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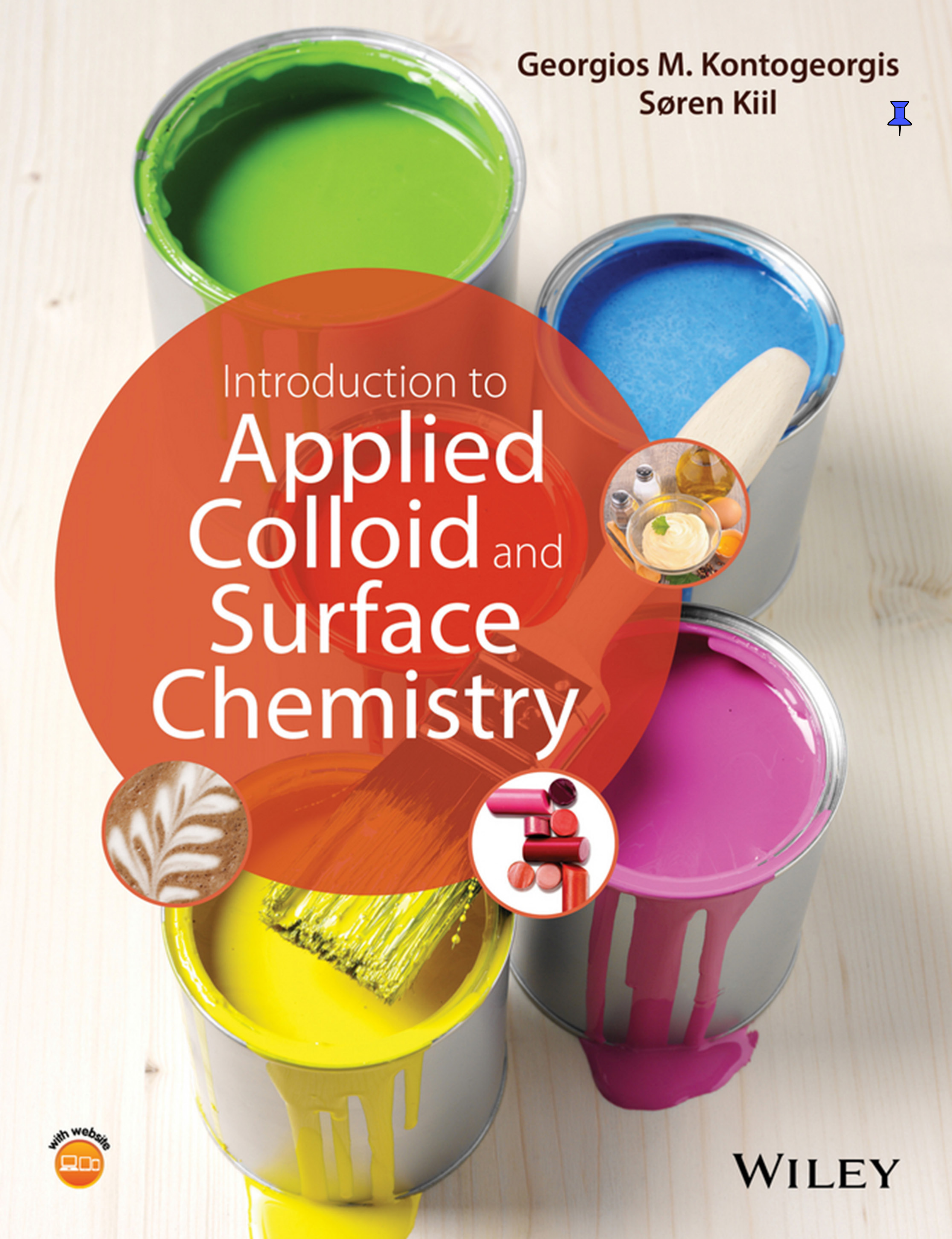

Introduction to Applied Colloid and Surface Chemistry

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Preface

Colloid and surface chemistry is a subject of immense importance and has implications both to our everyday life and to numerous industrial sectors from paints and materials to medicine and biotechnology.

When we observe nature, we are impressed by mosquitos and other small insects that can walk on water but are drawn into the water when detergents (soaps) are added in their neighbourhood. We are fascinated by the spherical shape of water and even more by the mercury droplets that can roll around without wetting anything. We know that for the same reasons we should use plastic raincoats when it is raining. We are also impressed by some of natural wonders like the "delta" created by rivers when they meet the sea and the non-sticky wings and leaves of butterflies, lotus and some other insects and plants. We are also fascinated by the blue colour of the sky and the red colour of the sunset.

When we are at home we are constantly surrounded by questions related to colloids or interfaces. We would like to know how detergents really clean. Why can we not just use water? Can we use the detergents at room temperature? Why do we often clean at high temperatures? Why do so many products have an expiration date (shelf-life) of a few days or weeks? Why can't milk last for ever? And why this "milky" colour that milk has? Is it the same thing with the well-known drink Ouzo? Why does Ouzo's colour change from transparent to cloudy when we add water? And what about salt? Why does it have such large effect on foods and on our blood pressure? Why do we so often use eggs for making sauces?

Those who have visited the famous VASA museum in Stockholm are impressed by the enormous efforts made in preserving this ship, which sank 400 years ago, after it was taken out of the sea. Why was a solution of poly(ethylene glycol) spayed on the ship?

Of course, similar problems occur in industries that focus on the development and manufacturing of a wide range of products ranging from paints, high-tech materials, detergents to pharmaceuticals and foods. In addition, here it is not just curiosity that drives the questions! Paint industries wish to manufacture improved coatings that can be applied to many different surfaces but they should also be environmentally friendly, e.g. should be less based on organic solvents and if possible exclusively on water. Food companies are interested in developing healthy, tasty but also long-lasting food products that appeal to both the environmental authorities and the consumer. Detergent and enzyme companies have worked in recent years, sometimes together, to develop improved cleaning formulations containing both surfactants and enzymes that can clean much better than before, working on more persistent stains, at lower temperatures and amounts, to the benefit of both the environment and our pocket! Cosmetics is also big business. Many of creams, lotions and other personal care products are complex emulsions and the companies involved are interested in optimizing their performance in all respects and even connecting consumer's reactions to products characteristics.

Some companies, often inspired by nature's incredible powers as seen in some plants and insects, are interested in designing surface treatment methods that can result in self-cleaning surfaces or self-ironing clothes; surfaces that do not need detergents, clothes that do not need ironing!

