Colloid and Surface Chemistry for Beginners

Colloid and Surface Chemistry for Beginners

By

Camillo La Mesa

Cambridge Scholars Publishing

Colloid and Surface Chemistry for Beginners

By Camillo La Mesa

This book first published 2026

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-1-0364-6699-2
ISBN (Ebook): 978-1-0364-6700-5

CONTENTS

FOREWORD

When involved with full-time scientific activity as researchers, we feel compelled to reduce early interests towards music and art. It is a hard decision, until one becomes acquainted that science is part of human life and it is creative as music and arts. It is not casual that scientists in the past shifted their interests from their activity to a different field. The brightest minds of *XVII* century, for instance, used arts to develop their unexpressed skills in the scientific disciples. At Galileo's time, for instance, the attitudes towards science and analytical thinking were severely forbidden in some parts of Italy and Spain, even though arts required substantial competences in mathematics, calculus and materials sciences. Great artists of that era like Bernini and Borromini had such capacities, although at different extent. The latter calculated the stability conditions required for building the high bronze baldachin in Saint Peter planned by his opponent Bernini; this is a pertinent example. In more recent times the attitudes of Richard Feynman (Nobel Graduate in Physics in 1965) towards samba and other Brazilian music, and painting, as well, were of substantial support in his scientific activity. Not forgetting Albert Einstein and his passion for playing the violin!

At the present time there is more scientific information available than in the past and we should take advantage of this, since creative attitudes are helpful in Physics, Chemistry and the arts too. This is why this book introduces items belonging to art, history and sciences. You shall appreciate this attitude, hopefully. Creativity is an essential part of modern scientific culture and the combination of sciences and artistic imagination may help and support us in these fields. Therefore, I introduced items related to the aforementioned aspects; I am pretty confident you shall appreciate these efforts.

An introductory course on Colloid and Surface Sciences proceeds in compulsory ways, where the fundamentals of Physics overlap with art and history. These fields enrich and supplement each other. This book is intended for People who are not yet fully involved in the aspects that colloids and many other scientific fields demand.

To stimulate the reader, articles reporting contributions from eminent scientists, sometimes awarded with Nobel Prize are introduced in the

References sections of chapters. Standing on the shoulders of giants is an excellent starting point to stimulate scientific curiosity.

I encourage you to take advantage of the physical, mathematical and humanities-based aspects disseminated here, together with a few pictures of some old scientific instruments.

Rome, 2025.

ACKNOWLEDGEMENTS

I thank my wife, Lyubov Bojko, for substantial support as a photographer.

I thank my dear friend Doctor Alberto di Tomassi for help in cleaning linguistic inconsistencies that were disseminated in the present contribution. In words, Alberto washed the manuscript in the waters of Thames river.

Thanks to my former students Dr. Giacomo Gente, Dr. Franco Tardani, Dr. Carlotta Pucci (Public University in Pisa University), Dr. Patrizia Andreozzi (working in Florence University) and many others.

I do not forget my deep friend and coworker Dr. Gianfranco Risuleo, who passed away in 2023. I also warmly thank Prof. Giuseppe Antonio Ranieri.

Without their substantial contributions this manuscript would not have been the same.

A BRIEF NOTE

As a dedicated collector of old-fashioned scientific instruments, I like to possess them and show them. In my opinion, old instruments are objects located at the boundaries between technics and art; discovering the procedure that led to their built-up favors the insatiable curiosity of those interested in science.

There is another good reason to use old instruments in demonstrating scientific concepts. That is, old-dated instruments are much more easily understood in functioning than automatized, modern, ones: I'd say they are "transparent". During the lessons I hold, pupils look at these old objects and ask "Truly? How do they work? How did they realize them?" That is the reason why old instruments explain the Physics underlying the instrumental design.

I must acknowledge that much merit of so much interest towards scientific old instruments is due to the outstanding capacity of the mechanicals, the glass-blowers and the great artisans active in Chemistry and Physics Departments at Sapienza University a long time ago.

I am confident you will appreciate my opinion on this regard.

CHAPTER I

INTRODUCTION TO THE FIELD AND SOME HISTORICAL NOTES

A perusal to human civilization puts in evidence that some colloids were well-known from our ancestors. To demonstrate such statements, let us remind that:

* Earthenware is in use from 40.000 years. Supposedly, a basket properly sealed with fresh clay accidentally fell on fire and gave origin to the first pot;
* Black carbon and $Fe(OH)_3$ pigments in Lascaux caverns, France, date to the same era;
* Dyes and lacquer from China, or Japan, are known from more than 4000 years;
* Soaps were used in the Babylonian age, *XX* century B. C. According to Julius Caesar, however, soap was known by Belgians, as he wrote in his "*Commentarii de Bello Gallico*". Caesar noticed that the boiling of beef fat and bones with potash, or K_2CO_3, gave a semi-solid material, ancestor of the actual *Marseille* soap. That process is a thermal hydrolysis of glycerides promoted by alkaline reactants as catalysts;
* Kajal is used in the middle East since over 5000 years ago, as documented by the half-length portrait of Queen Nefertiti. Kajal is a blend of galena (*PbS*), black carbon, hematite (*FeO*), and other inorganic dark pigments stabilized by acacia resin. The final result is a mixture of several different colloid particles stabilized by a natural polymer: in words, kajal is a hybrid colloid;
* from Homer's *Iliad* we know that only princesses could dress in purple, a dye obtained from murex, **Figure I.1**. The above conch was so precious to induce Phoenician merchants to sail well beyond Hercules' pillars, up to the Canary Islands! Later on, the *murex business* moved to Carthago, then to Rome, and became the symbol of imperial power;
* Etruscans and Romans modified bronze by surface functionalization and reaction. The technique implied pouncing bronze objects with sulfur, *S,*

powders, to get astonishing colors. See, for instance, the standing boxer, at Rome National Museum, **Figure I.2**;

* steel making belongs to the same category.

