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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*”).

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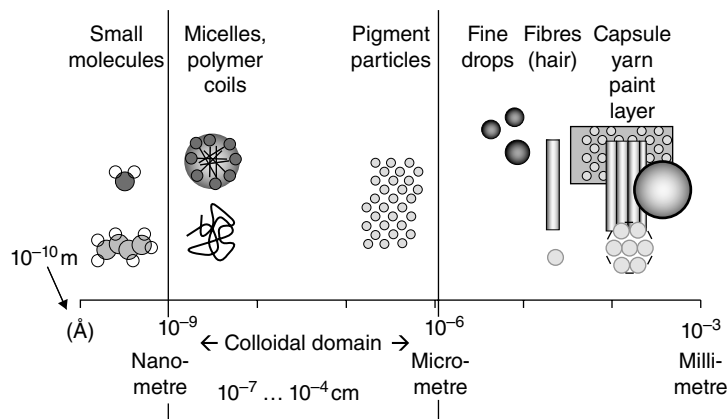


Figure 1.1 Scales in colloid and surface science. Typically, colloidal particles have one key dimension between 1 nm and 1 μ m (micrometre). Adapted from Wesselingh et al. (2007), with permission from John Wiley & Sons, Ltd



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



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

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).

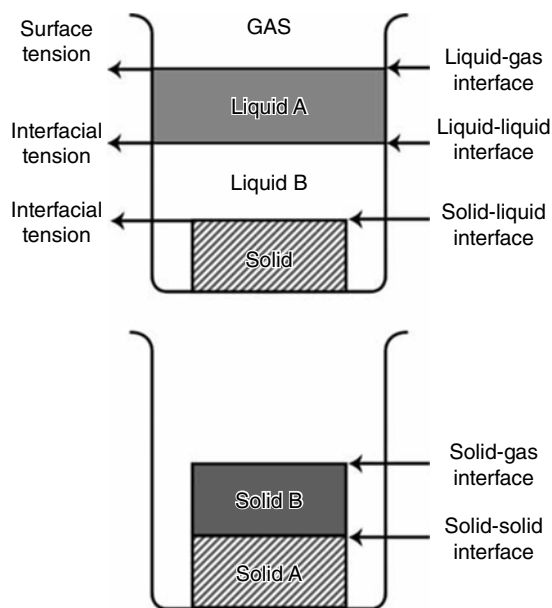


Figure 1.5 Surfaces and interfaces involving solids, liquids, and gases. An interface has a thickness of a few ångström ($1 \text{ Å} = 10^{-10} \text{ m}$)

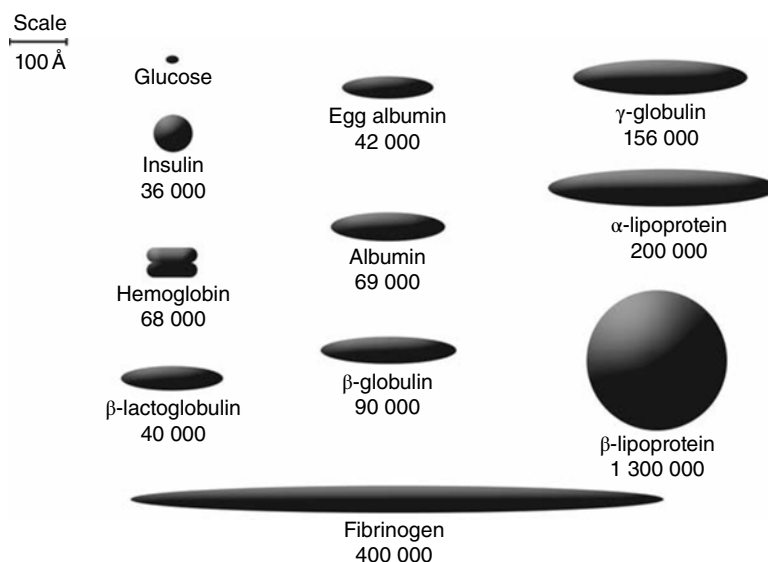


Figure 1.4 Different shapes of colloid particles with molecular weights provided in g mol^{-1} . Pr J. L. Onclev. Harvard Medical School

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 $0.2\ \mu\text{m}$ has a total particle surface area of $15\ 000\ \text{m}^2$. 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

