The Physics of Microdroplets
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The Physics of Microdroplets

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Preface

Capillary phenomena are intriguing. During the many years I (Jean) have spent with my colleagues working on microsystems for biotechnology, I have observed the difficulty to predict—and sometimes understand—the behavior of droplets and interfaces at the micro scale. First, optical observation is not straightforward—it is not easy to locate an interface seen from above in the microscope. Second, the analysis of the observed phenomena is complicated. In my personal experience, that was the case for pancreatic cells encapsulation in micro-flow-focusing devices, liquid-liquid extraction systems, digital microfluidics, capillary valves, spontaneous capillary flows in closed and open channels, in cracks, and between fibers.

And the difficulty is even more important for the conception of new microsystems. Questions such as “where is the interface going to anchor?” or “will the particles cross the interface?” or “will the interface de-pin when the capsule arrives?” or “will the capillary force be sufficient?” are repeatedly being asked. Although illustrious pioneers such as P-G. de Gennes, D. Quéré, G.M. Whitesides, and others have contributed to the knowledge of interface behaviors on a theoretical standpoint, much is left to understand for the engineer having to design a microchip or the student behind his computer or the biologist at his lab bench.

In this book, Ken and I have attempted to give the reader the tools for solving these capillary and surface tension problems, present theoretical tools derived from previous works of colleagues and our personal experience, as well as provide calculation tools through the Surface Evolver numerical program.

I first heard about Evolver at a Nanotech Conference in 2004 and its potential for two-phase microflows and droplets behavior. Although it cannot treat the dynamics of a flow, it can be used to predict the stable shape and location of droplets and interfaces. A typical example is that of a capillary valve where the bulging out of the interface directly depends on the applied pressure. Besides, useful information can be gained by considering that an interface or a droplet has not reached its equilibrium position: this is for example the case of spontaneous capillary flows or droplets moving up a step or a slope. Finally, at the microscale, interfaces are restored nearly immediately by capillary and surface tension forces, which frequently dominate the other forces like weight, viscosity, and inertia. This applies for example to self-alignment problems.

I started to work with Evolver for predicting the behavior of droplets in digital microfluidic systems. Because the electrowetting effect can often be translated into a capillary effect (capillary equivalence), Evolver is well suited to treat such problems. I had the fortune that the author of Surface Evolver, Kenneth Brakke, agreed to assist me with the handling of the numerical program and our cooperation was extremely fruitful. After a few years of working on this topic, as well on the theoretical, numerical and experimental aspects, I had the opportunity to write the book Microdrops and Digital Microfluidics in 2008.

But many capillary problems were still to be tackled outside the domain of digital microfluidics. I continued to use Evolver, again with Ken’s help. When our Evolver tool box was
sufficient, we thought that it could be useful to make it available to the scientific community and decided to write this new book with my publisher Martin Scrivener. The Evolver files corresponding to the examples and problems of this book are available for the reader at the internet address http://www.susqu.edu/brakke/physicsofmicrodrops.

We hope that our work will be useful to boost the developments of microfluidic systems and that this book will find an echo in the micro and nanotechnology world.

Jean Berthier, Grenoble, February 22, 2012
Kenneth A. Brakke, Susquehanna University, February 22, 2012
Introduction

From Conventional Single-phase Microfluidics to Droplets and Digital Microfluidics

Starting in the year 1980, microfluidics was at first a mere downscaling of macrofluidics. Its development was triggered by the emergence of biotechnology and materials science, imagined by visionary pioneers like Feynman [1], deGennes [2], Whitesides [3] and others. In particular, biotechnology was as a new science at the boundary of physics and biology. The goal was to give biological, medical and pharmaceutical research new automation tools to boost the development of new drugs, fabricate new body implants and increase the potentialities of fundamental research. In reality, this plan imagined by these first researchers has been extremely effective and produced even more discoveries than what was first expected. In a way, biotechnology developments bloomed according to Feynman’s words: “The best way to predict the future is to invent it.” The foreseen goals have required the downscaling of fluidic systems to the “convenient” size to work at the proper scale characteristic of a population of biologic targets. At the same time, it was found that the downscaling brought economy in costly materials, fluids, and devices; that sensitivity was increased and operating times were greatly reduced by the integration of many functions on the same microchip. Gradually, as microsystems based on microflows become conventionally used, new approaches were investigated that required even less volume of sample fluids. This trend to downscaling has promoted the development of new microfluidic approaches such as droplet and digital microfluidics. Reduction of the liquid vessel containing the biological targets was found to be possible by the use of microdroplets. New systems based on the confinement of biologic targets in extremely small vessels like microdrops are emerging. In such approaches the liquid volumes are reduced to a few picoliters.