There are many more other questions and applications! Why can we get more oil from underground by injecting surfactants? Can we deliver drugs for special cases in better and controlled ways?

All of the above and actually much more have their explanation and understanding in the principles and methods of colloid and surface chemistry. Such a course is truly valuable to chemists, chemical engineers, biologists, material and food scientists and many more. It is both a multi- and interdisciplinary topic, and as a course it must serve diverse needs and requirements, depending on the profile of the students. This makes it an exciting topic to teach but also a very difficult one. Unfortunately, as Woods and Wasan (1996) showed in their survey among American universities, a relatively small number of universities teach the course at all! This is a problem, as several universities try to "press" concepts of colloid and surface chemistry (especially the surface tension, capillarity, contact angle and a few more) into general physical chemistry courses. This is no good! This is no way to teach colloids and interfaces. This exciting topic is a science by itself and deserves at least one full undergraduate course and of course suitable books that can be used as textbooks.

This brings us to the second major challenge, which is to have a suitable book for teaching a course to undergraduate students of a (technical) university. More than ten years ago, we were asked to teach a 5 ECTS theory course on colloids and interfaces at the Technical University of Denmark (DTU). The time allocated for a typical 5 ECTS point (ECTS = European Credit System) course at DTU is one four-hour block a week during a 13 week semester, followed by an examination. This course is part of the international program of our university, typically at the start of M.Sc. studies (7^{th}–8^{th} semester) and can be followed by students of different M.Sc. programs (Advanced and Applied Chemistry, Chemical and Biochemical Engineering, Petroleum Engineering). B.Sc. students towards the end of their studies can also follow the course. In Denmark, students submit a written anonymous evaluation of the course at the end of semester, providing feedback on the teaching methods and course content, including course material (books used).

Our experience from 12 years of teaching the course is that we found it particularly difficult to choose a suitable textbook that could fulfil the course requirements and be appealing to different audiences and the increasing number of students. This may appear to be a "harsh comment". First of all, there are many specialized books in different areas of colloid and surface chemistry, e.g. Jonsson *et al.* (2001) on surfactants and Israelachvili (2001) on surface forces. These and other excellent books are of interest to researchers and also to students as supplementary material but are not suitable –and we do not think they were meant by these authors to be – as a stand-alone textbook for a general colloid and surface chemistry course. Then, there are some books, for example Hunter (1993) and Barnes and Gentle (2005), that focus either only on colloid or on surface science. There are, nevertheless, several books that, more or less, target to cover a large part of a standard colloid and surface chemistry curriculum. Examples are those written by Shaw (1992), Goodwin (2004), Hamley (2000), Myers (1991) and Pashley and Karaman (2004). Some of these could and are indeed used as textbooks for colloid and surface chemistry courses. Each of these books has naturally their own strengths and weaknesses. We have reported our impressions and those of our students on the textbooks which we have used in the course over the years in a previous publication (Kontogeorgis and Vigild, 2009) where we also discuss other aspects of teaching colloids and interfaces.

What we can state, somewhat generally, is that unlike other disciplines of chemical engineering (which we know well, both of us being chemical engineers) we lack in colloid and surface chemistry what we could call "classical style" textbooks and with an applied flavour. In other fields of chemical engineering, e.g. unit operations, thermodynamics, reaction engineering and process control, there are textbooks with a clear structure and worked out examples along with theory and numerous exercises for class or homework practice. We could not generalize that "all is well done" in the textbooks for so many different disciplines, but we do see in many of the classical textbooks for other disciplines many common features that are useful to teachers and of course also to students. As the structure in several of these disciplines and their textbooks is also rather established, things appear to be presented in a more or less smooth and well-structured way.

We felt that many of these elements were clearly missing from existing textbooks in colloid and surface chemistry and this book makes an attempt to cover this gap. Whether we succeed we cannot say a priori but the positive comments and feedback from the students to whom parts of this material has been exposed in draft form over the years is a positive sign.

Thus, this book follows the course we have taught ourselves and we hope that the content and style may be appealing to others as well, both colleagues and students. We would like to present the main elements of this book in two respects (i) content and (ii) style.

First of all, the book is divided approximately equally into a surface and a colloid chemistry part although the division is approximate due to the extensive interconnection of the two areas. The first two chapters are introductory, illustrating some applications of colloids and interfaces and also the underlying – for both colloids and interfaces – role of intermolecular and interparticle/intersurface forces. The next two chapters present the concepts of surface and interfacial tension as well as the "fundamental" general laws of colloid and surface science; the Young equation for the contact angle, the Young–Laplace and Kelvin equations for pressure difference and vapor pressure over curved surfaces, the Harkins spreading coefficient and the Gibbs equation for adsorption. We also present in some detail in Chapter 3 various estimation methods for surface and interfacial tensions, with special focus on theories using concepts from intermolecular forces. These estimation methods will be used later (Chapter 6) in applications related to wetting and adhesion. We hope that, already after Chapter 4, it will have become clear that colloid and surface chemistry have a few "general laws" and many concepts and theories, which should be used with caution. Another major result from these early chapters should be the appreciation of the Gibbs adsorption equation, as one of the most useful tools in colloid and surface chemistry. This is an equation that can link adsorption theories, two-dimensional equations of state (surface pressure–area equations) and surface tension/concentration equations. These will be fully appreciated later, in Chapter 7, where adsorption is discussed in detail, as well as in Chapter 14, which discusses multicomponent adsorption theories.

After Chapters 1–4 comes the discussion of surfactants (Chapter 5), solid surfaces with wetting and adhesion (Chapter 6) and adsorption (Chapter 7). In the surfactant chapter, we emphasize the structure–property relationships as quantified via the critical packing parameter (CPP) and the various factors affecting micellization and the values of the critical micelle concentration (CMC). The complexity of solid surfaces is discussed in Chapter 6. Wetting and adhesion phenomena are analysed with the Young equation and the theories presented in Chapters 3 and 4 but several practical aspects of adhesion are discussed as well. Chapter 7 provides a unified discussion of the adsorption at various interfaces. Thus, the similarities and differences (both in terms of physics and equations) of the adsorptions at various interfaces: gas–liquid, liquid–liquid, liquid–solid, solid–gas are shown. We discuss how information from one type of interface, e.g. solid–gas, can be used in analysing data in liquid–solid/liquid interfaces. Finally, the adsorption of surfactants and polymers which is crucial, e.g. in the steric stabilization of colloids, is presented in some detail. Quantitative tools like CPP have also a role here.

