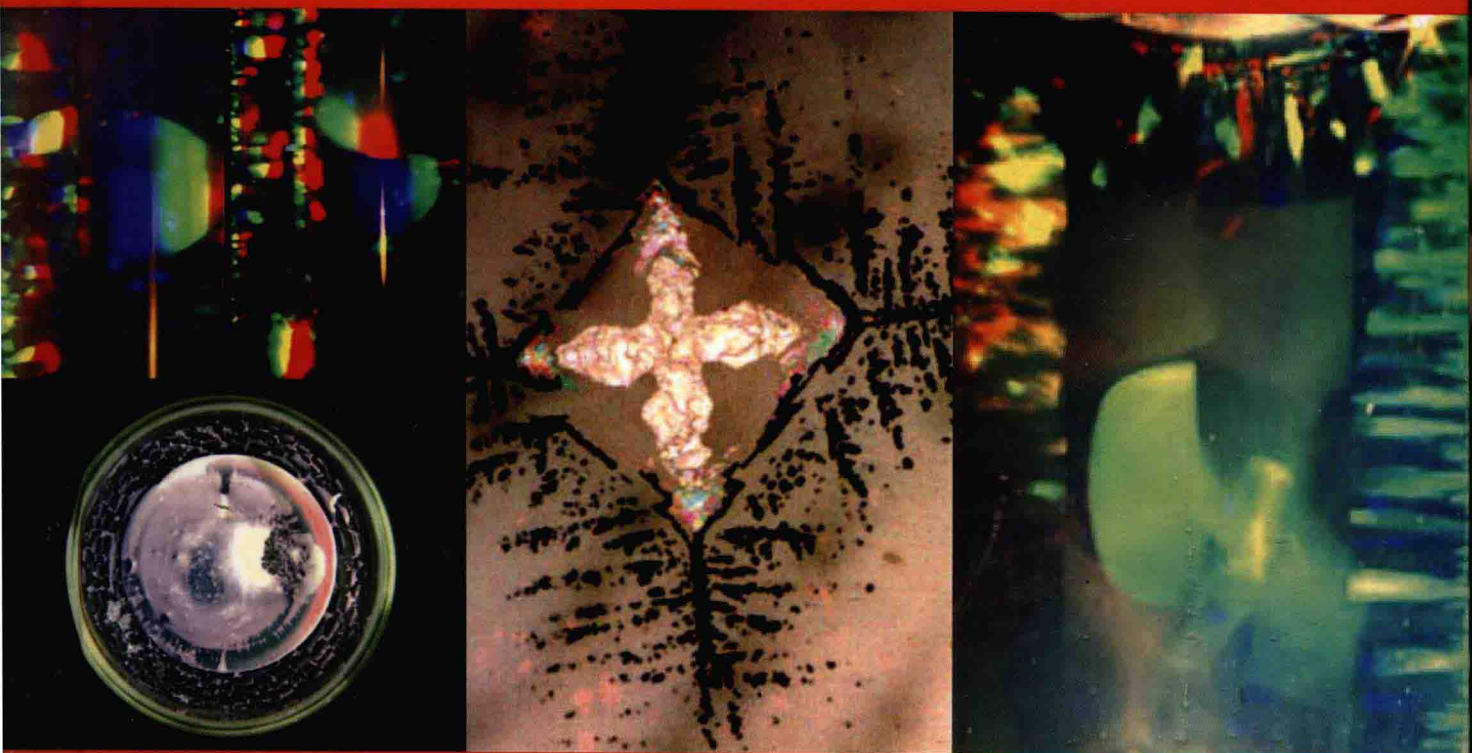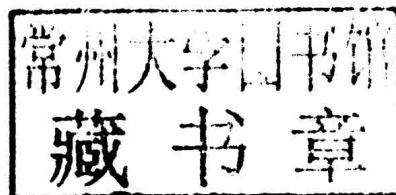# Colloidal Organization

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Colloidal
Organization

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Preface to the Edition

As is well known, colloidal and surface science was born in our usual life in nature and is one of the oldest sciences. A large number of colloidal systems exist in daily life such as clouds, fog, muddy water, milk, paint, and stained glass, as is described in this book. General sizes of colloidal particles range from several 10 nm to several millimeters. Most colloidal particles are not recognized with the naked eye, but are often observable through an optical microscope. Colloidal particles are small, but the ratios of the surface areas against their volumes are significant. Thus colloidal science developed rapidly in the field of surface science.