Domains of Application

Historically, genomics and proteomics were the first beneficiaries of the development of biotechnology, and now it is the turn of cellomics. Also, these developments have spread beyond the domain of biotechnology and created a “cloud” of new applications in other domains such as bioinformatics, bioengineering, tissue engineering, etc. At the same time, microfluidic techniques reached other domains, such as materials science, microelectronics and mechatronics. It has been quickly demonstrated that biochemical reactions such as PCR for the recognition of DNA can be performed with the same efficiency in droplets, with a lesser amount of replicas [4-6]. Proteins can be crystallized in droplets, resulting in a greater ability to investigate their structures by X-ray crystallography [7]. In biology, single cell research has become feasible, after encapsulating the cell in a droplet or a gelled (polymerized) droplet [8-10] or manipulating
cells on a digital microfluidic chip [11]. Chemical reactions can also be performed with very small amounts of chemical species inside droplets [12-14]. The use of droplet and digital microfluidics soon extended beyond the limits of biotechnology. Electrowetting droplets are now commercially used in optics as tunable lenses [15] and screen displays [16]. In mechatronics, electrowetting switches (or CFA, for "capillary force actuators") have been shown to be much more effective than electrostatic switches of the same size [17]. Self-assembly techniques using capillary forces produced by a droplet surface are currently used in materials science for manipulating gold nano-spheres for coating applications [18]. Self-alignment using capillary forces is also a promising approach to 3D-microelectronics, which is required to circumvent the present limitations of 2D assembly [19-21]. The examples are many showing the interest in microdrops.

Figure 1 Different applications using microdroplets: (a) droplets moved with magnetic beads for PCR application [6]; (b) protein crystallization in a microdrop (from [7], ©Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission); (c) encapsulated cells in a polymer-ized alginate matrix (photo courtesy CEA-LETI); (d) tunable lenses by Varioptics (from [15], courtesy Varioptics); (e) screen displays by Liquavista, (from [16], courtesy Liquavista); (f) schematic of a capillary force actuator (not to scale) [17].

Organization of the Book

This book is dedicated to the study of droplets and interfaces principally in a steady or quasi-steady state, although some dynamic considerations have been added when it was judged useful. The first chapter presents the general considerations leading to the concepts of surface tension and capillary forces, associated to the notions of surface energy and contact angle. Young’s and Laplace’s laws, which are the two “pillars” of any capillary approach, are described, commented and exemplified. The second chapter presents the theory of liquid surfaces in space, including some ways to prove certain surfaces are minimums of energy. Chapter 3 is devoted to the determination of the shape, surface area, and volume of droplets. In chapter 4, the shape and behavior of sessile droplets (droplets place on a solid surface) is investigated for many different configurations of chemical and geometrical surface inhomogeneities: drops at the boundaries between hydrophilic and hydrophobic substrates, or on geometrical inhomogeneities such as
steps or grooves or corners. The fifth chapter concerns the behavior of droplets in asymmetric geometries; in a first part, the Hauksbee problem is treated and an extension to hydrophobic surfaces is given. In a second part, the Concus-Finn relations are presented. In chapter 6, the behavior of droplets in microwells and closed microchannels is investigated. The cases of wetting and non-wetting plugs are treated as well as that of trains of droplets. Chapter 7 is dedicated to the phenomena of capillary rise, capillary pumping and capillary valving. In the first two parts, we analyze how capillary forces can contribute to moving a liquid in horizontal or vertical tubes. In the third part, we analyze the opposite: how to find a geometry that can stop a capillary flow. The focus of chapter 8 is open microfluidics, i.e. microflows partially guided by a solid wall, but also in contact with air or another liquid, which is becoming a very important issue in biotechnology; this type of microflow rely mainly on capillary forces and if necessary on electrowetting forces to move the fluid. Chapter 9 deals with the contact and potential engulfment of droplets and particles by interfaces. Examples pertaining to encapsulation of polymerized droplets and capillary assembly are presented. Chapter 10 is on digital microfluidics, a convenient way to manipulate droplets on a planar, or locally planar surface, which has seen many developments lately. We present the state of the art and new developments in this technique. In chapter 11, we treat an example of the use of capillary forces: the ongoing approach to 3D-microelectronics by assembling stacks of chips on a wafer. A promising approach to achieve chip positioning and alignment is that of capillary self-assembly.

