

科学前沿丛书

M. Daoud  
C.E. Williams (Eds.)

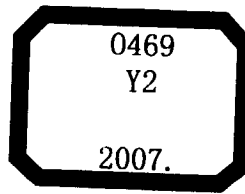
# Soft Matter Physics

软物质物理学

Springer

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Mohamed Daoud  
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*Editors*



# Soft Matter Physics

With 177 Figures, 16 of them in colour



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## 影 印 版 前 言

软物质过去常被称作复杂流体。自从 de Gennes 在其诺贝尔奖获奖演说中将其称作软物质以来，这个名称变得更为广泛。软物质包括聚合物、液晶、表面活性剂、胶体、乳状液、泡沫、颗粒物质以及生物大分子等分子体系。“软”是相对于“硬”而言的，但这还不能反映软物质的本质特征。软物质有这样两个主要特性：一是对非常弱的外界作用具有非常强的响应；二是非常小量的添加剂能够戏剧性地改变体系的性质。这两个特性使得软物质具有非常广泛的应用。

本书由法国著名学者 M. Daoud 和 C. E. Williams 主编，各个章节由工作在该领域的知名学者分别撰写，介绍了软物质物理的基本概念和各个不同的体系，涵盖了微滴、分形体系、胶体、表面活性剂及其在稀溶液中形成的胶束和膜、聚合物的合成及其物性、聚合物溶液、液晶等各种软物质体系。本书是第一本把这些初看似没有共性，但又具有相同的特征尺度、能量转移以及对外场响应的软物质体系放在一起讲述的书籍。

正如 de Gennes 在本书序言中所说，本书没有高深的理论，而是通过简单的具体实例，讲述实验与物理概念的关系。这些实例包括我们日常生活中所常见的洗涤剂、橡胶、乳状液、塑料、悬浮液中的颗粒等等。因此，这是一本深入浅出的导论性书籍，它面向的读者群为研究生、教师、科研工作者。诺贝尔奖金获得者 P. G. de Gennes 推荐此书并为之作序。本书在网络销售商 Amazon 上被列为五星级，是一本非常热销的书籍。

鉴于近年来软物质物理研究在国内外的迅速发展，我们将此书影印出版，供工作在相关领域的科研人员和学生进行学习、参考；同时，也可供物理、化学、生物、材料等学科的科研人员和学生拓展知识之用。

中国科学院化学研究所 研究员 严大东

2006 年 12 月

## Foreword

In a liquid crystal watch, the molecules contained within a thin film of the screen are reorientated each second by extremely weak electrical signals. Here is a fine example of soft matter: molecular systems giving a strong response to a very weak command signal.

They can be found almost everywhere. Soft magnetic materials used in transformers exhibit a strong magnetic moment under the action of a weak magnetic field. Take a completely different domain: gelatin, formed from collagen fibres dissolved in hot water. When we cool below 37°C, gelation occurs, the chains joining up at various points to form a loose and highly deformable network. This is a natural example of soft matter.

Going further, rather than consider a whole network, we could take a single chain of flexible polymer, such as polyoxyethylene [POE = (CH<sub>2</sub> CH<sub>2</sub> O)<sub>N</sub>, where  $N \sim 10^5$ ], for example, in water. Such a chain is fragile and may break under flow. Even though hydrodynamic forces are very weak on the molecular scale, their cumulated effect may be significant. Think of a rope pulled from both ends by two groups of children. Even if each girl and boy cannot pull very hard, the rope can be broken when there are enough children pulling.

POE, added to water at homeopathic dose levels, completely transforms its hydrodynamic properties (take, for example, the experiment devised by James in Toronto). We see here another aspect of soft matter: the fact that an additive, in very small quantities, can change everything. A whole practical area of science, called formulation, is based on the study of such additives, whether it be an ink, a paint, a medicine, or a product for treating vines. In this sense, soft matter physics is directly concerned with industrial problems.

But it also touches upon some quite fundamental questions, as we see from the history of long-chain molecules. It took a very long time just to realise that such things existed, a step taken by Staudinger in 1920; and then to establish that they are usually flexible, the fundamental idea put forward by Kuhn in 1940. Following this, their statistical conformations were described, the great triumph of Flory in the 1950s. And finally, the deep connection

between chain conformations and the trajectories of quantum particles was the superb idea, developed by Edwards in the 1960s, which meant that fifty years of theoretical knowledge acquired in atomic and nuclear physics could be transposed to polymers.

