Perspective

New Vistas in Dispersion Science and Engineering

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Introduction

Dispersion science holds the key to cost-effective manufacturing of an unimaginably large number of chemicals and consumer products, be it polymeric latexes, paints, inks, coatings, cosmetics and lotions, pharmaceuticals, ceramics, foams, gels, or emulsions. Consider also that thin films of colloidal dispersions are spread on solid surfaces to build magnetic, light-sensitive tapes and disks. Nanostructured materials, such as color-shifting inks, solar cells, light emitting displays, and biochemical sensors are other examples of the principles of dispersion science at work. It is also apparent that the control of industrial processes ranging from sedimentation, flocculation, and coagulation to the manufacture of advanced self-assembled materials can be greatly improved by a sound understanding of the factors that affect the quality and stability of colloidal dispersions.

We can examine dispersions at three scales: a submicroscopic scale (1 nm to 100 nm) that encompasses nanoparticles or surfactant aggregates called micelles, a microscopic scale (1 μm to 100 μm) that characterizes the size of liquid droplets or bubbles in emulsion and foam systems, and a macroscopic scale. Visualizing at three scales is useful, because forces operating at the submicroscopic scale between colloidal particles usually govern the stability of both micro- and macrodispersions. In addition to the interactions between colloidal particles, the interaction between particles and the surfaces confining them also strongly influences the structure and stability of colloidal dispersions. This is particularly true of concentrated dispersions where particles are more likely to come in close contact with one another and tend to become more ordered in the confines of their restricted environment.

It is becoming apparent that it is time to move beyond the classical model of dispersion stability, i.e., the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, which is limited to dilute systems and systems consisting of ions and solvent molecules without size in the supporting fluid (Russel et al., 1991). Many real systems and nontraditional systems of technological importance comprise colloidal particles of various sizes and concentrations and are under various external fields and spatial confinements as discussed in recent *AIChE Journal* Perspectives (Texter and Tirrell, 2001; Abbott, 2001; Stone and Kim, 2001). In all these systems, non-DLVO forces arise due to many-body interactions. The advent of new instrumentation, such as the surface force apparatus and the thin film capillary force balance as well as atomic force microscopy and total internal reflection microscopy, has permitted observations and measurements of long-range oscillatory (i.e., non-DLVO) forces in colloidal systems containing surfactants, polymers, their mixtures, and other colloidal particles. Semi-empirical approaches and simple approximate expressions for the calculation of structural forces have also been proposed (Kralchevsky and Denkov, 1995; Trokhymchuk et al., 2001). More sophisticated mathematical tools such as Monte Carlo simulations and molecular dynamics (as discussed in a recent *AIChE Journal* Perspective (de Pablo and Escobedo, 2002)), the integral equation method of statistical mechanics (Henderson and Lozada-Cassou, 1986), and the density functional theory (Evans, 1992) can now be used to model structure formation and thermodynamic properties of colloidal dispersions.

Beyond the Classical Paradigm

The DLVO theory, which balances the repulsive electrostatic double layer and the attractive van der Waals forces between particles, has long been the basis for explaining the structure and stability of colloidal dispersions. However, direct force-distance measurements in fluids confined between two mica sheets in a surface force apparatus made by Horn and Israelachvili (1981) clearly showed that the interaction between two surfaces becomes oscillatory as the particle surfaces are brought together because of the finite size of the solvent molecules.

Furthermore, these authors showed that the interaction energy is more repulsive than that given by the DLVO theory, which treats the supporting fluid as a continuum consisting of ions and solvent molecules without size. Kekicheff and coinvestigators (Parker et al., 1992; Richetti and Kekicheff, 1992; Kekicheff and Richetti, 1992) were among the first to directly measure the oscillatory structural force (OSF) in confined supramolecular fluids (such as micellar solutions and microemulsions) using the surface force apparatus. Their measurements showed that the period of oscillation is the effective size of the supramolecule.

