

Emulsion Science

BASIC PRINCIPLES

SECOND EDITION

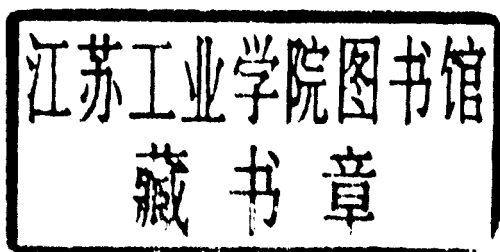
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Basic Principles

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 Springer

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Emulsion Science

Second Edition

Preface

Emulsions and Common Sense

Droplets of oil in water allow us to transport oil soluble materials (in a non viscous form) and ultimately to release them on a chosen target. Cosmetics, paints, foods, are often based on these “emulsions”.

But the droplets are fragile, and must be lucidly protected. Formulating an industrial emulsion implies numerous conditions: stability, efficiency, easy delivery, price, ... This is an art, and like all forms of art it requires experience and imagination. The present book provides both. It describes basic experiments on realistic model systems. I like this matter of fact approach. For instance, instead of beginning by formal discussions on interaction energies, the book starts with *methods of fabrication*. And, all along the text, the theoretical aspects are restricted to basic needs.

Of course (as always in a delicate subject like the present one) I have my own critiques on certain points in the presentation: for instance, in Section 5.3.1, coalescence is attributed to the thermal nucleation of a pore between two adjacent droplets. For me, discussing this channel is like discussing the sex of angels. Nucleation, in most physical systems, does not occur via plain thermal fluctuations. It involves external defects: a cosmic ray in a bubble chamber, or a dust particle in a condenser. I believe that the same holds for emulsions: dust particles (or small surfactant aggregates) control coalescence.

But these byzantine discussions on mechanism are beyond the point. This book is based on experiments. It does not claim to solve all problems (e.g: what is the real origin of Bancroft’s rule) but it presents them with common sense and precision. I am convinced that it will be of great help.

P.-G. de Gennes
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Introduction

Colloids comprise a very broad class of materials. Their basic structure consists of a dispersion of one phase into another one, in which the dispersed phase possesses a typical length scale ranging from a few molecular sizes up to several microns. Some colloids are thermodynamically stable and generally form spontaneously, whereas others are metastable, requiring energy for preparation and specific properties to persist. Metastable colloids are obtained by two main distinct routes: one is nucleation and growth, including precipitation, and the other is fragmentation. In both cases, as a consequence of the intrinsic off-equilibrium nature of this class of colloids, specific surface properties are required to prevent recombination. Surface-active species are generally employed to stabilize freshly formed fragments or growing nuclei, as they are expected to provide sufficient colloidal repulsive forces.

Emulsions are one example of metastable colloids. They are generally made out of two immiscible fluids, one being dispersed in the other, in the presence of surface-active agents. They are obtained by shearing two immiscible fluids, leading to the fragmentation of one phase into the other. Emulsion droplets exhibit all classical behaviors of metastable colloids: Brownian motion, reversible phase transitions as a result of droplet interactions, and irreversible transitions that generally involve the destruction of the emulsion. The droplet volume fraction may vary from zero to almost one: dense emulsions are sometimes called bilyquid foams since their structure is very similar to the cellular structure of air-liquid foams for which the continuous phase is very minor. From dilute to highly concentrated, emulsions exhibit very different internal dynamics and mechanical properties. When the emulsion is strongly diluted, droplets are agitated by Brownian motion [1,2], and the emulsion behaves as a viscous Newtonian fluid. When the emulsion is concentrated, namely above the random-close-packing volume fraction, which is 64% for monodisperse droplets, the internal dynamics are severely restricted and the emulsion behaves as a viscoelastic solid [3,4]. Simple direct emulsions are composed of oil droplets dispersed in water (O/W), while inverse emulsions are composed of water droplets dispersed in an oil continuous phase (W/O). Emulsions are in general made of two immiscible phases for which the surface tension is nonzero, and may in principle involve other hydrophilic-like or lipophilic-like fluids in the presence of suitable surface-active species, each phase being possibly

composed of numerous components. As an example, simple emulsions may also contain smaller droplets of the continuous phase dispersed within each droplet of the dispersed phase. Such systems are called double emulsions or multiple emulsions [5]. Simple emulsions may also contain solid dispersion within each droplet, as a possible route to produce magnetic colloids [6].

