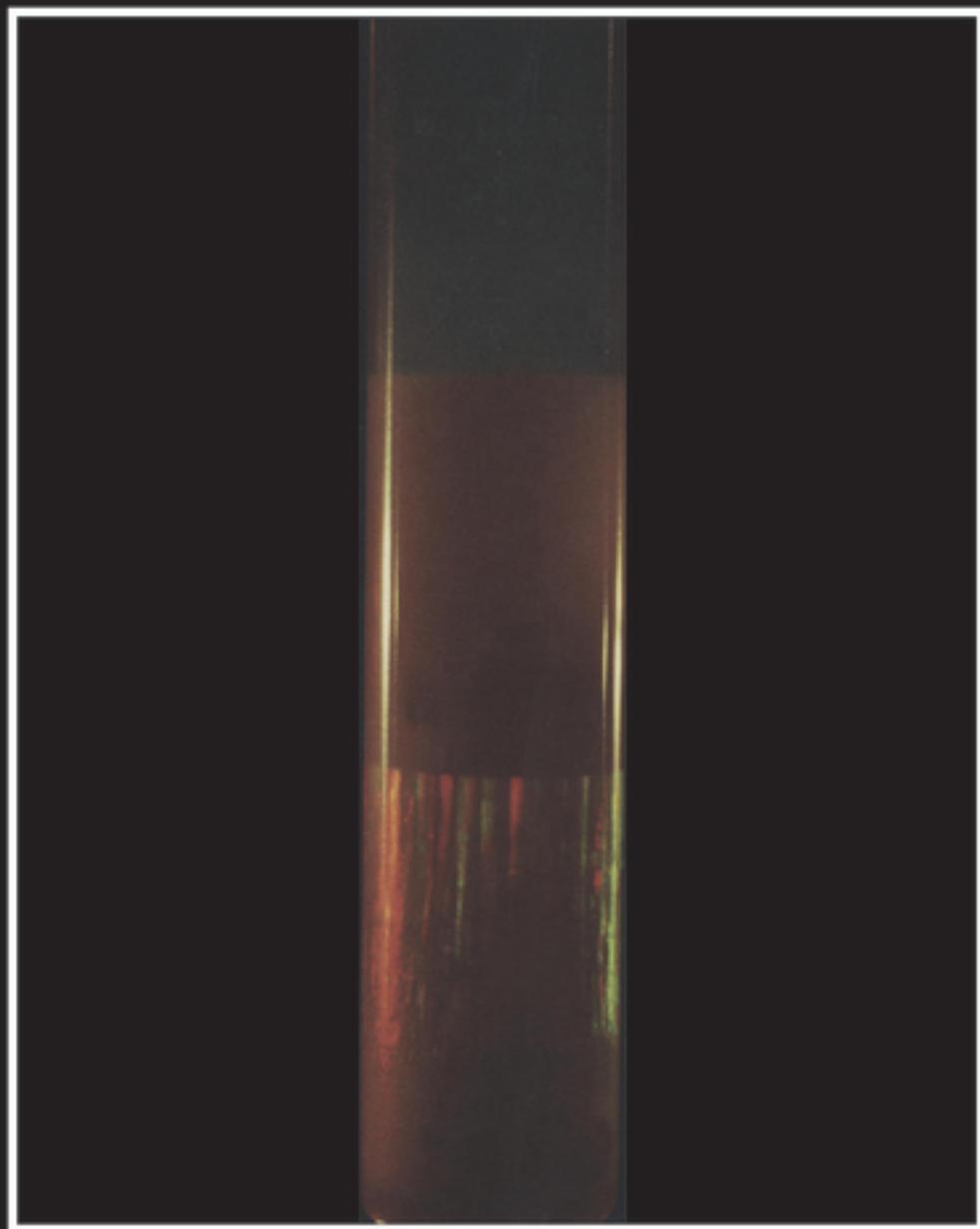


Colloidal Dispersions

W.B.RUSSEL, D.A.SAVILLE and W.R.SCHOWALTER



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Professor of Fluid Dynamics at the University of Cambridge

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To Priscilla, Joy, and Jane

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PREFACE

Colloid science has its roots in nineteenth- and early twentieth-century discoveries concerning the behavior of minute particles. Its early development was stimulated by controversies regarding the very existence of molecules. Scientific interest, along with technological and biological applications, fostered several definitive monographs and textbooks in the 1930s and 1940s. However, interest in the field declined within many academic circles after the Second World War, especially in the United States, despite continued and widespread industrial applications. The resurgence of interest that began in the early 1960s arose from mutually reinforcing events. New technological problems appeared in, for example, the manufacture of synthetic dispersions for coatings, enhanced oil recovery, the development of new fuels, environmental pollution, ceramics fabrication, corrosion phenomena, biotechnology, and separations processes. In addition, monodisperse suspensions of colloidal particles of diverse sorts became readily available and advances in our understanding of fluid mechanics on the colloidal scale burgeoned almost simultaneously. Further stimuli were provided by the appreciation by colloid scientists of advances in the theory of interparticle forces coupled with the development of several new experimental techniques. Forces and particle properties have long been difficult to measure accurately on the colloidal scale and numerical values were often the result of a long uncertain chain of inference. The new techniques made possible direct, accurate measurements of size, shape, and concentration, as well as the attractive and repulsive forces between surfaces separated by a few nanometers. The advancements made over the last thirty years convinced us of the need for a broad synthesis,

integrating recent discoveries with those of earlier times so as to treat dynamic as well as equilibrium properties of dispersions.

This book addresses the physical side of colloid science; the subjects range from the individual forces acting between submicron particles suspended in a liquid through the equilibrium and dynamic properties of the dispersion. The relevant forces include Brownian motion, electrostatic repulsion, attraction due to dispersion forces, attraction and repulsion caused by soluble polymers, and viscous forces arising from relative motion between the particles and the liquid. The balance between Brownian motion and the interparticle forces decides issues concerning stability and phase behavior in quiescent systems. Imposition of external fields alters the structure to produce complex effects, i.e., electrokinetic phenomena (electric field), sedimentation (gravitational field), diffusion (concentration/chemical potential gradient), and non-Newtonian rheology (shear field).

Our aim is to impart a quantitative understanding grounded in basic theory and coupled to experiments on well-characterized model systems. This provides the broad grasp of fundamentals which lends insight and helps develop the intuitive sense needed to isolate essential features of scientific and technological problems and to design critical experiments. The book is suitable both as a text for an advanced graduate course in chemical engineering, physical chemistry, physics, or applied mathematics, and as a reference for those doing industrial or academic research. Most of the material is accessible to those with a basic knowledge of mechanics and mathematics. Although exposure to fluid mechanics, statistical mechanics, and electricity and magnetism is assumed, the subjects in the book are introduced in a self-contained manner. Likewise, some facility with differential equations and vectors and tensors is required. Those interested in probing further can deepen their understanding by referring to the original works cited herein.

The book developed from complementary research interests among the authors, fostered initially by general grants from the Dreyfus and Xerox Foundations. This led to an advanced graduate course, first taught at Princeton in 1978 and now offered in alternate years. The writing began in earnest during WBR's tenure as the Olaf A. Hougen Professor in the Department of Chemical Engineering at the University of Wisconsin in 1984.

We are indebted to our students for their contributions, some of which appear explicitly in the text, as well as the interactions which advanced our understanding of the subject. In addition, we acknowledge the critical

reading and constructive comments on portions of the text by Chip Zukoski and Alice Gast. Finally, we thank Elizabeth B. Bixby for her ability to deal with what appeared to be an endless sequence of revisions; her threats of divine retribution helped make the process convergent.

W.B.R., D.A.S., W.R.S.
Princeton, September 1988

UNITS AND PHYSICAL CONSTANTS

The International Metric System ('SI', from the French, *Système Internationale d'Units*) used here employs the following base units:

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Amount	mole	mol
Electric current	ampere	A

The units derived from this set are:

Quantity	Unit	Symbol	Definition
Force	newton	N	1 kg m s^{-2}
Pressure	pascal	Pa	$1 \text{ kg m}^{-1} \text{ s}^{-2}$
Energy	joule	J	$1 \text{ kg m}^2 \text{ s}^{-2}$
Electric charge	coulomb	C	1 s A
Electric potential	volt	V	$1 \text{ kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$
Frequency	hertz	Hz	$2\pi \text{ rad s}^{-1}$
Capacitance	farad	F	$1 \text{ kg}^{-1} \text{ m}^{-2} \text{ s}^4 \text{ A}^2$

Of course the units of the derived quantities can be expressed in terms of one another, e.g.,

$$1 \text{ F} = 1 \text{ C/V.}$$

The fundamental laws involve a number of physical constants. Those used here are:

Constant	Symbol	Numerical value
Avogadro's constant	N_A	6.02552×10^{23} molecules/mole
Boltzmann's constant	k	1.38054×10^{-23} J/K
Magnitude of charge on an electron	e	1.60210×10^{-19} C
Permittivity of the vacuum	ϵ_0	8.854×10^{-12} C ² /N m ²
Planck's constant	$2\pi\hbar$	6.6256×10^{-34} J s
Speed of light	c	2.9979×10^8 m/s

Miscellaneous conversion factors

Standard acceleration due to gravity, g	9.8066 m/s ²
Atmospheric pressure	1.01325×10^5 Pa
kT/e at 298.16 K	25.69×10^{-3} V
1 molar solution, M	1 mol/(dm) ³
1 liter	1.0000028×10^{-3} m ³

Prefixes

Meters, kilograms, seconds and the like are not always convenient scales but various multiples are. The commonly used scale factors are listed below:

kilo,k	hecto,h	deca,da	deci,d	centi,c	milli,m	micro, μ	nano,n
10^3	10^2	10	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}

MATHEMATICAL SYMBOLS

The mathematical symbols denoting constants and variables of one sort or another are defined in the text at their point of introduction. Symbols used in equations are defined as follows:

Symbol	Meaning
\equiv	is identical to
$=$	is equal to
\sim	is asymptotically equal to (in some limit)
\approx	is approximately equal to
\leq	is less than or equal to
\ll	is much less than
\rightarrow	tends to
$f=O(\varepsilon)$	limit $f/\varepsilon < \infty$ as $\varepsilon \rightarrow 0$
$f=o(\varepsilon)$	limit $f/\varepsilon = 0$ as $\varepsilon \rightarrow 0$