OSF becomes apparent when the colloidal particles are confined in the gap between two macroscopic surfaces. Figure 1 shows the interaction between two macroparticles in the presence of small particles. These small particles can be solvent molecules, ions, solute molecules, or other colloidal particles. When the separation distance (i.e., gap) between surfaces of two suspended macroscopic particles is of the order of several colloidal particle diameters, the colloidal particles, due to Brownian motion, interact with the macroscopic surface. The wall induces ordering among the particles and this ordering propagates over several particle diameters. In the case of a film, the structured regions near the two opposing surfaces overlap giving rise to an OSF. This long-range structure induces a repulsive structural barrier that helps prevent the large particles from flocculating or coalescing. When the separation distance between two macroscopic particles is smaller than the diameter of the colloidal particles (i.e., so that no small particles can fit in the gap between the large particles), a net attractive force/depletion force between the large particles is expected due to the osmotic pressure difference between the bulk and confined regions. In general, the effective interaction induced by the small particles between two large (macroscopic) particles is found to be oscillatory, including both the attractive depletion and the repulsive structural barrier.

When the concentration of small particles is high, the structural stabilization barrier is high. Consequently the dispersion is stable. When the concentration of colloidal particles is low, the stabilization barrier is much less than the attractive depletion well, which leads to flocculation. Since the range of the structural and depletion forces is of the order of several diameters of colloidal particles (5–100 nm), they operate over length scales far greater than the DLVO forces (<5 nm), and, therefore, have a stronger influence on dispersion stability. We present below some relevant examples to illustrate the concepts discussed above, and especially point the way for future possibilities for chemical engineers to apply the tools devised by colloid chemists, materials scientists, and physicists to nanoparticle engineering.

Some Relevant Examples

During the past ten years, our research group has worked on several problems of interest to industry in which structural forces in colloidal dispersions appear to play an important role in one way or another. We have used the dynamic process of stratification, or multilayer microstructuring, in submicron thin liquid films to probe the long-range structural interactions in concentrated colloidal dispersions (Wasan et al., 2002). The knowledge gained from these studies has been applied to solve problems of practical interest such as particle suspension stability, foam and emulsion stability, demulsification, antifoaming, and oily soil removal (i.e., detergency).

Thin colloidal films

A thinning liquid film withdrawn from a colloidal suspension is a simple model that demonstrates the role of OSF in the phenome-