Professor Emer. Dr. Heinz Hoffmann (Bayreuth) kindly informed me of the following story. Dr. Wo. Ostwald, who made major contributions to colloid and surface science, wrote in his book *Licht und Farbe in Kolloiden*[1] that colloidal dispersion is not beautiful. During his age, backscattered and transmitted light and Mie scattering light were not enough to impress him with a sense of beauty.[2] I, on the other hand, was deeply impressed with the beauty of colloidal crystals. Colloidal science is now one of the most beautiful worlds of science. The term *beautiful* is not used so often in science. However, I like to use *beautiful* sometimes. Furthermore, I believe that the experience of a deep emotion during observation of new findings in nature in our life is also beautiful.

Colloidal organization has broad meaning, but *colloidal crystallization* and *ordered drying patterns* of colloidal dispersions are mainly described in this book. These two fields are typical systems representing colloidal organization, I believe. In a narrow sense, colloidal crystals are "ordered structures of colloidal particles in a suspension state." However, we should note that there exist eight kinds of colloidal dispersion systems: gas-in-liquid, gas-in-solid, liquid-in-gas, liquid-in-liquid, liquid-in-solid, solid-in-gas, solid-in-liquid, and solid-in-solid. Thus eight kinds of colloidal crystal systems are considered in a wide sense. Plasma crystals, opals, emulsion crystals, and gel crystals are typical examples of colloidal crystals in a wide sense. Ordered drying patterns are considered to be one of the colloidal crystals in the frozen (or fixed) states in a wide sense. When liquid-state colloidal crystals are dried on a substrate, drying processes from typical colloidal crystals to the solid-state colloidal crystals can be studied.

The main cause of colloidal organization is originated from the cooperative (or synchronized) and weak interactions among particles, substrate (or cell wall) and medium molecules. Particle–particle interactions are

influenced greatly by the electrical double layers extended around the particles, especially in colloidal crystallization in the aqueous media. Particle—medium interactions are important for colloidal crystallization and pattern formation through the electrical double layers and convectional and sedimentary motion of particles. Particle—substrate interactions are also important for colloidal organization. Without a vessel or interface, crystallization of suspensions does not take place spontaneously. Most dense crystal planes orient along the cell wall. Furthermore, colloidal crystallization is enhanced in a plane cell, but disturbed in a narrow capillary tube, for example. Among many contributions to colloidal organization, the most important factor is the cooperative thermal motion of colloidal particles, including all the relating components, colloidal particles, substrate, ionic species, and medium molecules. Atmospheric conditions such as temperature, humidity, pressure, external fields, and other factors are also important for the thermal motion. As is well known, thermal energies k_BT (k_B is the Boltzmann constant and T is the absolute temperature) given for all the components are essential factors for determining the properties of substances. Considering the previously described features of colloidal organization phenomena, careful experiments are necessary to obtain reliable results. For example, we must deionize the colloidal samples with coexistence of ion-exchange resins for more than 1 year to obtain the exhaustively deionized state of colloidal samples!

One of the main purposes of this book is to show the beautiful world of the colloidal organization to the readers. I believe careful experiments and observation are most important for understanding phenomena of colloidal organization. Explanation should follow the reliable observation. In this book, I have tried not to use complex equations, although I worry whether this was accomplished.

I deeply appreciate the guest researchers of the Institute for Colloidal Organization: Professor Akira Tsuchida and Hiroshi Kimura (Gifu University), Hiromi Kitano (University of Toyama), Kohji Yoshinaga (Kyushu Institute of Technology) and Etsuo Kokufuta (University of Tsukuba). The late Professor Emeritus Sei Hachisu (University of Tsukuba) is appreciated for his continuing encouragements and advice through our work. The late Professor Emeritus Ichiro Sakurada and other professors of Kyoto University are acknowledged for their kind comments. The late Professor Emeritus Ronald H. Ottewill (Bristol University) and Robert L. Lowell (University of Massachusetts) are acknowledged for their encouragement of our work. Professor Zoltan A. Schelly (University of Texas, Arlington), Thomas Palberg (University of Mainz), Maria Stoimenova (Institute of Physical Chemistry, Sofia, Bulgaria) and Peter A. Lovell (Manchester

University) are thanked sincerely for their discussions and comments. I acknowledge Dr. Anita Koch, Sarah J. Watson and Anitha Sivaraj of Elsevier for their kind support from arrangement to printing of this book. I thank my wife, Keiko, for her understanding and cooperation during the course of my research and writing.

