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W. B. Russel, D. A. Saville and W. R. Schowalter
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A SURVEY OF COLLOIDAL DISPERSIONS

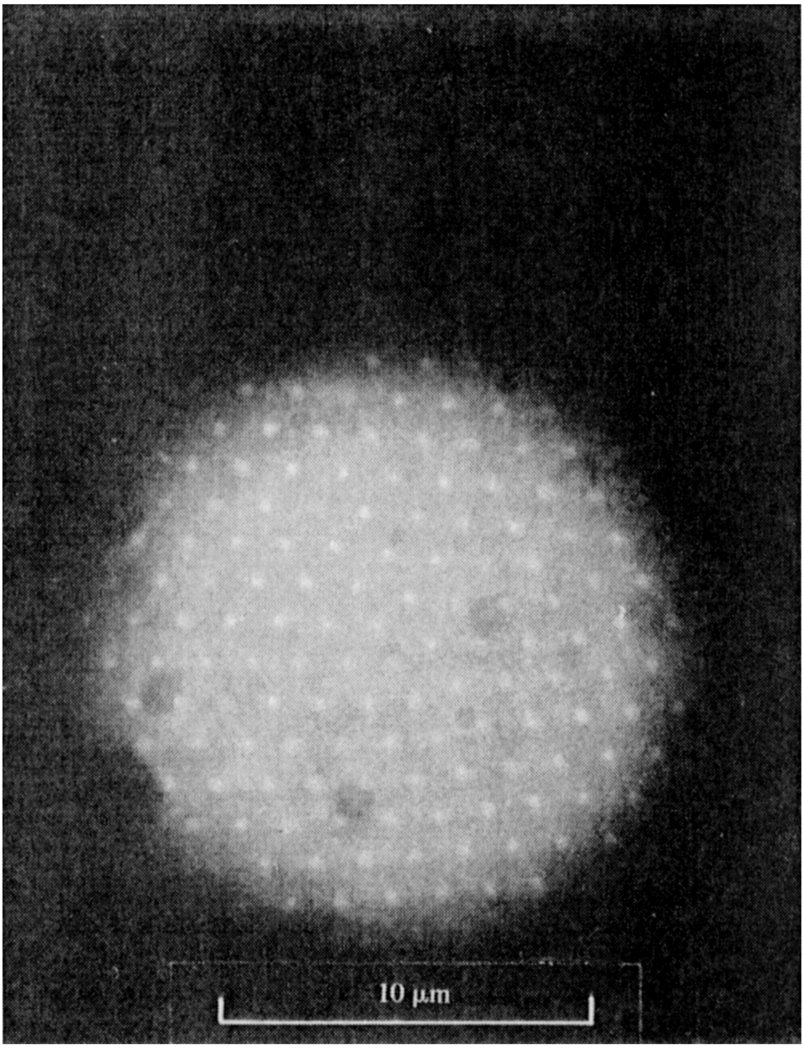
1.1 Colloidal phenomena

Colloidal particles dispersed in liquids exhibit astonishing properties. Dispersions such as the colloidal gold sol prepared by Faraday (1791–1867) over a century ago can persist almost indefinitely, yet the addition of salt would cause rapid, irreversible flocculation. In fact, for many dispersions the physical state, i.e. the stability or phase behavior, can be altered dramatically by modest changes in composition. This complex behavior stems from the different forces that act among the particles, determining their spatial distribution and governing the dynamics. Brownian motion and dispersion forces (arising from London–van der Waals attraction) would flocculate Faraday's gold sol were it not for electrostatic repulsion between the particles. The addition of salt increases the concentration of ions screening the surface charge, suppressing repulsion and allowing flocculation. Doublets and more complicated structures formed during flocculation have long lifetimes, since Brownian motion is too weak to overcome the strong attractive force between particles near contact. Indeed, removal of the salt does not usually lead to spontaneous redispersion, so mechanical means must be used.