A quite analogous story could be told about detergents or, as they are rather pompously called, surfactants. Soap bubbles fascinated Gibbs a hundred years ago, inspiring him to construct a thermodynamic theory of interfaces. In our own time, the discovery of vesicles, curious and flaccid objects, has opened up a whole new chapter in the science of surfactants. Extremely rich statistical problems are raised by these soft surfaces, and their analysis is a distant cousin of the string theories at present under development in elementary particle physics.

The aim of the present book is not to enter into the labyrinth of theory, but rather to show, using relatively simple examples, how concept and experiment relate today, with regard to everyday subjects, such as soaps, rubber, emulsions, plastic, grains in suspension, and so on. Thanks to all those who have taken part in this project, and especially to M. Daoud and C. Williams, patient shepherds for a capricious flock of researchers.

February 1995

*P.G. de Gennes*

## Preface

In the short time interval between the publication of "La Juste Argile" and "Soft Matter Physics", we were saddened by the fact that R. AUDEBERT passed away. He was a brilliant chemist and physical chemist working at the Ecole Supérieure de Physique et Chimie Industrielle de Paris. Besides his remarkable skills and intuition, he was also characterized by his availability and nice character. Even when overwhelmed with other work, he would always find time to listen and try to help. We would like to dedicate this book to his memory.

Clay, like many other materials, has to be prepared in a very specific way. If you add too much water, it is not good, because it flows. If there is not enough water on the other hand, it is too hard, and cannot be worked. Thus, there is a well defined proportion of water that has to be added in order to produce the perfect clay. Many other materials have similar properties and their practical use stems from this. Polymers, for instance – or plastics, as they were called not so long ago – have visco-elastic properties that allow the sample to take on any desired shape, and to keep that shape for extended periods of time. This is one of the key points in the use of these materials, not only as plastics, but also for fabrics, paints, adhesives, and several other existing applications; together with others to come, such as very light batteries for electric vehicles. Similarly for colloids, where wide applications exist in cosmetics and the food industry, to give but two examples. Or liquid crystals, commonly used in display devices that have completely changed the clock and watch making industry, for instance. All these new materials share common properties, such as strong reactivities with regard to certain external fields. Each of them has been studied for a long time as such. But gradually, the idea has emerged that they constitute a new class of materials. Because of their specific properties, this class was called "Soft Condensed Matter". Indeed, a liquid crystal is crystalline along some directions, but liquid along the others. Similarly, polymers are liquid on very long time scales, but solid on short ones. Therefore, they do not behave classically, but often in a non-linear way. Much of the physics be-

hind these systems is controlled not by averages but by fluctuations. In many instances, phase transitions are present, or the behavior of the system is closely related to what happens near a phase transition, even if none should actually occur. This is the case for polymer solutions or for the sol-gel transition, for instance. It then becomes important to determine whether or not there is any characteristic length or time in the material, and try to determine the relation between the latter and macroscopic properties. From this point of view, there are strong similarities between Soft Matter and phase transitions that occur at the Curie temperature, when a magnet loses its magnetization. This explains why the first systems that were considered were closely related to phase transitions. But later models – such as the so-called diffusion limited aggregation model – were growth models, which were not even at equilibrium. Thus both topics eventually split, and had independent evolutions. An important notion that proved to be very helpful, at least for modeling these materials, is that of fractals. These are nice models that are treated elsewhere, and may model perfectly soft matter, showing why the properties are so different from conventional ones. All these subjects have been taught at universities, usually at an advanced level. The purpose of this book is to present in a simple and direct way these materials in a single, hopefully didactic, work for a broader audience. It was felt that the time has come to try to reach students, college professors and engineers rather than just university professors. The various chapters in the book are devoted to those topics that we believe we understand best at the present time. They are written by experts in these fields, who have attempted to show basic effects through simple experiments, that might easily be carried out by anyone. Our goal was to present the bases that are common to all of these materials, and probably to others, and not to show the latest discoveries, which might fade away with time. A choice of topics had to be made: Wetting, Liquid Crystals, Polymers, Colloids, and Fractals. We believe that they are representative of the domain, and that they will help the reader move on to further study, even in topics that are not covered explicitly here. These topics are also the ones that were pioneered by de Gennes.