Figure I.1. Conch of Mediterranean Murex, *Bolinus brandaris,* according to Linnaeus. Purple color is extracted by prolonged boiling of the conchs and subsequent color concentration. Photo by Lyubov Bojko.

Figure I.2. Standing boxer, *I* century C. E. Located in Palazzo Massimo, National Rome Museum. Colors are due to pinching by *S* powders, and subsequent reaction with bronze components. The statue was recently cleaned to avoid adsorption of sulfo-bacteria and their proliferation onto folds. Photo by the author.

Iron has a *smectic* character (from the Greek word σμεγμα, meaning layered), obtained by immersing hot swords in animal blood or urine. Such dispersions are carbon- or nitrogen-rich fluids. Romans imported steel swords from Iberia 150 years B. C. [Wulff. 1965. 627-629.]. From the *VII* century C. E. renowned metallurgists acted in Damascus, where "*rigid*" steel was prepared, or in Arabic Spain. Toledo swords, in particular, had high elasticity and remained in use until the *XVIII* century. Among many famous owners, *Pope Alexander VI Borgia* was renowned for his splendid Toledo sword. It is not surprising, therefore, that steel craftsmen speculated on the magic of their art!

In the *XV* century procedures to get fine pigments were developed in Italy and the Netherlands. The workshops of *Andrea Verrocchio*, master of *Leonardo da Vinci*, and *Domenico Ghirlandaio*, *Buonarroti*'s one, both located in Florence, produced powders and colors finding use in water- or oil-based pigments. These products granted substantial coverage capacity and minimized the use of costly materials, as the famous "*lapis azul"*. For details on the renowned technological skills of Renaissance artists, see **Appendix I.A**.

In the afore-mentioned workshops craftsmen comminuted powders and stones to get fine pigments. They took a top-down strategy and transformed macroscopic objects to sub-microscopic powders. Nucleation operates in the reverse direction with respect to comminution, and gives colloids, as well. The latter bottom-up strategy dissolves materials undergoing chemical reactions and induces aggregation in small particles. Bottom-up modes were poorly used in the *XV* century; perhaps, pigments from water hyacinths gave the well-known "*blue indigo*". *Indigo* is unstable in white light, but was extensively used in coloring wool, or cotton; in France it is still a niche color.

The term *colloid,* from the Greek word κολλα (glue), was introduced less than 200 years ago. At that time there were vivid debates on the concept birthright; it is not casual if national scientific societies claimed their own scientists first discovered these systems. Thus, *Brown*, *Graham*, *Selmi*, *Zsigmondy*, *Gouy*, *van't Hoff*, *Ostwald* and many others were considered the field initiators in the respective countries. Each of the above scientists discovered some peculiar aspects inherent to the colloidal domain, see **Appendix I.B**. for more details.

The scattered discoveries that the above scientists presented cover many properties of what we currently define colloids. The dramatic increase of so many discoveries in less than 100 years is not surprising, given the physical variables that were screened, the easy access to relatively modern instruments, and the wide bunch of matrices that were considered in those

years. There was also intense and widespread interest from the first chemical companies. For instance, German factories synthetized paints and varnishes from the second half of *XIX* century, soon after companies as *BASF* and *BAYER* (the first producer of synthetic aspirin) settled.

At the end of *XIX* century there were not yet enough scientific competences for a unified theory, although taxonomic work was performed and primitive theories proposed. Such efforts did not univocally define the concept; more theoretical work and investigations were required. Today it is clear that an embracing definition of colloid applies to all states of matter, for systems differing in nature, composition, physical and chemical properties, as well. However, think how problematic it could have been for most *XIX* century scientists to put bubbles, biopolymers, metal hydroxides, soaps and pollens in a single class!

Our colloid ancestors had at their disposal dispersions finding use in steel and leather manufacturing, but also in producing inks, varnishes, potteries, jewelries, etc.; in other words, focus was on materials belonging to the colloidal domain. The preliminary information they reported on this subject came from matter flow through membranes. As glue, colloids are uncapable to cross membranes and cannot be crystallized; the actual definition comes from this fact. Peculiar too are the *lyophobic*/*lyophilic* character, solvent-hating or solvent-loving behavior, vividly discussed in the same years.

To our minds this attitude is funny, since people used technologies requiring colloid matter in bulk or on surfaces, but did not know how the preparations effectively worked. For instance, they ignored how soaps detached dirt from dresses. It is embarrassing that today many of us do not recognize the importance of colloid matter, even though materials with such character are of widespread utility. It is even more embarrassing to ignore that colloids have positive and negative effects on our daily life, although over 90% of air and water pollution arises from fine powders!

Colloids are met in all states of matter. For instance, the behavior observed in opals indicates that colloid organization does not depend on the state of matter, and that colloids can be dispersed in solids, liquids and gases. Below is listed a possible short list:

a) dispersed in solids are opals (a solid) in rocks, petroleum in sandstones, bubbles in polystyrene foams, etc.;
b) muds, oils and, eventually, water, or bubbles are dispersed in proper liquids;
c) solids (powders), or liquids (water micro-droplets) are dispersed in gases to give fogs or aerosols.

Mixtures of gases never ever produce colloids!