Another type of transformation occurs when ions are removed from electrostatically stabilized systems. Polymer latices in an electrolyte solution are milky-white fluids, but dialysis eliminates the ions and leads to iridescence owing to Bragg diffraction of visible light from an ordered structure (Fig. 1.1). Here the absence of screening allows long-range electrostatic repulsion to induce a disorder–order phase transition. Colloidal crystals contain defects and dislocations which permit flow as ordered structures at finite, but low, shear stresses. At higher stresses they melt and exhibit shear thinning (Rothen *et al.*, 1987).

Colloidal dispersions also exhibit a reversible phase transition in the presence of non-adsorbing polymer. Adding sodium polyacrylate to a suspension of polystyrene spheres, for example, causes particles to attract one another owing to osmotic pressure differences. The simplest explanation is that polymer molecules are excluded from the region between

Fig. 1.1. Micrograph of the ordered structure in a deionized polystyrene latex. The particles are 0.33 μm in diameter and the volume fraction of particles is 0.01. (From Kose *et al.*, 1973.)



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particles by steric effects, so the pressure is lower in the gap than on the portions of the particles accessible to the bulk solution. The osmotic pressure difference can cause the suspension to separate into a dense, ordered phase and a dilute, disordered phase (Fig. 1.2). Such equilibrium mixtures resemble those encountered with molecular fluids.

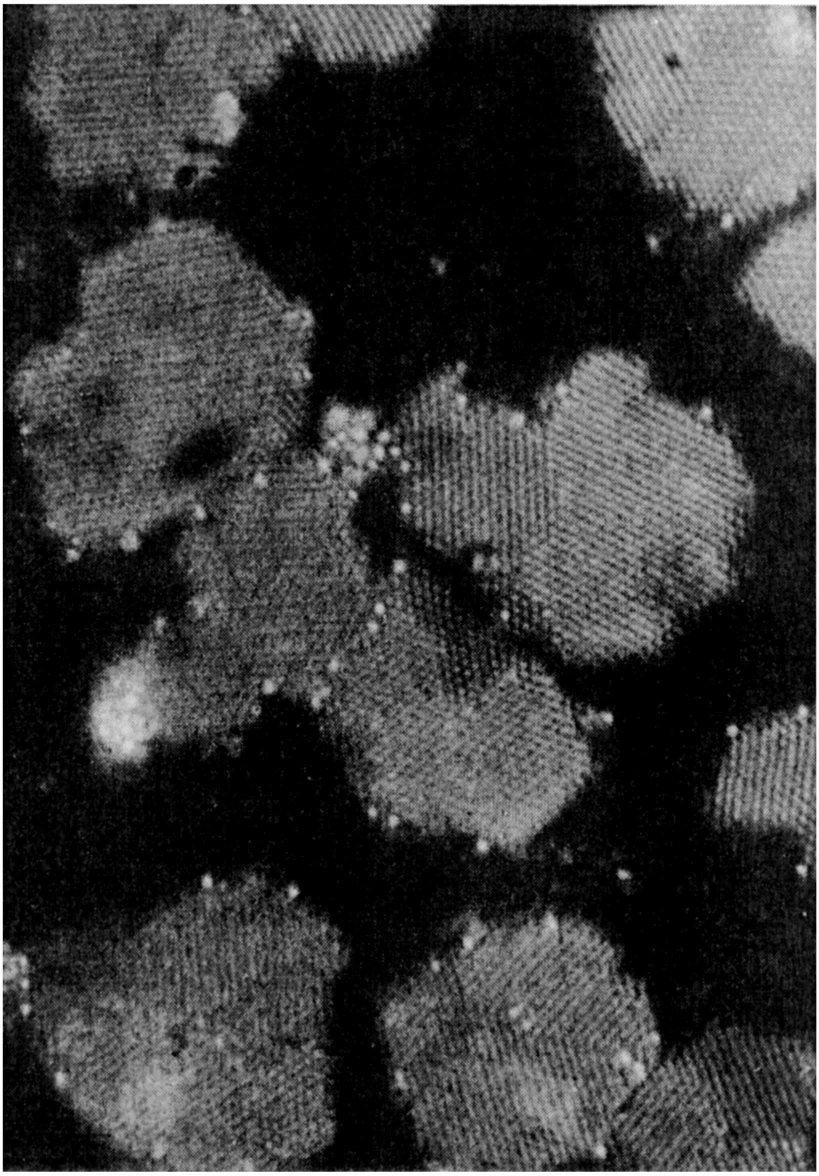
Colloidal systems display complex rheological behavior related to their thermodynamic non-ideality but do not show the substantial elastic recovery characteristic of polymeric liquids. Macromolecules recover from extensions several times their equilibrium dimensions, making polymer solutions very elastic. The relatively short range of interparticle forces precludes such behavior with colloidal dispersions. Dilute and moderately concentrated stable dispersions behave like low-viscosity liquids at low shear rates and may exhibit shear thinning. Changing the relative magnitudes of colloidal forces has dramatic effects. With aqueous latices, for example, lowering the ionic strength may increase the viscosity substantially as electrostatic repulsion comes into play. Alternatively, flocculated sols assume disordered structures which deform elastically under small strains, but fracture at higher strains and flow like liquids. Concentrated dispersions stabilized either electrostatically or polymerically form ordered layers under shear, and, at a critical shear stress, undergo an order–disorder transition as illustrated in Fig. 1.3. Each of these rheological properties stems from the interparticle forces responsible for the different types of phase behavior, with the added influence of hydrodynamic forces.