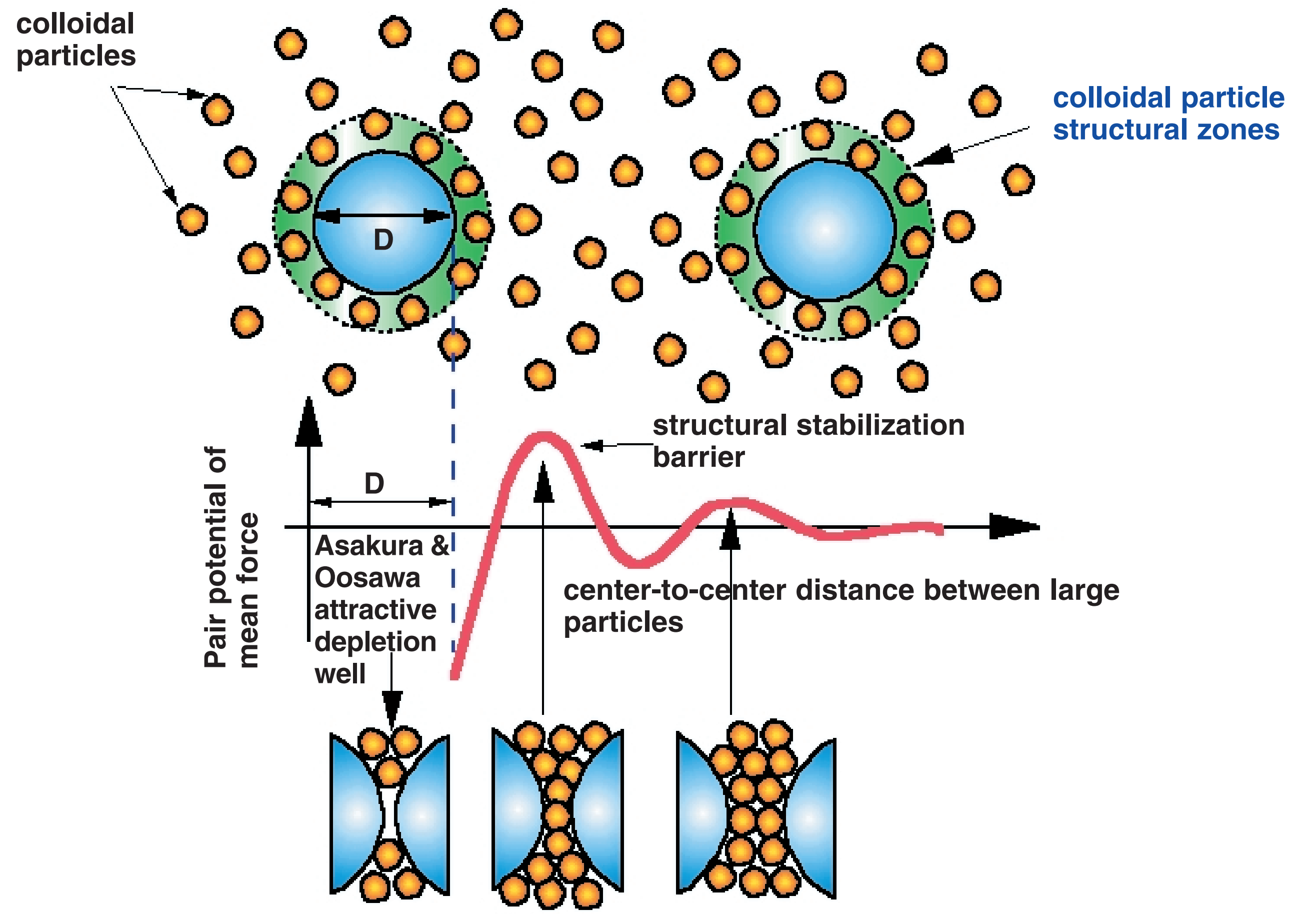

Figure 1. Structural force between two large particles immersed in colloidal suspension.

non of particle self-structuring in confined geometry (Wasan and Nikolov, 1999). Figure 2A depicts well-defined stripes (layers) of different colors in a vertical foam film formed from a monodispersed aqueous colloidal suspension of highly charged latex particles having a diameter of 156 nm. There are six to seven stripes seen in the figure. The stripes indicate that the film has a step-wise thickness profile (Figure 2B). Following the stripes, a sequence of diffuse, alternating green and red bands indicates a gradual change in film thickness (i.e., the film has a wedge profile) and the layered particle structure gradually becomes disordered. This figure also shows the diffraction patterns, which correspond to a predominantly two-dimensional (2-D) hexagonal packing structure (Figure 2C), which appears only at a film thickness corresponding to two- and one-particle layers. No such in-layer structure was observed for the film corresponding to three particle layers thick (Figure 2D). The practical implication of these results is that this colloid crystal-like, in-layer structure formation provides a structural barrier that prevents the coalescence of bubbles or droplets.