The physical state, electric charge and chemical composition of colloids and of the dispersing matrices are immaterial, at first sight, and do not allow to clarify the intrinsic features of what it is not a state of matter. This statement is undoubtedly true, although a self-professed expert in the field, a real goof, stated that colloids are the "*fourth state of matter*"! Believe me, it is not so.

At the end of the *XIX* century scientists were close clarifying many pertinent questions; they had the right physical and mathematical facilities to proceed along. However, the behavior of bubbles and foams, which are recognized parts of the colloid class, does not apparently fulfill the statements required to be included in such category. These vivid discussions look like rubbish today: we must convey, however, that such debates opened the way to further advances in the field.

There was the profound need of a great cultural leap forward with new ideas. Important articles on colloid matter appeared on German, French, English and American scientific journals from the end of the *XIX* century. In 1906, finally, *Wilhelm Ostwald*, full professor of Physical Chemistry at Leipzig University (Germany), founded the first journal fully devoted to colloids. Entitled *Zeitschrift für Chemie und Industrie der Kolloide (*Journal of Chemistry and Industry of Colloids*),* it took later the name *Kolloid Z. u. Z. Polym*. and is still known as *Colloid Polym. Sci*. It is not by chance if polymers are considered part of colloids, as they effectively are. Attempts to split the field in two parts dates to the late 20's of the past century, after H. Staudinger, later awarded with the Nobel Prize in Chemistry. Today, several dozen scientific magazines focus on colloidal matter; many others mostly deal with polymers.

Bubbles and foams exhibit very high surface to volume ratios; that is why the present branch of sciences matches in the denomination "*Colloid and Interface Science*". The term *Interface* refers to the thin separation layer among two adjacent phases. To demonstrate that the definition is valid, one may account for the enormous difference between the volume occupied by liquids restricted in bubbles to that pertinent to a foam, considered as a whole; this is a very difficult task to face with.

To clarify such statements, consider a homogeneous cube 10.00 *cm* long. The area of each side, A, is 100.0 cm^2, the total one 600.0 cm^2; the overall volume, V, 1000.0 cm^3. Cutting the cube in ten slides along three normal directions gives 1000 cubes long 1.0 *cm* each of them. The total surface has increased to 6000 cm^2, but the volume remains unchanged. In the comminution, there is a tenfold increase of surface, A, and of the surface to volume ratio, A/V! The effect continues proceeding along. For instance, 1.0

g TiO_2, a crystal grossly 6,0 *mm* large, gives very fine Titania powders upon comminution in a ball mill. The final product is used in painting on walls, and it is capable of covering uniformly a surface as high as 800 m^2 wide [Hanprasopwattana, Rieker, Sault and Datye. 1997. 165-175.]!

The surface to volume ratio, *A/V*, of colloids is incredibly high; it is not unusual, thus, that colloid matter has high surfaces, and noticeable chemical reactivity too. For instance, *pyrophoric Fe* powders easily burn in open air to give the corresponding oxides. *Fe* is not the only material having such properties. The extensive use of colloids in heterogeneous catalysis takes origin from the above considerations: efficient catalysts, luckily, do not undergo to the drastic oxidation met in pyrophoric iron.

High *A/V* ratios are intrinsically associated to the colloidal domain. Comminution gives entities with a nearly constant volume energy terms (we mean the energy intrinsically associated to a given volume of matter), and progressive contributions due to the surface state, which grow in direct proportion with the comminution degree.

The colloidal domain includes the following categories:

a) polymers, first investigated in detail by Hermann Staudinger [Muhlhaupt, 2004. 1072-1080.];
b) finely dispersed metallic powders;
c) some hydroxides (*Fe*, *Al*, *Cr*);
d) inorganic sulfides, as galena (*PbS*);
e) carbon-based nanoparticles as layered graphene, carbon nanotubes, fullerenes;
f) muds and clays;
g) surfactant aggregates and dispersed lipids;
h) emulsions, foams, bubbles, droplets;
i) biological structures as lungs, skin and bones;
j) sponges;
k) biological matter as pollens, red blood cells, viruses and bacteria.

At first sight bones are compact and solid; however, their porous inner structure finds substantial analogy with the shape of sponges and foams subjected to stresses. It is not unusual that bones' cells show significant deformation from the spherical shape. The fact that they are porous is extremely helpful for all animals, since the skeleton weight, the mineral body part, is minimized. At the same time, bones retain the mechanical properties as bulk hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, its major component [Olszta, Cheng, Jee, Kumar, Kim, Kaufman, Douglas and Gower. 2007. 77-116.]. The area on which forces are exerted is on the outer bones part, in

substantial analogy with what we observe on columns supporting the bridges on highways; as a rule, the mentioned columns are cave, in fact.

The forces controlling the supramolecular organization in colloids are covalent, non-covalent, electrostatic, and combinations thereof; their stability conditions have exactly the same meaning as in massive states. The case of surface to volume ratios is diriment. Above a certain A/V ratio, the energy contributions due to A terms dominate over the V-based ones. Drops nucleation is a worked example, since the surface and bulk energy contributions bear opposite sign. During the nucleation process, volume terms counteract surface tension and become dominant only from a certain particle size onward. Remind that volume terms are dimensionally cm^3, whereas surfaces are cm^2; hence they grow at a much different rate with the particles' radius.

Equilibrium is attained when the two terms become equal, that is when surface energy, indicated as G_A, and the volume one, G_V, obey the equality

$$G_A \leq |G_V| \quad (1.1)$$

The two terms in (1.1.) bear opposite sign; this is the reason for using the modulus. For a complete description of surface energy terms, see **Chapter II**.