References


1

Fundamentals of Capillarity

1.1 Abstract

In this first chapter, the fundamentals of capillarity are presented. We follow a conventional approach [1], first presenting surface tension of an interface, which is the fundamental notion in capillarity theory; this notion leads naturally to that of wetting, then to Laplace’s law, and to the introduction of Young contact angles and capillary forces. Next, different applications of capillary forces are shown, and the problem of the measurement of surface tensions is presented.

1.2 Interfaces and Surface Tension

1.2.1 The Notion of Interface

Mathematically speaking, an interface is the geometrical surface that delimits two fluid domains. This definition implies that an interface has no thickness and is smooth (i.e. has no roughness). As practical as it is, this definition is in reality a schematic concept. The reality is more complex, the boundary between two immiscible liquids is somewhat blurred and the separation of the two fluids (water/air, water/oil, etc.) depends on molecular interactions between the molecules of each fluid [2] and on Brownian diffusion (thermal agitation). A microscopic view of the interface between two fluids looks more like the scheme of figure 1.1. However,

![Figure 1.1 Schematic view of an interface at the molecular size.](image-url)

...
in engineering applications, it is the macroscopic behavior of the interface that is the focus of attention, and the mathematical concept regains its utility. At a macroscopic size, the picture of figure 1.1 can be replaced by that of figure 1.2, where the interface is a mathematical surface without thickness and the contact angle $\Theta$ is uniquely defined by the tangent to the surface at the contact line.

In a condensed state, molecules attract each other. Molecules located in the bulk of a liquid have interactions with neighboring molecules on all sides; these interactions are mostly van der Waals attractive interactions for organic liquids and hydrogen bonds for polar liquids like water [2]. On the other hand, molecules at an interface have interactions in a half space with molecules of the same liquid, and in the other half space interactions with molecules of the other fluid or gas (figure 1.3).

![Figure 1.2](image1.png)  
**Figure 1.2** Macroscopic view of the interface of a drop.

![Figure 1.3](image2.png)  
**Figure 1.3** Simplified scheme of molecules near an air/water interface. In the bulk, molecules have interaction forces with all the neighboring molecules. At the interface, half of the interactions have disappeared.

Consider an interface between a liquid and a gas. In the bulk of the liquid, a molecule is in contact with 4 to 12 other molecules depending on the liquid (4 for water and 12 for simple molecules); at the interface this number is divided by two. Of course, a molecule is also in contact with gas molecules, but, due to the low densities of gases, there are fewer interactions and less attraction than on the liquid side. The result is that there is locally a dissymmetry in the interactions, which results in an excess of surface energy. At the macroscopic scale, a physical quantity called "surface tension" has been introduced in order to take into account this molecular effect. The surface tension has the dimensions of energy per unit area, and in the International System it is expressed in J/m$^2$ or N/m (sometimes, it is more practical to use mN/m as a unit for surface tension). An estimate of the surface tension can be found by considering the molecules' cohesive energy. If $U$ is the total cohesive energy per molecule, a rough estimate of the energy
excess of a molecule at the interface is $U/2$. Surface tension is a direct measure of this energy excess, and if $\delta$ is a characteristic molecular dimension and $\delta^2$ the associated molecular surface area, then the surface tension is approximately