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April 22, 2015

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Introduction

1.1 Common Colloidal Dispersions

Colloidal and surface chemistry have always existed. Rain, fog, and mist are typical examples of liquid-in-gas—type colloidal dispersion. These types of colloidal dispersions are further distinguished depending on their sizes. In Japan, for example, they are named *moya* ("dry fog," smaller than 10 μm in diameter), *kiri* ($\approx$10-100 μm), *kirisame* ($\approx$100-300 μm), *sitosito-ame* ($\approx$0.3-1 mm), *ame* ("rain"; $\approx$1 mm), and *suko-ru* ("squall"; larger than 1 mm). *Ice-fog* is the dispersion of ice particles in the air (solid-in-gas type). *Cloud* refers to the concentration of water or ice particles ($\approx$2-40 μm) in the air. Gravity causes clouds to descend at the velocity of approximately 20 mm/min without wind; however, even a faint ascending air current can keep a cloud aloft for a long time. *Snow* is crystallized ice from saturated water vapor in a cloud and is a typical example of gas-phase crystallization. The maximum crystal growth rate of snow is approximately 30 μm/s and is surprisingly similar to that of colloidal crystallization.

Observation of snow crystals has a long history. Johannes Kepler (1571-1630) discussed why snow crystals are hexagonal (1611). Rene Descartes (1596-1650) observed and sketched many shapes of snow crystals (1637). Wilson Alwyn Bentley (1865-1931) and William Jackson Humphreys (1862-1949) published a famous book titled *Snow Crystals* (1931),[1] which included many beautiful pictures of snow crystals.

Ukichiro Nakaya (1900-1962), a famous scientist who studied snow, said, "Snow is a letter from the sky,"[2,3] meaning that the state of the sky becomes clear by studying the morphologic characteristics of snow crystals. He made the Nakaya diagram showing the relationship between various crystal structures of snow as a function of the degree of supersaturation and temperature of water vapor in the sky (Fig. 1.1). For example, hexagonal polyhedric snow crystals grow in a low supersaturation state of vapor, whereas various crystal structures, including needlelike, folding fan—like, sheathlike, and dendritic crystals, form in a state of high supersaturation. Fig. 1.1 is newly redrawn by the author based on several types of Nakaya diagrams reported previously.

Figure 1.1
Schematic representation of a Nakaya diagram of snow.
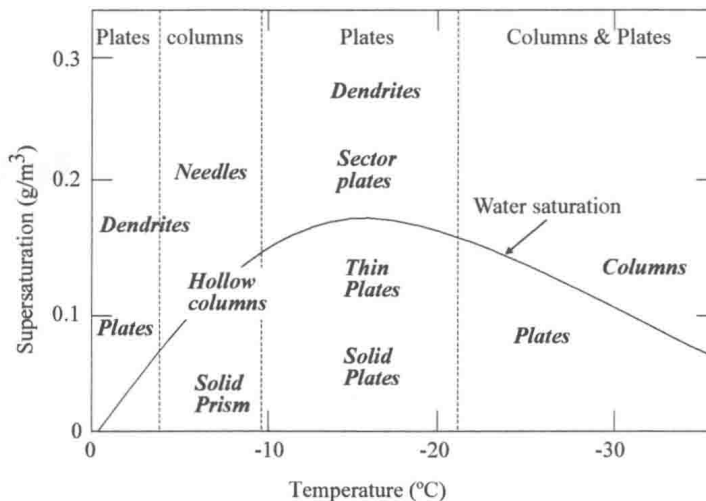
Smoke, the dispersion of the liquid-in-gas or solid-in-gas colloid type, is also familiar. *Smog* is a new word combing *smoke* and *fog,* and relates to the pollution problem. Mist and fume are also typical examples of colloidal dispersion systems in solid-in-gas and liquid-in-gas systems. Furthermore, *aerosol* is a general name for colloidal dispersions of solid-in-gas and liquid-in-gas systems. A large, red sunset may be beautiful, but this also means air pollution is a serious problem in the presence of colloidal particles.