1

A SURVEY OF COLLOIDAL DISPERSIONS

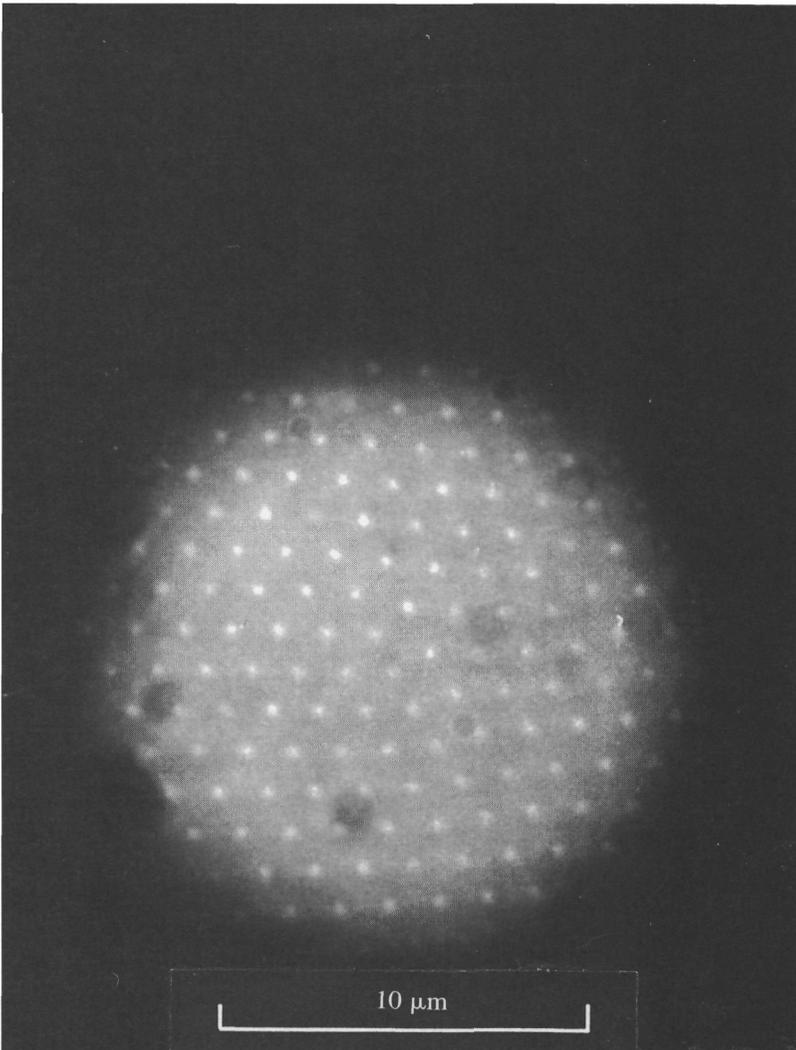
1.1 Colloidal phenomena

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 $0.33\ \mu\text{m}$ in diameter and the volume fraction of particles is 0.01. (From Kose *et al.*, 1973.)



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.

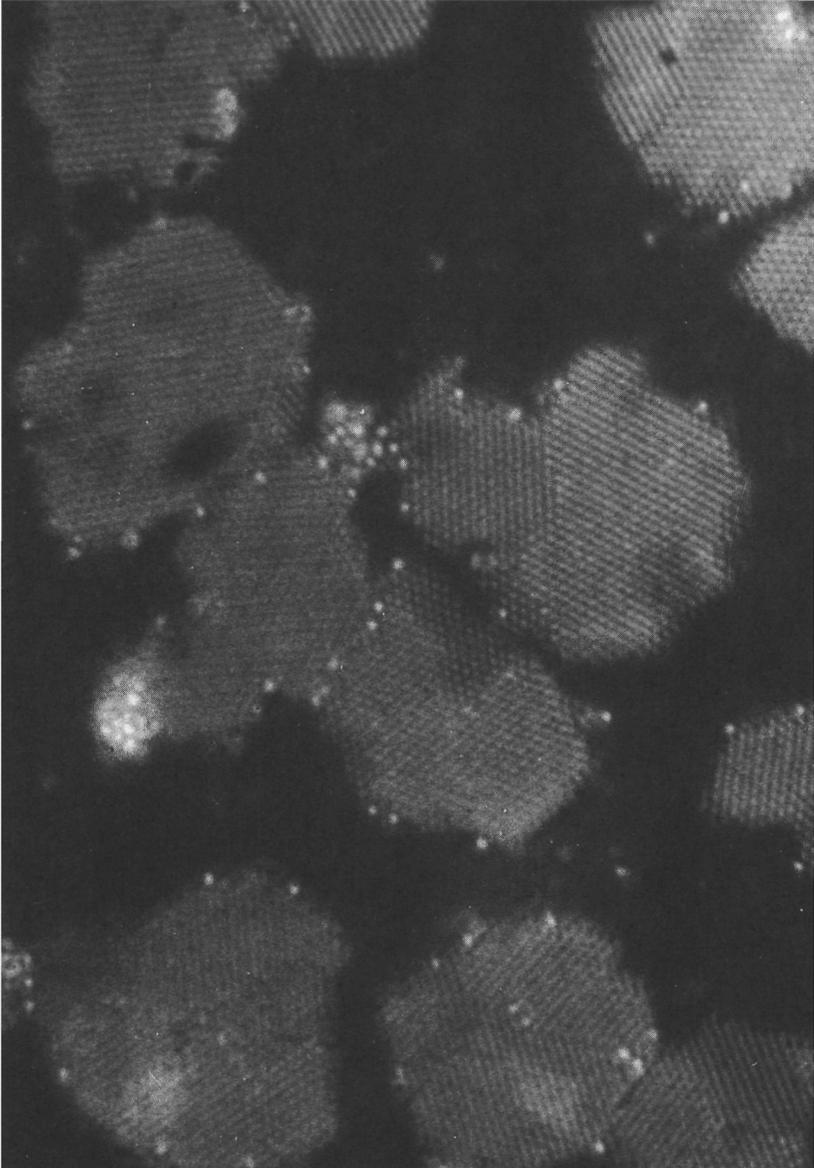
Sedimentation and Brownian motion of colloidal particles also reflect the balance of interparticle and hydrodynamic forces. Settling experiments produce states ranging from dilute random dispersions to dense sediments. The cover illustration depicts the sedimentation of silica particles in cyclohexane,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

4 *Colloidal dispersions*

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 $0.33\ \mu\text{m}$. (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.

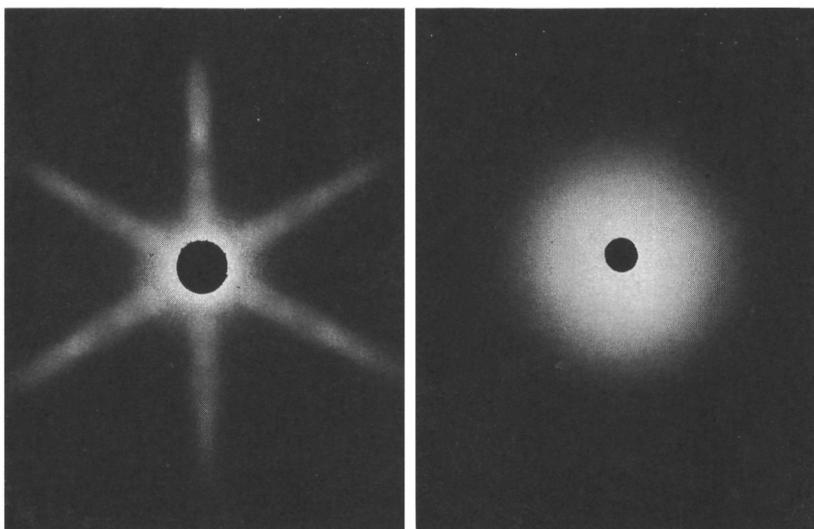
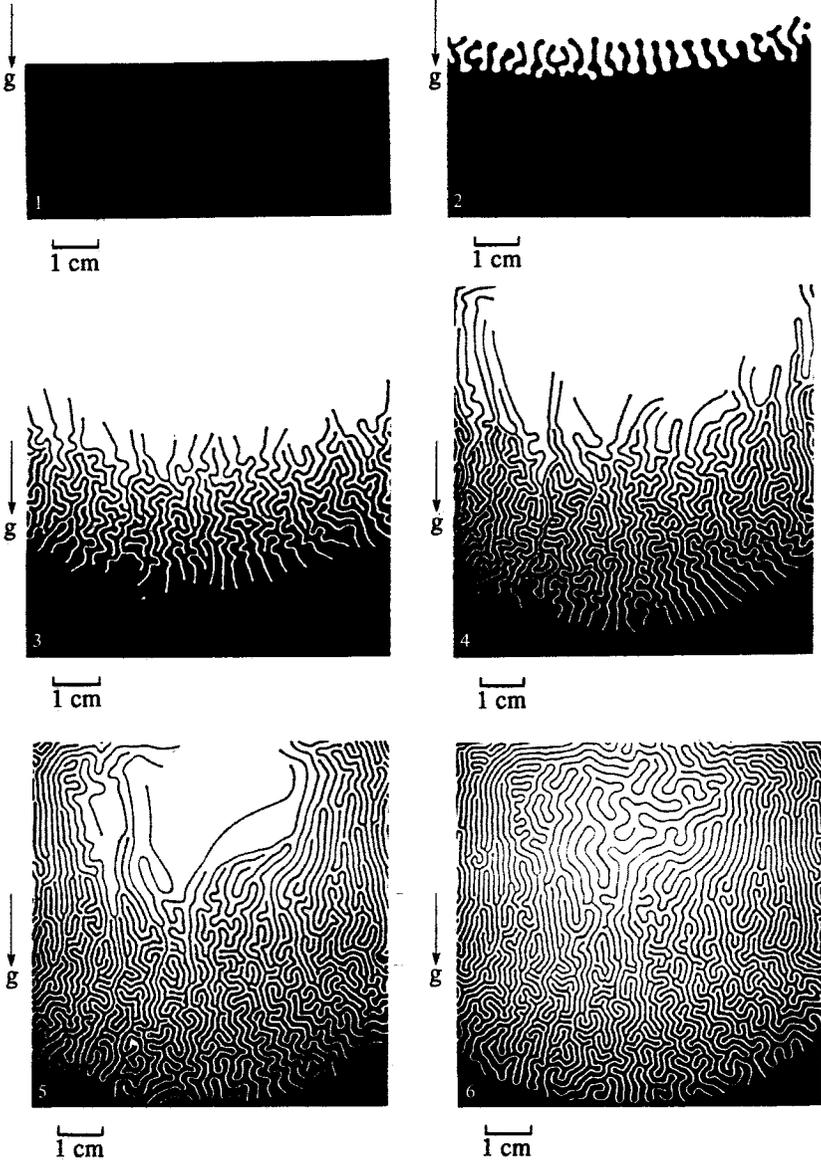


Fig. 1.4. Photographs of a labyrinthine instability developed by a magnetic field acting perpendicular to a thin vertical layer of ferrofluid. The field intensity increases from left to right. (From Rosensweig, 1985.)