January 1999  
Saclay – Paris,  
Orsay

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# 1. Droplets: Capillarity and Wetting

*F. Brochard-Wyart*

## 1.1 Introduction

Rain is falling outside. Water droplets run down the window pane leaving a trail of water behind them, and on the terrace large puddles have formed, where the drops which continue to fall create wavelets on the surface of the water, spreading out to the sound of the rain. Little necklaces of shiny droplets hang under the balustrade and the stems of the wysteria, slowly swelling, as if breathing, then falling suddenly to explode on the ground in a contracting splash of water. Rather than sink into the gloom of a rainy day, let us observe the magic of these droplets at closer quarters.

We shall tell a story of droplets and films, that could be lived out in your kitchen or bathroom, in a primary school and, in a more quantitative way, before a class at high school, or in a university. Capillarity is the study of moving interfaces which can deform so as to optimise their surface energy. Wetting is the study of the spreading of droplets when they are placed on a solid or liquid substrate.

We shall begin by introducing the fundamental physical quantities, together with the laws which govern them. We shall then describe five experiments which illustrate the static and dynamical properties of wetting. In each section, we shall indicate the equipment needed to carry out the experiments, as well as certain related industrial applications. In conclusion, some more specialised themes will be brought up: wetting on the nanometre scale, instability of the contact line, and the Marangoni effect, all of which require more sophisticated instrumentation.



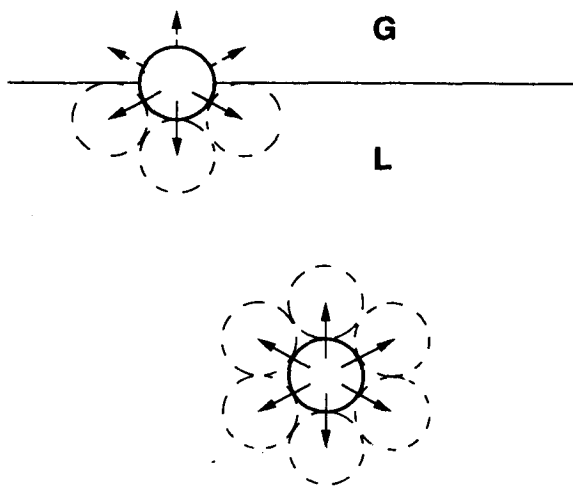
## 1.2 The Players and the Rules of the Game

### 1.2.1 Surface and Interfacial Tension

In a liquid, molecules are in a condensed state and experience cohesive interactions with neighbouring molecules (see Fig. 1.1). On the surface, a molecule remains in contact with only a half-space, and thereby loses about half of its cohesion energy  $u$ . This energy loss is the origin of the surface tension  $\gamma \approx u/a^2$ , where  $a^2$  is the mean area occupied by the molecule at the surface. For a simple liquid, where interactions are exclusively of van der Waals type, with  $u = 1/40$  eV and  $a = 3$  Å, we obtain  $\gamma \approx 40$  mJ m<sup>-2</sup>. Table 1.1 shows the values of  $\gamma$  measured for some liquids. In water, the high value  $\gamma = 72$  mJ m<sup>-2</sup> is due to the presence of hydrogen bonds. In the case of mercury, a liquid metal,  $u$  is large ( $\approx 0.3$  eV) and  $\gamma \approx 486$  mJ m<sup>-2</sup>. It is widely known that mechanical energy must be provided in order to create surface area, when making mayonnaise or beating eggs. Indeed,  $\gamma$  can be defined as surface work; to increase the surface area  $A$  by  $dA$ , work  $dW = \gamma dA$  must be done. In dimensions,  $[\gamma] = \text{EL}^{-2} = \text{FL}^{-1}$ . The usual units for  $\gamma$  are [mJ m<sup>-2</sup>]. Surface tension contributes to the work in thermodynamics, increasing the internal energy  $U$  or the free energy  $F$ :

$$\gamma = \left. \frac{\partial U}{\partial A} \right|_{S, V, n_i} = \left. \frac{\partial F}{\partial A} \right|_{T, V, n_i}$$

Surface tension can also be viewed as a force. Consider the experiment in which a rectangular frame with moveable side is dipped into soapy water (see Fig. 1.2). In order to move the side through  $dx$ , work  $dW = 2\gamma dx = 2\gamma dA$  must be done, the factor of two being due to the presence of two interfaces.  $\gamma$  is



**Fig. 1.1.** Physical origin of surface tension: a molecule at the surface loses part of its cohesive interaction compared with a molecule in the body of the liquid