Colloidal dispersion systems in the liquid phase are most familiar. For example, turbid water in a pond contains colloidal particles of soil. Mayonnaise and milk are typical examples of liquid-in-liquid–type colloidal systems. Most paints are solid-in-liquid–type dispersions. Coffee,[4,5] black tea,[6] green tea,[7] and Miso soup[8] are also solid-in-liquid–type colloidal dispersions. The monodispersed colloidal spheres are now available commercially thanks to the recent advancement in the field of synthetic colloidal chemistry. Fig. 1.2 shows typical colloidal crystals of polystyrene spheres (D1K88, 137 ± 16 nm in diameter) in the stock (*A*) and diluted (*B*) suspensions in a bottle and a test tube, respectively. Iridescent colors are beautiful. To remove most of the ionic impurities in the suspension as completely as possible, the stock suspension was deionized with the mixture of ion-exchange resins 10 years previously. The sample suspensions were prepared by diluting the stock suspension with deionized pure water and the ion-exchange resins were introduced again. The author found the viscosity of the sample suspension containing the resins increased with time and reached saturation after several years. Complete deionization of the sample spheres took such a long time because deionization is one of the equilibrium reactions proceeding between colloidal spheres and solid resins dispersed in the aqueous phase. Colorful single crystals are observed in Fig. 1.2, B.

Figure 1.2
Colloidal crystals of polystyrene spheres (D1K88, 137 ± 16 nm in diameter) in the stock (A, ϕ = 0.062) and diluted (B, 0.00053) suspensions.
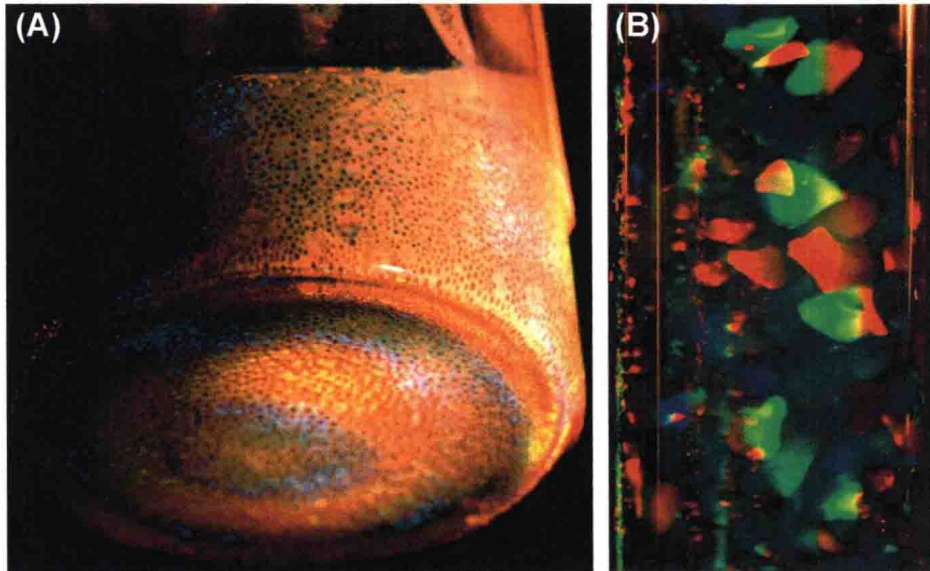
Fig. 1.3 shows one of the typical microscopic pictures of colloidal green tea leaves. In most Japanese hotels, a guest will find in her or his room a tea set to prepare green tea; the tea set is composed of green tea leaves in a paper filtering bag, a tea cup, and a water heater, for example. One day, after preparing tea and leaving it on the desk for several minutes, I was excited to find a broad ring forming in the cup. Fig. 1.4 shows typical examples of the broad ring patterns of green tea.[7] The broad rings of the hills created by accumulated green tea particles stayed on the inclined wall of the cup, and did not drop into the deepest central area. This was my first finding of

Figure 1.3
Microscopic observation of green tea leaves. Objective lens ×40, eye lens ×10; full scale is 25 μm. (From Okubo T: Sedimentation and drying dissipative structures of green tea. Colloid Polym Sci 285:331-337, 2006.)

Figure 1.4 Sedimentary patterns of green tea in the several cities in Japan. **A**, Sapporo, **B**, Yonezawa, **C**, Kumamoto, and **D**, Ishigaki in Japan. (**C** and **D** from Okubo T: Sedimentation and drying dissipative structures of green tea. Colloid Polym Sci 285:331-337, 2006.)

