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INTRODUCTION, THEORY, AND INSTRUMENTATION

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INTRODUCTION AND OVERVIEW

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1.1 INTRODUCTION

For many millennia, humankind has exploited matter in daily life. It has been only a few centuries since we have been able to engineer matter to control its properties. Over billions of years of evolution, nature has, however, engineered a material system to build its astonishing living constituents: "soft matter." Soft matter, as made by nature, is known to be versatile, adaptable, efficient, and—within the limits of our current knowledge—mysteriously capable of self-organizing and healing.

In spite of the fact that this book is not concerned with the theory of soft matter but rather with Raman spectroscopy and its capabilities in characterization of soft matter, we will briefly describe soft matter systems and their most important features and potentials in the following sections. Experimental characterization techniques utilized in investigating soft matter and the type of information they provide regarding the system will also be presented in Section 1.3.

Raman Spectroscopy for Soft Matter Applications, Edited by Maher S. Amer

1.2 WHAT SOFT MATTER IS

To start from the beginning, let us try to describe our universe from a materials scientist's viewpoint. We can say that the universe is made of energy and matter. These two entities are transformable into each other according to Einstein's famous equation, $E = mc^2$, and are bridged by another entity known to materials scientists as plasma. We usually classify matter into three different forms: solids, liquids, and gases. It can also be classified into two forms: hard matter (which includes metals and ceramics) and soft matter. It is scientifically safe to say that based on our deep understanding of molecular theory, many properties of hard matter are currently well understood. However, when it comes to soft matter, we have to admit that we are still on a steep learning curve.

If one asks the simple question, "what is soft matter?" the answer would not be so simple. Soft matter is a complex and flexible sort of matter referred to sometimes as "complex fluids." The term "fluids" should not be taken literally since soft matter is not necessarily fluids. Other terms such as "colloidal suspensions" and "colloidal dispersions" have also been used to describe soft matter [1]. The term describes a very wide range of matter including polymers, colloids, liquid crystals, emulsions, foams, biological tissues, as well as a wide variety of other materials such as milk, mayonnaise, and ice cream [2]. Soft matter systems can exhibit a drastic change in their mechanical, optical, and electrical properties as the result of very mild chemical or conformational changes in their structures [3]. To give a more quantitative description, it can be said that at ambient temperatures, molecular kinetic energy within a soft matter system is close to k_BT, a quantity that is much smaller than k_bT in a hard matter system[1] [4]. Considering structural features, soft matter systems exhibit a structural ordering intermediate between that of crystalline solids and liquids with a periodicity typically in the range of 1 nm to 1 μm. This makes soft matter systems ordered on the nano and/or the meso[2] length scales, depending on the system.

What really add to the importance of soft matter as a class of materials are the interesting theoretical analogies and behavior resemblances sometimes observed between them and other scientific fields. For example, S.F. Edwards [5] observed the correspondence between the

[1]Here, k_B is Boltzmann's constant and T is absolute temperature.

[2]Meso (Latin for "in between") scale covers lengths less than 1 μm and larger than 100 nm. Sometimes, it is extended down to a 10-nm limit in the literature.

conformations of a flexible chain and the trajectories of a nonrelativistic particle in the presence of external potential. He also showed that both systems are ruled by the same Schrodinger equation. This observation has been the key to all later developments in polymer statistics [3]. An interesting overlap in thought between the highbrow string theories and the descriptions of soaps has also been discussed [6].

Last, but definitely not least, it is possible to state that the most striking feature of soft matter is the ability to utilize it to create new forms of matter with properties we could only dream of a few decades ago. Microemulsions and liquid crystals are two good examples for such new forms of matter [7]. It is also expected to see, within our lifetime, more development for new forms of matter with novel engineered properties and adaptively controlled structure that we can as yet only imagine. The recently reported [8] colloidal crystals exhibiting negative Poisson's ratio that can be controlled in the range of 1 to 2 is a good example. Such ability is crucial for utilization in other advanced applications such as narrowband rejection filters, nanosecond optical switches, and sensors [9].

