An introduction to Interfacial Engineering G.J.M. Koper



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Department of Chemical Engineering Faculty of Applied Sciences Delft University of Technology © VSSD First edition 2007 corrected 2009, 2011

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Preface

In 2004 the first course on Interfacial Engineering was given a the chemical engineering department DelftChemTech of Delft University of Technology. Before that time, there was some coverage with colloidal systems in courses on physical chemistry and a voluntary course on "disperse systems". The idea was to give a course that would deal with colloidal phenomena while giving a good perspective on technological applications. Hence the name Interfacial Engineering. The teaching goal of the course was set at a decent level: after studying the course, the students should be able to critically assess the relevant scientific literature.

This first course was developed simultaneously with prof. dr. Theo van de Ven (McGill University, Montreal), who was a visiting professor of the department at the time. A significant amount of course material was generated from which the students could study, but a textbook covering all topics of the course was not available. Over time, the idea developed to write one myself. The result of half a year writing text while teaching the course is what you are reading now. The book is still under construction. Many ideas have been put into this book and the coverage is not fully balanced yet. Also, the text will not be without flaws. Therefore, any suggestion or correction will be welcomed so that in a following print more accuracy will be attained.

The contents of the book can be roughly divided into two parts. The first part contains the basic knowledge required to deal with colloidal systems albeit that some technological issues are discussed. These are the chapters 1 - 5. With these chapters, there is a bundle of worked exercises, taken from the author's own experience and from other textbooks, that will be available upon request. The chapters 6 - 8 deal with technologies such as emulsification, film formation and flotation. In these last chapters some new fundamental issues are discussed where necessary but the emphasis is on the application.

In a half-semester course – of weekly 2 consecutive lecture hours – one chapter is discussed per week, sometimes together with some exercises. The last three chapters are discussed in conjunction with scientific papers from the contemporary literature. This teaches the students how to use their knowledge with published material and how to extract key information for a given process. Particular attention is paid on how to read a scientific paper, how to extract information from it, and how to evaluate its significance. A method has been developed to do this systematically. Subsequently, some calculations are made with the material presented in the paper where it does occur that another conclusion is drawn than in the paper. The exam for the students consists of the assessment

of a - small - scientific paper and some relevant calculations.

Most of the information in this book is not mine. It is the accumulated knowledge of the field and I acknowledge all contributors: there are too many to name and I feel indebted to them all. My role has been to make a selection of topics and to organize and discuss these in such a way as to teach chemical engineers the essentials about colloid science and its technological applications.

Finally, I thank all who have helped me writing this book and Delft University of Technology for their support. Last but not least I thank my wife and children for their patience: they had to suffer my absence during long evenings of working to finish this work.

Ger Koper, Leiden, 5 March 2007.

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Chapter 1

Introduction

1.1 Nature of the colloidal state

The challenge of Interfacial Engineering is the wide range of length scales that it deals with, see figure 1.1. On the one hand there are the molecules of which their typical length scale is in the Ångstroms. On the other hand there is the size of the mixing vessel or reactor of which the length scale is meters or more. In almost all practical situations, there is at least one particular length scale — the colloidal length scale — that is associated with the degree of dispersion in the system. This colloidal length scale is in the range of $10^{-9} - 10^{-3}$ m and encompasses the range that is currently exploited by the "nanoscientists".



Figure 1.1 Length scales operative in Interfacial Engineering.

The term *colloid* stems from the greek word $\kappa o \lambda \lambda \alpha$ that means glue and refers to classical colloids as protein or gelatin solutions. Using a membrane, colloids can be distinguished from molecules in the classical experiment depicted in figure 1.2.



Figure 1.2 Classical experiment to distinguish colloids from molecular solutions.

A *colloidal system* or *colloid* is an essentially multiphase — usually two-phase — system, such as paint or milk, in which one of the phases is dispersed in the other. In such systems the *colloidal particles* have at least one dimension in the colloidal range. A

special class is formed by solutions of high polymers which are in fact molecular solutions but where the globules are nevertheless in the colloidal range. The two constituting phases can either be solid, liquid or gas and hence many types of colloids are possible, see table 1.1. In this table there is one entry, $g \subset G$, that has question marks; consider this as a question to ponder ...