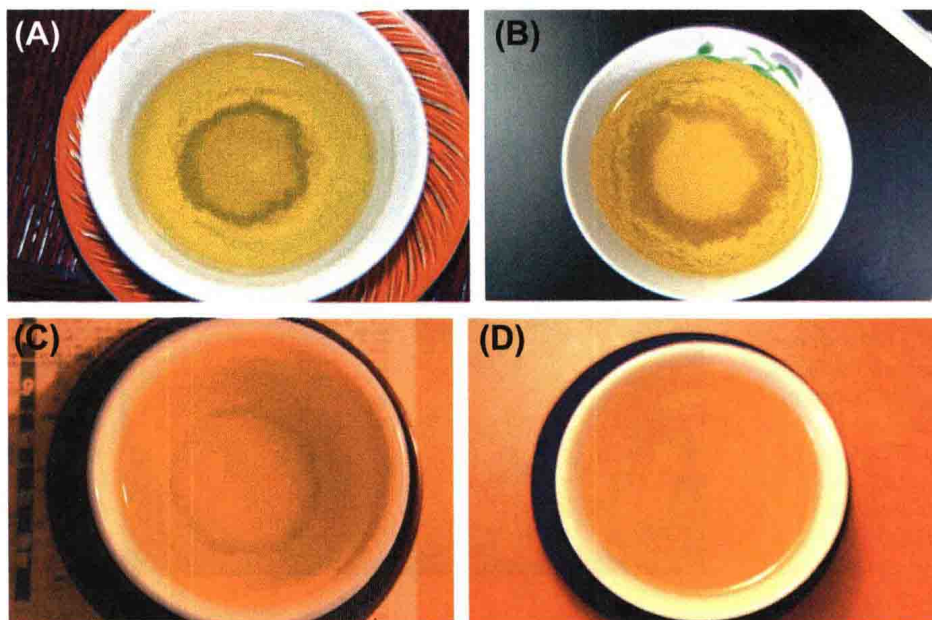sedimentation patterns. The sedimentary patterns were always observed irrespective of the kind of particles, cup, and observed places. The smaller the colloidal particles, the larger the broad rings that form up the inclined wall. Therefore approximate information on the size distribution of the particles is available from the sedimentary broad ring patterns. The details are described in Chapter 5.

Biologic polymeric substances are grouped into three categories: proteins (polypeptides), polysaccharides, and polynucleotides. Many are assemblies of anionic polyelectrolytes. Spherical proteins of hemoglobin and fibrous collagen or keratin exist in the state of solid-in-liquid—type colloidal systems.

Sponge, hydrated silica gel, and stained glass are typical examples of gas-in-solid, liquid-in-solid, and solid-in-solid systems, respectively. Stained glass is the beautiful colloidal system composed of metal particles 100 to 300 nm in diameter dispersed in a glass solid.[9] An example of stained glass is shown in Fig. 1.5. Stained glass can be seen almost anywhere. Only light in a certain range of wavelengths is transmitted through the stained glass by the quantum effect, and the transmitted light is colorful (e.g., reddish, greenish, or yellowish, depending on the kind of the metal particles). Usually, a stained glass window in a church is beautiful when we see it in the daytime. Many years ago, I was impressed to find beautiful stained glass when I looked at a lighted church in the evening. Table 1.1 describes examples of colloidal
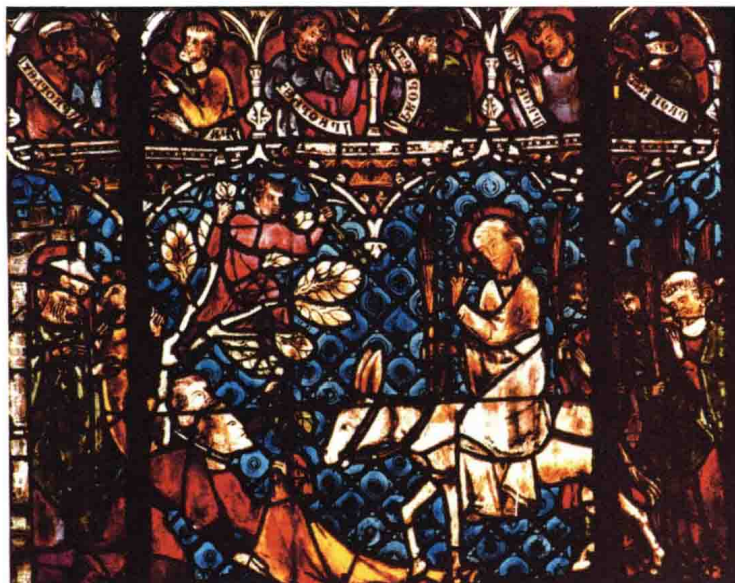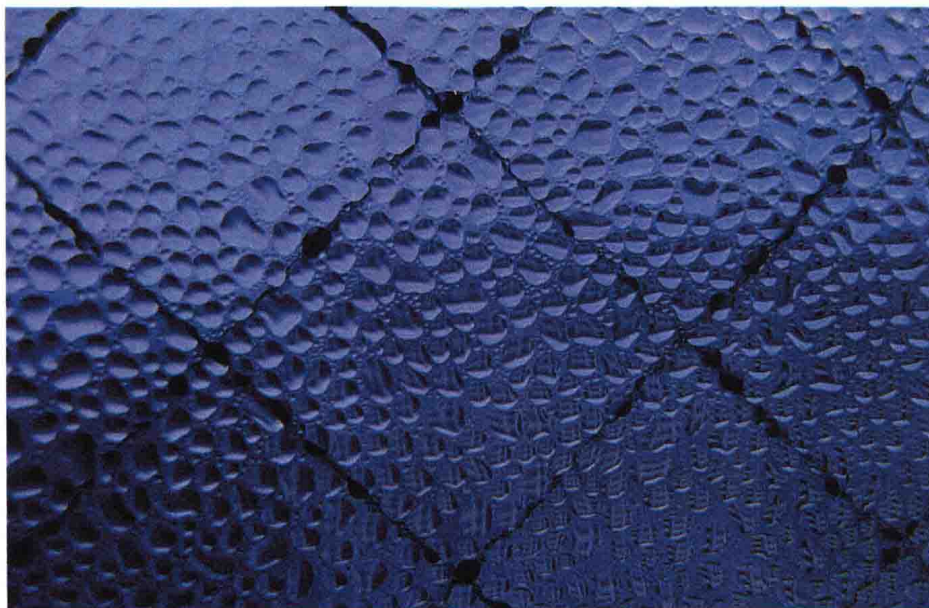
Figure 1.5
A typical example of stained glass in Notre-Dame Cathedral, Strasbourg, France.