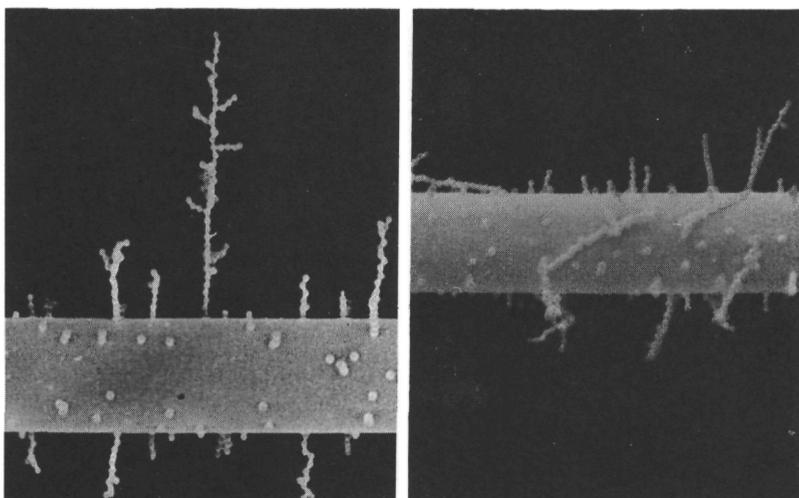
isolation or interacting with others in a pairwise manner. In the chapters that follow the salient features of those phenomena are set out and then integrated into a broad theory of colloidal behavior. To establish a context, the historical foundations are reviewed next, followed by a discussion of the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

[†] 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.)



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.

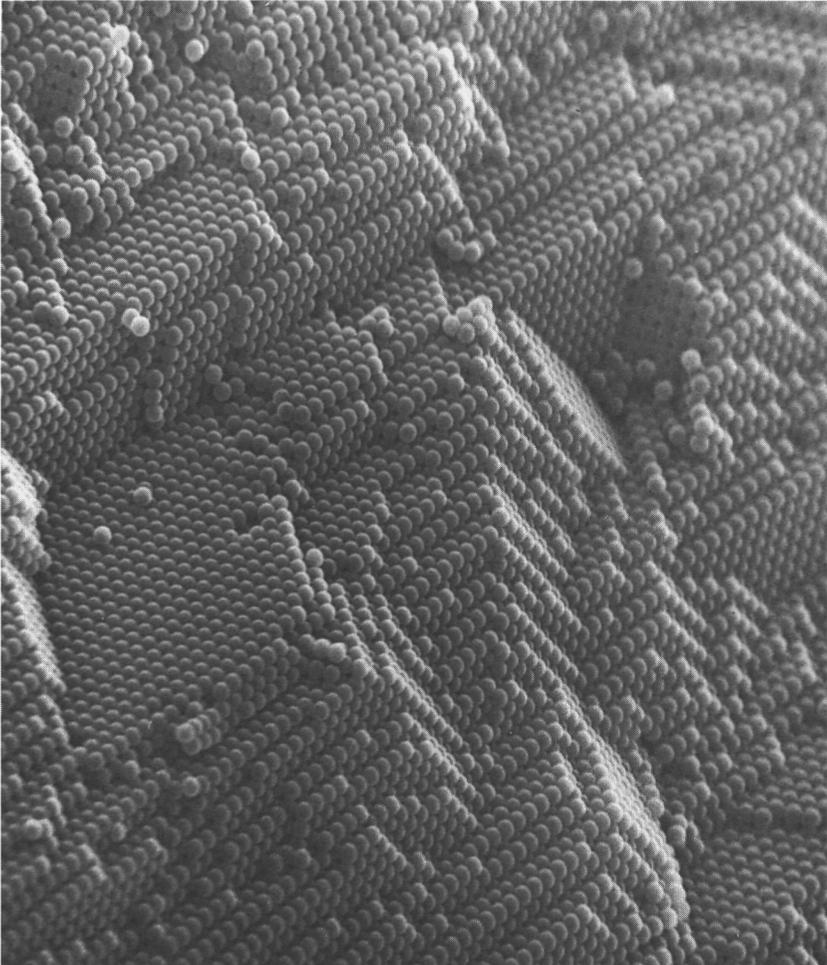
Another key development has been the direct measurement of interaction forces. Early efforts by Derjaguin *et al.* (1954) and Overbeek & Sparnaay (1954) were limited by the roughness of the fused quartz and polished glass surfaces employed. Tabor & Winterton (1969) recognized that cleaved muscovite mica 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

[†] 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.)



behavior. Ninham & Parsegian (1968) then devised tractable ways of applying the theory quantitatively to colloidal systems. Predictions based on measurements of the dielectric spectra for mica now agree with forces measured across a vacuum with the crossed cylinder apparatus (White *et al.*, 1976).

The need to disperse particles at high ionic strengths or in non-aqueous solvents led to improved techniques for polymeric stabilization in the 1960s. Naturally occurring macromolecules have been employed since ancient times, but the development of block and graft copolymers revolutionized the practice. These molecules combine an insoluble component for attachment to the particle surface and a soluble chain for stabilization. The pioneering work of Napper and colleagues (Napper, 1983) has revealed the close relation between the stability of the dispersion and the solution properties of the stabilizing block.

New developments in the statistical mechanics of the liquid state, coupled with synthesis of new model systems, also influenced colloid science. Silica spheres coated with octadecyl chains and dispersed in cyclohexane (Stober, Fink and Bohn, 1968; Iler, 1979) behave much like the hard spheres described by both analytical theories and computer simulations. Furthermore, perturbation theories (Barker & Henderson, 1967; McQuarrie, 1976), originally developed to deal with Lennard-Jones potentials in the liquid state, provide a convenient means for predicting phase transitions and other thermodynamic properties of concentrated colloidal dispersions.

Our detailed understanding of hydrodynamic effects on Brownian motion is another contemporary development. Although Langevin (1908) used Stokes' law to analyze the dynamics of Brownian particles, discrepancies between this approach and corresponding analyses of molecular motions were not resolved until the early 1970s. On the experimental side, rapid advancements in light-scattering techniques profoundly improved our understanding, particularly in concentrated dispersions. Photon correlation spectroscopy (dynamic light scattering) now provides a rapid, accurate method for measuring diffusion coefficients both for sizing particles and for understanding interactions between particles (see Berne & Pecora, 1976).

The full description of viscous interactions between a pair of particles is also of recent vintage; Happel & Brenner (1965) give a comprehensive review of the situation through the early 1960s. The detailed treatment necessary for understanding colloidal systems followed from work by Goldman, Cox & Brenner (1966) on a pair of spheres moving through a

quiescent fluid and Lin, Lee & Sather (1970) on spheres in a linear shear flow. This knowledge of the fluid mechanics advanced our understanding of Brownian diffusion, colloid stability, sedimentation, and rheology.

All these topics will be examined in detail in subsequent chapters, but first it is useful to consider the classification of colloids and the relative magnitudes of the various forces.

1.4 The classification of colloids

Graham used the term colloid to distinguish types of matter, but it later became apparent that colloids are not separate types, but matter in a particular state of subdivision, in which effects connected with the surface are pre-eminent. The terms lyophobic and lyophilic were introduced in the early literature to distinguish sols that were extremely sensitive to small amounts of electrolyte from those that were not. Gold and Prussian blue sols, for example, were called lyophobic ('liquid hating'); sols that required a large amount of salt to produce coagulation, e.g. albumin or gum arabic, were called lyophilic. Kruyt (1949) gives an extensive survey of the historical development of the subject and Shaw (1970) describes modern aspects. A simpler classification will be used in this book, viz.: particles, macromolecules, and molecular assemblies. Silver halide and gold sols, along with clays and polymer latex particles, fall into the first category. Such particles can be treated as rigid bodies and the details of their internal structure ignored when analyzing the dynamics. Macromolecular solutions, where the conformation of the molecule reflects the nature of the solvent, exemplify the second category. Micelles and microemulsions epitomize the third.

Particle size and shape are of considerable importance in setting the properties of a colloidal system. The simplest shape, a sphere, is characteristic of emulsions, latices, some protein molecules, and gold and silica sols. Clay particles such as kaolinite are plate-like, while attapulgite is rod-like. The treatment in the following chapters is restricted to spherical particles, in part because modest departures do not alter the qualitative features of the phenomena so that non-spherical particles can be modelled in terms of an equivalent sphere. Moreover, comprehensive results are available only for spheres.

Particle sizes in colloidal systems generally range from 1 nm to 10 μm . Table 1.1 shows some representative particle dimensions.

To furnish insight into the relative importance of the forces we can look into representative orders of magnitude. The thermal energy of molecular chaos may be interpreted as a Brownian force with a magnitude of $O(kT/a)$;

Table 1.1. Typical particle sizes

μm			
10^2		Sand	Pulverized coal
10^1	↑ Mist and fog	Silt	Red blood cells
10^0		Clay	Paint pigment
10^{-1}	↓		Latices
		Colloidal silica	Coiled macromolecules
10^{-2}			Carbon black
10^{-3}		Colloid gold	Micelles

here a denotes a representative length, k stands for Boltzmann's constant (1.381×10^{-23} J/K), and T for the absolute temperature. Additivity of London-van der Waals forces on an atomic or molecular scale yields a force between macroscopic bodies, the dispersion force, which is $O(A_{\text{eff}}/a)$. The Hamaker constant, A_{eff} , depends on the nature of the particles and the intervening fluid. Electrostatic forces between two particles are moderated by ions in the intervening fluid, but an order of magnitude follows from Coulomb's law as $\epsilon\epsilon_0\zeta^2$; ϵ is the dielectric constant of the fluid, ϵ_0 the permittivity of free space (8.85×10^{-12} C/V m), and ζ the electrostatic potential of the particles. Viscous forces on a particle moving at a velocity U through a medium of viscosity μ are $O(\mu a U)$, according to Stokes' law, and inertial forces are $O(a^2 \rho U^2)$. Finally, if $\Delta\rho$ represents the difference between the density of the particle and the fluid, then the gravitational body force on the particle is $O(a^3 \Delta\rho g)$. To compare magnitudes we use the values listed in Table 1.2 and compute ratios of the several forces.