Туре	Name	Examples
$(intern \subset extern)$		
$s \subset G$	aerosol	smoke
$l \subset G$	aerosol	mist, hair spray
$g \subset G$?	?
$s \subset L$	sol	ink, paint
$l \subset L$	emulsion	milk, mayonnaise
$g\subset L$	foam	shaving foam
$\mathbf{s} \subset \mathbf{S}$	solid dispersion	pearls, ruby glass
$l \subset S$	solid emulsion	ice cream, butter, bitumen
$\mathbf{g} \subset \mathbf{S}$	solid foam	marshmallows, PUR foam

Table 1.1 Possible combinations of phases to form colloids

The dispersions may form either spontaneously, such as protein solutions, after mixing or require significant energy input, such as the case with emulsions. In the first case, the dispersion is called *reversible* or *lyophilic*¹. The other case is called irreversible or *lyophobic*².

An important aspect of colloidal systems is the specific surface. As an example, first consider the simple situation of a dispersion of spherical particles with uniform radius a = 3 nm. The *volume fraction* or *fill factor* is $\phi = 0.1$. The specific surface area is now given by

$$A_{sp} = \frac{3\phi}{a} \tag{1.1}$$

which in this particular case evaluates as

$$A_{sp} = \frac{3 \times 0.1}{3 \cdot 10^{-9}} \text{ m}^2 / \text{ m}^3 = 10^8 \text{ m}^2 / \text{ m}^3$$

In other words, a volume of only 1 mL of this dispersion has a surface area of 100 m^2 , which is of the same order of magnitude as the surface area of a lecture room.

The proof of the above expression is as follows. Let the number of particles in a volume V be N, then the total volume occupied by the particles is $V_d = 4\pi Na^3/3$ and the total surface area is $A_d = 4\pi Na^2$. Using that $\phi = V_d/V$ the specific area is obtained as

$$A_{sp} = \frac{A_d}{V} = \frac{A_d}{V_d} \times \frac{V_d}{V} = \frac{3}{a} \times \phi$$

¹The term lyophilic means solvent-loving, which in the case of water becomes hydrophilic

²The term lyophobic means solvent-hating, which in the case of water becomes hydrophobic

which is the expression given in eq. 1.1.

Care has to be taken in the usage of the term specific area. The one usage, discussed above, is the specific area per unit volume of dispersion. Another usage is the specific area per unit mass of *dispersed material*.

1.2 Microscopic colloidal behavior

The experienced interfacial engineer has some simple tools at hand to distinguish a molecular solution from a dispersion. The phenomena described below are both fundamental in nature but very practical in their application.

1.2.1 Osmotic pressure

The classical experiment to measure molar masses of polymers is of very good use to colloid scientists as it can provide in a relatively simple way information about the mass as well as the size of the dispersed particles. The set-up requires a semi-permeable mem-



Figure 1.3 Osmotic pressure experiment.

brane that does not allow the dispersed particles to go from the vertical tube to the reservoir below, see figure 1.3. The height h is directly related to the osmotic pressure Π , due to the dispersion, by

$$\Pi = \rho g h$$

with ρ the mass density of the solvent and g the gravitational constant. Van 't Hoff's law relates this osmotic pressure to the mass concentration C of dispersed material by

$$\frac{\Pi}{RT} = \frac{C}{M} \left(1 + B_2 C + \ldots \right) \tag{1.2}$$

where the second virial coefficient B_2 has been added. The molar mass M of the dispersion is related to the particle mass M_p by

$$M = N_A M_p$$



Figure 1.4 Analysis of osmotic pressure experiment, various second virial coefficient conditions.

with $N_A = 6.0 \cdot 10^{23}$ Avogadro's number. The second virial coefficient is related to the effective interaction volume of the dispersion. For hard spheres, the second virial coefficient is equal to

$$B_2 = 4\frac{V_p}{M_p}$$

with V_p the particle volume. But the second virial coefficient can also vanish which is equivalent to the situation at the Boyle temperature in gases: the repulsive and attractive interactions balance. For polymers such situation is called the *theta solvent conditions* and similarly in colloidal dispersions the situation is largely dependent on solvent conditions. In a good solvent, the virial coefficient is not negative. When the second virial coefficient is negative, attractive interactions dominate, sometimes leading to thermodynamically stable flocculation, see figure 1.4.