Chapter 8 starts the presentation of colloidal properties. Chapters 8 and 9 discuss the kinetic, optical and rheological properties of colloids and we illustrate how measurements on these properties can yield important information for the colloidal particles especially their molecular weight and shape.

Chapters 10 and 11 are devoted entirely to aspects of colloid stability. First, the essential concepts of the electrical and van der Waals forces between colloid particles are presented with special emphasis on the concepts of the zeta potential, double-layer thickness and Hamaker constants. Then, the DLVO theory for colloidal stability is presented. This is a major tool in colloid chemistry and we discuss how stability is affected by manipulating the parameters of by the classical DLVO theory. Chapter 11 closes with a presentation of kinetics of colloid aggregation and structure of aggregates. Chapters 12 and 13 are about emulsions and foams, respectively – two important categories of colloid systems where DLVO and other principles of colloid and surface science are applied. In this case, DLVO is often not sufficient. Steric forces and solvation effects are not covered by the classical DLVO and their role in colloid stability is also discussed in Chapter 12.

Chapter 14 presents three theories that can be used for describing multicomponent adsorption. This is a very important topic, which unfortunately is only very briefly touched upon in most colloid and surface chemistry books. It is also a rather advanced topic which may be omitted in a regular course. The same can be said for Chapter 15, which presents in some more detail, compared to previous chapters, theories for interfacial tension and their strengths and weaknesses are discussed.

Finally, we close with a concluding chapter and some remarks on research aspects in colloid and surface chemistry.

In terms of style, we have attempted to provide a book for those students/engineers/scientists interested in a first course about colloids and interfaces. We have decided to cover the most important topics in a generic form, rather than emphasizing specific applications, e.g. of relevance to food or pharmaceuticals. Nevertheless, many applications are illustrated via the exercises and selected case studies. Each chapter starts with an introduction and ends with a conclusion, when needed with links to what will be seen next. The basic equations are presented in the main text but to avoid "focusing on the trees and losing the forest" the derivations of some equations are, when we feel necessary, added as appendices in the corresponding chapters. Some of these derivations, e.g. those in Chapters 4, 10 and 14, require advanced knowledge of thermodynamics but our aim is to have the main principles and applications of colloids and interfaces understood also by those students who do not have extensive background in thermodynamics or electrochemistry. We have included several worked-out examples dispersed in the various chapters and many exercises at the end (with answers in the book website). A full solution manual is available to instructors from the authors. We have deliberately selected a large variety of problem types, which illustrate different aspects of the theory but also a variety of calculation techniques. Thus, the problems vary from simple calculations – demonstrations of the general laws of the applicability of theories – to derivations, problems from industrial case studies and a range of combined/review problems which are presented at the end of the book.

We have decided, largely because we had to draw a line with respect to book size and purpose at some point, to limit this book on theoretical aspects without extensive discussions of experimental equipment and techniques used in colloid and surface chemistry. Experiments are extremely important for colloids and interfaces and fortunately certain key properties can be readily measured. Even though we do not discuss them extensively we believe, however, that it is important for the student to know which properties can indeed be measured and which cannot – and for which theories are very important. A comprehensive table for this is included in Chapter 1.

We mentioned that we tried to "write a book with a purpose", to balance theory and applications, to present the basic principles of colloid and surface chemistry in an easy to understand way, suitable for students and beginners in the field and with the applied flavour in mind. But we are not aware if we have succeeded. We certainly tried and it has been enjoyable for us to write a book in this way and on this very exciting topic.

If part of this excitement is passed to our readers, students, colleagues and engineers, we have certainly succeeded.

We wish to thank many colleagues for their contribution to this book. We are particularly grateful to Professor Martin E. Vigild who participated together with us in the teaching of the course on "colloid and surface chemistry" over many years and his influence and input is to be found in many places in this book.

Finally, we would like to thank The Hempel Foundation for financial support of this book project. This has enabled us to hire one of our former students, Emil Kasper Bjørn, to help us prepare many of the figures in the book.

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DTU Chemical Engineering
Copenhagen, Denmark, February 2015

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Useful Constants

Acceleration of gravity, $g = 9.8066\ \mathrm{m \cdot s^{-2}}$

Avogadro Number, $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$

Boltzmann's constant, $k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$

Relative permittivity (or dielectric constant) of water at 20 °C = 80.2

Relative permittivity (or dielectric constant) of water at 25 °C = 78.5

Dielectric permittivity of vacuum, $\varepsilon_o = 8.854 \times 10^{-12}\ \mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$

Dipole moment unit, 1 *D(ebye)* = $3.336 \times 10^{-30}\ \mathrm{C \cdot m}$

Electronic (elementary) charge, $e = 1.602 \times 10^{-19}\ \mathrm{C}$

Ideal gas constant, $R_{ig} = 8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (= $N_A k_B$)

Ideal gas volume, $V = 22414\ \mathrm{cm^3 \cdot mol^{-1}} = 2.2414 \times 10^{-2}\ \mathrm{m^3\ mol^{-1}} = 22.414\ \mathrm{L \cdot mol^{-1}}$ (at s.t.p, 0 °C, 1 atm)

"Natural" kinetic energy, $k_B T = 4.12 \times 10^{-21}\ \mathrm{J}$ (298 K)

Planck's constant, $h = 6.626 \times 10^{-34}\ \mathrm{J \cdot s}$

Viscosity of water at 20 °C, $10^{-3}\ \mathrm{N \cdot s \cdot m^{-2}} = 10^{-3}\ \mathrm{kg\ m^{-1} \cdot s^{-1}}$

Viscosity of water at 25 °C, $8.9 \times 10^{-4}\ \mathrm{N \cdot s \cdot m^{-2}} = 8.9 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$