In situations represented by this set of parameters, repulsive forces dominate attraction, so a suspension of such particles should be stable. Viscous and Brownian forces appear to influence matters equally, but sedimentation and inertia should not be important. Nevertheless, it must be recognized that this approach overlooks an important fact: individual forces depend differently on particle separation. For example, the screened electrostatic repulsion between flat surfaces decays exponentially, whereas the dispersion force varies inversely with the cube of the separation when

Table 1.2. *Magnitudes of the characteristic forces; $a = 1 \mu\text{m}$, $\mu = 10^{-3} \text{kg/m s}$, $U = 1 \mu\text{m/s}$, $\rho = 10^3 \text{kg/m}^3$, $\Delta\rho/\rho = 10^{-2}$, $g = 10 \text{m/s}^2$, $A_{\text{eff}} = 10^{-20} \text{Nm}$, $\zeta = 50 \text{mV}$, $\varepsilon = 10^2$*

electrical force	$\frac{a\varepsilon\varepsilon_0\zeta^2}{kT}$		
Brownian force		\approx	10^2
attractive force	$\frac{A_{\text{eff}}}{kT}$		
Brownian force		\approx	1
Brownian force	$\frac{kT}{\mu U a^2}$		
viscous force		\approx	1
gravitational force	$\frac{a^3 \Delta\rho g}{\mu U a}$		
viscous force		\approx	10^{-1}
inertial force	$\frac{\rho a^2 U^2}{\mu U a}$		
viscous force		\approx	10^{-6}

the surfaces are close together. Accordingly, attraction due to the dispersion force may predominate at one separation while electrostatic repulsion dominates the interaction at another. Moreover, viscous effects are so strong a function of separation that as two surfaces are forced together, the resistance to further diminution of the gap diverges. Clearly, a more careful study is warranted.

1.5 An overview

Our presentation focuses on dynamic and thermodynamic properties of colloidal dispersions. Because the behavior is complex, study of idealized situations makes it easier to understand key factors. For example, the motion of isolated spheres provides the simplest model for particles interacting with external fields, while the study of pairs of spheres exemplifies the effects of interparticle forces. Although our approach is theoretical and relies on mathematical analyses of model problems, we endeavor to give experimental foundations full weight.

The hydrodynamic factors are set out in Chapter 2, focusing on the behavior of spheres. Solutions to complicated problems are constructed from singular solutions of the Stokes equation because this illustrates the basic physics better than, say, mathematical techniques that rely on separation of variables. Since pair interactions are so important, the motion of two spheres is studied in detail.

Brownian motion is taken up in the third chapter by using the Langevin equation to analyze the motion of an individual particle. This is followed by a complementary statistical treatment. Comparison of the two approaches establishes that the overall process can be characterized by hydrodynamic mobilities calculated from the Stokes equation, despite the unsteady nature of the detailed motion. An analysis of pairs of spheres shows how pair mobilities describe the Brownian motion of interacting particles as well as the translation and rotation of a doublet consisting of two touching spheres. Brownian motion can be studied experimentally using light-scattering techniques as well as macroscopic observations. A sampling of experimental results demonstrates the agreement between experiment and theory when electrostatic and dispersion forces are negligible.

The treatment of interparticle forces begins with electrostatics in Chapter 4. Maxwell's equations are taken as axioms and magnetic effects ignored. A brief description of homogeneous dielectrics sets the stage for a detailed study of situations where fully ionized electrolytes are present. The structure of the diffuse layer adjacent to a charged surface is analyzed first, followed by an inquiry into the electrostatic forces between plates and spheres. Ion densities adjacent to a charged surface follow the Boltzmann distribution, so the equations for the electrostatics are non-linear. Thus, approximations must be used to obtain explicit expressions for the electrostatic part of the interparticle potential. Comparison with results from exact numerical solutions and experimental data helps define the range of validity of the various approximations.

Dispersion forces are less familiar, so Chapter 5 begins by describing interactions between two oscillating dipoles. This shows how the interaction energy varies with separation and forms the basis for a microscopic treatment of condensed phases involving a pairwise summing of dipole interactions. The result is an analytical form for the interaction potential which characterizes the material properties in terms of the Hamaker constant. A different methodology is required to account for the many body interactions neglected in this microscopic theory. The continuum theory based on the dielectric response of the different phases rectifies the shortcomings of the microscopic approach and provides the interaction potential between macroscopic bodies, including the effect of electromagnetic retardation and the intervening electrolyte. The chapter closes with a discussion of the experimental test of the theory using the crossed-cylinder apparatus with mica surfaces and simplified forms for the interaction potential.

Soluble polymers, either free in solution, attached to the colloid surface

at one end, or adsorbed reversibly at a number of points along the polymer backbone, also mediate particle-particle interactions. Forces due to polymer-polymer interactions are analyzed in Chapter 6 by combining thermodynamic and statistical mechanical methods. The task is to describe how the interactions produce a non-uniform polymer distribution in the solution around each particle. Alteration of this distribution by particle-particle interactions produces an interparticle force. Our understanding of such forces is less developed than for electrostatic or dispersion forces. Thus, although the theory can explain some features of the phenomena, many important details remain to be worked out.

Electrokinetic phenomena derived from the relative motion between a charged surface and an ionic solution reflect the electrical characteristics of the diffuse charge cloud and the particle surface. Chapter 7 presents a detailed survey of the behavior of individual particles and suspensions. Electrophoresis is taken up first to explain how static and dynamic situations differ. Though measurements of electrophoretic mobility traditionally serve to characterize the charge on colloidal particles, measurements of the electrical conductivity or the complex impedance can serve the same purpose. The former characterizes the suspension in terms of its response to a steady field, whereas the real and imaginary parts of the impedance reflect a frequency-dependent conductivity and dielectric constant. Dielectric relaxation arises from polarization and relaxation processes in the diffuse layer and on the particle surface. Attention is focused on dilute systems, since theories for concentrated systems are not highly developed. Detailed comparisons between theory and experiment are limited to the static conductivity, because measurements of the complex impedance are clouded by interpretation problems at present.

Electrostatic forces, dispersion forces, and polymer-induced forces are combined into an interparticle potential in Chapters 8 and 9 to assess colloid stability. Electrostatic stabilization refers to a metastable condition where kinetic factors control the persistence of the system. Rates of doublet formation due to Brownian motion and shear are analyzed and compared to experimental results. Now that it is possible to evaluate the electrostatic and dispersion contributions to the interaction potential independently, measurements of doublet formation rates test the theory unambiguously instead of simply serving to estimate the Hamaker constant. For polymerically stabilized systems we concentrate on incipient Brownian flocculation, using the theory developed in Chapter 7 to rationalize the qualitative features of the experiments.

Colloidal systems also undergo reversible phase transformations, which

are addressed in Chapter 10 using a statistical mechanical approach to calculate thermodynamic properties. A perturbation theory based on the behavior of hard spheres explains the order–disorder transition for charged spheres that produces the iridescence noted earlier. Phase transformations involving two fluid phases or a fluid and a solid phase are produced by dissolved polymer for both electrostatically and polymerically stabilized dispersions. These can be predicted from the weak attraction induced by the presence of non-adsorbing polymer.

The last four chapters describe dynamic processes where colloidal forces are central features: particle capture on stationary objects (Chapter 11), sedimentation (Chapter 12), diffusion (Chapter 13), and rheology (Chapter 14). In each instance the emphasis is on ways interparticle forces affect dynamics. For example, it is very difficult to bring two surfaces into contact in the presence of viscous forces. Particle inertia can produce capture, but the speeds of particles in liquids rarely exceed the threshold where capture begins. Thus, without an attractive interaction most filtration processes would be very inefficient. Chapter 11 deals with the ways interparticle forces alter particle paths so as to promote or inhibit capture.

Sedimentation in a closed container produces complex structures, as the Frontispiece amply demonstrates. Here consideration must be given to the effect of particle number density, the external force field, and interparticle potential on the settling velocity, Brownian motion, and the microstructure of the sediment. For example, a purely repulsive interaction hinders settling whereas attraction promotes it. Moreover, the microstructure of the suspension is set by Brownian motion and the interparticle force in the absence of the external field, but this structure is altered by the settling process. Thus, the speed of the process and the evolution of sediment structure depend crucially on colloidal forces. These issues are taken up in Chapter 12.

As noted earlier, the diffusion process in concentrated dispersions is very sensitive to interparticle forces. Chapter 13 first addresses gradient diffusion by distinguishing hydrodynamic and thermodynamic effects through a generalized Stokes–Einstein equation. Then self-diffusion coefficients are defined through the mean-square displacement of a Brownian particle in the presence of neighbors. Theoretical expressions relate the ‘short-time’ and ‘long-time’ behavior to the interparticle forces and hydrodynamic interactions. At finite particle concentrations, the self-diffusion and gradient diffusion coefficients differ because of different weightings of the various interactions. These diffusion coefficients can be measured by a combination of photon correlation spectroscopy and other techniques.

The rheology of colloidal suspensions is discussed in the final chapter. The presentation begins with a description of the phenomena and their classification using dimensional analysis. The utility of this approach is then demonstrated by correlating sets of experimental data for dispersions of hard, charged, polymerically stabilized, and weakly flocculated spheres. Then pair-interaction theories are developed that describe the non-equilibrium microstructure and the bulk stress in dilute systems. The good agreement with experimental results confirms the general applicability of the approach.

Our treatment centers on simple systems, primarily those involving monodisperse spherical particles with well-defined interactions at dilute concentrations. Dispersions of technological importance are often concentrated and polydisperse, with oddly shaped particles and a variety of uncharacterized components. Much of the difficulty encountered with these systems lies in simply identifying the components present and sorting out the important forces. These problems are formidable, and theoretical descriptions of the type developed here will rarely apply quantitatively. Nevertheless, it is clear that the relation between fundamental knowledge and technology is synergistic; each profits from the stimulus of the other. A broad understanding of the fundamentals does provide insight and helps develop the intuitive sense needed to isolate essential features of technological problems and design critical experiments. Providing that fundamental knowledge is the purpose of this book.