The destruction of emulsions may proceed through two distinct mechanisms. One, called Ostwald ripening, is due to the diffusion of the dispersed phase through the continuous phase. This mechanism does not involve any film rupture; instead, there is a continuous exchange of matter through the continuous phase, which increases the average droplets diameter while reducing their number. The other mechanism, called coalescence, consists of the rupture of the thin liquid film that forms between two adjacent droplets. This rupture requires the formation of a hole within the thin film which then grows, resulting in the fusion of two adjacent droplets. This ultimately leads to a total destruction of the dispersed system, since two macroscopic immiscible phases are recovered. The lifetime of emulsions is increased by the presence of surface-active species, which are known to cover the interfaces and to delay both coalescence and Ostwald ripening. As a matter of fact, the metastability of emulsions is strongly correlated to the presence of these surface-active species at their interfaces. Because the lifetime of these materials may become significant (longer than one year) they become good candidates for various commercial applications.

Emulsions are widely used in a variety of applications because of their ability to transport or solubilize hydrophobic substances in a water continuous phase. All kinds of surface treatments will take advantage of emulsion technology: painting, paper coating, road surfacing, and lubricating. Because homogeneous mixtures of two immiscible fluids may be obtained, organic solvents may be avoided when solubilizing hydrophobic substances into water. When the mixture is applied, water evaporates and is safely released into the atmosphere, while the dispersed phase concentrates and ultimately leads to the formation of a hydrophobic film (painting, paper coating, lubricating). Moreover, emulsion technology drastically simplifies the pourability of many hydrophobic substances. Indeed, at ambient temperature some material may be almost solid whereas by dispersing it within small droplets in water it remains fluid at room temperature. One famous example is bitumen used for road surfacing. Emulsions are also involved in the food and cosmetic industries because of their rheological properties which may vary from an essentially Newtonian liquid to an elastic solid. Moreover, they are also efficient drug carriers (medicines, food, and pesticides) for various types of targets. Indeed, double direct emulsions will allow transporting a water soluble molecule within the internal water droplets throughout a water continuous phase.

All these applications have already led to an important empirical control of these materials, from their formation to their destruction. Besides this empirical background which is considerably widespread among the various specific applications, the basic science of emulsions is certainly progressing and we aim within this book to give an overview of the most recent advances.

The production of emulsions is certainly one of the most important aspects related to the industrial use of these materials. After a review of the available and currently employed techniques, this book aims to present advances in making controlled size emulsions at a large scale and rate production. It will be shown that controlled shear applied to a polydisperse emulsion can transform it into a monodispersed one through Rayleigh instability (Chapter 1). Interdroplet forces, from long range to very short range, are of prime importance in understanding the collective behavior of emulsion droplets. A variety of interactions that occur between these liquid colloids are described. Repulsive interactions between droplets are directly measured by using the magnetic chaining technique, providing detailed descriptions of steric and electrostatic forces (Chapter 2). Soft attractions and particularly the depletion induced interactions are described, as well as the resulting equilibrium phase transitions that can also be used to fractionate polydisperse emulsions. Strong adhesion is also explored through the measurement of contact angles, for a variety of interfaces and compositions, as well as the very characteristic gelation transition that takes place in the regime of deep attractive interaction quench (Chapter 3). Because emulsion droplets are deformable they can span droplet volume fraction from zero to almost one. We present the basic physics that governs both compressibility and shear elasticity of dense emulsions as a function of droplet packing and the nature of adsorbed species from short surfactants to macromolecules and solid particles. When droplets are still capable to slip under stress, the role of disorder has been revealed to be of most importance and to dictate the subtle scaling of the shear elastic modulus (Chapter 4). Understanding the lifetime and destruction of emulsions is obviously a crucial aspect. The various scenarios of destruction are reviewed and correlated to the two well accepted limiting mechanisms: coalescence and diffusion or permeation. The basic understanding of thermally activated hole nucleation, which is responsible for coalescence, is presented, in close relation with the nature of the adsorbed species (Chapter 5). The very rich domain of double emulsion is discussed. A detailed description of these materials is presented owing to their very promising potential in various applications, in addition to their remarkable contribution in understanding the metastability of thin films (Chapter 6). At that stage of understanding, the scientific background about emulsions can direct their potential use to new fields of applications: droplets can act either as minute substrates or reservoirs. They can also be manipulated by applying external forces to selectively sort desirable products, or to create local stress-controlled conditions. Liquid droplets can compartmentalize minute amounts of defined reactants, either to screen a large compound library or parallelize a directed process imposed by confinement. We present in Chapter 7 some particularly promising examples of new applications of emulsions in nano or microtechnologies, related to biotechnologies, biophysics, and processing of high-tech materials for micro-optics.