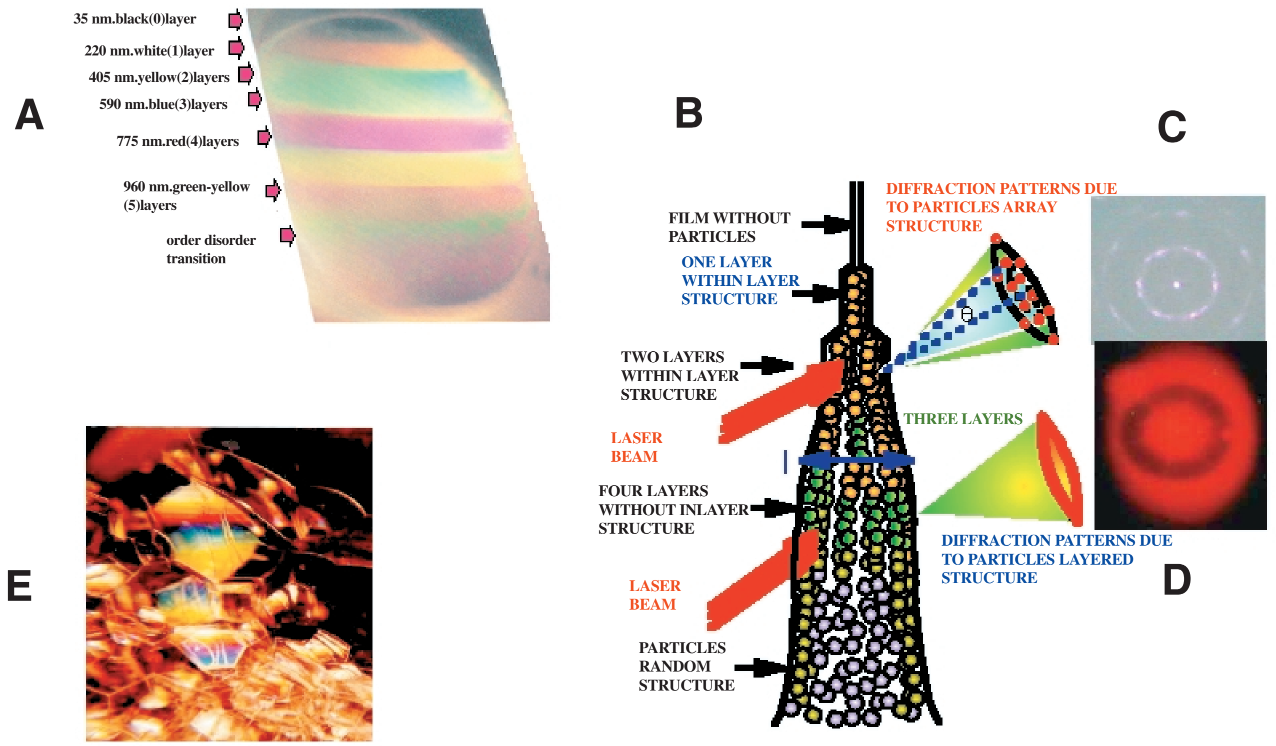

Figure 2. **(A) Well-defined stripes of different colors in a vertical foam film formed from 44 vol. % monodispersed latex suspension with 156-nm-dia.; (B) latex particle layering and structuring inside thinning vertical film; (C), (D) diffraction patterns revealing particle structural transition from layered to 2-D in-layer hexagonal packing; (E) capturing of foam lamellae with color stripes; foam generated from a solution of 20 vol. % silica particles with diameter of 19 nm.**

We investigated particle layering and in-layer structure formation in thin films, which consist of the plane surfaces with particles sandwiched between them, by theoretical modeling using Monte Carlo simulations (Chu et al., 1994). These results reveal that the particle density near the walls of the film is much higher than that in the bulk, and it is periodic in nature, the period of oscillation being equal to the diameter of the particle. The in-layer structure depends on particle concentration, as well as on the position of the layers in the film and on the film thickness. When the particle concentration is low, the particles inside a given layer pack randomly and form a liquid-like 2-D structure without order. As the particle concentration increases, a structural transition takes place from a liquid-like, in-layer structure to a colloid crystal-like, in-layer structure. In fact, at concentrations higher than 40 vol. %, a 2-D hexagonal structure within layers two particles thick was found, which is consistent with our light diffraction experiments for a foam film withdrawn from a 44 vol. % latex suspension (Figure 2C). In summary, the sequence of the particle structural transitions in a thin film of fixed thickness with increasing concentration is as follows: disorder → layering → in-layer ordering for surface layer → in-layer ordering for the middle layer → bulk type of ordering, i.e., Kirkwood-Adler transition. The structural disjoining pressure (i.e., the pressure exerted by small particles on the film surface) is oscillatory, and the period of oscillation is nearly the effective size of the particle. These theoretical findings on the OSF were independently confirmed by measurements in a foam film using the thin film balance technique (Bergeron and Radke, 1992). Below, we discuss the effects of OSF on the stability of micro- and macrodispersions, and the oily soil removal process (i.e., detergency).