References

- Barker, J. A. & Henderson, D. (1967). Perturbation theory and equation of state for fluids: I, The square well potential. *J. Chem. Physics* **47**, 2856–61. II, A successful theory of liquids. *Ibid.* **47**, 4714–21.
- Berne, B. J. & Pecora, R. (1976). *Dynamic Light Scattering*. Wiley.
- Chapman, D. L. (1913). A contribution to the theory of electrocapillarity. *Phil. Mag.* **25**(6), 475–81.
- de Boer, J. H. (1936). The influence of van der Waals forces and primary bonds on binding energy, strength and orientation, with special reference to some artificial resins. *Trans. Faraday Soc.* **32**, 10–38.
- Derjaguin, B. V., Titijevskaia, A. S., Abrikosova, I. I. & Malikina, A. D. (1954). Investigations of the forces of interaction of surfaces in different media and their application to the problem of colloid stability. *Disc. Faraday Soc.* **18**, 24–41.
- Derjaguin, B. V. & Landau, L. D. (1941). Theory of the stability of

- strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim. URSS* **14**, 633-62.
- Einstein, A. (1906). On the theory of Brownian movement, in *Investigations on the Theory of Brownian Movement* (ed. R. Furth). Dover, 1956. A translation of a paper appearing in *Ann. d. Phys.* **19**, 371-81.
- Goldman, A. J., Cox, R. G. and Brenner, H. (1966). The slow motion of two identical arbitrarily oriented spheres through a viscous fluid. *Chem. Eng. Sci.* **21**, 1151-70.
- Gouy, G. (1910). Sur la constitution de la électrique à la surface d'un electrolyte. *J. Phys. Radium* **9**, 457-68.
- Hamaker, H. C. (1937). London-van der Waals attraction between spherical particles. *Physica* **4**, 1058-72.
- Hardy, W. B. (1900). A preliminary investigation of the conditions which determine the stability of irreversible hydrosols. *Proc. Roy. Soc. Lond.* **66**, 110-25.
- Happel, J. & Brenner, H. (1965). *Low Reynolds Number Hydrodynamics*. Prentice-Hall.
- Helmholtz, H. von (1879). Studien über electrische grenschichten. *Ann. der Physik und Chemie* **7**, 337-87.
- Hoffman, R. L. (1972). Discontinuous and dilatant viscosity behavior in concentrated suspensions. I. Observations of flow instability. *Soc. of Rheology, Transactions* **16**, 155-73.
- Iler, R. K. (1979). *The Chemistry of Silica*. Wiley.
- Israelachvili, J. N. (1985). *Intermolecular and Surface Forces*. Academic Press.
- Israelachvili, J. N. & Tabor, D. (1972). The measurement of van der Waals dispersion forces in the range 1.5 to 130 nm. *Proc. Roy. Soc. Lond.* **A331**, 19-38.
- Kose, A., & Hachisu, S. (1976). Ordered structure in weakly flocculated monodisperse latex. *J. Colloid Interface Sci.* **55**, 487-98.
- Kose, A., Ozka, M., Takano, K., Kobayashi, Y. & Hachisu, S. (1973). Direct observation of ordered latex suspension by metallurgical microscope. *J. Colloid Interface Sci.* **44**, 330-8.
- Kruyt, J. R. (1949). *Colloid Science*, vols. I & II. Elsevier.
- Langevin, P. (1908). Theory of Brownian motion. *C. R. Acad. Sci.* **146**, 530-3.
- LeNeveu, D. M., Rand, R. P. & Parsegian, V. A. (1976). Measurement of forces between lecithin bilayers. *Nature* **259**, 601-3.
- Lifshitz, E. M. (1955). The theory of molecular attractive forces between solids. *Soviet Physics JETP* **2**, 73-83.
- Lin, C. J., Lee, K. J. & Sather, N. F. (1970). Slow motion of two spheres in a shear field. *J. Fluid Mech.* **43**, 35-47.
- Matijevic, E. (1976). Preparation and characterization of monodisperse metal hydrous oxide sols. *Prog. Colloid & Polymer Sci.* **61**, 24-35.

- McQuarrie, D. A. (1976). *Statistical Mechanics*. Harper & Row.
- Napper, D. H. (1983). *Polymeric Stabilization of Colloidal Dispersions*. Academic Press.
- Ninham, B. W. & Parsegian, V. A. (1970). van der Waals forces. Special characteristics in lipid-water systems and a general method of calculation based on Lifshitz theory. *Biophysical J.* **10**, 646-63.
- Oak, M.-J., Lamb, G. E. R. & Saville, D. A. (1985). Particle capture on fibers in strong electric fields. *J. Colloid Interface Sci.* **106**, 490-501.
- Overbeek, J. Th. G. & Sparnaay, M. J. (1954). Coagulation and flocculation, II. Classical coagulation. London-van der Waals attraction between macroscopic objects. *Disc. Faraday Soc.* **18**, 12-24.
- Perrin, J. (1910). *Brownian Motion and Molecular Reality*. Taylor & Francis, London.
- Rosensweig, R. (1985). *Ferrohydrodynamics*. Cambridge University Press.
- Rothen, F., Jorand, M., Koch, A.-J., Dubois-Violette, E. & Pansu, B. (1987). Dislocations in Colloidal Crystals in *Physics of Complex and Supermolecular Fluids* (ed. S. Safran & N. A. Clark), pp. 413-45. Wiley.
- Schulze, H. (1882). Schwefelarsen im wässriger Lösung. *J. Prakt. Chem.* **25**, 431-52.
- Shaw, D. J. (1970). *Introduction to Colloid and Surface Chemistry*, 2nd edn. Butterworths.
- Smoluchowski, M. von (1903). Contribution à la théorie de l'endosmose électrique et de quelques phénomènes corrélatifs. *Bulletin International de l'Académie des Sciences de Cracovie* **8**, 182-200.
- Smoluchowski, M. von (1917). Versuch einer mathematischen Theorie der Koagulationkinetik kollider lösungen. *Z. Phys. Chem.* **92**, 129-68.
- Stöber, W., Fink, A. & Bohn, E. (1968). Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* **26**, 62-9.
- Tabor, D. & Winterton, R. H. S. (1969). Direct measurements of normal and retarded van der Waals forces. *Proc. Roy. Soc. Lond.* **A312**, 435-50.
- Vanderhoff, J. W., Vitkuske, J. F., Bradford, E. B. & Alfrey, T. (1956). Some factors involved in the preparation of uniform particle latexes. *J. Polymer Science* **20**, 225-34.
- Verwey, E. J. W. & Overbeek, J. Th. G. (1948). *Theory of the Stability of Lyophobic Colloids*. Elsevier.
- White, L. R., Israelachvili, J. N. & Ninham, B. W. (1976). Dispersion interaction of crossed mica cylinders: a reanalysis of the Israelachvili-Tabor experiments. *J. Chem. Soc. Faraday Trans. 1* **72**, 2526-36.

2

HYDRODYNAMICS

2.1 Introduction

Because colloidal particles generally reside in a viscous fluid, the behavior of a dispersion is strongly influenced by hydrodynamic forces generated by the relative particle–fluid motion. Although many hydrodynamic effects can be deduced from the behavior of an isolated particle, the disturbance it causes decays so slowly with distance that interparticle effects are seldom negligible. Consequently, hydrodynamic forces transmitted from one particle to another through a viscous fluid must be understood. Interactions, as well as the behavior of isolated particles, are discussed here. The presentation is not meant to be a scaled-down text on hydrodynamics, but is intended to provide tools to deal with phenomena encountered in colloidal systems.

The next section presents the basic differential equations governing the behavior of an incompressible Newtonian fluid and an analysis of the relative importance of viscous and inertial effects. The analysis of two simple flows illustrates some basic principles about the kinematics of fluid motion. Then we turn our attention to flows for which inertial effects are negligible, Stokes flows. Special emphasis is given to singular solutions resulting from forces applied at points in the fluid. Subsequent sections deal with isolated spheres and two interacting spheres, first in a quiescent fluid and then in fluid undergoing laminar shear flow.

Throughout this chapter, most of our attention will be fixed on situations where spatial accelerations are unimportant, and conditions under which this is valid will be set forth. Time-dependent situations are analyzed for small-amplitude motions to illustrate the effect of particle accelerations. This serves to establish the validity of quasi-static approximations where temporal effects enter only insofar as they refer to changes in particle configurations.

2.2 Description of the motion of continuous media

For the applications of interest here, the classical laws of Newtonian mechanics suffice. However, the fluid between colloidal particles is a continuum and the mass-point mechanics of elementary physics is inappropriate. Instead, the momentum conservation principle is applied to a stationary control volume through which fluid may enter or leave.

It is convenient to divide the forces acting in the fluid into body forces and contact forces. Gravitational and electrostatic body forces are relevant to colloidal dispersions. For the present we include only that represented by \mathbf{g} , the gravitational force per unit mass, and leave electrostatic forces to Chapter 4. Thus the body force \mathbf{F}_g acting on a volume V is

$$\mathbf{F}_g = \int_V \rho \mathbf{g} dV, \quad (2.2.1)$$

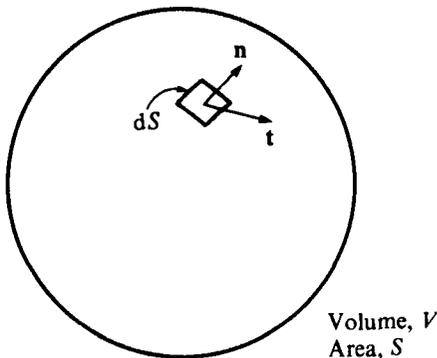
where ρ is the density of the fluid. Contact forces act at the bounding surface of a control volume (Fig. 2.1). If \mathbf{t} is the stress, i.e. force per unit area acting over an infinitesimal portion dS of the surface S enclosing V , then the contact force is

$$\mathbf{F}_c = \int_S \mathbf{t} dS. \quad (2.2.2)$$

$\mathbf{F}_c + \mathbf{F}_g$ is equated with the rate of change in momentum associated with the volume V .

The stress vector \mathbf{t} depends on the orientation of the area over which it acts. For example, in a fluid at rest $\mathbf{t} = -p\mathbf{n}$ since the only contact force is a pressure, acting normal to any surface. For this reason \mathbf{t} is associated with the outer surface normal \mathbf{n} shown in Fig. 2.1. For a fluid in motion, \mathbf{t} will

Fig. 2.1. Stress vector acting as a contact force on a surface enclosing V .



not be aligned with \mathbf{n} , but can be shown to be a linear vector function of \mathbf{n} (Batchelor, 1967, Ch. 1).