Important unit relationships

$\mathrm{N = J\ m^{-1} = kg\ m\ s^{-2}}$

$\mathrm{J = N\ m = kg\ m^2\ s^{-2}}$

$\mathrm{J = kg\ m^2\ s^{-2}}$

$\mathrm{Pa = N\ m^{-2}}$

$\mathrm{V = J\ C^{-1}}$

Symbols and Some Basic Abbreviations

Latin

A	surface area, m^2
A, A_{123}, A_{121}, A_{11}, A_{22}	Hamaker constants, J
A_{eff}	effective Hamaker constant, J
ΔA	change in surface area, m^2
AB	acid-base (interactions, concept)
A_0	area occupied by a gas molecule, m^2
A_{spec}	specific surface area, typically in m^2/g
a	energy parameter in two- or three-dimensional equations of state
a	acceleration, m/s^2
a_0	area of the head of a surfactant molecule, m^2
B	parameter in the Langmuir equation
B_1	first Virial coefficient, m^3/kg
B_2	second Virial coefficient, $m^6/(kg \cdot mol)$
b	co-volume parameter in two- or three-dimensional equations of state
C,c	molar concentration (often in mol/L or mol/m^3) or concentration (in general)
C	parameter in the BET equation
CCC	critical coagulation concentration, mol/L
CFT	critical flocculation temperature, K
CMC	critical micelle concentration, mol/L
CPP	critical packing parameter
d, d_p	(particle) diameter (and d can also be distance), m
D	diffusion coefficient, m^2/s
D_o	diffusion coefficient of equivalent unsolvated spheres, m^2/s
E	electric field strength, V/M
E	elasticity, J/m^2 or mN/m
E	entry coefficient, J/m^2 or mN/m
e	electronic (unit) charge, C
EO	ethylene oxide
F	foam number
F	force, N
F_V	viscous force, N
f	friction(al) coefficient, kg/s
f_0	friction(al) coefficient of unsolvated sphere, kg/s
f_{RPM}	rounds per minute (centrifuge), min^{-1}
g	acceleration of gravity, m/s^2
h_c	critical rupture thickness, m
H	distance between two particles or surfaces or films, m
HB	hydrogen bonds/hydrogen bonding
HLB	Hydrophilic-lipophilic balance
HSP	Hansen solubility parameter $(cal/cm^3)^{1/2}$
I	ionization potential, J
I	ionic strength, mol/m^3
IEP	isoelectric point
K_L	equilibrium adsorption constant, m^3/mol
K_{ow}	octanol-water partition coefficient
k	parameter in the Langmuir equation
k_B	Boltzmann constant, J/K
$k_2{}^o$	rate constant, $m^3/(numbers \cdot s)$
l	parameter in the Hansen/Beerbower equation
l_c	length of a surfactant molecule, m
LA	Lewis acid
LB	Lewis base
M	molar mass (molecular weight), kg/mol
MW	molecular weight, kg/mol
m	mass (of colloid particles), kg
n_i^σ	number of molecules at surface, $numbers/m^2$

n	refractive index
n	molar amount, mol
n	number of particles per volume, m^{-3}
n_o	initial number of particles per volume, m^{-3}
N_A	Avogadro number, 6.0225×10^{23} molecules/mol=mol^{-1}
N_{agg}	Aggregation (or aggregate) number of a micellar structure
[P]	Parachor
P	(vapour) pressure, Pa
P^{sat},P_o	equilibrium vapour pressure over a flat surface ("ordinary" vapour pressure), Pa
PZC	point of zero charge
PIT	phase inversion temperature, K
R_{ig}	ideal gas constant, 8.314 J/(mol·K)
R	particle of drop radius, m
R	Hansen radius of solubility $(cal/cm^3)^{1/2}$
R_o	initial radius of bubble, m
R_g	radius of gyration, m
R_f	roughness factor
R_f	horizontal film length, m
R	radius of curved surface (spherical particle, droplet, bubble), m
Re_p	particle Reynolds number
r	intermolecular distance, m
S	Harkins spreading coefficient, N/m or mN/m
S_{eq}	solubility of gas in liquid, mol/(m^3·Pa)
s	solubility, mol/L
s	sedimentation coefficient, s
SDS	sodium dodecyl sulphate
T	temperature, K
t	time, s
t	plate thickness, m
$t_{1/2}$	half life, s
T_{br}	T/T_b (T_b = boiling temperature)
V	molar volume, m^3/mol
V	volume per g of solid, m^3/g
V	potential energy (F=−dV/dH), J or J/m^2
V_A	attractive potential energy, J or J/m^2
V_R	repulsive potential energy, J or J/m^2
V_m	maximum volume occupied by a gas (in adsorption in a solid), cm^3/g
V_{max}	maximum value of potential energy, J or J/m^2
V_g	gas volume at standard T & P conditions (=22414 cm^3/mol)
v_{av}	average drainage velocity, m/s
V_F	volume of foam, m^3
V_L	volume of liquid, m^3
W	work, J
W	stability ratio
x	mole fraction
x	distance (e.g. in centrifuge), m
$\bar{x}$	Brownian end-to-the-end distance, m
u	velocity (of a colloid particle), m/s
Q	quadrupole moment
w	weight fraction
vdW	van der Waals (forces)
z, z_i	ionic valency (including sign)

Greek

α_0	electronic polarizability, C·m^2·V^{-1}
β	parameter in the Zisman equation
γ	surface or interfacial tension, N/m or J/m^2
$\gamma\infty$	infinite dilution activity coefficient
γ_o	water (solvent) surface tension, N/m or J/m^2
Γ_i	adsorption of compound (i), mol/g
Γ_{max}	maximum adsorption, mol/g
δ	solubility parameter $(cal/cm^3)^{1/2}$
δ	adsorbed layer thickness, m
δ	film (lamella) thickness, m
ΔP	pressure difference across a curved surface / capillary pressure, Pa
ΔG	Gibbs energy change (and of micellization), J/mol
Δh	height change (osmotic pressure), m
ΔH	Enthalpy change (and of micellization), J/mol
ΔH^{vap}	Enthalpy of vaporization, J/mol
ΔS	Entropy change (and of micellization), J/mol
ε_0	permittivity of free space (vacuum), $8.854 \cdot 10^{-12}$ $C^2 \cdot J^{-1} \cdot m^{-1}$
ε	relative permittivity (dielectric constant)
ζ	zeta potential, V
η	viscosity (of dispersion medium), kg/(m·s)
η_o	viscosity of particle-free medium, kg/(m·s)
η_r	relative viscosity

η	number of particles per unit volume, m^{-3}
η_0	start number of particles per unit volume, m^{-3}
ϑ	contact angle
θ	theta temperature, K
κ^{-1}	Debye length (double-layer thickness), m
μ	electrophoretic mobility, $m^2 \cdot V^{-1} \cdot s^{-1}$
μ	dipole moment, C·m
π	surface pressure ($=\gamma_w - \gamma$), N/m or mN/m
π_{sv}	spreading pressure ($=\gamma_s - \gamma_{sv}$), N/m or mN/m
π, Π	osmotic pressure, Pa
ρ	(molar) density (mol/m^3) or number density
ρ_L	density of liquid, kg/m^3
σ	surface
σ	shear stress, N/m^2
σ_o	charge density, C/m^2
φ	correction parameter in the Girifalco-Good equation
φ_G	volume fraction of gas
φ_L	volume fraction of liquid
ψ_0	surface potential, V
ω	angular acceleration, s^{-1}