$$\gamma \approx \frac{U}{\delta^2}. \quad (1.1)$$

This relation shows that surface tension is important for liquids with large cohesive energy and small molecular dimension. This is why mercury has a large surface tension whereas oil and organic liquids have small surface tensions. Another consequence of this analysis is the fact that a fluid system will always act to minimize surface area: the larger the surface area, the larger the number of molecules at the interface and the larger the cohesive energy imbalance. Molecules at the interface always look for other molecules to equilibrate their interactions. As a result, in the absence of other forces, interfaces tend to adopt a flat profile, and when it is not possible due to boundary constraints or volume constraints, they take a rounded shape, often that of a sphere. Another consequence is that it is energetically costly to expand or create an interface: we will come back on this problem in Chapter 10 when dividing a droplet into two "daughter" droplets by electrowetting actuation. The same reasoning applies to the interface between two liquids, except that the interactions with the other liquid will usually be more attractive than a gas and the resulting dissymmetry will be less. For example, the contact energy (surface tension) between water and air is 72 mN/m, whereas it is only 50 mN/m between water and oil (table 1.1). Interfacial tension between two liquids may be zero: fluids with zero interfacial tension are said to be miscible. For example, there is no surface tension between fresh and salt water: salt molecules will diffuse freely across a boundary between fresh and saltwater.

The same principle applies for a liquid at the contact of a solid. The interface is just the solid surface at the contact of the liquid. Molecules in the liquid are attracted towards the interface by van der Waals forces. If the attractions to the solid are strong, the liquid-solid interface has negative surface energy, and the solid is said to be wetting or hydrophilic (or lyophilic for non-water liquids, but we will use the term hydrophilic for all liquids). If the attractions are weak, the interface energy is positive, and the solid is non wetting or hydrophobic (or lyophobic).

Usually surface tension is denoted by the Greek letter $\gamma$, with subscripts referring to the two components on each side of the interface, for example $\gamma_{LG}$ at a Liquid/Gas interface. Sometimes, if the contact is with air, or if no confusion can be made, the subscripts can be omitted. It is frequent to speak of "surface tension" for a liquid in contact with a gas, and "interfacial tension" for a liquid in contact with another liquid. According to the definition of surface tension, for a homogeneous interface (same molecules at the interface all along the interface), the total energy of a surface is

$$E = \gamma S, \quad (1.2)$$

where $S$ is the interfacial surface area.

In the literature or on the Internet there exist tables for surface tension values [3,4]. Typical values of surface tensions are given in table 1.1. Note that surface tension increases as the intermolecular attraction increases and the molecular size decreases. For most oils, the value of the surface tension is in the range $\gamma \approx 20 - 30$ mN/m, while for water, $\gamma \approx 70$ mN/m. The highest surface tensions are for liquid metals; for example, liquid mercury has a surface tension $\gamma \approx 500$ mN/m.
Table 1.1 Values of surface tension of different liquids in contact with air at a temperature of 20 °C (middle column, mN/m) and thermal coefficient α (right column, mN/m/°C).

<table>
<thead>
<tr>
<th>liquid</th>
<th>(\gamma_0)</th>
<th>(\alpha)</th>
</tr>
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<tbody>
<tr>
<td>Acetone</td>
<td>25.2</td>
<td>-0.112</td>
</tr>
<tr>
<td>Benzene</td>
<td>28.9</td>
<td>-0.129</td>
</tr>
<tr>
<td>Benzylibenzoate</td>
<td>45.95</td>
<td>-0.107</td>
</tr>
<tr>
<td>Bromoform</td>
<td>41.5</td>
<td>-0.131</td>
</tr>
<tr>
<td>Chloroform</td>
<td>27.5</td>
<td>-0.1295</td>
</tr>
<tr>
<td>Cyclohexane</td>
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<td>-0.121</td>
</tr>
<tr>
<td>Cyclohexanol</td>
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<td>-0.097</td>
</tr>
<tr>
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<td>-0.103</td>
</tr>
<tr>
<td>Dichloroethane</td>
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<td>-0.143</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>Ethylene-Glycol</td>
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<td>-0.089</td>
</tr>
<tr>
<td>Isopropanol</td>
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<td>-0.079</td>
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<tr>
<td>Iodobenzene</td>
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<td>-0.112</td>
</tr>
<tr>
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<td>Mercury</td>
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<td>-0.205</td>
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<tr>
<td>Methanol</td>
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<td>-0.077</td>
</tr>
<tr>
<td>Nitrobenzene</td>
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</tr>
<tr>
<td>Perfluorooctane</td>
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<tr>
<td>Polyethylen-glycol</td>
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</tr>
<tr>
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<tr>
<td>Pyrrol</td>
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</tr>
<tr>
<td>Toluene</td>
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</tr>
<tr>
<td>Water</td>
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<td>-0.1514</td>
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</table>
1.2.2 The Effect of Temperature on Surface Tension