Dispersion stability

The phenomena of particle layering and the in-layer colloid structure formation, for example, offer a novel colloidal stabilization mechanism for macrodispersions such as foams and emulsions. We have produced aqueous foams in surfactant-free particle suspensions using nanosized silica particles. We observed particle layering (i.e., stratification) in a real foam generated from a solution of 20 vol. % silica particles with diameters of 19 nm. The photograph (Figure 2E) clearly captures the multibanded pattern associated with stabilization of the curved foam lamella. The practical importance of film microstructuring is that the lifetime of foams and emulsions with stratifying films is much longer.

An important factor that affects the small particle structuring and layering phenomenon in confined films is the polydispersity in particle size. Polydispersity has a significant effect on the structural disjoining pressure. Studies have shown that a 20% polydispersity in particle size can decrease the structural barrier of the OSF by a factor of 3, while the effect on the depletion well is smaller (Chu et al., 1995, 1996a). This suggests that a simple way to destabilize a stable foam is to increase polydispersity of the suspension or simply add a small amount (e.g., 1 vol. %) of larger sized particles. The larger particles trapped inside the foam lamella weaken the structure of colloidal particles, decrease the OSF, and destabilize the foam lamella, reducing the foaminess (Bindal et al., 2002). This method was recently applied to develop a new antifoamer to suppress severe foaming in the radioactive waste vitrification process for immobilization of nuclear wastes at the Defense Processing Facility at the Savannah River Technology Center in Aiken, S.C (Lambert, 2000).

We have investigated the impact of OSF on the stability of concentrated food dispersions by using the Kossel diffraction technique (Xu et al., 1998). The effective potential of interaction between fat particles in the presence of caseinate micelles was determined from the measured structure factors. When low shear was applied to the emulsion, the casein particles appeared to form microlayers between fat particles, thereby improving dispersion stability. The emulsion was modeled using the integral equation method of statistical mechanics. The theoretical results verified the role of structural forces in stabilizing large particles (fat globules) by the small particles (casein micelles).

The addition of a nonadsorbing polymer has been known to destabilize a stable colloidal dispersion since the pioneering work of Asakura and Oosawa (1958), who identified this mechanism as a depletion force. In recent years, experiments carried out using a variety of colloidal systems have demonstrated the importance of a depletion force in destabilizing colloidal dispersions. However, there are very few studies that explore the role of both structural and depletion forces in stabilizing and destabilizing a given dispersion. Recently, the role of these oscillatory forces in a nearly hard-sphere binary mixture of large (330 nm) and small (38 nm) silica particles dispersed in a fluid medium has been investigated by measuring the sedimentation rates of large particles (2 vol. %) as a function of small particle concentration (Chu et al., 1996b; Xu et al., 1997). Results revealed that a low volume concentration of small particles (varying up to 30 vol. %) can destabilize larger particles due to the attractive depletion force leading to an increase in sedimentation rate. However, at higher concentrations of small particles (greater than 30 vol. %), the confinement-induced structural forces prevented large-sized particles from approaching each other, thereby stabilizing the large particle suspension, as evidenced by the much lower sedimentation rate. Davis et al. (1989) had also observed earlier that particles, particularly if they are small, form well-ordered (e.g., hexagonal) structures during sedimentation. These findings suggest that the ordering of small particles around larger ones can have an important effect on the dispersion's stability. Tohver et al. (2001) showed that it is possible to stabilize uncharged large colloidal particles by introducing highly charged nanoparticles into the system. The nanoparticles form a "halo" around each colloidal particle and the repulsion between the halos of each colloidal sphere stabilizes the suspension.