Superscripts and subscripts

A	attraction/attractive
AB	acid/base interactions
adh/A	adhesion
ads	adsorption
coh	cohesion
crit	critical (in critical surface tension, different from critical point
c	critical
d	dispersion
dw	dirt-water
ds	dirt-solid
eff	effective
exp	experimental
EO	ethoxylate group
i	gas, solid or liquid in expressions for surface or interfacial tensions
ind	induction
j	gas, solid or liquid in expressions for surface or interfacial tensions
ij	gas/liquid, liquid/liquid, liquid/solid or solid/solid in expressions for interfacial tension
g	gas
h	hydrogen bonding
H_g	mercury
l,L	liquid
lg	liquid-gas
LW	London/van der Waals
m	mixture
m	metallic bonding/forces
max	maximum
mix	mixing
o	oil (in the "broader" sense used in colloid and surface science)
OA	oil-air interface
OW	oil-water interface
[P]	parachor
p	polar or particle
R	repulsion/repulsive
r	reduced (e.g T_r=T/T_c)
sat	saturated
s	solid
s	steric
sd	solid-dirt
spec	specific (forces/contribution)
sl	solid-liquid interface
surf	surfactant
spec	specific (non-dispersion) effects e.g. due to polar, hydrogen bonding, metallic,…
sw	solid-water
sv	solid-vapor (with vapor coming from liquid)
theor	theoretical
w	water
WA	water-air interface
+	acid effects (van Oss-Good theory)
−	base effects (van Oss-Good theory)
1	particle or droplet
2	medium

About the Companion Web Site

This book is accompanied by a companion website

www.wiley.com/go/kontogeorgis/colloid

This website includes:

- PowerPoint slides of all figures from the book for downloading
- Solutions to problems

1

Introduction to Colloid and Surface Chemistry

1.1 What are the colloids and interfaces? Why are they important? Why do we study them together?

Colloid and surface chemistry is a core subject of physical chemistry. It is a highly interdisciplinary subject, of interest to diverse fields of science and engineering (pharmaceuticals, food, cosmetics, detergents, medicine and biology, up to materials and microelectronics, just to mention a few). Being challenging to teach, it is often either incorporated or presented very briefly in general physical chemistry courses or, even worse, completely neglected (Panayiotou, 1998).

Colloidal systems have a minimum of two components. Colloidal dispersions are systems of particles or droplets with the "right dimensions" (the dispersed phase), which are dispersed in a medium (gas, liquid or solid). The medium is called the continuous phase, which is usually in excess. But which are the "right dimensions"? The particles or droplets have dimensions (or one key dimension) between (typically) 1 nm and 1 μm and their special properties arise from the large surfaces due to precisely these dimensions (Figure 1.1).

However, sometimes even larger particles, with diameters up to 10 or even up to 50 micrometre (μm), e.g. in emulsions, or very small particles as small as 5×10^{-10} m can present colloidal character. Thus, despite the above definition, it is sometimes stated that "If it looks like and if it acts like a colloid, it is a colloid".

Colloids are characterized by their many interesting properties (e.g. kinetic or optical) as well as by observing their stability over time.

The characteristic properties of colloidal systems are due to the size of the particles or droplets (i.e. the dispersed phase), and not to any special nature of the particles. However, their name is attributed to Thomas Graham (Figure 1.2), who was studying glue-like (gelatinous or gum-like polymeric) solutions (from the Greek word for glue which is "*colla*").

Introduction to Applied Colloid and Surface Chemistry, First Edition. Georgios M. Kontogeorgis and Søren Kiil.

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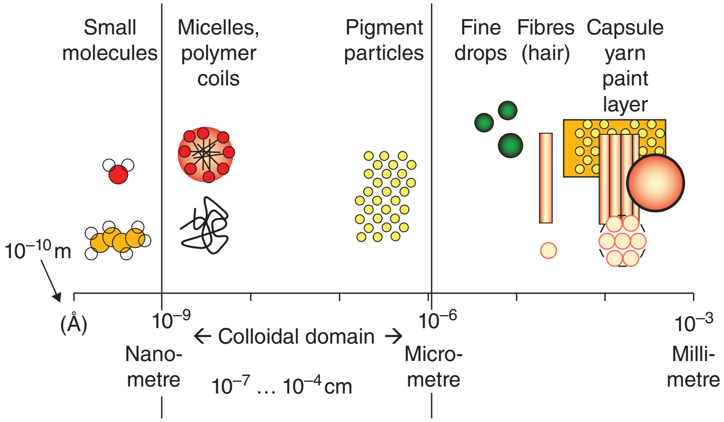

Figure 1.1 *Scales in colloid and surface science. Typically, colloidal particles have one key dimension between 1 nm and 1 µm (micrometre). Adapted from Wesselingh* et al. *(2007), with permission from John Wiley & Sons, Ltd*

Figure 1.2 *Thomas Graham (1805–1869), the pioneer in the study of colloidal systems, used the term "colloids" derived from the Greek word for glue ("colla"). He thought that their special properties were due to the nature of the compounds involved. Later, it was realized that the size of particles (of the "dispersed phase", as we call it) is solely responsible for the special properties of colloidal systems. (Right) T. Graham, H407/0106. Courtesy of Science Photo Library*

Many colloidal systems like milk are easily identified by their colour, or more precisely their non-transparent appearance (Figure 1.3). The optical properties of colloids are very important, also in their characterization and study of their stability – as discussed in later chapters.

Colloidal particles (or droplets) are not always spherical. They can have various shapes (e.g. spherical and rod- or disk-like), as shown in Figure 1.4. Proteinic and polymeric molecules are usually large enough to be defined as colloid particles. Moreover, their shape may be somewhat affected by solvation (hydration) phenomena, where solvent molecules become "attached" to them and influence their final properties. Solutions of proteins and polymers may be stable and they are classified as lyophilic colloids. Many colloidal particles (e.g. Au or AgI) are (near) spherical, but others are not. For example, proteins are often ellipsoids, while many polymers are random coils.

1.1.1 Colloids and interfaces

What about surfaces and interfaces? Colloidal systems are composed of small particles dispersed in a medium. The fact that these particles have such small dimensions is the reason that a huge surface (interfacial) area is created. Their high interfacial area is the reason why colloidal systems have special properties and also why we study colloids and interfaces together. As shown in Figure 1.5, the surfaces or interfaces are sometimes considered to be “simply” the ”dividing lines” between two different phases, although they are not really lines; they *do* have a certain thickness of a few Å (of the order of molecular diameters).

