These consist mostly of concentrated suspensions and emulsions. To control the rheology of the formulation is important for the long-term physical stability, as well as applications in the spray tank.

Liquid detergents: These consist of concentrated surfactant solutions in which solids such as phosphates and silicates are dispersed. Rheology modifiers are required to prevent separation and facilitate dispersion on dilution.

At a fundamental level, it is important to relate the bulk rheology of dispersions to the interaction forces between the particles or droplets. Some progress has been made as a result of the possibility of directly measuring the interaction energies between macroscopic bodies, using for example the surface force apparatus and the technique of atomic force microscopy (AFM).

Within this book, the text is organized as follows. In Chapter 2, attention is focused on the colloidal aspects of dispersions, both of the solid–liquid (suspensions) and liquid–liquid type. The three main energies involved – namely, double-layer repulsion, steric interaction, and van der Waals attractions – will be considered. A combination of these energies provides energy–distance curves that can be used to describe the stability/flocculation of dispersions. The different states of suspensions and emulsions will also be described, highlighting the structure of the concentrated dispersions that are produced on standing. Particular attention will also be given to the sedimentation of suspensions and creaming of emulsions. The flocs that can be produced as the result of a lack of stability are described, and both strong and weak flocculation can be distinguished in these dispersions. Subsequently, Chapters 3 and 4 describe the basic principles of rheology in relation to both steady-state and viscoelastic behaviors, and also provide details of the experimental techniques that may be applied for their investigation. Rheology is well recognized as the study of the deformation and flow of matter. Typically, steady-state measurements are carried out using shear rate-controlled rheometers, where the shear is gradually increased while simultaneously measuring the stress produced, so as to produce flow curves of shear stress and viscosity versus shear rate. The curves obtained may then be analyzed by using different models, so as to produce the various rheological parameters such as yield value, viscosity, and shear thinning index. The viscoelastic measurements (which are referred to as "low-deformation measurements") are carried out using highly sensitive rheometers that are capable of applying low torques (stress) or oscillation at a variety of amplitudes and frequency. For this, three main types of investigation can be applied: (i) strain relaxation after the application of constant stress (referred to as "creep measurements"); (ii) stress relaxation after a sudden application of strain; and (iii) dynamic or oscillatory techniques. In the latter case, a sinusoidal strain (with amplitude γ_o) or stress (with amplitude σ_o) is applied at a frequency ω (rad s^{-1}), and the sign waves of strain and stress (or stress and strain) are compared so as to obtain the phase angle shift, δ. In this way, the various rheological parameters can be obtained as a function of amplitude and frequency, and the elastic and viscous components of the system thus obtained, with a variety of models being used to analyze the results. The basic laws that govern the rheology of a dispersion are also described, whilst avoiding – as much as possible – the use of complex mathematical analyses. The rheology of suspensions is discussed in Chapter 5, by describing the four main forces – hard-sphere, electrostatic, steric, and van der Waals attractions – where the rheological behavior of each system is described using the well-known theories of rheology of dispersions. The rheology of emulsions, which have some features in common with suspensions, is detailed in Chapter 6. Due to the fluid nature of the interface, it is also necessary to consider the interfacial rheology that results from surfactant and/or polymer adsorption. The deformability of the emulsion droplets must also be considered, particularly at the high volume fraction of the emulsion.

Finally, a section will be devoted to the rheology of highly concentrated emulsions (high internal-phase emulsions, HIPE), whereby the rheology of emulsions during flow and the break-up of drops will also be described. Consequently, Chapter 8 is devoted to rheology modifiers, thickeners, gels, and liquid crystalline structures, and considers the application of rheological measurements to assess and predict the long-term physical stability of dispersions, which is especially important in their industrial application.

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