Fine Particles: Science and Technology

Egon Matijević, Guest Editor

Introduction

Some readers may wonder about the reasons for having two issues focus on fine particles. Hopefully, this introduction and the articles to follow will offer the necessary justification.

It is fully expected by everybody, professional or laic, that the properties of matter will change if its chemical composition is altered. It is less frequently recognized that many characteristics of materials can be dramatically affected by varying dimensions, yet countless examples in everyday life clearly demonstrate such phenomena. Consider water in droplet form. Driving in rain creates little problem, providing the car has working windshield wipers. In contrast fog, which consists of droplets of much smaller size, represents one of the major hazards in transportation. Obviously, the optical properties of the same matter have greatly altered with diminution. In another example, it is well known that finely dispersed carbon is an excellent adsorbent, a property used in gas masks and in many industries as a purifying agent. Large-sized lumps of such carbon would be useless in these applications.

The effect of particle size on properties of materials can be readily understood from a simple consideration. The total energy of any system, (E_{tot}), consists of two contributions, the internal energy, E_i, and the surface energy, E_s.

$$E_{tot} = E_i + E_s = e_i V + \gamma A$$

where e_i is internal energy per unit volume, and γ is the interfacial energy per unit surface area, while V and A are the total volume and area of the dispersed matter, respectively.

The contributions of the two terms are not always equal; depending on the conditions, one or the other may prevail. It is easily seen that the dominance of these contributions depends on the geometric factor. The above equation, expressed per unit volume, reads

$$(E_{tot})_v = e_i + \gamma(A/V)$$

Since e_i and γ are intrinsic properties of a material, the only variable quantity is A/V. If this ratio is large, the second term becomes significant (e.g., $A/V \sim 10^4 - 10^7\ cm^{-1}$). The properties of matter are greatly affected by the surface energy contribution to the total energy of the system. It is obvious that the large value of A/V can be achieved by having one, two, or three dimensions rather small, resulting in films, fibers, and fine particles. This series of articles concerns itself only with the last case, where the above cited A/V range corresponds to particle sizes of a few nanometers to a few micrometers.

Monodispersed Systems

In reading the articles to follow, note the consistent emphasis on the uniformity of particles. Indeed, a major effort is currently being placed on developing techniques to prepare dispersions of powders of different shapes and chemical composition, consisting of particles of narrow size distribution. This trend has been promoted for both academic and application reasons.

Scientists engaged in colloid research have been fascinated with "monodispersed" systems ever since this state of matter was recognized last century. Faraday prepared the now famous gold sols of different color as early as 1857 and understood their particulate nature. The synthesis of many different uniform dispersions of elements (sulfur, selenium, silver, etc.) or compounds (silica, tungstic acid, barium sulfate, etc.) has been reported in the literature over the years. All these preparations were based on the "trial and error," with no common underlying scientific principles. The only exceptions were polymer colloids of different chemical compositions, commonly known as latexes, which have been produced in large quantities as exceedingly uniform spherical particles by emulsion or dispersion polymerizations.

In view of the interest in such systems, much effort has been invested in developing processes and techniques that would yield well-defined colloidal dispersions. The emphasis in these, more recent, studies has been on certain scientific principles which include physical, chemical, or combined physical-chemical approaches. As a result, a large library of inorganic or organic materials is now available, which consists of amorphous or crystalline, simple or composite particles of different shapes, of narrow size distribution with modal sizes in the colloidal range. Some recent review articles describe and refer to many such systems.[1-5] Dispersions of uniform particles have been made of metals, of metal (hydrous) oxides, sulfides, selenides, phosphates, carbonates, etc., and of nonmetallic compounds. Some of these fine particles may have more than one anion or cation in their structure. It is also possible to generate uniform coated particles, in which the core and the surface layers differ in chemical composition.

T. Sugimoto's article reviews some of the procedures for preparing monodispersed systems in general, while M. Figlarz and colleagues deal specifically with well-defined metal particles. A.J.I. Ward and S.E. Friberg describe the novel approaches in employing lyotropic systems to generate colloidal dispersions.