Figure 1.3 *A non-colloidal (water) and a colloidal liquid system (milk)*

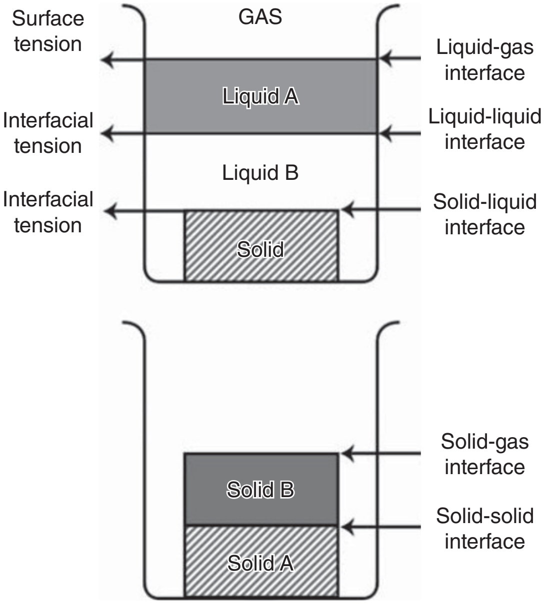

Figure 1.5 *Surfaces and interfaces involving solids, liquids, and gases. An interface has a thickness of a few ångstrøm (1 Å = 10^{-10} m)*

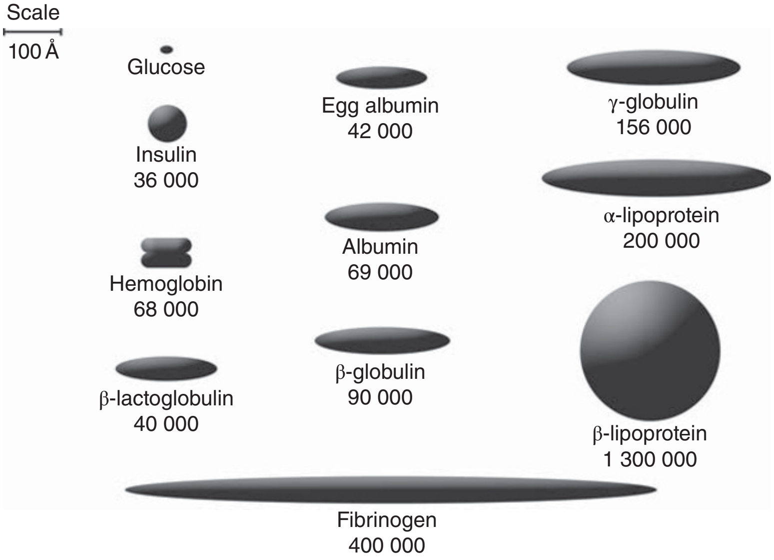

Figure 1.4 *Different shapes of colloid particles with molecular weights provided in g mol^{-1}. Pr J. L. Onclev. Harvard Medical School*

We often use the term ”surfaces” if one of the phases is a gas and the term “interface” between liquid–liquid, liquid–solid and solid–solid phases. All of these interfaces are important in colloid and surface science, in the understanding, manufacturing or in the application of colloidal products. However, there are many applications in surface science which are not directly related to colloids.

The huge interface associated with colloids is the reason why colloid and surface chemistry are often studied together. Colloidal dimensions imply that there are numerous surface molecules due to the large surfaces present. For example, 1 litre of a latex paint suspension containing 50% solids with a particle size of 0.2 μm has a total particle surface area of 15 000 m^2. However, to form such huge interfaces, e.g. by dispersing water in the form of droplets in an oil, we need “to do a lot of work”. This work remains in the system and thus the dispersed phase is *not* in the lowest energy condition. There is a natural tendency for droplets to coalesce and for particles to aggregate. To maintain the material in the colloidal state, we need to manipulate the various forces between particles/droplets and achieve stability. Colloidal stability is one of the most important topics in colloid chemistry.

1.2 Applications

Colloids and interfaces are present and of importance in many (everyday) products and processes, ranging from food, milk and pharmaceuticals to cleaning agents, and paints or glues (Figure 1.6). These are