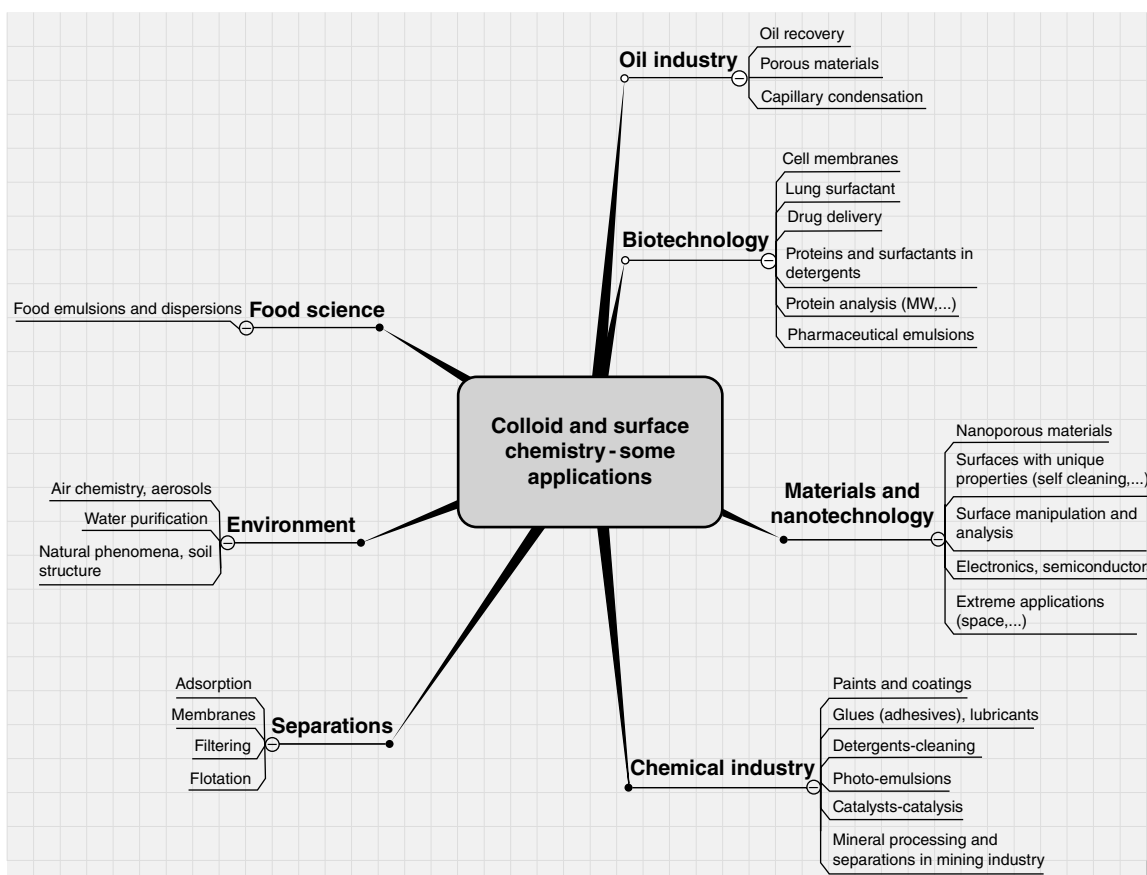


Figure 1.6 Selected applications of colloid and surface chemistry

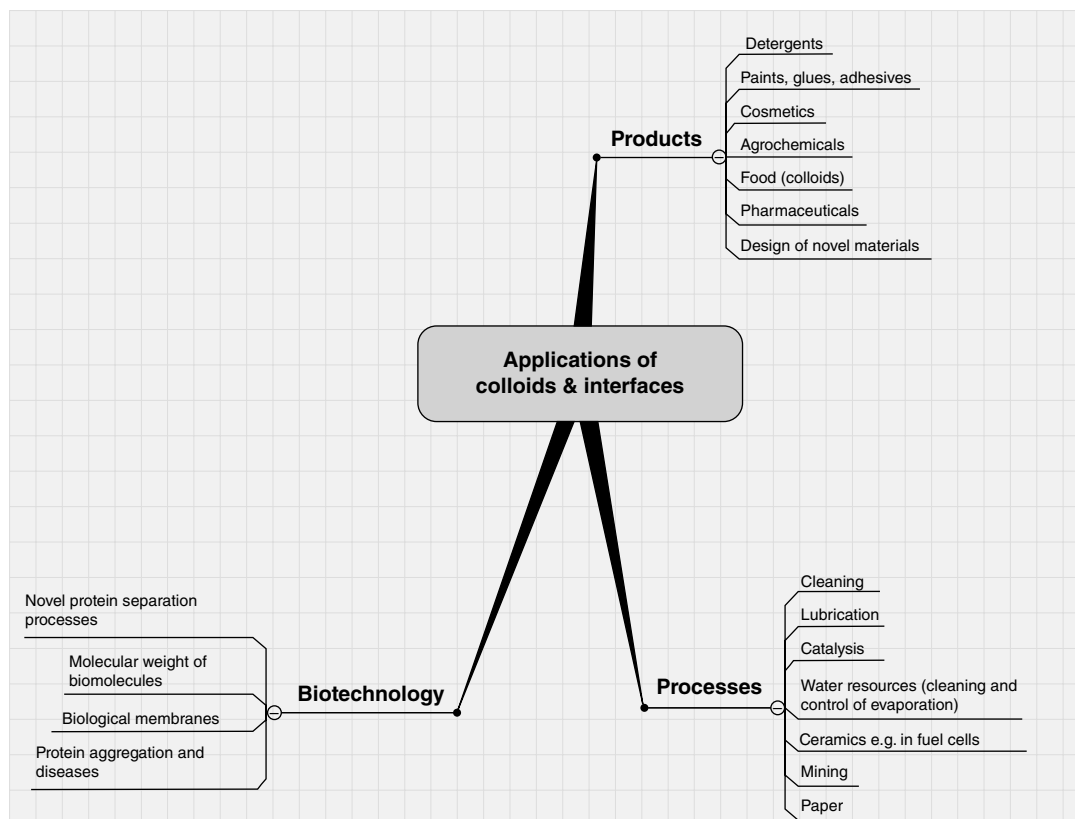


Figure 1.7 A few applications of colloids and interfaces related to various types of products and processes

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



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

"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

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

Table A1 (continued)

Property	Can we measure it? (How?)	Can we estimate it? (How?)	Comments – applications
Interparticle forces and colloid stability	Yes (surface force apparatus, AFM and other methods for stability, e.g. Turbiscan)	Yes (DLVO theory)	Stability of all types of colloids (paints, food colloids...)
Molecular weight of polymers and proteins	Yes (many methods, e.g. ultracentrifuge and osmotic pressure)		Characterization of high molecular weight molecules
Creaming and sedimentation of suspensions and emulsions	Yes (Turbiscan)	Yes (Stokes equation for dilute dispersions)	Stability of colloids
Critical coagulation concentration	Yes (series of experiments adding salts in colloidal dispersions until coagulation occurs)	Yes (DLVO theory)	Stability of colloids
Determining emulsion type		Yes (HLB and Bancroft rule)	Emulsion design

Problems

Problem 1.1: Colloids in everyday life and colloid types

Give at least three examples of products with colloids from your everyday life, and describe for each the nature and function of the components. You can use Table 1.1 for inspiration.

Describe the following colloidal categories, by naming the state/form and function of their components: dispersion, aerosol, micelle, emulsion, foam, paste, gel, latex. Place the examples you gave above into one of these categories.

Problem 1.2: Which ones are colloids?

You have the following three ingredients available:

- oil (a liquid)
- polymer (a low molecular hydrophobic liquid)
- water (a liquid)

You are allowed to mix/blend two ingredients together into one sample. How many of the three resulting

binary blends could be classified as colloids? For each sample state why/why not. In addition, give details about what the criterion could be to judge whether or not the blend is a colloid. For the samples you have classified as colloids you should give the correct term for the type of colloid the sample belongs to.

Problem 1.3

Try to characterize an interface in terms of thickness, molecular arrangement and importance for product properties.

Problem 1.4

Try to mix 100 ml of (preferably unskimmed) milk with 100 ml of vinegar. What do you observe? Explain what you think has happened (compare this with the Ouzo example in Figure 1.8).

Problem 1.5

What particle shapes are possible for colloids? Give some examples.

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