1.3 CHARACTERIZATION TECHNIQUES OF SOFT MATTER

A necessity for the understanding and further development of a new class of materials is a powerful characterization technique capable of interrogating such system on an appropriate length scale. A number of experimental methods were employed in investigating the structure and performance of soft matter systems. Such experimental techniques include microscopy, spectroscopy, scattering methods, rheology, calorimetry, and surface structure probes such as atomic force probe (AFP or AFM) and scanning tunneling probe (STP or STM). In the following sections, we will briefly describe these experimental techniques. The rest of the book is dedicated to Raman spectroscopy and its applications in investigating different classes of soft matter.

1.3.1 Microscopy and Surface Probes

Since the length scale of interest in soft matter is the nano-/mesoscale, optical microscopy (with a Rayleigh limit $\lambda/2$ on the spatial resolution) suffers from serious resolution limitations as a structural analysis method. However, the technique can be useful in viewing aggregated structures larger than 1 μm formed in the system. Polarized optical microscopy was also found useful to identify birefringent structures

rather than examining the structures themselves in cases such as spherulites in polymers. Certain optical imaging methods such as differential interference contrast (DIC) that relies on the interference between light waves reflected from different regions (with different birefringence or thickness) in the sample, were developed and used as identification techniques in plants and biological samples [10]. Recent development in near-field scanning optical microscopy (NSOM) techniques with a spatial resolution in the range of $\lambda/20$ has allowed better characterization of the structure in soft matter.

Electron microscopy (both in transmission and scanning modes TEM and SEM) provides a good means for examining the structure down to sub-nanometer resolution. Elaborate sample preparation, and the no fluid restriction in transmission electron microscopy (TEM) (due to high vacuum required in the microscope chamber) impose restrictions on the type of soft matter samples that can be examined using such techniques. The development of environmental scanning electron microscopy (ESEM) and field emission (FESEM) has greatly aided in investigating the structure of soft matter.

Surface probe microscopy (SPM) techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), with their atomic resolution, have proven to be invaluable in characterizing surface structures in soft matter on the nanoscale. The force probing function in AFM was also used to measure local mechanical constants (such as local stiffness) in soft matter as well.

1.3.2 Scattering Methods

Scattering of light, as well as X-rays and neutrons, was used to investigate the structure of soft matter. Static light scattering, especially small angle light scattering (SALS) can be used to determine the particle size. Data analysis in this case will depend on the particle size relative to the wavelength of the light (λ). Dynamic light scattering can also be employed to measure relaxation times and translational diffusion coefficients in soft matter.

X-ray and neutron scattering measurements can also be used to probe the structure of soft matter on a much smaller level (Typically 1 Å). Wide-angle X-ray scattering (WAXS) with scattering angles (2θ) larger than 10° has been successfully utilized in investigating structures and crystallinity in soft mater such as polymers. Small-angle X-ray spectroscopy (SAXS) with scattering angles (2θ) smaller than 10° has been used to characterize structures in the range of 5 to 100 nm within soft matter as well. Small-angle neutron scattering (SANS) is very

similar to SAXS in principle and has also been extensively utilized in structural investigations of soft matter. A fundamental difference between the two techniques, however, arises from the fact that X-ray scattering intensity depends on electron density distribution in the scattering medium while neutron scattering intensity depends on nuclear scattering length density. Hence, SANS can clearly distinguish between hydrogen atoms ^{1}H and deuterium atoms ^{2}H, and has been utilized extensively in characterizing soft matter structure by deuterium substitution in parts that need to be investigated.

1.3.3 Rheology and Calorimetry

Rheology was utilized to investigate mechanical deformation and flow characteristics of soft matter under stress. Flow behavior, i.e. of Newtonian, non-Newtonian, or Bingham nature, of soft matter is usually determined by rheology studies and can be correlated to its structure. Calorimetric studies, however, are used to investigate phase transitions in soft matter. Differential scanning calorimetry (DSC) is the most widely used technique to investigate soft matter phase transitions, determine transition temperatures, and to measure the associated transition enthalpy.

