

# New Developments in Colloid Science

D.A. Weitz and W.B. Russel, Guest Editors

## Abstract

This introductory article reviews the topics covered in this issue of *MRS Bulletin* on New Developments in Colloid Science. Colloidal particles have a long history of importance in a broad range of applications in technology and materials processing. They can be made from many different materials and suspended in a wide variety of solvents. The rheological properties of colloidal suspensions have traditionally been of primary concern in their technological applications, and our understanding of these properties continues to evolve. However, new uses of colloidal particles are also emerging. Because they can be produced to a precise size, colloidal particles are now also being used in novel ways as building blocks for engineering completely new materials, including high-precision filters, controlled-porosity substrates, and photonic devices. In addition, new methods are evolving to alter the shape of the particles and create controlled structures with nonspherical particles. New experimental techniques are allowing improved measurement and increased understanding of the structure, properties, and behavior of colloidal suspensions. Significant progress continues to be made, and the potential uses of colloidal particles continue to grow. This issue presents a snapshot summary of recent developments in this field.

**Keywords:** *colloids, colloidal materials, rheology, suspensions.*

Colloids are small solid particles dispersed in a medium, typically a fluid. Colloidal particles have a long history of importance in a broad range of applications in technology and materials processing, extending from the pigments used in ancient inks to the photonic-bandgap materials being developed today.

Particles can be made from many different materials and suspended in a wide variety of solvents. The typical size of colloidal particles ranges from nanometers to micrometers. Because of this small size, thermal energy induces Brownian motion of the particles, and the resultant dynamics can play an important role in the properties of the suspension. The typical volume fraction of solids in a colloidal suspension can vary from a small fraction of a percent to more than 60%. The consequences on the suspension behavior as the volume fraction increases are still not completely understood, yet they are of great fundamental interest and practical importance.

Colloidal suspensions have considerable technological importance. They represent a means of making solid or highly viscous materials flow like low-viscosity fluids; this is because the solid or high-viscosity

material is contained in the colloidal particles while the rheological properties are dominated by the continuous-phase fluid in which the particles are dispersed, which can have a relatively low viscosity. Colloidal suspensions are also of great scientific interest, motivated not only by their technological applications but also by their potential use as models to investigate the collective phase behavior of systems in which Brownian motion produces an equilibrium state, to explore fundamental questions of packing and geometry, and to fabricate new structures using the colloidal particles as building blocks. This issue of *MRS Bulletin* focuses on new developments in colloid science that illustrate some areas of current active interest.

One area of particular effort recently is the use of colloidal particles as precursors in engineering new structures; this has been called colloid engineering and forms a major theme in this issue. Colloidal particles can be made with exquisite precision in their size. Furthermore, interparticle interactions can be precisely controlled through a combination of surface treatment, solvent choice, or the addition of other materials, such as nonadsorbing

polymers, that induce an effective interparticle attraction when excluded from the gap between neighboring particles; this is called the depletion interaction.

One of the most exciting areas of current colloid research is the use of this high degree of control to create new structures. Recent work has also focused on the use of other interactions and forces to modulate the behavior of the particles in order to gain further control over the nature of the structures produced. This has led to a new class of methods called "directed" assembly that represents variants on the self-assembly techniques that are so successful in colloid engineering. Recent developments in this field are summarized in the article by van Blaaderen that opens this issue. The author provides an interesting overview of the state of the field for different forms of directed assembly. He focuses primarily on the use of additional stresses to help direct self-assembly; these vary from the presence of a hard wall that restricts the states of the colloidal suspension to the application of relatively large forces by means of electric and magnetic fields, surface stresses induced by drying, order imposed by patterned surfaces, and gravitational effects. One is struck by the variety of interactions and the range of effects that can be harnessed to achieve such fine control of the structures that form.