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1

Emulsification

1.1. Introduction

Emulsification consists of dispersing one fluid into another, nonmiscible one, via creation of an interface. Properties of emulsions (e.g., stability, rheological properties) and their industrial uses are governed not only by variables such as temperature and composition but also by the droplet size distribution. The highest level of control consists of producing “monodisperse,” that is, narrow size distributed emulsions with a tunable mean size. From a fundamental perspective, monodispersity has allowed significant progress in emulsion science as will be shown throughout this book. Monodispersity also opens perspectives for new technological applications that are reviewed in Chapter 7. Usually, industrial emulsification is empirically controlled and the purpose of this chapter is to provide fundamental concepts that support such empirical knowledge.

In the first part, we briefly review some possible routes to fabricate emulsions such as high-pressure homogenization and membrane, microchannel and spontaneous emulsification. Then, the basic principles of the phase inversion temperature (PIT) method are presented and the influence of different parameters such as surfactant concentration and stirring intensity is discussed. The following section is devoted to emulsification via application of a controlled shear. The mechanism of drop rupturing and the conditions leading to monodispersity are described. From fundamental studies on shear emulsification, some useful strategies for formulators can be proposed and we shall explain how they can be exploited to produce monodisperse materials of technological interest.

1.2. High-Pressure Homogenization

High-pressure homogenization (microfluidization) is widely used for producing dairy and food emulsions. It consists of forcing the two fluids or a coarse premix to flow through an inlet valve, into a mixing chamber, under the effect of a very high pressure. The fluids undergo a combination of elongation and shear flows, impacts, and cavitations. Despite the complexity of the mechanisms involved [1],

the size distributions are usually reproducible with a mean size ranging from 50 nm to 5 μm .

Emulsification by high-pressure homogenization results from a dynamical equilibrium between breakup promoted by drop deformation resulting from the high speed flow and of recombination (coalescence) promoted by collisions. Numerous studies have been performed [2–6] to determine the effect of stabilizing agent concentration (protein or surfactant), applied pressure, number of cycles on the droplets size and emulsion stability. Taisne and Cabane [6] have developed a refractive index contrast matching technique allowing the determination of oil exchange between the droplets. They were able to distinguish two regimes of emulsification in a high-pressure homogenizer depending on the surfactant concentration C_{surf} . In the **“surfactant-poor” regime** ($C_{\text{surf}} < \text{CMC}/10$ where CMC is the critical micellar concentration), the average drop size, d , only weakly depends on the applied pressure. Lobo and co-workers [7] have elaborated a quantitative method based on the dilution of a fluorescent excimer signal during oil exchange to determine the number of coalescence events during emulsification. They showed [8] that a high level of coalescence leads to emulsions with average diameters ranging from 0.3 to 2 μm depending on the surfactant concentration. Drops are first fragmented at a low size and then coalesce because of insufficient interfacial coverage. In the **“surfactant-rich” regime** ($C_{\text{surf}} > 10 \text{ CMC}$), the average droplet diameter d is lower, typically varying from 50 to 350 nm, and is almost independent of the surfactant concentration [6, 8, 9]. Even though coalescence can not be completely arrested in a high-pressure homogenizer, a low level of recombination is attained [6, 8]. Hence, the size is determined mainly by droplet fragmentation and scales with the applied pressure P_h as:

$$d \propto P_h^{-\alpha} \quad (1.1)$$

where the power law α typically varies between 0.6 and 0.9 [6,10,11]. Brösel and Schubert [4] showed that during the deformation and breakup of a single drop, almost no surfactant molecules adsorb at the new interface because the adsorbing time is larger than that of disruption. Surfactant adsorbs between two breakup events, thus lowering the interfacial tension and facilitating further rupturing. The existence of two regimes can be generalized to protein-stabilized emulsions: larger sizes are obtained by drop coalescence for low protein concentrations [2]. Other parameters may influence the final droplet size distribution: (1) an increasing number of passes reduces the size distribution width [12,13], (2) whatever the emulsifier (surfactant or proteins), large dispersed phase volume fractions favor collisions and recombinations but the droplet volume fraction ϕ has little influence on the average size for $\phi < 30\%$.