The dependence of the stress vector on \mathbf{n} complicates derivation of an equation for momentum conservation, but the difficulty can be overcome through the linear relationship between \mathbf{n} and \mathbf{t} . Defining a stress tensor, $\boldsymbol{\sigma}$, as a linear operator that transforms the unit normal into the stress vector \mathbf{t} yields (Batchelor, 1967, Ch. 1)

$$\mathbf{t} = \boldsymbol{\sigma} \cdot \mathbf{n}. \quad (2.2.3)$$

For the fluids dealt with here, the stress tensor is symmetric.

Conservation of momentum dictates that the rate of change of momentum in an arbitrary volume V equals the net force acting on the volume. With (2.2.1–3) and the divergence theorem, it is straightforward to show that

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot (\rho\mathbf{u}\mathbf{u}) = \rho\mathbf{g} + \nabla \cdot \boldsymbol{\sigma}; \quad (2.2.4)$$

\mathbf{u} is the local fluid velocity.

Similarly, one can derive a differential statement of mass conservation,

$$\frac{\partial\rho}{\partial t} + \nabla \cdot (\rho\mathbf{u}) = 0. \quad (2.2.5)$$

However, until further stipulations are made regarding the stress tensor and the density the model is incomplete.

We will be concerned solely with fluids of constant density, for which (2.2.5) reduces to

$$\nabla \cdot \mathbf{u} = 0. \quad (2.2.6)$$

This restriction (usually expressed by describing the fluid as incompressible) creates a problem because the equation of state for an incompressible fluid is indeterminate, and a unique definition of pressure is not possible. Thus only pressure differences or pressure gradients are meaningful.

For a Newtonian fluid of constant density,

$$\boldsymbol{\sigma} = -P\boldsymbol{\delta} + \mu[\nabla\mathbf{u} + (\nabla\mathbf{u})^T], \quad (2.2.7)$$

where μ denotes the shear viscosity of the fluid. Thus the stress is equal to the isotropic pressure plus a symmetric linear tensor function of the velocity

gradient. Combining (2.2.7) with (2.2.4) and (2.2.6) results in the Navier–Stokes equation,

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u}. \quad (2.2.8)$$

This form of the equation assumes a constant viscosity and absorbs the effect of gravity into a dynamic pressure, p ,

$$p = P + \Phi, \quad (2.2.9)$$

with Φ being a scalar potential given by $\rho \mathbf{g} = -\nabla \Phi$. Equations (2.2.6) and (2.2.8) are the basic equations governing the motion of an incompressible Newtonian fluid.

A complete description requires boundary conditions. Application of the conservation principles shows that the normal component of the velocity, and, in the absence of interfacial tension, the stress vector, are continuous across interfaces. Experience shows that the tangential velocity is also continuous for the situations under study.

Before attempting solutions, it is instructive to write the equations in dimensionless form. Defining characteristic quantities as velocity, U , length, L , time, L/U , and denoting dimensionless quantities by overbars, e.g., as $\bar{x} = x/L$, gives

$$Re \left(\frac{\partial \bar{\mathbf{u}}}{\partial \bar{t}} + \bar{\mathbf{u}} \cdot \bar{\nabla} \bar{\mathbf{u}} \right) = -\bar{\nabla} \bar{p} + \bar{\nabla}^2 \bar{\mathbf{u}}, \quad (2.2.10)$$

where

$$\bar{p} \equiv \frac{pL}{\mu U},$$

$$Re \equiv \frac{\rho UL}{\mu}.$$

It is clear that a single dimensionless group, the Reynolds number, Re , indicates the importance of inertia relative to viscous forces.

Integral properties of the flow can also be converted to dimensionless forms. For example, the force acting on a suspended particle becomes

$$\begin{aligned} \mathbf{F} &= \int_S \boldsymbol{\sigma} \cdot \mathbf{n} dS \\ &= \mu UL \int_{S_0} \bar{\boldsymbol{\sigma}} \cdot \mathbf{n} dS, \end{aligned} \quad (2.2.11)$$

identifying the appropriate dimensionless force as $\mathbf{F}/\mu UL$.

There are several reasons for writing hydrodynamic equations in dimensionless form. As we have just seen, it makes possible, via inspection, an assessment of regimes in which the physics is dominated by one or another force. For example, for $Re \ll 1$, viscous forces dominate the effects of inertia, while for $Re \gg 1$ inertia is predominant, although subtle viscous effects often play significant roles. Second, it is the basis for similarity analysis, which capitalizes on the fact that the dimensionless velocities and pressure, as well as integral quantities such as forces, depend only on the dimensionless independent variables and groups appearing in the governing equations. The latter includes the boundary conditions, i.e. continuity of velocity and stress vector across interfaces. Here additional groups can enter, e.g., a viscosity ratio for two fluid phases in contact, the Froude number U^2/Lg for a free surface, or the aspect ratio of an anisotropic body. However, for the rigid spheres of primary interest here the dimensionless force defined above depends only on \bar{t} , Re , and the geometrical factors. In later chapters similarity analysis is used repeatedly to present experimental data efficiently for situations in which non-hydrodynamic forces introduce additional dimensionless groups.

For low-viscosity liquids such as water, inertial effects are negligible only if the flow is slow or the dimensions of interest are small. For example, water flowing at 0.1 m/s through an array of 1 mm diameter fibers produces $Re \approx 100$. In cases such as this, inertia cannot be ignored. However, for colloidal particles suspended in such a flow, the appropriate Reynolds number depends on the particle size and the relative velocity between the particle and the fluid, which is generally much less than the fluid velocity. Even for 1 μm spheres moving at 0.1 m/s, the Reynolds number is small, i.e. $Re \approx 10^{-1}$. Hence inertia is generally negligible for flows on the scale of colloidal particles.

To set the stage for later descriptions of the dynamics of colloidal particles, we next examine two characteristic macroscopic flows. The first, steady laminar shear, illustrates the kinematics to which colloidal particles can be subjected. The second, potential flow past a sphere, introduces the concepts of streamlines and stream functions and represents a prototype flow for discussions of particle collection in Chapter 11.

2.3 Two simple flow fields

Steady laminar shear

One of the simplest flow fields is generated in the fluid between parallel infinite planes moved parallel to each other, as shown in Fig. 2.2.

For a constant velocity U , the Navier–Stokes equations reduce to

$$0 = \mu \frac{\partial^2 u}{\partial y^2}. \tag{2.3.1}$$

Thus, from (2.3.1) and the no-slip boundary conditions on the planes,

$$u = U \frac{y}{d}. \tag{2.3.2}$$

Although (2.3.2) was obtained for a Newtonian fluid, the result is valid for any fluid for which the stress is determined by the history of the velocity gradient.

The idealization shown in Fig. 2.2 is a prototype for certain viscometers. The relationship between shear stress and velocity gradient is readily found from measurements of the wall shear stress, or the drag, on one of the planes at various values of U . For a Newtonian fluid, defined by (2.2.7), it follows from (2.3.2) that

$$\sigma_{xy}(y) = \mu \frac{du}{dy} = \mu \frac{U}{d}. \tag{2.3.3}$$

Hence the (constant) slope of the relation between shear stress and velocity gradient equals the viscosity of the fluid.

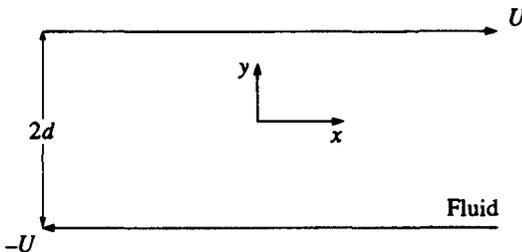
The velocity profile (2.3.2) is a special case of the general linear velocity field,

$$\mathbf{u} = \mathbf{\Gamma} \cdot \mathbf{x}, \tag{2.3.4}$$

where $\mathbf{\Gamma}$ is the constant velocity gradient tensor $\nabla \mathbf{u}^T$. Indeed, the velocity near a point \mathbf{x}_0 can be expressed through a Taylor series expansion as

$$\mathbf{u} = \mathbf{u}(\mathbf{x}_0) + (\mathbf{x} - \mathbf{x}_0) \cdot \nabla \mathbf{u}(\mathbf{x}_0) + \dots \tag{2.3.5}$$

Fig. 2.2. Laminar shear flow.



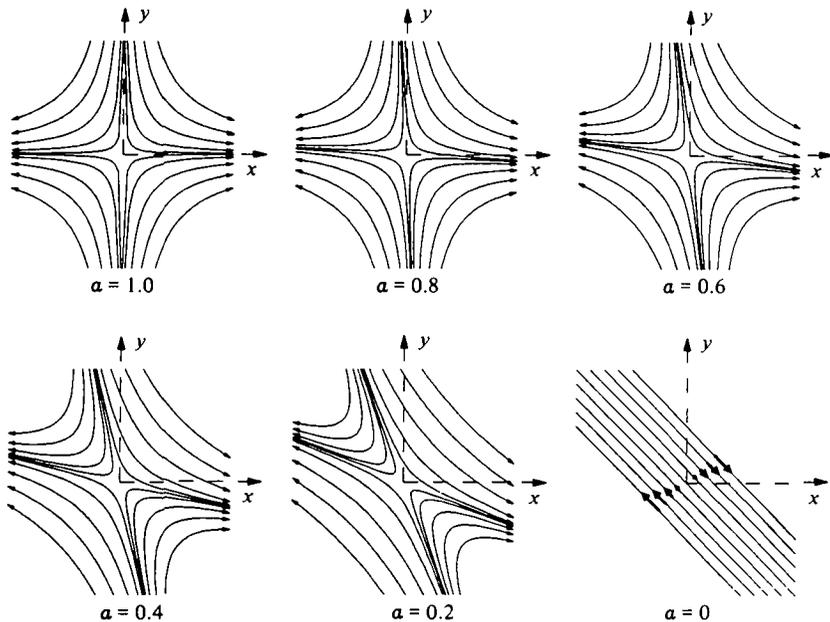
The first two terms suffice to describe the velocity field experienced by a colloidal particle with dimension $a^2 \ll |\mathbf{u}(\mathbf{x}_0)| / |\nabla^2 \mathbf{u}(\mathbf{x}_0)|$.