Sedimentation and Brownian motion of colloidal particles also reflect the balance of interparticle and hydrodynamic forces. Settling experiments produce states ranging from dilute random dispersions to dense sediments. The cover illustration depicts the sedimentation of silica particles in cyclohexane, showing five distinct regions:

clear fluid at the top;
a region of particles settling at the initial, dilute concentration;
a dense, disordered region of particles still settling freely;
an iridescent, ordered region; and
an opaque, disordered sediment.

This complex behavior reflects a combination of kinematic processes stemming from the concentration dependence of the settling velocity and thermodynamic factors responsible for the order–disorder transition. Brownian motion is equally sensitive to interparticle forces, but the effects are more subtle. For example, in an electrostatically stabilized system, the

Fig. 1.2. An equilibrium two-phase structure formed in a polystyrene latex with 0.000 37 per cent (by weight) sodium polyacrylate. Particle diameter is 0.33 μm. (From Kose & Hachisu, 1976.)



mutual-diffusion coefficient increases rapidly as the ionic strength is lowered, but the self-diffusion coefficient decreases. Both effects can be measured accurately by photon correlation spectroscopy.

Electric and magnetic fields affect dispersions in various ways. When the particles are charged, externally applied electric fields move them relative to the fluid (electrophoresis). From this motion the net electric charge on a particle can be ascertained. Electrophoresis can also be used to separate particles via the relative motion between particles of different charge. Another illustration is furnished by the behavior of ferrofluids, colloidal magnetic particles dispersed in a liquid. Magnetic fields alter the rheology of such dispersions and induce labyrinth-like patterns (Fig. 1.4).

Interactions between colloidal particles and macroscopic bodies are also governed to a large degree by colloidal forces. Small particles moving past a larger object are influenced by both electrostatic and dispersion forces, and the fate of individual particles is controlled by the delicate balance between viscous and interparticle forces. Striking configurations are possible, as illustrated in Fig. 1.5.

Our understanding of colloid dynamics and phase behavior is based largely on knowledge of the behavior of individual particles, either in

Fig. 1.3. Diffraction patterns from monodisperse suspensions in simple shear between parallel discs (Hoffman, 1972). The photograph on the left shows the diffraction of white light from an ordered structure below the critical shear stress; the other photograph shows the pattern above the critical shear stress.