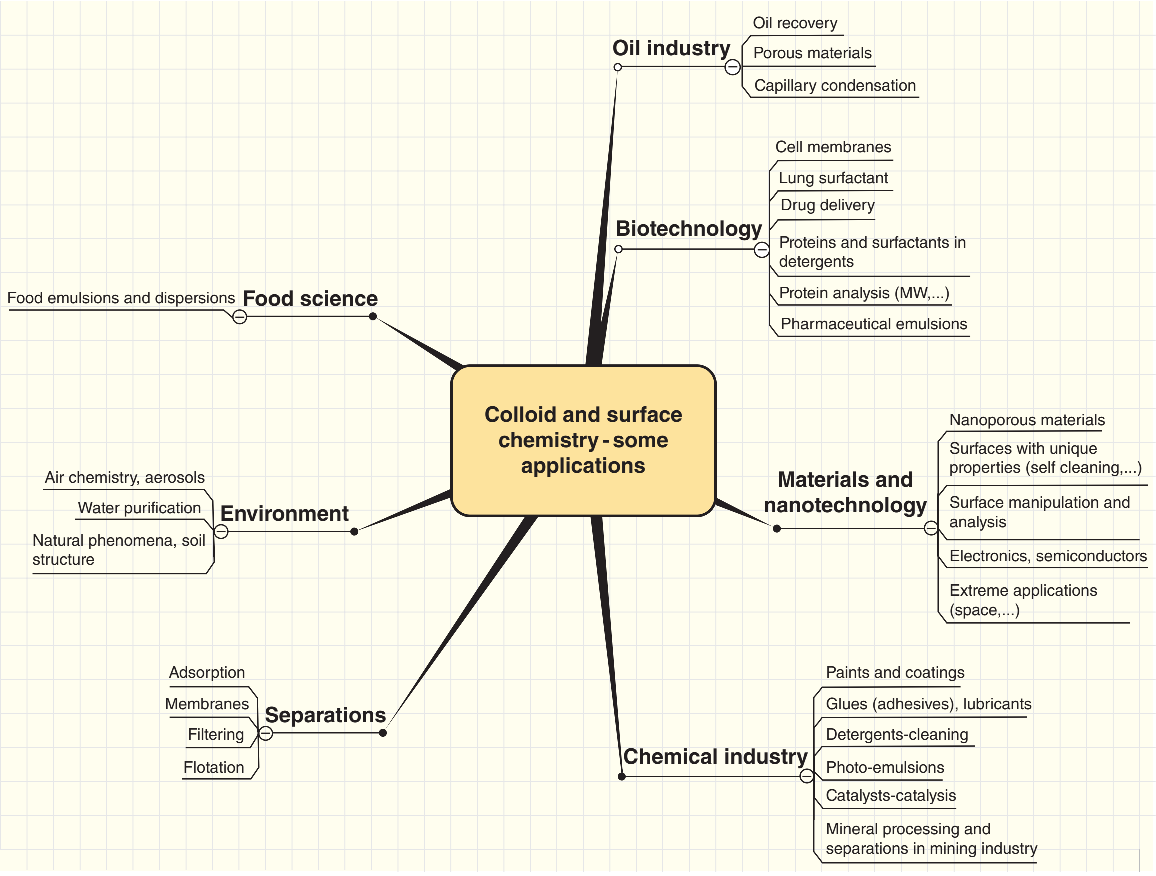

Figure 1.6 *Selected applications of colloid and surface chemistry*

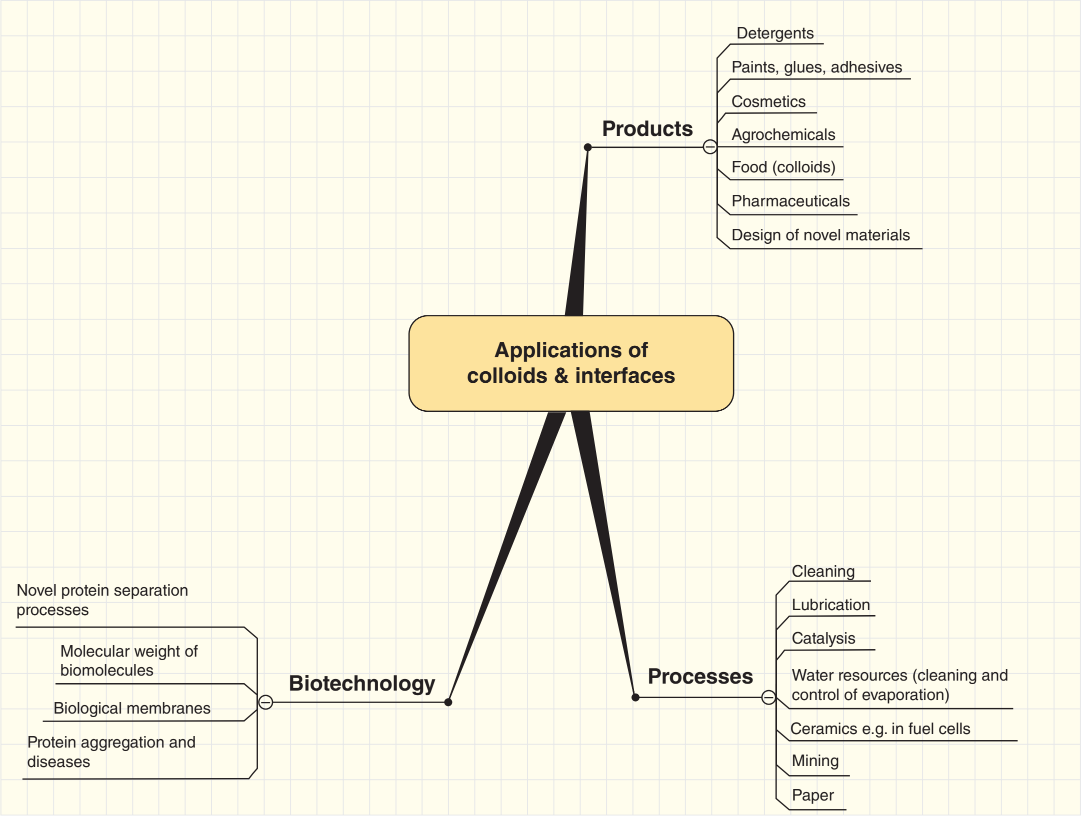

Figure 1.7 *A few applications of colloids and interfaces related to various types of products and processes*

some examples of what we call "structured products". Most of these products are colloidal systems, e.g. milk (liquid emulsion) or paint (emulsions or dispersions). The production and/or use of many colloidal-based products involve knowledge of surface science, e.g. the adhesion of glues and paints or cleaning with detergents. Most of these everyday "consumer" products are rather complex in the sense that they contain many components, e.g. polymers, solids, surfactants, and water or other solvents. As already mentioned, colloids and interfaces are linked and they are best studied together. Figure 1.7 shows some interrelations.

1.3 Three ways of classifying the colloids

Colloids (or colloidal dispersions) can be classified according to the state of the dispersed phase and the dispersion medium (gas, liquid, solid), see Table 1.1, or according to their stability. The most well-known colloids are emulsions (both phases are liquids), dispersions (solid particles in a liquid medium), foams (gases in liquids), liquids in solids (gels) and aerosols (liquids or solids in a gas).

The common colloidal dispersions (e.g. food or paint) are thermodynamically unstable, while association colloids (surfactants) and polymer/protein solutions are thermodynamically stable. In addition, there can be multiple or complex colloids which are combinations of the above, e.g. dispersion, emulsion, surfactants and/or polymers in a continuous phase. Finally, network colloids, also called gels, are sometimes considered to be a separate category.

Lyophobic (i.e. solvent hating) colloids are those in which the dispersoid (dispersed object) constitutes a distinct phase, while lyophilic colloids refer to

Table 1.1 *Examples of colloidal systems, i.e. one type of compound, e.g. solid particles or liquid droplets, in a medium. Different combinations are possible depending on the phase of the particles (dispersed phase) and the (dispersion) medium they are in. Two gas phases will mix on a molecular level and do not form a colloidal system.*

Dispersed phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fog, mist, liquid sprays
Gas	Liquid	Foam	″Chantilly″ cream, shaving cream
Liquid	Liquid	Emulsion	Milk, mayonnaise, butter
Solid	Liquid	Dispersion	Toothpaste, paints
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Gel	Pearl
Solid	Solid	Solid dispersion	Pigmented plastics, bones

Modified from Shaw (1992), Pashley and Karaman (2004), Hiemenz and Rajagopalan (1997) and Goodwin (2009).

single-phase solutions of macromolecules or polymers. Lyophobic colloids are thermodynamically unstable. These terms describe the tendency of a particle (in general a chemical group or surface) to become wetted/solvated by the liquid (=lyo- or hydrophilic in the case of water). Certain colloids like proteins have an amphiphilic behaviour as there are groups of both hydrophobic tendency (the hydrocarbon regions) and hydrophilic nature (the peptide linkages and the amino and carboxyl groups).