Table 1.1 Types of Colloidal Dispersions

		Dispersion Solutes		
		Gas	**Liquid**	**Solid**
Dispersion medium	**Gas**	————	**Aerosol** Fog, mist, cloud	**Aerosol** Smoke, smog
	Liquid	**Foam** Foam	**Emulsion** Mayonnaise, milk	**Solid dispersion** Paint, coffee
	Solid	**Solid foam** Sponge	**Solid emulsion** Hydrated silica-gel	**Solid dispersion** Stained glass

systems grouped by the combination of the interfaces formed between the solute and the medium. Gas-in-gas systems do not exist in equilibrium, because gas and gas are mixed homogeneously and no interfaces between gas and gas exist.

We should note here that there exist many ordering phenomena relating to the colloidal organization in nature. Fig. 1.6 shows dewdrops observed on a window glass within a house in the winter season. Here, the distribution looks somewhat ordered. Interfacial tensions between air and water, water and glass, and air and glass control the shape, size, and distribution of the droplets. Watching the synchronized self-organization processes is interesting. Self-organization phenomena are classified into two groups: (1)

Figure 1.6
Patterns of
dewdrops formed
on a window glass
in winter.

dissipative structures in a nonequilibrium state and (2) consecutive structures in equilibrium. Most self-organization phenomena in nature are in the first group, and are exemplified by the fractal networks of rivers and mountains, and the chevron patterns that appear in a bacterium colony of *Escherichia coli*. In the laboratory, examples include the hexagonal convection cell (Benard cell), Belousov-Zhabotinsky reaction patterns, and the film formed by drying liquids, among others. The ordering of dewdrops in Fig. 1.6 are grouped into the dissipative structures. However, there have been few laboratory studies of the dissipative structure. Most of the self-organized structures studied have been the second group of conservative structures in equilibrium. Fast micellization of surfactant molecules and crystallization of proteins and metals are the typical examples for the second group. To understand the complex ordering phenomena in nature, the systematic study of the dissipative structures in laboratory scale is very important.

It is well known that the ratio of surface area of a substance against its volume increases substantially with decreasing size. Surface area and volume of a sphere in radius r are $4\pi r^2$ and $(4/3)\pi r^3$, respectively, and the area per volume of a sphere is $4\pi r^2/[(4/3)\pi r^3] = 3/r$. The ratio will be very large when the value of r comes close to zero. Thus more significant surface phenomena occur as the size of a solute decreases. This is a main reason why colloidal particles are studied so often in surface chemistry. However, we should note that the surface forces per unit of surface area, of course, do not depend on the size of solutes. Even for a very large solute, such as a man coming in contact with

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