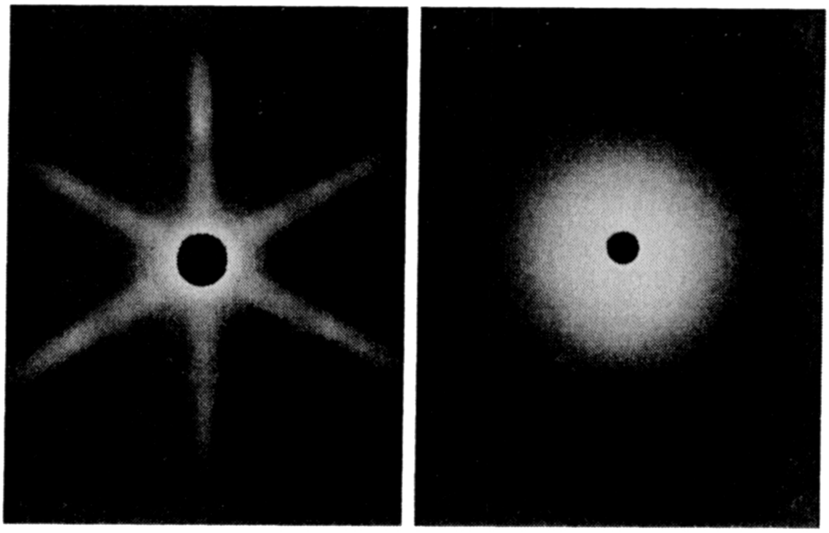


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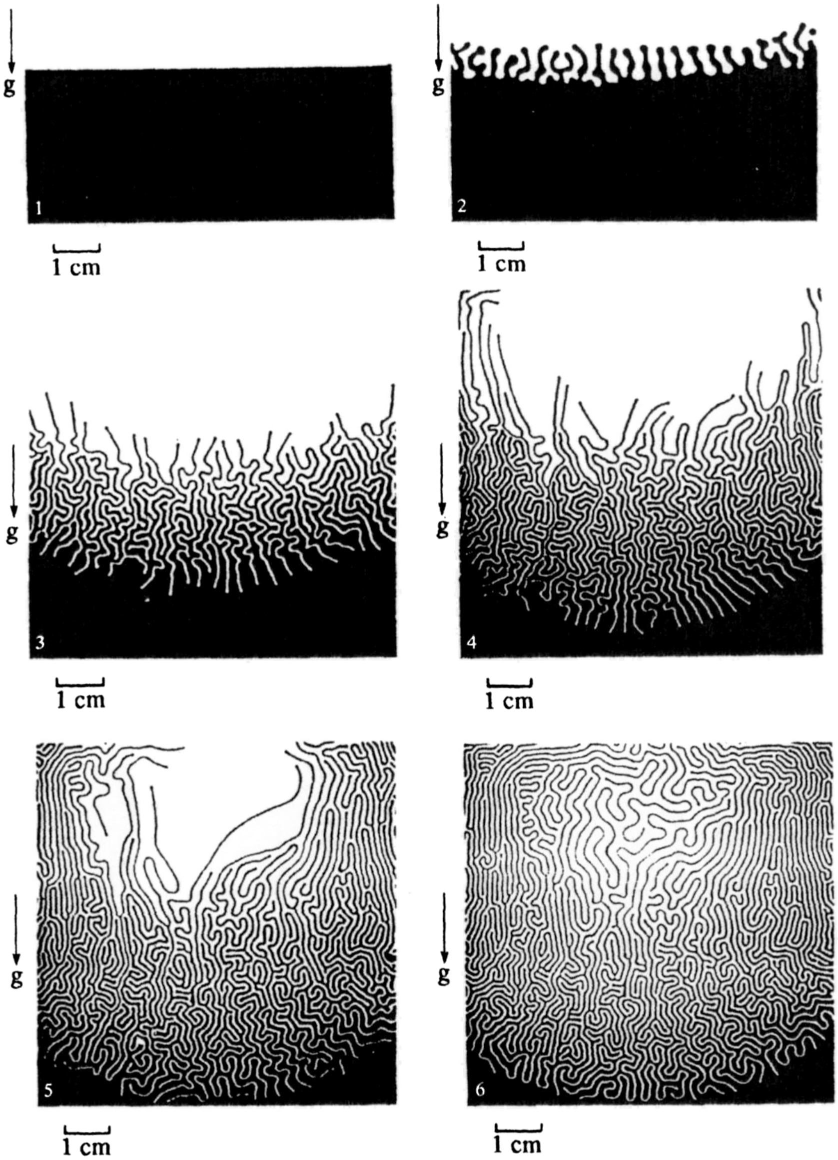
Fig. 1.4. Photographs of a labyrinthine instability developed by a magnetic field acting perpendicular to a thin vertical layer of ferrofluid. The field intensity increases from left to right. (From Rosensweig, 1985.)