Oily soil removal and detergency

Soil remediation, oily soil removal (i.e., detergency), and enhanced oil recovery are some of the processes that require a better understanding of the spreading on solid surfaces of structured fluids containing colloidal particles such as surfactant micelles. Traditional understanding is that the presence of surfactants in the aqueous washing medium reduces the interfacial tension at the oil/water interface causing the three-phase contact line to move to restore the balance of forces. However, experimental data (Kao et al., 1988) exist that suggest "lifting up" of the oil is possible by structural forces arising due to the self-organization of nanosized surfactant micelles in the three phase contact region (i.e., the wedge film).

The figure on the cover shows the interference patterns produced from an oil droplet (of 10 μL) placed on a glass surface observed by reflected light using a differential microscope (Wasan and Nikolov, 2003). Parallel, regular, continuous lines depict the topology of the wedge film regions. This figure depicts the three-phase contact angle dynamics during the various stages of oil droplet removal from the glass in the presence of an aqueous anionic sodium lauryl sulfate micellar solution (40% effective volume or 0.1 mol/L).

The micellar solution seeps between the oil and the glass surface. The speckled band between the dark and light areas in this figure shows the formation of small water lenses (white spots encircled by dark fringes) between the oil and solid surface. In effect, two contact regions are established: the first, between the oil droplet, the solid surface and the aqueous surfactant solution (outer region), and the second, between the oil droplet, solid surface and the aqueous film with lenses (inner region). A prewetted aqueous film with lenses forms between the two regions. The thickness of the speckled band increases with time; the inner contact line recedes more rapidly than the outer contact line. Eventually, the oil droplet is separated completely from the solid surfaces by a thick aqueous film with a dimple. These observations clearly suggest a new mechanism of soil removal from solid surfaces using micellar fluids, where the structural disjoining pressure arising due to micelle ordering in the confined geometry of the wedge drives the aqueous film in the region between the inner and outer contact lines and the aqueous micellar solution spreads on the solid surface, detaching the oil drop.

To test the role of micellar interaction in the oil detachment process, a small amount of electrolyte (0.1 mol/L NaCl) was added to the same micellar fluid. However, the drop did not detach from the solid surface. This was unexpected because the interfacial tension in the oil-aqueous micellar solution interface decreases with added salt, and, as a result, the droplet shrinks. So according to the classical model, this reduction in tension should have enhanced the separation process. However, in fact what happens is that at high electrolyte concentrations, the effective micellar diameter, and, thereby, the micelle volume fraction, decrease due to the shrinkage of the electrical double layer around each micelle. Therefore, the magnitude of the OSF (i.e., the structural disjoining pressure) diminishes, thereby reducing the driving force for the detachment of the drop. OSF leading to the ordering of particles has implications in processes as diverse as the spreading of colloidal fluids on solids (Churaev et al., 2001) to building nanostructured materials on a solid surface (Aksay et al., 1996), and to the adhesion of living cells on surfaces.

Outlook

The previous examples illustrate the potential importance of OSF in particle ordering in bulk, as well as in confined colloidal systems. Although our understanding of OSF and particle self-assembly has increased greatly in the past few years, much more remains to be done. Colloidal suspensions are receiving increasing attention from scientists, because they are ideal systems for modeling various problems in statistical physics. Colloidal particles driven by Brownian motion, for example, rapidly sample their accessible configurational space and can be regarded as analog computers, which allow real-time simulation to model the processes of nucleation, crystallization, melting, freezing, etc. In addition, experimental studies on colloidal systems have provided a valuable understanding of the thermodynamic behavior underlying phase transitions (Hug et al., 1995). In a study of phase behavior of colloidal particles conducted in outer space, Cheng et al. (2001) found that in the absence of sedimentation and convection effects, particles tend to crystallize near the random close pack limit without the formation of a glassy phase.

Engineers have begun to extend the understanding of the fundamental issues of self-assembly to particles encountered in real-life by moving away from simple models like hard spheres and accounting for realistic interaction potentials between particles. Piech and Walz (2002) have performed calculations of the force of interaction between macrosurfaces immersed in a suspension of charged colloidal particles using an electrostatic repulsive potential. They found that the OSF calculated compared well with direct measurement of the force between the macrosurfaces. Trokhymchuk et al. (2002) have considered the case of a more concentrated dispersion of large particles and used a screened electrostatic interaction to represent the charged micelles (particles), which are commonly used surfactants.