Fundamental Studies

Monodispersed colloids are invaluable in the quantitative assessment of properties that depend on the particle size and shape. Such systems are also useful in the elucidation of mechanisms of solid phase formation and particle growth. The latter studies can greatly contribute to a better understanding of various processes involving interfaces, such as adsorption, adhesion, (hetero)-coagulation, corrosion, and catalysis, to mention a few. Indeed, a large volume of work in recent literature is devoted to such studies, using well-defined dispersions. Several areas of interest will be briefly mentioned here.

First, determining the size or size distribution of an assembly of fine particles may not be a simple task. While electron microscopy is an indispensable tool in this discipline, one must keep in mind that sample preparation, as well as exposure to high vacuum and to the electron beam, can sometimes drastically alter the system. There is little choice when sizing dispersed solutes of different shapes; one has to depend on electron microscopy. However, the size distribution of spherical particles of narrow size distribution can be determined by nondestructive optical techniques, such as light scattering or photon correlation spectroscopy. If data, obtained by electron microscopy and by optical means agree, the likelihood of having reliable information on size is greatly enhanced.[6] Indeed, we still do not have a reliable standard for calibration of electron microscopes by a well-defined powder!

Determining the chemical mechanism of the formation of a solid phase in a homogeneous solution is an arduous task, especially when dealing with inorganic systems involving ions that have high tendency for complexation. Only a limited number of cases yielded sufficient experimental evidence to suggest chemical processes responsible for particle formation.[7,8] In part the difficulty lies in the scarcity of thermodynamic information on the complex species of interest.

One of the major tasks of fine particle science is to develop some general principles that would allow predicting the properties of products from the composition of complex solute precursors in a precipitating system. Some inroad in this direction has been made by J. Livage and his collaborators as reviewed in the January 1990 *MRS BULLETIN*. Obviously, for any quantitative attack on this problem we need a number of well-defined dispersions of different particle compositions and shapes. As yet no known principles exist which would allow us to predict particle morphology from a set of experimental conditions. The same reagents at a slightly varied temperature of pH may yield entirely different products in terms of composition and shape.[9,10] In contrast, relatively minor adjustments may result in materials of the same chemical stoichiometry, but different geometries.[11]

In the precipitation of solids of mixed internal composition, such as oxides containing two or more different cations, we still need to establish the relationship of the concentration ratios of reactants in solution and in the solid phase. We also face the question of whether the particles are internally homogeneous, or if the composition changes from the center to the periphery.[12]

An ideal system to study various reactions in liquids or solids is the single particle electrodynamic balance, pioneered by E.J. Davis and reviewed in the January *1990 MRS BULLETIN*. A single particle represents the only truly "monodispersed" system. Modern spectroscopy techniques allow elucidation of processes with microquantities of materials in a most sensitive manner.

It is known that optical properties of matter depend strongly on particle size and shape, in addition to chemical composition and structure of a dispersion. Having spherical particles of narrow size distribution now makes it possible to quantitatively evaluate the color, its purity and saturation, as well as other optical properties of such systems, using the Mie theory.[13]

The elucidation of magnetic properties as a function of particle morphology and size is another area where uniformity of the powders has been an essential condition, as described by M. Ozaki in this issue.

The electrokinetic phenomena of dispersions present intriguing problems of solid/solution interfaces. Sophisticated equipment based on different principles is available for the determination of electrophoretic mobilities. If the measurements are properly done, excellent agreement is obtained for a well-defined system with different instrumentation.[14] Again, there is still need for a good standard that could be used as a reference for people working with various techniques and equipment.

Last but not least, it should be mentioned that monodispersed sols are essential in studies of the oldest problems of colloid science: coagulation and heterocoagulation. These processes are not treated in this series because numerous articles are available in the literature and the fundamental aspects are discussed in every textbook on colloids.

A related problem dealing with particle adhesion, which theoretically represents a special case of interactions between unlike particles, is discussed by N. Kallay in the January 1990 *MRS BULLETIN*.

Applications

In addition to the exploitation of monodispersed colloids in fundamental research or as models to elucidate processes in environmental control, corrosion, etc., the usefulness of these materials has become increasingly evident. Some of the well-defined powders are employed in the manufacture of known products, but with improved properties, while others are developed for new uses, especially in high technology. A few examples of these developments are offered here.

The significance of the morphology of silver bromide grains in photographic emulsions has been best illustrated in the development of high-speed films. Sugimoto's review emphasizes the role of fine particle science in photographic applications of silver halides.