The electric properties of colloids are active in one, two or three directions. Such lucky chance is because electric fields are radial. Electrostatics works not only for small particles, but operates among large surfaces, regardless of how close they are. The presence of charges at moderate distances is ubiquitous in colloid chemistry and it gives origin to a state defined as *double layer*; in many aspects, the double layer is an electric capacitor. As it will be shown later, the foundations of the double layer theory, and the subsequent stability of dispersed matter, become helpful in several practical applications.

According to what stated above, it is evident that all the features of the colloid matter can be expressed combining thermodynamic, statistical thermodynamics and electrostatic contributions. Therefore, it is possible to use physical terms as potentials, energies, and to define the most relevant features of the colloidal domain. This is what we shall do, applying, when required, the foundations of differential calculus, integrals and other physical and mathematical relations to colloid matter.

Primitive pictures of surfaces, interfaces, and of their main features are indicated below. A point to be discussed in more detail deals with electrostatics; thus, the electrical double layer and the related *DLVO* theory shall be extensively discussed. The acronym *DLVO* comes from the names of the scientists which developed the theory, that is Deriaguin, Landau

(Nobel Graduate in Physics in the year 1962), Verwey and Overbeek. The theory was developed independently by Dutch and Russian scientists in the years around the *WW II*, when exchange of scientific information was practically impossible. When comparison between such contributions became possible, it came out that the results obtained from the two groups were practically inter-exchangeable and complementary [Verwey and Overbeek. 1999.], [Deriaguin, Churaev and Muller. 1987.], [Landau. 1969. 386-411.].

Colloid particles are *intrinsic* (the term means "as such") entities; they can be inorganic, association-based, several composites, but also muds, pastes, emulsions and microemulsions. The single categories are discussed separately below. Experimental methods and techniques characterizing the single categories are briefly outlined in the following chapters. Physical and mathematical approaches are introduced in the pertinent sections, when necessary. The important field of food colloids is dealt with in a separate chapter. Restoration and cultural heritage, which are part of Colloid Sciences, are randomly mentioned throughout the book. At a first view, some chapters are more descriptive than others. Perhaps, efforts have been made to make the chapters of comparable difficulty.

The primary goal of this book is to show the ubiquitous nature of colloid matter. Our body, for instance, contains several tissues and organs belonging to that class. Thus, bones, red blood cells, lungs, bile, muscles (whose long fibers are arranged in liquid crystalline order), skin and the circumvolutions of brain are worth being mentioned. Some tissues are solid, others semi-solid, others can be dispersions, or solutions. Not only human tissues are like that; all animal types (vertebrates, fishes, and insects) are built-up by organized assemblies of colloid entities. It is not surprising, therefore, that modern biomedicine considers colloid sciences the starting point of the tissues' organization in histology, anatomy and physiology.

Heterogeneous catalysis and nanotechnologies have much to deal with colloid chemistry. This is why substantial knowledge on the fundamentals of Colloid Sciences is ineludible in different fields of *Biology*, heterogenous organic synthesis and catalysis, *Physical Chemistry*, and *Soft Matter Physics* [De Gennes. 1992. 842-845.]. Even engineers and personnel involved in the restoration of antiquities are interested in the field. Restoration, in fact, takes care of the surface state of statues, paintings, frescoes, mosaics, jewels, and of the inherent surface cleaning procedures, which change in different cases. Motor engineers, conversely, use ceramics surface-covered by very thin metal layers to get catalyzers finding use in combustion engines [Haag, Burgard, Amer and Ernst. 2008. 202-221.], and reactors, as well. As such, the two aspects are complementary. In both

cases, the processes occur on a thin metal-covered surface; oxidation occurs in the first case, chemical reactions in the second.

Such efforts arrived at convergence after the WW *II*, with the discovery of plastic matter, synthetic surfactants and so on. From a heuristic viewpoint a great push was due to a pioneering contribution by Richard Feynman [Feynman. 1960. 22-23.], who convinced his followers towards what we currently define nanotechnologies. His important contribution stating that "there's plenty of room at the bottom" led us to our actual knowledge in the field.

Techniques characterizing colloid systems are reported in the following chapters. Often the descriptions rely on old-dated equipment. From a pupil's viewpoint, old instruments are much more easily understood; it is as if they look "*transparent*" to our eyes. The description of some techniques does not fit completely in a single chapter, and is split in more chapters. Information on the electrical aspects of colloid matter, for instance, is not circumscribed to **Chapter IV**, since the reported techniques find use in many different colloid systems. Viscosity finds use in two- and three-dimensional cases; we show the similarities and differences occurring in two such states.

The book is written in plain form and is apt to undergraduate students. It does not need the physical competences required by the books of Adamson [Adamson and Gast, 1994.], Evans and Wennerstroem [Evans and Wennerström, 1999.], Israelachvili [Israelachvili, 2011.], Vold [Vold and Vold, 1983.] and of Everett [Everett, 2019.], to which interested pupils may refer. Information from specialized articles is reported in the text, when necessary.