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isolation or interacting with others in a pairwise manner. In the chapters that follow the salient features of those phenomena are set out and then integrated into a broad theory of colloidal behavior. To establish a context, the historical foundations are reviewed next, followed by a discussion of the general character of colloidal forces.

1.2 Historical notes

In his 1861 paper, 'Liquid Diffusion Applied to Analysis', Thomas Graham (1805–69) described two classes of matter, crystalloids and colloids. This classification differentiated between substances that would diffuse through a membrane separating water from an aqueous solution (crystalloids), and those which would not (colloids).[†] The crystalloid class included salt, sugar, and other substances that crystallize, while albumin, gum arabic, gelatin, and the like belonged to the colloid class. Graham also described how to disperse normally insoluble substances by a method called dialysis. Prussian blue, which is soluble in oxalic acid but insoluble in water, is an example of such a material. During dialysis with Prussian Blue, oxalic acid is replaced by water moving through the membrane, yet the

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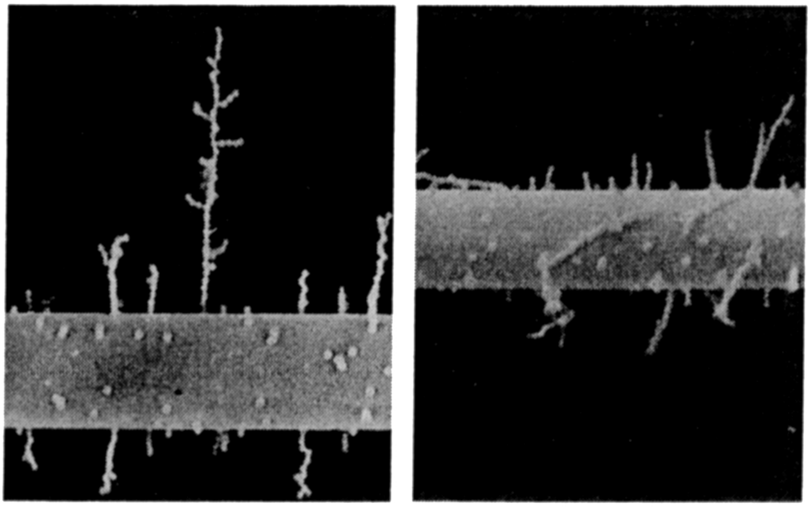
[†] From the Greek κόλλα, meaning glue.

Fig. 1.5. Dendritic structures built up of 1 μm polystyrene spheres stacked on a 20 μm nylon fiber. The particles were collected from an aerosol using a strong transverse electric field and are held in place by the strength of the dispersion force at close separations. (From Oak, Lamb, & Saville, 1985.)



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solution remains clear. Graham coined the term sol for the substance that did not dialyze.

Although Graham's techniques were original, colloids had been observed and studied much earlier. Seventeenth-century alchemists produced sols by treating gold chloride solutions with reducing agents and Berzelius (1779–1848) studied silicic acid, sulfur, and metallic sulfides. One of the most important observations was Faraday's discovery that small particles could be detected by focusing light into a conical region. This led to the development of the ultramicroscope by Zsigmondy & Siedentopf in 1903. Studies with this instrument probed the nature of the erratic motion of individual particles first observed by Robert Brown (1773–1858) and ascribed to the impact of molecules of the suspending medium. The molecular basis of the motion was settled when Perrin (1870–1942) summarized extensive observations in his book *Brownian Movement and Molecular Reality* (1910). The supporting theory was presented almost simultaneously by Einstein (1879–1955), who analyzed the sedimentation–diffusion equilibrium (Einstein, 1906) and Langevin (1872–1946), who treated the dynamics (Langevin, 1908).