The value of the surface tension depends on the temperature. The first empirical equation for the surface tension dependence on temperature was given by Eötvös in 1886 [5]. Observing that the surface tension goes to zero when the temperature tends to the critical temperature $T_C$, Eötvös proposed the semi-empirical relation

$$\gamma = \left( \frac{1}{v_L} \right)^{\frac{2}{3}} (T - T_C),$$

(1.3)

where $v_L$ is the molar volume. Katayama (1915) and later Guggenheim (1945) [6] have improved Eötvös’s relation to obtain

$$\gamma = \gamma^* \left( 1 - \frac{T}{T_C} \right)^n,$$

(1.4)

where $\gamma^*$ is a constant for each liquid and $n$ is an empirical factor, whose value is $11/9$ for organic liquids. Equation (1.4) produces very good results for organic liquids. If temperature variation is not very important, and taking into account that the exponent $n$ is close to 1, a good approximation of the Guggenheim-Katayama formula is the linear approximation

$$\gamma = \gamma^* (1 + \alpha T).$$

(1.5)

It is often easier and more practical to use a measured reference value $(\gamma_0, T_0)$ and consider a linear change of the surface tension with the temperature,

$$\gamma = \gamma_0 (1 + \beta (T - T_0)).$$

(1.6)

Comparison between (1.4) and (1.6) for $\gamma = 0$ at $T = T_C$ requires

$$\beta = -\frac{1}{T_C - T_0}.$$  

(1.7)

Relations (1.5) and (1.6) are shown in figure 1.4. The value of the reference surface tension $\gamma_0$ is linked to $\gamma^*$ by the relation

$$\gamma^* = \gamma_0 \frac{T_C - T_0}{T_0}.$$ 

(1.8)

Typical values of surface tensions and their temperature coefficients $\alpha$ are given in table 1.1.

The coefficient $\alpha$ being always negative, the value of the surface tension decreases with temperature. This property is at the origin of a phenomenon which is called either Marangoni convection or thermocapillary instability (figure 1.5). If an interface is locally heated by any heat source (such as radiation, convection or conduction), the surface tension is reduced on the heated area according to equations (1.5) or (1.6). A gradient of surface tension is then induced at the interface between the cooler interface and the warmer interface. We will show in section 1.3.7 that surface tensions can be viewed as forces; as a consequence, there is an imbalance of tangential forces on the interface, creating a fluid motion starting from the warm region (smaller value of the surface tension) towards the cooler region (larger value of the surface tension). This surface motion propagates to the bulk under the influence of viscosity. If the temperature source is temporary, the motion of the fluid tends to homogenize the temperature and the motion gradually stops. If a difference of temperature is maintained on the interface,
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Surface tension

\[ \gamma = \gamma^* (1 + \alpha T) \]

\[ \gamma = \gamma_0 (1 + \beta (T - T_0)) \]

Figure 1.4 Representation of the relations (1.5) and (1.6).

Figure 1.5 Sketch of interface motion induced by a thermal gradient between two regions of the surface. The motion of the interface propagates into the bulk under the action of viscous forces.

the motion of the fluid is permanent; this is the case of a film of liquid spread on a warm solid. Depending on the contrast of temperature between the solid surface and the liquid surface, the motion of the liquid in the film has the morphology of convective rolls, hexagons or squares. Figure 1.6 shows hexagonal patterns of Marangoni convection in a film of liquid heated from below [7]. The white streamlines in the left image show the trajectories of the liquid molecules.

1.2.3 The Effect of Surfactants

"Surfactant" is the short term for "surface active agent". Surfactants are long molecules characterized by a hydrophilic head and a hydrophobic tail, and are for this reason called amphiphilic molecules. Very often surfactants are added to biological samples in order to prevent the formation of aggregates and to prevent target molecules from adhering to the solid walls of the microsystem (remember that microsystems have extremely large ratios between the wall areas and the liquid volumes). Surfactants diffuse in the liquid, and when reaching the interface they are captured because their amphiphilic nature prevents them from escaping easily from the interface. As a consequence, they gather on the interface, as is sketched in figure 1.7, lowering the surface tension of the liquid.

As the concentration of surfactants increases, the surface concentration increases also.