Textual Reference to the Introduction

1.1. Wulff, Hans E. 1965. "Technology and Culture". Baltimora, Ma. USA. John Hopkins University Press. No 6: 627-629.
1.2. Hanprasopwattana, A.; Rieker, T.; Sault, A.G., and Datye, A.K. 1997. "Morphology of titania coatings on silica gel." Catal. Lett., No 45:165-175.
1.3. Muhlhaupt, Rolf. 2004. "Hermann Staudinger und der Ursprung der Makromolekularen Chemie." Angew. Chem., No 116:1072-1080.
1.4. Olszta, M.J. Cheng, X.; Jee, S.S.; Kumar; Y.Y. Kim, Y.Y.; Kaufman, M.J.; Douglas, E.P. and L.B. Gower, L.B. 2007. "Bone structure and formation: A new perspective". Mater. Sci. Engin. R. Rep., No 58: 77-116.
1.5. Verwey, E.J.W., and Overbeek, J.Th.G. 1999. "Theory of the Stability of Lyophobic Colloids". Dover, UK. Dover Books on Chemistry.

1.6. Deriaguin, Boris V., Churaev, Nikolai V., and Muller, Viktory N. 1987. “Surface Forces”. Heidelberg, FRG. Springer.
1.7. Landau Lev Davidovich. 1969. “Collected Works”. Moscow (USSR). Nauka: Vol. I, 386-411.
1.8. De Gennes, Pierre Gilles. 1992. “Soft Matter (Nobel Lecture)”. Angew. Chem., No 31: 842-845.
1.9. Haag, S., Burgard, M., Amer, J. and Ernst. B. 2008. “Thin palladium layer deposited on ceramic materials: application in hydrogen transport and catalytic membrane process”. Intern. J. Surface Sci. Engin., No 2: 202-221.
1.10. Feynman, Richard. 1960. “There’s plenty of room at the bottom”. Caltech Eng. Sci. No. 23: 22-23.
1.11. Adamson, Arthur W. and Gast, Alice P. 1994. “Physical Chemistry of Surfaces”, 6th Ed. New York, USA. Wiley.
1.12. Evans, Donald Fennel, and Wennerström, Hakan. 1999. “The Colloidal Domain - where physics, chemistry, biology, and technology meet”. 2nd Ed.; New York, USA. Wiley-VCH.
1.13. Israelachvili, Jacob N. 2011. “Intermolecular and Surface Forces”. 3rd Ed. New York, USA. Academic Press.
1.14. Vold, Robert D., and Vold, Majorie J. 1983. “Colloid and Interface Chemistry”. Reading, Mass. USA. Addison-Wesley.
1.15. Everett, Douglas E. 2007. “Basic Principles of Colloid Science”. 2nd Ed. London, UK. Royal Society of Chemistry Paperbacks.

Appendix I.A

A brief historical note

When the Middle Ages were close to their end, sciences were not developed yet, but artistic and craftsmen technologies became extremely advanced. Such expertise, including some knowledge of mathematics, was of current use in art, and in manufacturing materials, as in wool and leather goods making.

Distinguished artists of the Renaissance age had deep competences in Euclidean geometry, studied three dimensions and perspective, in vivo human anatomy and operated, if required, with several branches of metallurgy, including cannon making. Because of the possible war with Turks, they transferred competences from bronze making towards such activity. Renaissance artists used basic aspects of the at-yet unknown inorganic chemistry, developed architecture, civil engineering and hydraulics.

Some of them wrote comedies, poems and sonnets. Others had philosophical debates, built up and played musical instruments; see Raffaello's paintings in Vatican, for instance. Another example is Leonardo da Vinci; this outstanding painter, architect, engineer, sculptor, and so forth, was engaged as musician in the court of Sforza dukes, Milan, between the end of XV and the beginning of the XVI century. His musical skills, however, are not much known.

In addition, many artists had a deep knowledge of the foundations of ballistics (and mechanics of bodies in motion), repaired antiquities, excelled in drawing, painting, and sculpture. Some, as the adventurer Benvenuto Cellini, took up swords. Thus, most distinguished Renaissance artists were not limited in competences to arts, as Frederick Engels, friend and supporter of Karl Marx, wrote.

Appendix I.B

Ancestors of Colloid Sciences

The scientists listed below discovered fundamental aspects of colloid chemistry. The list includes chemists, physicists, and biologists. It is not casual that Colloid Sciences are at the boundaries between these scientific fields, and close to materials sciences and engineering. The following list is incomplete, and other scientists are mentioned in the text.

- Robert Brown (British botanist): described the phenomenon known as Brownian motion in dispersions of pollen, in 1827, when observing pollens with the aid of an optical microscope.
- Francesco Selmi (Italian chemist): described "pseudo-solutions" of starch and albumin, and the coagulation of Prussian blue, in the years 1844-1847.
- Michael Faraday (British physicist): excellent experimentalist, prepared stable dispersions of colloidal gold in 1857. He presumably took inspiration by former suggestions of Paracelsus.
- Thomas Graham (Scottish chemist): described the effusion laws in gases and solutions and showed that colloids do not cross membranes. Active in the years 1864-67.
- Jacobus E. Van't Hoff (Dutch chemist): discovered the laws of osmotic pressure across membranes, in 1887, and discussed most theories of solutions. He talked about "The power of imagination in sciences". Nobel Graduate in 1901.

- Louis-Georges Gouy (French physicist): developed the electrical double-layer theory, later known as Stern-Gouy-Chapman approach. Active between the XIX and XX centuries.
- Wilhelm Ostwald (German/Lectonian chemist): developed the concept of mole, the dilution laws, the equilibrium theory, and the fundamentals of heterogeneous catalysis. He founded the first scientific journal on Colloid matter. Nobel Award in 1909.
- Richard A. Zsigmondy (Austrian physicist): studied gold hydrosols and capillary condensation. Developed the ultra-microscope, at the end of XIX century. Nobel in 1925.