1.3.4 Spectroscopy

Different spectroscopic techniques have been utilized in characterizing soft matter. Techniques such as nuclear magnetic resonance (NMR), dielectric spectroscopy, infrared spectroscopy, and Raman spectroscopy have all been proven powerful techniques in characterizing and understanding soft matter. Here, the ability of such spectroscopic techniques will be briefly introduced.

NMR has been utilized to probe chain local microstructure and to determine the number average molecular weight and the dynamics of segmental motion in polymers, as well as composition of copolymers. The technique was also used to provide information on orientational ordering in liquid crystals, and to determine translational self-diffusion coefficient in amphiphiles and colloids' dilute solutions.

Dielectric spectroscopy with its very wide range of frequency coverage (10^{-5} to 10^{10} Hz) provides information complementary to that provided by rheology. Dielectric spectroscopy, however, can cover much higher frequencies than that covered in rheology and thus becomes the technique of choice when dynamic mechanical properties of soft matter need to be probed at high frequency range.

Infrared spectroscopy is known to be a complementary technique to Raman spectroscopy. The technique is used extensively for identification purposes in soft matter. In addition, the technique is used to provide information regarding chain branching, tacticity, length of unsaturated groups in polymer as well as information regarding hydrogen bond network formation in surfactant and colloidal solutions. Polarized infrared spectroscopy, as in Raman spectroscopy, can also be used to determine the orientation of a particular chemical bond within a soft mater system.

1.4 OVERVIEW OF THE BOOK

In Chapter 2, Philippe Colomban, and Gwénaël Gouadec of CNRS, Paris, France, give a simplified overview of the Raman scattering theory and elements of Raman instrumentation. In Chapter 3, Giriprasath Gururajan and Amod A. Ogale of Clemson University discuss Raman applications in polymer films and its ability to conduct *in situ*, real-time characterization of the films. Specialized instrumentation for this application and the impact of Raman characterization on better processing of polymer films are discussed. In Chapter 4, Robert Young and Steve Eichhorn of University of Manchester, England, review Raman applications in investigating synthetic and natural polymer fibers and their composites. Information provided by Raman spectroscopy regarding the structure and mechanical properties of such fibers including their composites, as well as the potential of Raman spectroscopy techniques in investigating nanocomposites, is discussed. In Chapter 5, Oihana Elizalde and Jose Ramon Leiza of BASF, Germany, and University of the Basque Country, Spain, respectively, review emulsions and emulsion polymerization, and Raman spectroscopy applications in this branch of soft matter. A study of liquid crystals and their characterizations using Raman spectroscopy is given in Chapter 6 by Naoki Hayashi of Fuji Photo Film Co., Japan. In Chapter 7, Maher S. Amer of Wright State University discusses foams, their structure, importance, and the information that can be provided by Raman spectroscopy regarding this important class of matter. In Chapter 8, Søren Balling Engelsen and his team from the University of Copenhagen, Denmark, review Raman applications in the food industry and the characterization capabilities of the Raman technique in this field.

Medical applications of Raman spectroscopy are discussed in the third section of this book. In Chapter 9, Peter Fratzl of Max Planck Institute of Colloids and Interfaces, and his coauthors S. Gamsjäger and

E.P. Paschalis of Ludwig Boltzmann Institute of Osteology, Austria, and M. Kazanci of St. Francis Xavier University, Canada, discuss the capabilities, potentials and impact of Raman spectroscopy imaging on bone characterization and investigation. Raman applications in cancer studies and the invaluable information provided by the technique are discussed in Chapter 10 by Hiro-o Hamaguchi of the University of Tokyo and his coauthors of Kao corporation, Tokyo Metropolitan Hiroo Hospital, and Toho University School of Medicine, Japan.

This book is intended as a reference for experienced researchers working in any of the aforementioned branches of soft matter, and as a guide for researchers and graduate students preparing to investigate and explore the amazing world of soft matter.

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