1.2.2 Brownian motion and diffusion

When a particle is forced to move through a liquid, the velocity v it acquires is proportional to the applied force F. This is essentially Stokes' law and it reads

$$v = \frac{F}{f} \tag{1.3}$$

The proportionality factor f is called the *friction factor* which for a sphere³ is given by

$$f = 6\pi\eta a \tag{1.4}$$

with *a* the radius of the particle. The friction that the particle experiences in the liquid arises from the hydrodynamic momentum transfer which in itself is mediated by collisions of liquid molecules with the moving particle surface.

³Even though many (colloidal) objects are not spheres, one still uses expressions for spheres to obtain the correct order of magnitude in the absence of a more accurate value.

1. Introduction

But there is an additional effect of these collisions. Even at rest, there is a fluctuating momentum transfer from the liquid molecules to the particle and as a consequence the particle exhibits irregular motion, the so called *thermal motion* or *Brownian motion*. The time average of the momentum transfer vanishes, but there is a noticeable effect on the position of the particle. In a given time lapse Δt the uncertainty in the center-of-mass position of the particle has increased by an amount

$$\Delta r = \sqrt{6D\Delta t} \tag{1.5}$$

The proportionality constant D in the above equation is the diffusion coefficient of the particles, which is related to its friction factor by the *Einstein relation*

$$D = \frac{k_B T}{f} \tag{1.6}$$

in which $k_B = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant or molecular gas constant and *T* is the absolute temperature of the liquid. It is important to note that Brownian motion is a chance process and hence there is no way to predict the actual distance covered by a particle. The only statement one may make is that after a time lapse Δt there is a high probability to find the body within a sphere of radius $\sqrt{6D\Delta t}$. Colloquially one says: the particle has "diffused" over a distance $\sqrt{6D\Delta t}$.

It is easy to see that the Brownian motion of a tennisball will not be too impressive, but for a 3 nm sphere the diffusion coefficient is about $72 \cdot 10^{-12}$ m²/s so that after a second "it diffuses" a distance of approximately 20 micrometer which is about 700 times its size!



Figure 1.5 Sedimentation in a colloidal dispersion.

Now, consider a liquid colloidal dispersion in a transparent vessel as in figure 1.5 where the dispersed phase has a higher mass density than the liquid. After some time, a density gradient will set in so that the dispersed phase is denser at the bottom of the vessel than at the top. In the extreme case all the dispersed mass is at the bottom, which is called *sedimentation*. The situation where the dispersed phase has a lower mass density is called *creaming* because the density gradient is opposite. The density profile c(z) has the same functional form as the barometric height distribution

$$c(z) = c(z_0) \exp\left\{-\frac{gV_P \Delta \rho}{k_B T}(z - z_0)\right\}$$
(1.7)

in which g is the gravitational constant, $\Delta \rho$ is the mass density difference between dispersed phase and continuous phase, and V_p particle volume.

It is customary to derive the above expression using the Boltzmann distribution known from statistical thermodynamics. As an illustration that equilibrium phenomena are actually due to balancing fluxes, let us consider the particle flux due to gravity alone. The mass of one particle is $m_p = \Delta \rho V_p$ and hence the gravitational force on the particle is $F_z = m_p g = g V_p \Delta \rho$. The velocity that the particle will acquire due to this force is given by $v_z = F_z/f$ with f its friction factor. The total flux of particles moving with gravity is given by $J_z = cv_z$, where it is assumed that the particles do not hinder each other.

Due to the movement of particles with gravity, a particle concentration gradient will develop. According to Fick's law, this will give rise to an opposite flux given by $J_D = -D\nabla c$.

In stationary state — equilibrium — the two fluxes balance which leads to the differential equation

$$\frac{dc}{c} = -\frac{gV_p\Delta\rho}{k_BT}dz$$

of which the solution is given in equation 1.7.

For some systems, the particle density gradient is easily visible whereas for others spectroscopic techniques are required.

1.2.3 Tyndall effect and light scattering

Wherever there are optical density variations, there are refractive phenomena. In the case of colloidal systems the density fluctuations take place at length scales which are comparable to the wavelength of visible light. Therefore, colloidal systems scatter visible light very much like a ray of sun in a dark room is visible through the light scattering dust particles in its pathway. A demonstration of this phenomenon is depicted in figure 1.6 where a "laser pointer" is used to send a beam of light through two vessels, one containing a colloidal dispersion and the other a pure solvent. A typical way to assess the light scattered by a colloidal solution is by means of a standard visible light spectrometer. Such an instrument measures the light loss along an optical path of length d through a calibrated cuvette containing the dispersion. According to Lambert-Beer's law the light loss leads to a transmission factor

$$T = \exp\{-(\kappa + \tau)d\}$$
(1.8)

with κ the absorption and τ the *turbidity*. Here, the case of light absorption is discarded because most – but not all – colloidal dispersions are "dielectric". It is noteworthy, however, that light scattering manifests itself as absorption in a spectrometer but also to the human eye. A good example is ruby glass which appears red to the observer even though there is no light absorption. One observes a color due to the fact that light of the other