CHAPTER II

SURFACE PHASES

II.A. Introduction

The concept of a fluid surface is not intuitive. In analogy to solids, a surface is represented as a Mathematical entity; no thickness and inalterability are its major peculiarities. Fluid surfaces are more mobile than one could expect, since molecules therein freely move on the mentioned surfaces, which are equipotential, escape from bulk toward the surface, move to the gas or return to the surface. This complex behavior does not depend on the presence of gases or vapors; it depends on composition, P and T. The surface phase adsorbs molecules from the gas, takes up species from the bulk and releases them in bulk phases. The same holds true when two immiscible fluids are in contact; thus, the two cases shall be considered jointly. Any surface phase is a few molecular diameters thick. Molecular motions are fast and occur on very short time scales, in the time required for diffusion [Chandler. 1974. 246-251.].

To ensure coexistence among phases between two immiscible fluids, we accept that thermodynamic equilibrium always exists (*N.B.* In thermodynamic terms, tiny amounts of A-type molecules are present in a medium made by B-type ones, and vice-versa.). Equilibrium with gas is affected by the latent heat of evaporation (ΔH_{vap}), by that of condensation (ΔH_{cond}), by molecular diffusion from/toward the bulk, eventually by some chemical reactions, and by their combination, as well.

The number of events occurring at the same time in the different phases requires thermodynamic equilibrium conditions. These are troublesome problems to face with, since events occur in different phases, each with its own peculiar features. Exchange of matter between phases is extremely fast on an experimental time scale, and equilibrium exists. If not, one could observe the phase(s) disappearance. In what follows, the not-yet defined surface phase is considered an autonomous entity. The stability of that phase results from a huge number of individual events ensuring equilibrium to multi-phase systems.

Conditions for thermodynamic equilibrium require the:

1- Molecular transfer from gas to surface, governed by the latent heat of condensation, ΔH_{cond};
2- The transfer from surface to gas, driven by the latent heat of vaporization, ΔH_{vap};
3- The molecular motions along the surface, from the bulk to surface transfer and the reverse. The first is diffusion-driven, others from fluctuations in composition, hence in chemical potentials. Motions over surfaces are two-dimensional, when bulk ones are three-dimensional. In the latter case, motions can be anisotropic, if motions in one direction differ from the others.
4- The chemical potential of a component in these phases, including the surface, is univocally defined from the overall composition, *P* and *T*. At equilibrium, chemical potentials, μ_i, are the same in all phases [Silbey, Alberty, Papadantonakis and Bawendi. 2022. Chapt. VI, 179].

One can write equilibrium conditions for all processes occurring in the mentioned phases. Despite molecules chaotically move much faster than we may imagine, the surface tension, γ (dynes cm-^{1}), is the resultant of processes taking place in the surface, and it remains fixed if T, and, to a lesser extent, P are constant. To now, pure substances are considered; however, the theory can be safely extended to mixtures. The chemical potentials of different species, each referred as μ_i, must be accounted for.

For a one component system, the energy required to increase the surface of its liquid is controlled only by *T* and *P*. For a pure liquid the surface tension, γ, is $\gamma(T, P)$ and represents the work term required to increase the surface area. Dimensions are energy/area, *G/A* (*dynes cm*$^{-2}$). It is possible to define γ as a work per unit line, *F/L*. At first glance the definitions do not seem comparable to each other; perhaps, they have exactly the same meaning and are numerically equivalent if the two relations are expressed in *dynes cm*$^{-2}$, or in *milliNewton m*$^{-1}$ units, respectively.

Such hasty hypothesis is evident from the relation

$$\gamma = G/A = FL/A = F/L \quad \text{(II.1)}$$

Therefore, equivalence is at hand if *G* is expressed in *joules*, *A* in *cm*^{2}, *F* in *Newton*, and *L* in *cm*.

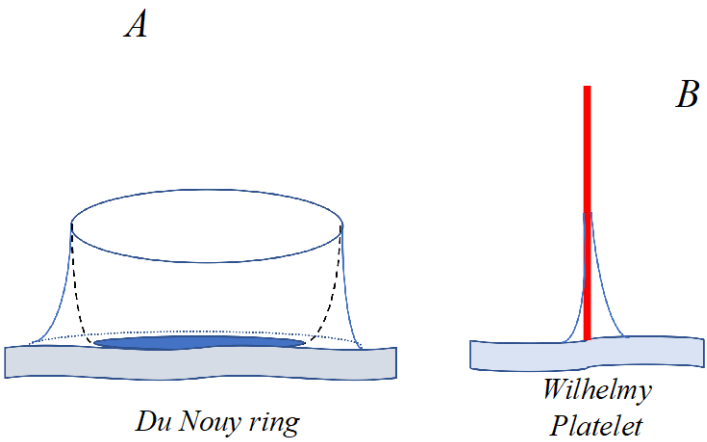

Figure II.1. *Left side, A.* A Du Nouy ring emerging from a liquid with an adsorbed liquid layer: the fluid is displayed in light blue. *Right side, B.* A Wilhelmy platelet drawn normal to the paper sheet has an adsorbed liquid layer. The platelet is in red color. For simplicity, anchoring of the platelet, or the ring, to measuring devices is not indicated. In both cases, the surface area increases upon mechanical action.

II.B. Basic Instruments

Below is indicated how to measure γ with dedicated instruments. Imagine having rings, or platelets, immersed in water, solutions, quicksilver, benzene, or else. The molecular forces acting on the immersed objects occur along the contact line with the liquid, on all sides that these objects share in common with the fluid, **Figure II.1**. The increase in area upon application of a force reported in the above Figure is intentionally extreme. Whatever the effect really is, the increase in area requires the action of mechanical work to balance the forces acting on surface molecules. The effect continues until the liquid layer around the ring breaks down. The effect is equivalent to the mechanical work balancing surface tension, γ. For these reasons such methods are termed *balance methods*.