The discovery that naturally occurring colloidal particles were charged dates to an 1809 study by Reuss, who noted the motion of clay particles in an electric field. Linder and Picton found in 1892 that synthetic sols of sulfur, ferrocyanides, gold, silver, or platinum are negatively charged, while oxide sols of iron, chromium, aluminium, and cerium are positive. The role of added electrolytes in suppressing the effects of charge and promoting flocculation was elucidated by Schultz (1882) and Hardy (1900). Their work provided strong evidence that the stability of aqueous dispersions derived from electrostatic repulsion. Nevertheless, no theory existed to describe the screened repulsion or relate the particle's charge to its mobility in an electric field, even though Helmholtz (1821–94) had already formulated his model of the molecular condenser. His analysis of the movement of liquid through a capillary under the action of an electric field introduced the notion of the ζ-potential to describe the electrostatic state of a surface (Helmholtz, 1879). Smoluchowski (1872–1917) derived his celebrated formula relating the ζ-potential to the electrophoretic mobility (Smoluchowski, 1903) by recognizing the similarity between the motion produced by an external electric field acting on a small particle (electrophoresis) and on a liquid in a capillary (electro-osmosis). As a result, the ζ-potential could be measured by timing the motion of a particle viewed through a microscope. Though the electric charge could be estimated, the effect of electrolyte on the double-layer thickness was still not understood.

The theory of screening of the surface charge by the diffuse charge cloud was developed by Gouy (1910) and Chapman (1913), thereby relating the thickness of the layer to the ionic strength of the solution.

After it was known that dispersions could be flocculated by screening the electrostatic repulsion with excess electrolyte, Smoluchowski (1917) deduced expressions for the rate of formation of small aggregates by Brownian and shear-induced collisions. However, the structure of the attractive interparticle potential was unknown until de Boer (1936) and Hamaker (1937) developed a theory based on pairwise summation of the intermolecular forces. Representing the total interparticle potential as the sum of the attractive and repulsive components then led to a detailed theory of colloid stability. Activity within several groups culminated in the theory published by Derjaguin & Landau (1941) in the Soviet Union and Verwey & Overbeek (1948) in the Netherlands.

1.3 Recent developments

Progress in colloid science has been stimulated by several important developments since the early 1950s, beginning with the synthesis of model colloids (Vanderhoff *et al.*, 1956).[†] Highly monodisperse latices with diameters of 0.05–3.0 μm can be formed of various polymers by emulsion polymerization. Inorganic dispersions made from hydrous metal oxides (Matijevic, 1976) and silica particles (Iler, 1979) provide a variety of particle types and shapes. Consequently, complications due to polydispersity are avoided and theories can be tested cleanly. Particle size analysis has been speeded immensely through easy access to scanning electron microscopes; see Fig. 1.6.

Another key development has been the direct measurement of interaction forces. Early efforts by Derjaguin *et al.* (1954) and Overbeek & Sparnaay (1954) were limited by the roughness of the fused quartz and polished glass surfaces employed. Tabor & Winterton (1969) recognized that cleaved muscovite mica provides a molecularly smooth surface, and this increased the accuracy of the measurement considerably. Later work by Israelachvili & Tabor (1973) produced a greatly improved instrument, leading to measurements that resolve events on the scale of a nanometer or so using crossed cylinders covered with mica sheets. The experimental results using this device and independent measurements on lipid bilayers (LeNeveu, Rand & Parsegian, 1976) have confirmed both the attractive

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[†] See Vanderhoff (1964), *Preprint, Div. of Organic Coatings and Plastics Chemistry* 24 (2) 223–32, for an account of the almost accidental discovery of monodisperse latex dispersions.

and the repulsive interactions, as well as revealing complex structural forces at separations comparable to molecular dimensions (see Israelachvili, 1985).

A deeper theoretical understanding of attractive forces emerged during the same period. Early theories based on the assumption of pairwise additivity failed to account for many-body interactions important in condensed phases. Lifshitz (1955) resolved the problem by developing a continuum theory in which materials were characterized by their dielectric

Fig. 1.6. Ordered arrays formed from filtered latex suspensions. (Photo from Interfacial Dynamics Corporation, Portland, Oregon.)