Figure 1.6 Demonstration of the Tyndall effect. On the left side a colloidal dispersion and on the right side the pure solvent.

wavelengths is scattered in all directions and hence very little reaches the eye. In particular, this means that colloidal systems may show a different color upon reflection and on transmission, a phenomenon used in the famous Lycurgus cup⁴.

For not too dense systems, the turbidity of colloidal dispersions is proportional to the concentration, i.e.

$$\tau = cS \tag{1.9}$$

The proportionality constant is called the *scattering cross section S* which, for not too large and dense particles, is proportional to an optical contrast factor and volume squared

$$S \propto \left[\frac{n^2 - 1}{n^2 + 2}\right] V_p^2 \tag{1.10}$$

with *n* the relative refractive index. For larger particles the scattering cross section is a complex function of wavelength, scattering angle, refractive index and particle size which is fully described by the Mie theory⁵. An extremely useful consequence of the above equations is, that the turbidity of a colloidal suspension of given volume fraction is directly proportional to the product of volume fraction and particle volume and hence to particle size cubed, i.e. $S \propto \phi V_p = \phi a^3$.



Figure 1.7 Colloidal phenomena in the environmental sciences.

1.3 Applications

1.3.1 Environmental sciences

Due to the strong attachment of chemicals such as heavy metals, radionuclides, pharmaceuticals to the solid phase of porous media it was for a long time assumed that the transport of these chemicals by the water phase would be extremely slow. Recent fieldand laboratory-scale observations have shown that mobile colloidal particles such as microbes, humic substances, clays, and metal oxides, can act as pollutant carriers and thus provide a much more rapid transport pathway for strongly sorbing contaminants, see figure 1.7. These observations have led to an enormous upsurge of colloid science in this field.

1.3.2 Liposomes as colloidal cargo carriers

Whereas emulsions consist of one liquid phase dispersed into the other, such as oil in water, dispersions of liposomes allow for an aqueous phase to be dispersed in another aqueous phase. As such, liposomes are used as containers to transport drugs, vitamins or special proteins through the human body, see figure 1.8. In the colloid literature the word liposome is rarely found, the particular structure formed by surfactant molecules is called *vesicle* in that domain.

There are many fields in which liposomes are used or proposed for use, such as cosmetics, medicine and in the field of genetic engineering. In all cases, the main issue is to

 $^{^4}A$ picture movie and a description is available from the British Museum in London, see http://www.thebritishmuseum.ac.uk/science/lycurguscup/sr-lycugus-p1.html .

⁵see Bohren, C. F. and Huffman, D. R. *Absorption and Scattering of Light by Small Particles*. New York: Wiley, 1983. There are various web sites giving computational aid to evaluate the scattering cross section.



Figure 1.8 Liposomes as colloidal cargo carriers.

prevent the cargo from entering into the continuous phase where it might degrade for instance by oxidation. In other cases, direct exposure to for instance the blood circuit might activate anti-immune reactions before the target is reached. Novel systems have special receptors that allow targeted release of the cargo.

1.3.3 Sol-gel technology

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid sol into a solid gel phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials. An overview of the sol-gel process is presented in a simple graphic work⁶ depicted in figure 1.9.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a sol. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the sol is cast into a mold, a wet gel will form. With further drying and heat-treatment, the gel is converted into dense ceramic or glass articles. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called "aerogel" is obtained. As the viscosity of a sol is adjusted into a proper viscosity range, ceramic fibers can be drawn from the sol. Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

⁶Adapted from http://www.chemat.com/



Figure 1.9 Various routes in sol-gel technology.

1.3.4 Food technology

Traditionally, colloid science has evolved mainly from two technological areas: food processing and detergency. Many colloid experts, up till recently, could be found in industrial research laboratories. The applications in food processing are so numerous, that it is currently evolving as a popular branch of science⁷.

⁷See the website http://khymos.org/ and for the dutch http://www.kokenchemie.nl