1.3. Membrane Emulsification

Membrane emulsification [14] consists of forcing the dispersed phase to permeate into the continuous phase through a membrane having a uniform pore

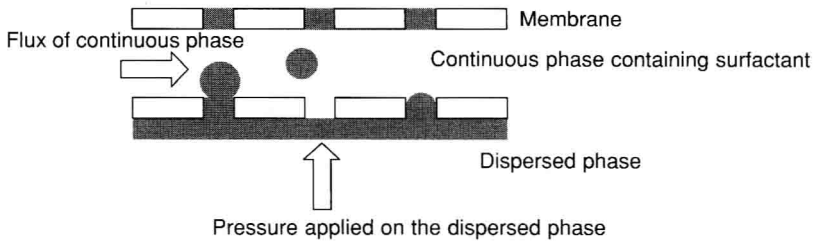


FIGURE 1.1. Schematic principle of membrane emulsification.

size distribution. The dispersed phase is pressed perpendicular to the membrane while the continuous phase is flowing tangential to the membrane (Fig. 1.1). Although easy in principle, membrane emulsification is dependent on many parameters such as membrane properties, fluxes, and formulation, all influencing the emulsion size distribution. To obtain a monodisperse emulsion, the membrane pores must themselves have a narrow size distribution [15]. Usually, the drop size is proportional to the pore size [16–18]. The choice of membrane porosity is the result of a compromise: if the pore density is too large, coalescence of freshly formed drops is likely to occur, increasing polydispersity; conversely, if the pore density is too low, the production rate is insufficient [19]. The dispersed phase should not wet the membrane coating and consequently a hydrophilic membrane should be used to produce an oil-in-water (O/W) emulsion [16,20]. High continuous phase velocity and low interfacial tension will promote small drops [19–27]. The pressure to be applied to the dispersed phase depends on both the interfacial tension [21] and the membrane pore size. A compromise between high pressures promoting either large drops or a dispersed phase jet and low pressures decreasing the production rate should be found. For a more detailed review on membrane emulsification of simple and double emulsions, the reader can refer to [28] and [29] and references therein.

1.4. Microchannel Emulsification

Microchannel technology allows fabrication of monodisperse emulsions with an average droplet diameter ranging from 10 to 100 μm [30,31]. The principle is reminiscent of membrane emulsification. The dispersed phase is forced into the continuous phase through microchannels manufactured via photolithography. A scheme of a microchannel device is shown in Fig. 1.2. The use of a high-speed camera and a microscope allows direct observation of the flow and of the emulsification process [32,33]. The phase to be dispersed is pushed through a hole in the center of the plate in such a way that it passes through the microchannels and inflates on the terrace in a disk-like shape. When it reaches the end of the terrace, the phase falls onto the well and a drop detaches. The spontaneous detachment and relaxation into the spherical drop are driven by interfacial tension. Outstanding

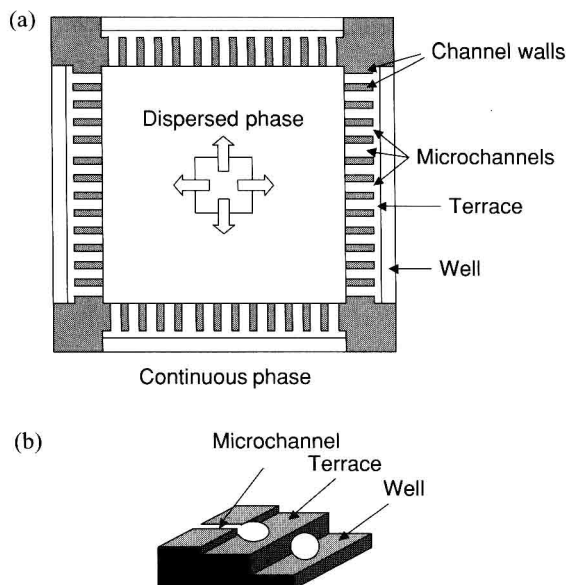


FIGURE 1.2. Schematic principle of microchannel emulsification. (a) Top view; (b) side view.

monodispersity is obtained by this process. Direct, reverse, and multiple emulsions [34] can be developed. As for membrane emulsification, an O/W emulsion is produced using hydrophilic microchannels, whereas producing a W/O emulsion requires a hydrophobic device [35]. The influence of various parameters on droplet size and monodispersity has been studied:

- The geometry of the device is important; the terrace length and microchannel depth are size-determining factors.
- At low flow velocity of the dispersed phase, the interfacial tension does not influence the droplet diameter but it affects the time-scale parameters for droplet formation [35–37]; the detachment time becomes shorter at high interfacial tension (low surfactant concentration) [38].
- The surfactant type (anionic, nonionic) is indifferent [39], but cationic surfactants should be avoided to produce O/W emulsions because they lead to complete wetting of the dispersed phase on the microchannel plate.

More complex geometries have been developed [40] and the influence of the geometrical structure has been examined. Although straight-through microchannel emulsification has been developed [39,41], the production rates are still low compared to those obtained with standard emulsification methods. However, the very high monodispersity makes this emulsification process very suitable for some specific technological applications such as polymeric microsphere synthesis [42,43], microencapsulation [44], sol–gel chemistry, and electro-optical materials.