Later we will see that the motion of a particle depends on the nature of Γ . For the present it is instructive to express Γ for a two-dimensional flow in terms of a shear rate γ and a parameter α as

$$\Gamma = \frac{1}{2}\gamma \begin{bmatrix} 1+\alpha & 1-\alpha & 0 \\ -1+\alpha & -(1+\alpha) & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2.3.6)$$

in a Cartesian coordinate system. The effect of α on the flow structure is clearly evident from Fig. 2.3. Negative values of α denote an increasing amount of rotation, with a purely rotational flow for $\alpha = -1$. Simple shear flow corresponds to $\alpha = 0$ with the axes rotated by 45° relative to (2.3.2). The case of $\alpha = 1$ is a two-dimensional extension where a small particle placed in the flow experiences no rotation but is subjected to tensile and compressive forces. This contrasts with simple shear, for which stretching, compression, and rotation all take place.

Fig. 2.3. Streamlines for various values of $0 \leq \alpha \leq 1.0$ (Stone, Bentley, & Leal, 1986).



Potential flow past a sphere

Another interesting flow is that past a stationary sphere. Just such situations occur when particles in suspension encounter a stationary obstacle. Here the large-scale motion must be known before the paths of individual particles can be ascertained. Individual particle trajectories are analyzed in Chapter 11; here we delve into the structure of the motion and illustrate the concepts of streamlines and stream functions.

Imagine the situation when a sphere is placed in a flow with a uniform velocity \mathbf{U} . If the Reynolds number is large and the flow steady, temporal accelerations and viscous effects can be ignored over most of the region around the sphere. The uniform flow is irrotational, i.e., $\nabla \times \mathbf{u} = \mathbf{0}$, and, in the absence of viscous effects, this characteristic is preserved (see, for example, Batchelor, 1967, §§2.7 and 6.8). Hence the velocity can be written as the gradient of a scalar potential, ϕ , as

$$\mathbf{u} = \nabla \phi. \quad (2.3.7)$$

From (2.2.6) and (2.3.7) it follows that

$$\nabla^2 \phi = 0. \quad (2.3.8)$$

Situations in which (2.3.8) is valid form a class of flows known as potential flows. For a rigid impermeable sphere of radius a with $\mathbf{u} \rightarrow \mathbf{U}$ far from the sphere, the solution of Laplace's equation is

$$\phi(\mathbf{r}) = \mathbf{U} \cdot \mathbf{r} \left(1 + \frac{a^3}{2r^3} \right); \quad (2.3.9)$$

\mathbf{r} is the position vector measured relative to the sphere center and $r^2 = \mathbf{r} \cdot \mathbf{r}$. From this expression it is straightforward to obtain the radial and angular components of the velocity as

$$u_r = U \cos \theta \left(1 - \frac{a^3}{r^3} \right)$$

and (2.3.10)

$$u_\theta = -U \sin \theta \left(1 + \frac{a^3}{2r^3} \right).$$

Note that the normal velocity is zero at $r = a$, since the sphere is impermeable, but the tangential velocity is non-zero.

One might expect (2.3.10) to furnish a good approximation to the steady flow of a real (i.e. viscous) fluid at sufficiently high Reynolds numbers, as noted earlier. This is indeed true, except near the surface of the sphere and

downstream. Viscous effects alter the structure in a thin boundary layer near the surface, so as to satisfy the no-slip condition, and play a role in separation of the flow, which leads to formation of a wake.

Equations (2.3.10) can be used to introduce streamlines and stream functions. For an incompressible fluid, the continuity equation for two-dimensional or axisymmetric flows can define a scalar function, ψ , whose derivatives yield the velocity. In an axisymmetric flow, the relation between the stream function and velocity is expressed as (Batchelor, 1967, §2.3)

$$u_r = \frac{1}{r^2} \frac{\partial \psi}{\sin \theta \partial \theta}, \quad u_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \tag{2.3.11}$$

in spherical polar coordinates. Thus, the continuity equation,

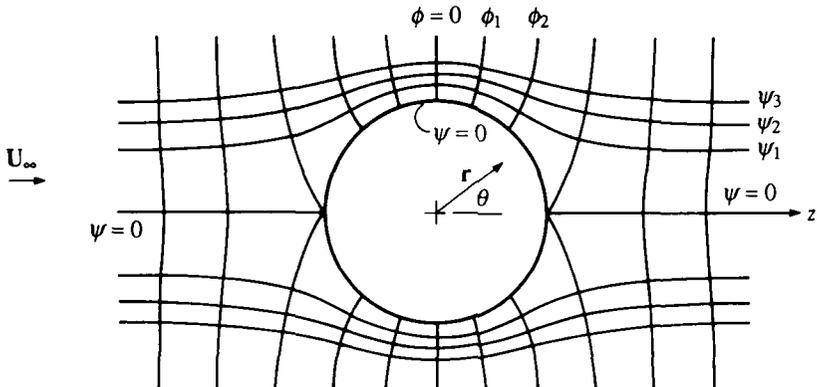
$$\frac{1}{r^2} \frac{\partial}{\partial r} r^2 u_r + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (u_\theta \sin \theta) = 0, \tag{2.3.12}$$

is satisfied identically by (2.3.11). Integrating the expressions given in (2.3.11) with the velocity from the potential flow solution shows that the stream function for this flow is

$$\psi = \frac{1}{2} U r^2 \sin^2 \theta \left(1 - \frac{a^3}{r^3} \right). \tag{2.3.13}$$

Figure 2.4 depicts streamlines in a plane through the axis of the sphere aligned with the flow direction, the z -axis. Note that the lines $\theta = 0$ and π coincide with the streamline $\psi = 0$ for $r > a$ and that the stream function is zero on the surface of the sphere. The points on the surface $r = a$ at $\theta = 0$ and

Fig. 2.4. Streamlines and equipotential lines for potential flow past a sphere at rest.



π are stagnation points, where the velocity is zero and the flow divides and then converges as it passes around the sphere.

It is also easy to show that the lines of constant ϕ are perpendicular to the lines of constant ψ . Accordingly, the velocity is tangent to the streamlines and no fluid flows across streamlines. To illustrate the connection between the stream function and the volumetric flow rate, imagine a surface formed by rotating a line of constant ψ around the z -axis to form a stream tube. Two such stream tubes delineate an annular region within which the volumetric flow rate must be constant. A plane intersecting the center of the sphere perpendicular to the flow, i.e., the plane $\theta = \pi/2$, intersects the two stream tubes on circles with radii r_1 and r_2 . Since the local normal to the plane, \mathbf{n} , is in the direction of the incident flow, \mathbf{U} , the flow rate through the annular ring is

$$\int_{r_1}^{r_2} \mathbf{u} \cdot \mathbf{n} 2\pi r \, dr = 2\pi \int_{r_1}^{r_2} (-\sin \theta) u_\theta r \, dr = 2\pi \int_{r_1}^{r_2} \frac{\partial \psi}{\partial r} \, dr = 2\pi(\psi_2 - \psi_1).$$

Hence, the flow rate through a stream tube depends only on the difference of the stream function on the two stream surfaces.

In this section viscous effects were neglected on the grounds that $Re \gg 1$; slow flows will be analyzed next to show how viscous effects modify the flow structure when $Re \ll 1$.

2.4 Characteristics of Stokes flow

In §2.2 we noted that for many problems relevant to colloid science the Reynolds number is small. There, to a good approximation, the flow is governed by the Stokes equations,

$$\begin{aligned} \nabla \cdot \mathbf{u} &= 0, \\ \nabla p &= \mu \nabla^2 \mathbf{u}. \end{aligned} \tag{2.4.1}$$

Two features of the Stokes equations deserve particular attention. Since the low Reynolds number approximation eliminates the time derivative in (2.2.8), solutions of the equations with time-dependent boundary conditions provide pseudo-steady descriptions of the motion. Second, the set (2.4.1) is linear. Therefore, solutions to a complicated problem can often be synthesized by superposition of solutions to simpler problems. Indeed, the superposition concept is fundamental to some important solution methods.

Consider, now, several issues central to solution of the Stokes equations for motion involving one or more spheres. Sphere motion is conveniently expressed as a combination of the translational velocity \mathbf{U}_0 of a sphere

center and the rotational velocity $\boldsymbol{\Omega}$ of the sphere about its center. Then the velocity of the surface of a sphere centered at \mathbf{x}_0 is

$$\mathbf{U} = \mathbf{U}_0 + \boldsymbol{\Omega} \times (\mathbf{x} - \mathbf{x}_0). \quad (2.4.2)$$

The viscous forces over the surface of a sphere give rise to a net force \mathbf{F} on the sphere

$$\mathbf{F} = \int_{S_0} \boldsymbol{\sigma} \cdot \mathbf{n} dS, \quad (2.4.3)$$

and a torque \mathbf{L} about the sphere center

$$\mathbf{L} = \int_{S_0} (\mathbf{x} - \mathbf{x}_0) \times \boldsymbol{\sigma} \cdot \mathbf{n} dS. \quad (2.4.4)$$

The integration is over the sphere surface S_0 and \mathbf{n} is the unit normal, taken as positive outward. In some situations the value of \mathbf{U} for one or more spheres with specified forces and torques is needed. This is known as the *mobility* problem. However, it is also possible to seek the force (or torque) on the spheres when the motion is specified. This is the *resistance* problem.

There are numerous methods for solving the Stokes equations for spheres moving in a Newtonian fluid. Separation of variables leads to Lamb's general solution (Lamb, 1932) with spherical harmonics used to represent the velocity and pressure fields. Happel & Brenner (1965, pp. 62–78) describe the methodology in some detail.

A second approach draws upon solutions to the Stokes equations generated by a point force, a force dipole, etc. These solutions are known as fundamental or singular solutions. To solve a particular problem, the singular solutions are combined so as to meet the boundary conditions in question. This approach is well suited to problems associated with colloid dynamics and will be used extensively, e.g. in Brownian motion (Chapter 3), electrokinetics (Chapter 7), and sedimentation (Chapter 12).

2.5 Singular solutions to the Stokes equations

Certainly the most important solution of the Stokes equations is that which describes the flow caused by a sphere moving due to an applied force \mathbf{F} through an unbounded quiescent fluid. Sufficiently far from the sphere, one expects the same velocity and pressure fields as those due to a concentrated force of equal magnitude. Thus the point force solution represents a 'far-field' approximation and provides a basic building block for the superposition method mentioned above.