The terms hydrophobic and hydrophilic can also be used for surfaces. Both surfaces and colloid particles can "change" character from hydrophilic to hydrophobic and vice versa. For example, clean glass surfaces are hydrophilic but they can be made hydrophobic by a coating of wax, as discussed by Pashley and Karaman (2004). In addition, the hydrophobic (hydrocarbon) droplets in an oil-in-water emulsion can be made hydrophilic by the addition of protein to the emulsion – the protein molecules adsorb onto the droplet surfaces.

Unstable colloids can be kinetically stable (i.e. stable over a limited time period). The stability of colloids, one of their most important characteristics, is discussed in Chapters 10 and 11.

1.4 How to prepare colloid systems

There are various ways to "trick" particle formations and create a colloidal system. The most important ones are the ”aggregation” of molecules or ions and "grinding" or "milling" methods, typically in a mill/stirrer with the application of shear stress and adding some dispersants, e.g. surfactants. Other methods are based on the precipitation or the reduction of the solubility of a substance in a solvent such as in the case of the well-known Greek drink Ouzo (Figure 1.8), whose

Figure 1.8 *Ouzo, an example of a colloidal system. The reduced transparency upon addition of water is due to the reduction of anise oil solubility in alcohol*

opaque colour when water is added is due to the reduction of the alcohol content. In Ouzo's standard state (conventional alcohol content) the drink is colourless because the anise oil fully dissolves in the alcohol. But as soon as the alcohol content is reduced (by adding water), the essential oils transform into white crystals, which you cannot see through (like in milk, another classical colloidal system). The same phenomenon occurs when it is stored in a refrigerator. But Ouzo resumes its former state as soon as it is placed at room temperature.

Typically, the colloids need, after their preparation, to be purified e.g. to remove the electrolytes that destabilize them and there are many techniques for doing that. Among the most popular ones are the dialysis, the ultrafiltration, the size exclusion chromatography (SEC) and the gel permeation chromatography (GPC). The basic separation principle is the size difference between the colloid and the other substances that need to be removed.

1.5 Key properties of colloids

Colloidal systems are special and exciting in many ways. They have very interesting kinetic, rheological and optical properties (Chapters 8 and 9) which are important for their characterization (determination of molecular weight and shape) and application. But their most important feature is possibly the large surface area, and this is why these systems are often unstable (or metastable). The stability of colloids involves the relative balance between the attractive van der Waals and the repulsive forces; the latter are often due to the electrical charge that most colloid particles have. The van der Waals attractive forces in colloids are much stronger than those between molecules and lead to aggregation (instability), but there are (fortunately) also repulsive electrical forces, when the particles are charged, which "help stability". There are other types of repulsive forces, e.g. steric, solvation. Manipulating colloidal stability implies knowing how we can change or influence the various forces, especially the van der Waals attractive and the electrical and steric repulsive forces.

We emphasize, thus, from the start that almost all lyophobic colloids are in reality metastable systems. When we use the term "stable" colloids throughout this book, we imply a kinetically stable colloid at some arbitrary length of time (which can be, for example, two days or two years! depending on the application).

1.6 Concluding remarks

Colloids and interfaces are present and important in many (everyday) products and processes, ranging from food, milk and pharmaceuticals to cleaning agents and paints or glues. They are intimately linked and are best studied together. Colloids have many important, exciting properties of which stability is possibly the most important. Some properties of colloids and interfaces can be measured while others cannot and are obtained best via theories/models. An overview of what can be measured and what cannot in colloid and surface science is given in Appendix 1.1.

Colloids can be classified according to the phase (gas, liquid, solid) of the dispersed phase and the dispersion medium or according to their stability. Colloidal dispersions are thermodynamically unstable, while association colloids (surfactants) and polymer/protein solutions are stable. The former are often called lyophobic (hydrophobic if the dispersion medium is water) and the latter lyophilic (hydrophilic) colloids. These terms can be also used for surfaces.

Crucial in the study of both colloids and interfaces is knowledge of the forces between molecules and particles or surfaces and this is discussed next. While, as explained, a strict division is not possible, Chapters 3–7 discuss characteristics and properties of interfaces (surface and interfacial tensions, fundamental laws in interfacial phenomena, wetting & adhesion, surfactants and adsorption), while Chapters 8–13 present the kinetic, rheological and optical properties of colloids, as well as their stability and also a separate discussion of two important colloid categories, emulsions and foams.

Appendix 1.1

Table A1 *Overview of what can be measured and what can be calculated in the area of colloid and surface chemistry*

Property	Can we measure it? (How?)	Can we estimate it? (How?)	Comments – applications
Surface tension of pure liquids and liquid solutions	Yes (Du Nouy, pendant drop, Wilhelmy plate, capillary rise)	Yes (parachor, solubility parameters, corresponding states)	Wetting, adhesion, lubrication
Interfacial tension of liquid–liquid interfaces	Yes (Du Nouy)	Yes (many methods, e.g. Fowkes, Hansen, Girifalco–Good)	Surfactants
Surface tension of solids		Yes (Zisman plot; extrapolation from liquid data, solubility parameters, parachor)	Wetting and adhesion
Interfacial tension of solid–liquid and solid–solid interfaces		Yes (many methods, e.g. Fowkes, Hansen, van Oss–Good)	Wetting, adhesion, characterization and modification of surfaces… (paints, glues…)
Contact angle between liquid and solid	Yes (many goniometers and other methods)	Yes (combination of Young equation with a theory for solid–liquid interfaces)	Wetting, adhesion, characterization and modification of surfaces…
Critical micelle concentration of surfactants	Yes (change of surface tension or other properties with concentration)		Detergency
Surface or zeta potential of particles	Yes (micro-electrophoresis)		Stability of colloidal dispersions
Adsorption of gases/liquids on solids	Yes (many methods)	Yes (many theories, e.g. Langmuir, Brunauer–Emmett–Teller (BET), Freudlich)	Stability, surface analysis
Topography of a surface	Yes (AFM, STM)		Surface analysis and modification
HLB (hydrophilic–lipophilic balance)		Yes (group contribution methods, solubility parameters)	Design of emulsions including stability of emulsions and determining the emulsion type
Work of adhesion	Yes (JKR, AFM)	Yes (the ideal one is via Young–Dupre and similar equations)	Adhesion, detergency