Despite the tremendous advances in the use of other means to influence particle interactions and therefore the structures that form, one feature of colloidal particles has until very recently remained unchangeable: their shape. The typical shape of a colloidal particle can be qualitatively understood as resulting from the surface energy of the particle, which very strongly drives the interface to be spherical. This places fundamental limitations on the structures that can be built and the nature of the problems that can be addressed with colloidal particles. An important limitation comes in making photonic-bandgap structures.

Photonic-bandgap structures are to photons what semiconductors are to electrons; properly designed structures would have a band of wavelengths where photons would not propagate due to the interference effects of the ordered structure. However, it is becoming increasingly obvious that a complete photonic band will not be achieved in the visible wavelengths using the ordered structures that can be created with a single set of spherical particles. Of course, one way to circumvent this limitation is to mix particles of different sizes and create binary alloy crystal structures. However, in their article, Manoharan and Pine present some very elegant work that introduces a completely new method

of obtaining macroscopic quantities of nonspherical particles. These particles are formed from spherical particles whose local packing is controlled by encapsulating them in emulsion droplets that are then collapsed by drying. Intriguingly, such packings lead to well-defined and highly reproducible structures or clusters. The nature of such clusters is itself a challenging question, and the packing of these clusters into larger structures with long-range order offers an important opportunity to create completely new materials.

The interactions between colloidal particles also play a critical role in determining the overall structure of the suspension. Typically, very weak interactions are required to achieve ordered structures. This is because thermal energy allows particles to explore phase space and achieve the lowest-energy structure, which is often an ordered structure; thus, the thermalization of the particles in response to Brownian motion is essential to allowing them to self-assemble. As a result, interparticle interaction energies must typically be around  $k_B T$ , the thermal energy, to ensure that the particles can explore their phase space. However, the interparticle interaction energies are often far greater than  $k_B T$ . In this case, attractive interactions will drive the particles together to form local clusters, and these clusters can span space to form connected networks or colloidal gels. The structures that result are typically kinetically trapped and remain disordered indefinitely. Such structures are quite commonly encountered in technical applications of colloidal particles when attractive interactions drive the formation of extended structures. The behavior of these structures is not well understood.

Recently, however, applications of mode coupling theory to attractive interactions have provided considerable insight into this behavior, as summarized in the article by Poon. In the absence of attraction, increasing the volume fraction leads to a kinetic arrest that constrains Brownian motion and produces the hard-sphere colloidal glass transition at  $\phi_g \approx 0.58$ , where  $\phi_g$  is the glass volume fraction. Intriguingly, however, a very weak attraction can actually suppress the glass transition at volume fractions of  $\phi_g \approx 0.58$  or slightly higher, with a solid reemerging only at an even stronger attraction. Poon describes recent work investigating this behavior and discusses attempts to rationalize the behavior at all volume fractions and interaction energies within mode coupling theory. This approach may help describe a wide range of behaviors in concentrated colloidal suspensions.

Finally, since the control of the rheological properties of colloidal suspensions is so critical to their technological uses, it is also appropriate to review recent progress in our understanding of rheology. This is covered in the final article in the issue, by Wagner and Bender. Although dispersions generally flow easily at moderate solids fractions, the viscosity at low stresses necessarily diverges near transitions to the solidlike phases discussed by Poon. Under those conditions, simultaneous interactions among many particles create structures—the unit cell of a crystal or the cage of a glass—that transmit forces in a way that opposes large deformations. Thus, the immediate response is elastic; only on longer time scales might the structure relax and allow flow. Thus, one can employ a measurement of the short-time response,

in terms of a high-frequency elastic modulus, to estimate the strength and range of the interparticle potential. If, instead of gently shearing the dispersion, one applies a large stress, viscous forces can overwhelm the thermodynamic or interparticle forces and push the particles close together. Often this produces a reversible shear thickening, with the viscosity increasing sharply by an order of magnitude or more as the shear rate remains roughly constant. Wagner and Bender attribute this to the formation of clusters held together by viscous forces and estimate the onset from a simple balance between viscous and interparticle forces. Techniques that use devices such as the surface forces apparatus, atomic force microscopy with colloidal probes, and laser tweezers offer complementary means for measuring the interparticle forces directly. An understanding of such interactions is very useful in enabling full technological exploitation of concentrated colloidal suspensions.