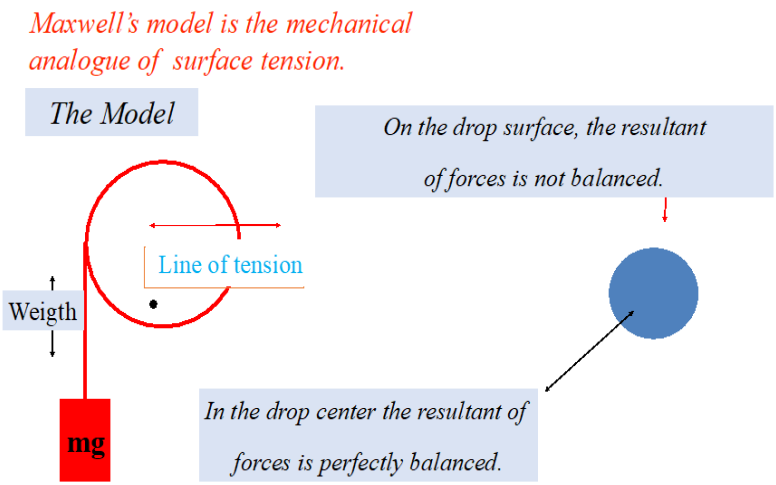

Figure II.2. The surface tension acts on a spherical drop, according to J.C. Maxwell (who developed the electromagnetic field theory). The line of tension, in red, moves along the surface and is counteracted by the red object, placed normal to it. In the center of a sphere, right part of the figure, forces in action are balanced and their resultant is zero.

Surface tension minimizes the fluid area: the mechanical work counteracts this tendency. That is the reason why drops and bubbles are grossly spherical. That shape, in fact, ensures the minimum surface area for a given volume. The same considerations arise from Maxwell's scheme of surface tension, **Figure II.2**. Methods measuring the surface tension are the *Wilhelmy* plate (of metal, glass or mica), or the *Du Nouy* ring one, respectively, **Figure II.3**. The *Du Nouy* ring is built with platinum, to remove the adsorbed surface-active impurities by firing.

The *pendant drop* method uses a *stalagmometer*; it has similarity with stalagmites in caverns.

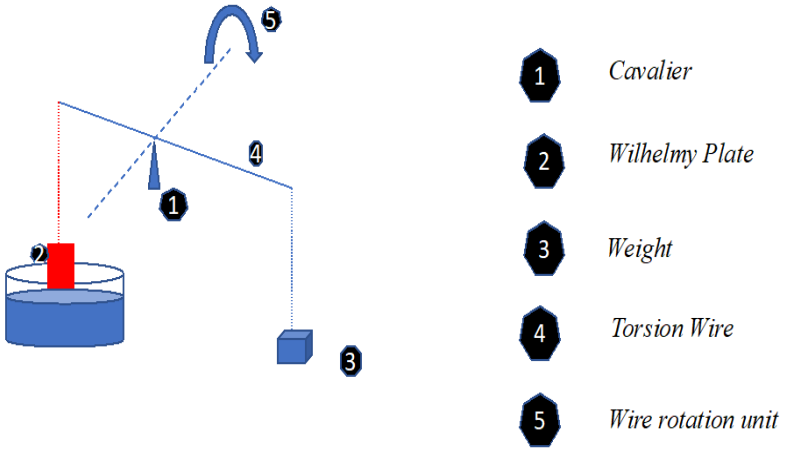

Figure II.3. Essential components of surface balance methods. The fundamental parts of the instrument are indicated in the right-hand side of the figure.

In the pendant-drop method a liquid is put in a glass ball of known volume terminating in a thin tube from which the liquid flows. An orifice is on the tube. The liquid exits from an orifice in the center of a highly polished glass disk of known diameter, placed at the tube end. Before falling by gravity, the liquid spreads on the glass, covers it, nucleates in a lens, grows and forms a drop, which detaches under the combined action of surface tension, tending to reduce drop size, and drop weight, operating in the reverse direction. When equilibrium among two such forces is lost, the drop falls and is recovered. Several drops are counted and weighted. To proceed along, it is required to know the effective area of the glass-polished surface, of the liquid column height in the tube, T, and so on.

Many instruments are based on the "*stalagmometric*" method drawn in **Figure II.4**.

II.C. Thermodynamic foundations.

The surface energy is mostly related to T, when P plays a minor role. Surface tension decreases with T, and vanishes at the critical point [Jensen. 2001. 1369-1371.], [Nagle. 1975. Chapt. 1, 1-66.]. Any liquid in equilibrium with its vapor has an interface, existing well above its boiling point. If not, it would be impossible to have pressure cookers!

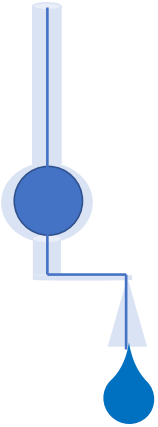

Figure II.4.A stalagmometer. In blue is the liquid in the reservoir, in the falling drop, and in capillaries.