Oseen (1927) employed Green's functions to obtain the point force solution. Although that approach permits an appreciation of the physics of the problem, the derivation is less direct than an alternative route, using Fourier transforms. We follow the latter approach as outlined by Ladyzhenskaya (1969, pp. 50-1).

To determine the velocity and pressure fields induced in an infinite expanse of fluid we use the Dirac delta function (Stakgold, 1968, p. 5) to represent a force \mathbf{f} imposed at the origin. Two properties of the delta function are

$$\int \delta(\mathbf{x}) dV = 1, \quad (2.5.1)$$

and the convenient sifting property for some function $g(\mathbf{x})$,

$$\int g(\mathbf{x}) \delta(\mathbf{x}) dV = g(\mathbf{0}). \quad (2.5.2)$$

Then the Stokes equations can be written as

$$\nabla \cdot \mathbf{u} = 0; \quad \nabla p = \mu \nabla^2 \mathbf{u} + \delta(\mathbf{x}) \mathbf{f}. \quad (2.5.3)$$

The solution to (2.5.3) is one of the fundamental solutions to the Stokes equations mentioned above.

The key to solving (2.5.3) is to recognize some special relations between the Dirac delta function and Fourier transforms. Recall that a function $\mathbf{f}(\mathbf{x})$ and its Fourier transform $\hat{\mathbf{f}}(\mathbf{q})$ are related by (Stakgold, 1968, pp. 36ff.)

$$\hat{\mathbf{f}}(\mathbf{q}) = \int \mathbf{f}(\mathbf{x}) e^{i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x} \quad (2.5.4)$$

and

$$\mathbf{f}(\mathbf{x}) = \frac{1}{(2\pi)^3} \int \hat{\mathbf{f}}(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{q}. \quad (2.5.5)$$

Integrations are over the full three-dimensional space of the integration variable. From these relations and the properties of $\delta(\mathbf{x})$ one can show that

$$\delta(\mathbf{x}) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{q}. \quad (2.5.6)$$

$$\nabla^2 \frac{1}{4\pi x} = \nabla^4 \frac{x}{8\pi} = -\delta(\mathbf{x}), \quad (2.5.7)$$

and hence

$$\frac{1}{4\pi x} = \frac{1}{(2\pi)^3} \int \frac{1}{q^2} e^{-iq \cdot x} dq \quad (2.5.8)$$

and

$$\frac{x}{8\pi} = -\frac{1}{(2\pi)^3} \int \frac{1}{q^4} e^{-iq \cdot x} dq, \quad (2.5.9)$$

where $q^2 = \mathbf{q} \cdot \mathbf{q}$, $x^2 = \mathbf{x} \cdot \mathbf{x}$. Taking the Fourier transform of (2.5.3) yields

$$\mathbf{q} \cdot \hat{\mathbf{u}} = 0; \quad -\mu q^2 \hat{\mathbf{u}} + iq \hat{p} = -\mathbf{f}. \quad (2.5.10)$$

Solving separately for $\hat{\mathbf{u}}$ and \hat{p} gives

$$\hat{\mathbf{u}}(\mathbf{x}) = \frac{1}{\mu q^2} \left(\mathbf{f} - \frac{(\mathbf{q} \cdot \mathbf{f}) \mathbf{q}}{q^2} \right) \quad (2.5.11)$$

and

$$\hat{p}(\mathbf{x}) = i \frac{\mathbf{q} \cdot \mathbf{f}}{q^2}.$$

To invert the transformed solution we use (2.5.8) and (2.5.9) to obtain

$$\mathbf{f} \cdot \nabla \frac{1}{4\pi x} = -\frac{i}{(2\pi)^3} \int \frac{\mathbf{f} \cdot \mathbf{q}}{q^2} e^{-iq \cdot x} dq \quad (2.5.12)$$

and

$$\mathbf{f} \cdot \nabla \nabla \frac{x}{8\pi} = \frac{1}{(2\pi)^3} \int \frac{\mathbf{f} \cdot \mathbf{q} \mathbf{q}}{q^4} e^{-iq \cdot x} dq.$$

Then, from (2.5.11) and (2.5.12) we find

$$\mathbf{u}(\mathbf{x}) = \frac{1}{8\pi\mu} \left(\frac{\delta}{x} + \frac{\mathbf{x}\mathbf{x}}{x^3} \right) \cdot \mathbf{f} \quad (2.5.13)$$

and

$$p(\mathbf{x}) = \frac{1}{4\pi x^3} \mathbf{x} \cdot \mathbf{f}.$$

The δ symbol refers to the unit tensor. In rectangular Cartesian coordinates with the basis \mathbf{i} , \mathbf{j} , \mathbf{k} ,

$$\delta = \mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j} + \mathbf{k}\mathbf{k}. \quad (2.5.14)$$

The multiplier of \mathbf{f} in (2.5.13) is called the Oseen tensor, \mathbf{I} ,

$$\mathbf{I} = \frac{1}{8\pi\mu x} \left(\boldsymbol{\delta} + \frac{\mathbf{x}\mathbf{x}}{x^2} \right), \quad (2.5.15)$$

and \mathbf{f} is often expressed in terms of a strength α as

$$\mathbf{f} = 8\pi\mu\alpha. \quad (2.5.16)$$

The force \mathbf{f} (and often the velocity field (2.5.13) due to \mathbf{f}) is called a Stokeslet of strength α .

The Stokeslet is not the only singular solution of the Stokes equations; derivatives of the Stokeslet are also fundamental solutions. For example, if \mathbf{d} is an arbitrary constant vector then $(\mathbf{d}\mathbf{f}) : \nabla\mathbf{I}$ represents the velocity field of a Stokes doublet (Chwang & Wu, 1975). The doublet also provides far-field behavior for flows involving small force-free particles. These fields can be separated into two parts, viz:

$$(\mathbf{d}\mathbf{f}) : \nabla(\mathbf{I}, \mathbf{x}/4\pi x^3) = (\mathbf{u}, p)_s + (\mathbf{u}, p)_c. \quad (2.5.17)$$

The first set of velocity and pressure fields is known as the stresslet, i.e.,

$$\begin{aligned} \mathbf{u}_s &= \frac{1}{8\pi\mu} \left(\frac{1}{x^3} \mathbf{S} : \boldsymbol{\delta} \mathbf{x} - \frac{3}{x^5} \mathbf{x} \cdot \mathbf{S} \cdot \mathbf{x} \mathbf{x} \right), \\ p_s &= \frac{1}{4\pi} \left(\frac{1}{x^3} \mathbf{S} : \boldsymbol{\delta} - \frac{3}{x^5} \mathbf{x} \cdot \mathbf{S} \cdot \mathbf{x} \right), \end{aligned} \quad (2.5.18)$$

where

$$\mathbf{S} = \frac{1}{2}[(\mathbf{d}\mathbf{f}) + (\mathbf{f}\mathbf{d})].$$

Note that this definition of the stresslet corresponds to that of Batchelor (1970) for situations where \mathbf{S} is traceless. The stresslet represents a straining motion with principal axes in the $\mathbf{d} + \mathbf{f}$, $\mathbf{d} - \mathbf{f}$, and $\mathbf{d} \times \mathbf{f}$ directions. An integral of the stress vector over a surface encompassing the singularity vanishes, showing that the stresslet exerts no force on the fluid. However, the integral of the moment of the stress vector does not vanish and

$$\int_S [\boldsymbol{\sigma} \cdot \mathbf{n}\mathbf{x} - \mu(\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u})] dS = \mathbf{S}, \quad (2.5.19)$$

when \mathbf{S} is traceless. This result will prove useful shortly in calculating the bulk stress in a suspension of colloidal particles.

The other part of the doublet is called the couplet and represents a torque applied to the fluid by the singularity. Here

$$\mathbf{u}_c = \frac{\mathbf{L} \times \mathbf{x}}{8\pi\mu x^3}, \quad p_c = 0. \quad (2.5.20)$$

where

$$\mathbf{L} = \mathbf{f} \times \mathbf{d}. \quad (2.5.21)$$

The moment applied by the couplet is

$$\int_S \mathbf{x} \times \boldsymbol{\sigma} \cdot \mathbf{n} dS = -\mathbf{L}. \quad (2.5.22)$$

2.6 Dynamics of isolated spheres

In many applications the full velocity field is not needed, but, as we have already noted, only the force on a particle or some other integrated characteristic of the flow. For these purposes a set of expressions known as Faxen's laws can be useful. To derive these we follow the approach of Batchelor (1972), based on the velocity field due to a point force, (2.5.13).

Consider a rigid sphere of radius a and surface S_0 immersed in a fluid with velocity field $\mathbf{u}_\infty(\mathbf{x})$ in the absence of the sphere. The sphere is centered at \mathbf{x}_0 , translates with velocity \mathbf{U}_0 and rotates about its center with angular velocity $\boldsymbol{\Omega}$. Owing to its motion the sphere affects the fluid through forces distributed over its surface, $\mathbf{t}(\mathbf{x})$ per unit area. From (2.5.13) the velocity field at \mathbf{x} is now $\mathbf{u}_\infty(\mathbf{x})$ plus that generated by the superposition of forces $\mathbf{t}(\mathbf{x}') d\mathbf{x}'$, or

$$\mathbf{u}(\mathbf{x}) = \mathbf{u}_\infty(\mathbf{x}) - \int_{S_0} \mathbf{I}(\mathbf{x} - \mathbf{x}') \cdot \mathbf{t}(\mathbf{x}') d\mathbf{x}'. \quad (2.6.1)$$

At the surface of the sphere this must match the sphere velocity given by (2.4.2). Thus,

$$\mathbf{U}_0 + \boldsymbol{\Omega} \times (\mathbf{x} - \mathbf{x}_0) = \mathbf{u}_\infty(\mathbf{x}) - \int_{S_0} \mathbf{I}(\mathbf{x} - \mathbf{x}') \cdot \mathbf{t}(\mathbf{x}') d\mathbf{x}'. \quad (2.6.2)$$

Integration of (2.6.2) over the sphere surface results in

$$\int_{S_0} \mathbf{t}(\mathbf{x}') d\mathbf{x}' = \mathbf{F} = \frac{3\mu}{2a} \int_{S_0} [\mathbf{u}_\infty(\mathbf{x}) - \mathbf{U}_0] d\mathbf{x}. \quad (2.6.3)$$