Colloid science is one of the oldest topics of scientific investigation. Some historical perspective is described in van Blaaderen's article, focused mostly on the early part of the last century. However, colloid science dates back well before that: Faraday was studying colloidal gold in the mid-1800s. Today, significant progress continues to be made, and the potential applications and uses of colloidal particles continue to grow. Thus, this issue of *MRS Bulletin* should be viewed as only a snapshot summary of recent developments in colloid science. It seems highly likely that progress will continue at a rapid pace comparable to that of the last five years, clearly demonstrating the robustness of this field. □

**David A. Weitz**, Guest Editor for this issue of *MRS Bulletin*, is a professor of physics and applied physics in the Physics Department and in the Division of Engineering and Applied Sciences at Harvard University. His research interests are focused on experimental soft condensed-matter physics, and he has done extensive research in colloidal physics. Weitz received a PhD degree in physics from Harvard and then spent almost 18 years as a physicist at Exxon Re-

search and Engineering Co. He was a professor of physics at the University of Pennsylvania for nearly four years before joining the Harvard faculty in 1999.

Weitz can be reached at the Dept. of Physics and DEAS, Pierce 231, Harvard University, 29 Oxford St., Cambridge, MA 02138, USA; and by e-mail at [weitz@deas.harvard.edu](mailto:weitz@deas.harvard.edu).

**William B. Russel**, Guest Editor for this issue of *MRS Bulletin*, is a professor of chemical engineering and dean of

the graduate school at Princeton University. His research team has touched on a range of phenomena in colloidal dispersions and complex fluids, with the link between rheology and phase behavior, including the effects of soluble polymers, providing a continuing theme. Recent work has delved into cracking and other complications encountered in latex film formation and instabilities that generate novel sub-micrometer patterns in thin polymer films. He is a member of the



**David A. Weitz**

National Academy of Engineering and the American Academy of Arts and Sciences.

Russel can be reached at the Dept. of Chemical

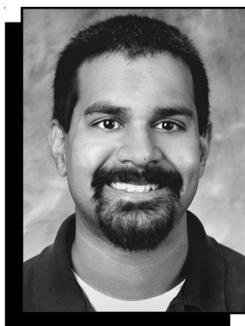


**William B. Russel**

Engineering, Room A-225, Princeton University, Princeton, NJ 08544, USA; and by e-mail at [wbrussel@princeton.edu](mailto:wbrussel@princeton.edu).



**Jonathan W. Bender**



**Vinothan N. Manoharan**



**David J. Pine**



**Wilson C.K. Poon**



**Alfons van Blaaderen**



**Norman J. Wagner**

**Jonathan W. Bender** is an assistant professor of chemical engineering at the University of South Carolina. His research interests are centered on metal and polymer nanotribology, contact mechanics and adhesion, rheology of colloidal suspensions, and lubrication by macromolecular solutions. He obtained his PhD degree in chemical engineering from the University of Delaware in 1995, focusing on the microstructural origins of shear thickening of colloidal suspensions. After industrial positions with Exxon Chemical Co. and Lord Corporation, he completed two postdoctoral positions in physics and materials science at North Carolina State University.

Bender can be reached at the Department of Chemical Engineering, Swearingen Research Center, University of South Carolina, Columbia,

SC 29208, USA; tel. 803-777-5025 and e-mail [benderjw@enr.sc.edu](mailto:benderjw@enr.sc.edu).

**Vinothan N. Manoharan** is a PhD student in chemical engineering at the University of California, Santa Barbara. His thesis research involves the fabrication of photonic crystals by colloidal self-assembly. Manoharan received his BSE degree in chemical engineering from Princeton University.