Beyond understanding the essential role of OSF in stability of dispersions, the most important question before us is how to tailor particle interactions to engineer self-assembling nanomaterials. Colloidal suspensions are basic systems to assemble nanomaterials. To develop nanomaterials with desirable structural and optical characteristics, for example, suspensions of nanosized particles are spread on solid surfaces. Depending on the type of confined geometry—cylindrical, spherical, channel, slit, etc.—OSF will drive colloidal particles to self-assemble into different types of packing-linear, spiral, layer, 2-D cubic, 2-D hexagonal, etc. In this manner, it generates different types of particle structures (Whitesides and Grzybowski, 2002). The phenomenon of nanoparticle structure formation under confinement is of considerable interest in both science and technology (Vettiger and Binnig, 2003). The nature of OSF must be further explored to learn how to optimize interaction patterns of nanoparticles in order to engineer nanomaterials and devices such as quantum dots and quantum wires (Taton and Norris, 2002).

By combining OSF and external force fields, it is possible to manipulate particle structures. Pieranski (1980) was the first to combine external fields (capillary pressure and electrostatic force) to form a quasi-2-D colloidal system using charged polystyrene spheres at the water/air interface. Since then, many advances in the understanding of ordering phenomena of colloidal suspensions under the combined action of external fields and confinement have taken place (Trau et al., 1996; Zahn and Maret, 1999; Nikolaides et al., 2002).

Study of the ordering of colloidal particles in confined spaces is also relevant to understanding transport processes in micropores, used in industrial processes such as filtration (Shen et al., 1994) and the transport of water and ions through biomembranes (Crozier et al., 2001). Understanding the nature of OSF will point toward ways to enhance filtration. In membrane filtration of suspensions, the colloidal particle/particle interactions and colloidal particle/membrane surface interactions lead to a concentration-polarization effect, which reduces the rate of filtration (Petsev et al., 1993).

There is a complex interplay between hydrodynamic forces caused by the flow field and the tendency of particles to self-assemble. For instance, Bowen and Wilson (2002) show that in a colloidal fluid flowing through a cylindrical capillary, particles above a certain size tended to arrange themselves in a line away from the confining walls. Although the charge on the particles was expected to prevent their alignment at the wall, it was observed that the particle-free zone was orders of magnitude thicker than the Debye length of the solution. This suggests that while particles do tend to assemble for entropic reasons, there is no simple rule to predict their behavior especially in dynamic situations. Another illustration of this complexity comes from Wei et al. (2000) who demonstrated that normal Fickian diffusion rules do not apply in highly confined geometries even for particles as large as 3 μm. They used a magnetic field to study the movement of paramagnetic particles within the narrow confines of a circular trench and found strong deviation from Fickian law and an observance of what is called “single file diffusion”.

Microfluidic devices offer another example of the effect of confinement on behavior of colloidal fluids. Manipulating fluids that have networks of microchannels is crucial in the design and fabrication of microfluidic devices for applications in bioassays, microreactors, and chemical, medical, and biological sensing (Terray et al., 2002). Fluid surface and rheological properties, especially wetting and fluid structure, are changed significantly when system dimensions are reduced below submillimeter scales. For example, when a complex fluid, such as blood, flows into a capillary system, its rheology and wettability change as a result of the confinement structures. Further research on the topic of transport in confined geometries may improve our understanding of the processes involved in the movement of ions across biological membranes, as well as the movement of chemical species in molecular sieves. Knowledge of the role of OSF in complex fluid structuring and wetting will help improve the functionality of microfluidic devices.

We have merely scratched the surface when it comes to applying the concepts of particle layering or self-assembly to understanding processes like crystallization, filtration and sedimentation or to building materials of desired structural and optical properties. As we obtain a deeper understanding of the forces involved in arranging colloidal particles, the opportunities for chemical engineers to apply those results multiply.

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