Ozaki discusses the importance of the shape and structure characteristics of uniform magnetic particles. The best performance of different recording materials requires such powders to meet certain rather restricted specifications, now achievable.

New requirements for pigments and inks in high-speed printing and in other uses will make tools of fine particle science indispensable, if improved products are to be achieved. As mentioned previously, it is now quite feasible to design pigments of predictable qualities, with respect to both optical characteristics and mutual interactions between the particles or between the particles and the substrates. It is also possible to replace pigments that have been declared toxic with colored materials representing no danger to health. Furthermore, the properties of monodispersed pigments can be controlled by producing coated particles in which cores and surface layers may vary in size and optical parameters. Finally, the surface charge characteristics of such fine particles can be adjusted by small amounts of additives.

The role of colloids in various ceramics applications has now been generally recognized and discussed in numerous articles in a spectrum of journals. Some aspects of the problems of interest are addressed by T.A. Ring in the January *1990 MRS BULLETIN*. It has become evident that the quality and reproducibility of products can be more readily achieved by starting with well-defined powders of known properties. It has also been demonstrated that processing of powders (e.g., compaction, sintering, etc.) can in many cases be done more efficiently and at a lower temperature if the raw solids consist of uniform particles of a given size. Needless to say, ceramics represents a broad range of materials of diverse uses, but it tends to be compartmentalized in practice, depending on the specific interest of investigators or manufacturers. Thus, requirements placed on precursor powders depend on application and may vary widely. Obviously, different properties of matter will be needed when dealing with electro-optical, capacitor, piezoelectric, magnetic, composite, superconducting, structural, or other ceramic materials. In some cases whiskers are preferable; in others spheres may be preferable or essential. Fine particle science has progressed sufficiently to meet at least some of these challenges.

The importance of fine particles in catalysis is well known. For example, it has been finally well documented that the catalytic effect of palladium in electroless plating, which is essential to modern electronic industry, is due to the presence of exceedingly small particles of this metal on the surfaces that need to be coated.[15]

Another exciting, fast developing area of colloid applications is in medicine, especially for diagnostic purposes and novel disease treatments.

Much effort is invested in developing immunization procedures using magnetic dispersions. Small magnetic particles, coated with an antibody layer, are used to provide large specific surface area for sorting and separating select viruses, bacteria, and other cells from a mixture of populations. Similarly, particles of appropriate magnetic properties, coated with a suitable coupling agent that specifically binds red blood cells, can be used for a fast clinical blood analysis. The presence in body fluids of selected immunochemically responsive substances, such as antibodies or antigens, provides useful medical information for testing pregnancy, syphilis, and blood factors. Immune reagents tagged with magnetic particles offer a safe and sensitive way to detect these analytes.

Specific interactions with solids can be used directly in disease treatment and drug therapy. For example, myeloma cells can be purged from the bone marrow *ex vivo* using monoclonal antibodies coupled to magnetic immunobeads.

Biologically active material can be released in a controlled manner from microspheres through semipermeable membranes. Tiny magnetic particles can be incorporated into such microcapsules for directional drug delivery to specific body areas. Much effort in this area focuses on cancer therapy. Bringing the anticarcinogenic drug incorporated in a particulate carrier to the tumor site enhances the therapeutic effectiveness while minimizing the toxicity to the rest of the body.

In all these applications, specific requirements regarding carrier particle size, shape, and other properties (e.g. magnetic, adsorptive, electrokinetic, etc.) are essential.

All the uses of fine particles I've mentioned represent just a few examples from a wealth of areas that could have been cited.

Conclusion

While tremendous progress has been made in the science and technology of fine particles, much has yet to be done. Indeed, in many areas of this discipline we are still at the onset of new developments. Elucidation of the properties and mechanisms of formation of monodispersed colloids will not only help us to better understand Nature, but contribute greatly to the well being of humanity.

From the applications point of view, it is now essential that the engineers develop methods for scaling up and continuous processing of well-defined powders, based on the newly established fundamental principles for preparing such materials.

In view of so many different aspects of fine particle science and technology, it is obvious that the topics in these issues had to be restricted. I hope that the articles to follow will encourage and stimulate scientists and engineers to attack problems in this discipline, which are both fascinating and useful.

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