Manoharan can be reached by e-mail at [vinny@umail.ucsb.edu](mailto:vinny@umail.ucsb.edu).

**David J. Pine** is professor and chair of chemical engineering and a professor of materials at the University of California, Santa Barbara. His research interests encompass the structural, rheological, and optical properties of complex fluids, including colloidal suspensions, emulsions, surfactant solutions, and polymer solutions. He

received his PhD in physics from Cornell University and has held positions at the University of Pittsburgh, Haverford College, and Exxon Corporate Research Laboratories.

Pine can be reached at the Department of Chemical Engineering, University of California, Santa Barbara, CA 93106-5080, USA; tel. 805-893-7383 and e-mail [mrl.ucsb.edu](mailto:mrl.ucsb.edu).

**Wilson C.K. Poon** graduated in physics and theoretical physics from Cambridge University in 1984, where he stayed on to complete a PhD degree in 1988 on spectroscopic studies of mineralogical phase transitions. After lecturing for a year at Portsmouth Polytechnic, he moved to the University of Edinburgh in 1990 to continue his study of solid-state phase transformations. When Peter Pusey joined the faculty

in 1991, Poon joined him to set up a soft condensed-matter research effort, focusing on the study of model colloidal suspensions. Now, with Stefan Egelhaaf, the group uses a variety of experimental techniques (light, neutron and x-ray scattering, microscopy, and rheo-optics) to study phase behavior, dynamics, metastability, deformation, and flow in soft and biological matter, with strong collaboration with theorists and simulators led by Mike Cates.

Poon can be reached at the School of Physics, University of Edinburgh, JCMB, Kings Buildings, Mayfield Road, Edinburgh EH9 3JZ, Scotland; and by e-mail at [wckp@ph.ed.ac.uk](mailto:wckp@ph.ed.ac.uk).

**Alfons van Blaaderen** is a professor in the Department of Physics and Astronomy at Utrecht University and heads the Soft Condensed Matter group, together with Arnout Imhof and Marjolein Dijkstra, which is part of the Debye Institute. His research interests focus on the development and use of colloidal model systems in both fundamental and applied studies. Van Blaaderen obtained his PhD degree in physical chemistry in 1992 at Utrecht University. In 1992–1993, he worked as a postdoctoral researcher at Utrecht while also studying physics there. Subsequently, he worked for almost two years in a postdoctoral post at what was then AT&T Bell Laboratories (Murray Hill, N.J.) and is now part of Lucent Technologies. Before his appointment in the Department of Physics at Utrecht in 1999, he worked in the

Department of Chemistry as an associate professor and as group leader at the FOM Institute AMOLF (Amsterdam).

Van Blaaderen can be reached at Soft Condensed Matter, Dept. Physics & Astronomy, Debye Inst., Utrecht University, Princeton pl. 5, 3584 CC Utrecht, the Netherlands; e-mail [a.vanblaaderen@phys.uu.nl](mailto:a.vanblaaderen@phys.uu.nl) and Web site [www.colloid.nl](http://www.colloid.nl).

**Norman J. Wagner** leads an active research group in the field of rheology, complex fluids, particle technology, and nanotechnology in the Department of Chemical Engineering at the University of Delaware. His research areas include the effects of applied flow on the microstructure and material properties of colloidal dispersions, polymers, self-assembled surfactant solutions, and combinations thereof. Wagner was a senior Fulbright scholar at the University of Konstanz, Germany, and a guest professor at the ETH Zurich. His research is partly supported by the International Fine Particle Research Institute, and he is active in the Society of Rheology and the American Institute of Chemical Engineers (AIChE). He has delivered international keynote lectures and has taught many short courses on colloidal suspension rheology and particle science and engineering.

Wagner can be reached at the Center for Molecular and Engineering Thermodynamics, Dept. of Chemical Engineering, University of Delaware, Newark, DE 19715, USA; and by e-mail at [wagner@che.udel.edu](mailto:wagner@che.udel.edu). □