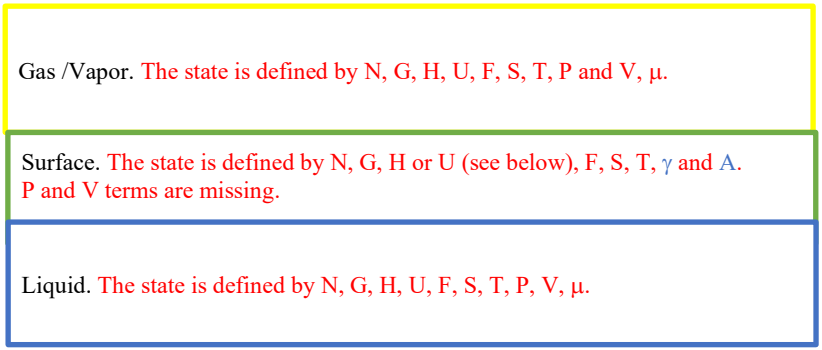

Figure II.5. Three phases in equilibrium. The massive ones, in yellow and blue, are defined by *G*, *H*, *U*, *V*, number of moles, *N*, and chemical potentials. The surface phase, in green, does not contain volume terms, replaced by surface energy cones. The chemical potentials in the surface phase are missing and are obtained by dγ, thanks to the Gibbs adsorption isotherm.

Figure II.5 schematically draws three coexisting phases, a liquid, in blue, a surface, in green, and a gas (vapor), in yellow. For each phase it is possible to draw thermodynamic equations, using the differential energy forms. In particular, the equality

$$dG = \gamma dA \quad \text{(II.2)}$$

occurs in the surface phase. It implies

$$G_S = (\partial G/\partial A)_{P,T} = \gamma \quad \text{(II.2')}$$

where G_S is the surface Gibbs energy (energy per unit area).

In reversibility conditions, at T and P constant, one gets

$$dQ = TdS = TS_S\, dA \quad \text{(II.3)}$$

S_S defines the surface entropy, $S_S = (\partial S/\partial A)_T$. The dispersion of Q from that phase becomes

$$T\, S_S = (\partial Q/\partial A) \quad \text{(II.4)}$$

which, combined with Eq. (2.2'), gives

$$(\partial G_S/\partial T) = -\, S_S = (\partial \gamma/\partial T)_P \quad \text{(II.5)}$$

Therefore

$$H_S = G_S + TS_S = \gamma + T(\partial \gamma/\partial T) = \gamma + (\partial \gamma/\partial lnT) \quad \text{(II.6)}$$

The relation is approximated by

$$H_S = U + PV \sim U_S \quad \text{(II.7)}$$

Eq. (II.7) is valid because no PV-like work occurs in mathematical surfaces. One could use the Helmholtz free energy, F, in place of the Gibbs one. In fact, F does not contain PV terms. Perhaps, habits force us to use G. In the limits set up by the above convention, one may write

$$U_S \sim \gamma + (\partial \gamma/\partial lnT) \quad \text{(II.8)}$$

The equation implies that γ is related to the surface energy, U_S, decreases with T and vanishes at the critical point, where no distinction between gas and liquid phases occurs. **Figure II.6** shows the links between phase diagram and surface tension. (See **Appendix II** and **Figures II.A** and **II.B** therein for more details).

There is an urgent need of more specifications. We define the variables to consider when a surface phase is in equilibrium with a gas and/or a liquid. The total volume of the system is

$$V_{tot} = V_l + V_g \quad \text{(II.9)}$$

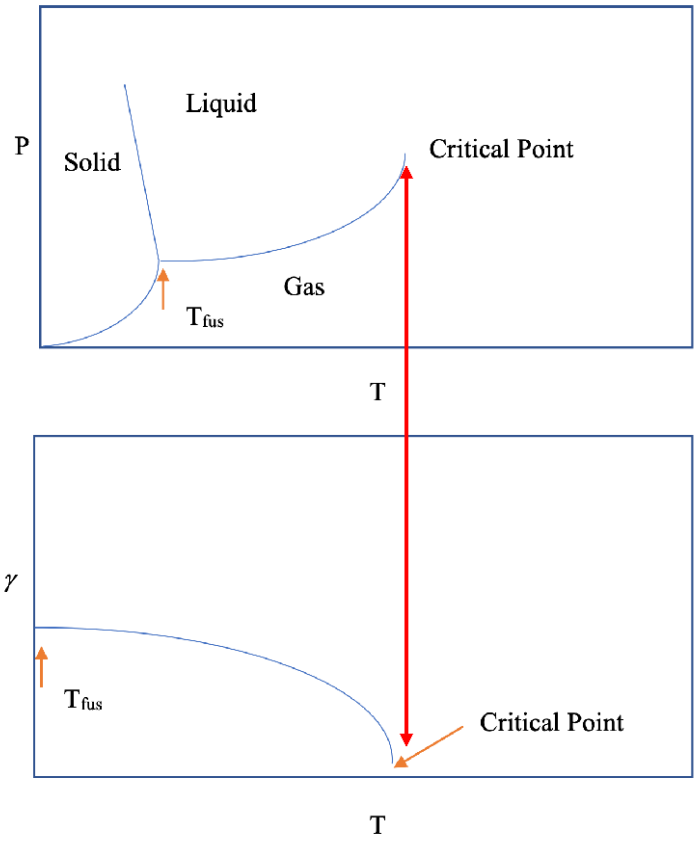

Figure II.6. Simplified phase diagram of pure water in the *P-T* plane, *upper graph*, and the dependence of the surface tension of distilled water, γ, on temperature, *lower graph*. The effect of pressure on γ is much less relevant compared to *T* and can be neglected. To clarify the statements given in the text, the graphs were unified and the location of critical points was indicated by a red arrow.