

Chapter 1

Microhydrodynamic Phenomena

1.1 Objective and Scope

Every student of science and engineering knows that a particle in a vacuum subject to an external force \mathbf{F}^e undergoes an acceleration \mathbf{a} given by Newton's famous law, $\mathbf{a} = \mathbf{F}^e/m$, where m is the mass of the particle. The particle trajectory is obtained immediately upon two integrations, and thus the fate of the particle can be determined. Every student of fluid dynamics learns that in a fluid medium, viscous resistance of the fluid decreases this acceleration so that the particle soon attains a terminal velocity. This resistive force, usually referred to as the hydrodynamic drag, \mathbf{F}^H (*hydrodynamic* because water is the most prevalent example), is linear with respect to the instantaneous particle velocity relative to the fluid, so long as the particle is small, the fluid is sufficiently viscous, the motion is slow, or a combination of the above. Unfortunately, the hydrodynamic drag is shape-dependent, so the particle trajectories are no longer described by a lumped parameter like the mass. Instead the drag calculation involves the solution of a boundary value problem for the velocity, with the shape of the particle entering into the solution through the boundary conditions on the particle surface. For a small sphere of radius a moving with a relative velocity \mathbf{U} through a fluid of viscosity μ , this procedure yields the Stokes law, $\mathbf{F}^H = -6\pi\mu a\mathbf{U}$.

Determining the motion of a particle or particles in bounded and unbounded flow is a central problem in the world of microhydrodynamics and the main objective of this book. The motion of the particles dictates the evolution of the suspension microstructure. The microstructure or multiparticle configuration in turn shapes the forces acting on the particles (which induce further motion). Thus the division of the subject matter (*i.e.*, colloid or particulate science) into hydrodynamics and statistical mechanics is somewhat arbitrary. Readers interested in a more complete treatment of the natural sciences that form the basis for understanding suspension phenomena are directed to [37, 42]. In some sense, this book provides an expanded view of the purely hydrodynamic aspects

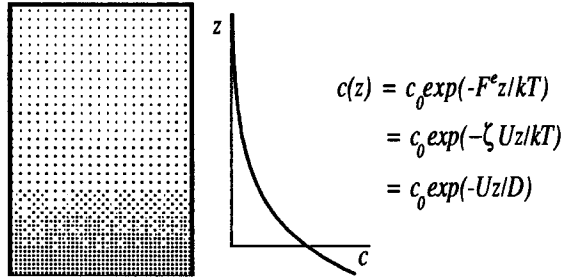


Figure 1.1: Brownian motion and an external field.

of the subject.

Since inertia plays a negligible role on the microscale, the hydrodynamic force balances the external forces, and the simplest paradigm may be stated as

$$\text{motion} \leftrightarrow \mathbf{F}^H = -\mathbf{F}^e.$$

In other words, if we know the relation (linear in our context) between particulate motion and the hydrodynamic force, we can determine the action of known external forces on the motion, or used in the opposite direction, infer the nature of unknown forces by observing the motion of the particle or particles. As in any introductory statements, there are qualifications. This simple paradigm applies only to noncolloidal particles, which are typically larger than a micron (10^{-6}m) but not so large that fluid inertia is important. This view is the fundamental underpinning of many important industrial operations, including flotation operations in ore processing [38], particle filtration operations common to many industries (an excellent review of particle capture from low-speed laminar flows is given by Spielman [41]), and aggregation and deposition of pulp fibers in paper manufacturing [40], to name a few.

In the colloidal size range (from the smallest continuum length scale such as the size of large globular protein molecules, to 0.1 microns) particle Brownian motion caused by the thermal agitation of the solvent molecules is important, and the particle motion is no longer deterministic. However, here also we have a role for the central theme of this book, the mobility relation between the particle motion and forces. The effect of Brownian motion in a liquid can be viewed as a diffusive process, an idea dating back to the early era of Einstein [13], with the diffusion coefficient given by kT/ζ , where k is the Boltzmann constant, T is the absolute temperature, and ζ^{-1} is the mobility of the particle. Thus the diffusion coefficient of a sphere of radius a is given by $D = kT/6\pi\mu a$.

To understand the source of this relation, we consider the situation depicted in Figure 1.1. A suspension of large particles will simply settle out and form a precipitated layer at the bottom of container. Colloidal particles, on the other hand, are subject to Brownian motion, and the formation of a concentration

gradient is hindered by the action of Brownian motion; the flux of particles moving from the region of higher concentration will be greater than that from the region of lower concentration. In an equilibrium situation, the upwards flux due to Brownian motion, $-Ddc/dz$ must balance the flux due to gravity, $(\zeta^{-1}F^g c)$. (The velocity is given by $\zeta^{-1}F^g$, by definition of the mobility ζ^{-1} .) The resulting distribution $c(z)$ is the Boltzmann distribution only if $D = kT/\zeta$. The link between diffusivity and mobility is readily extended to rotary Brownian motion (a rotary Brownian diffusion coefficient related to the rotary mobility times kT) and diffusion for an assembly of particles [2, 8].

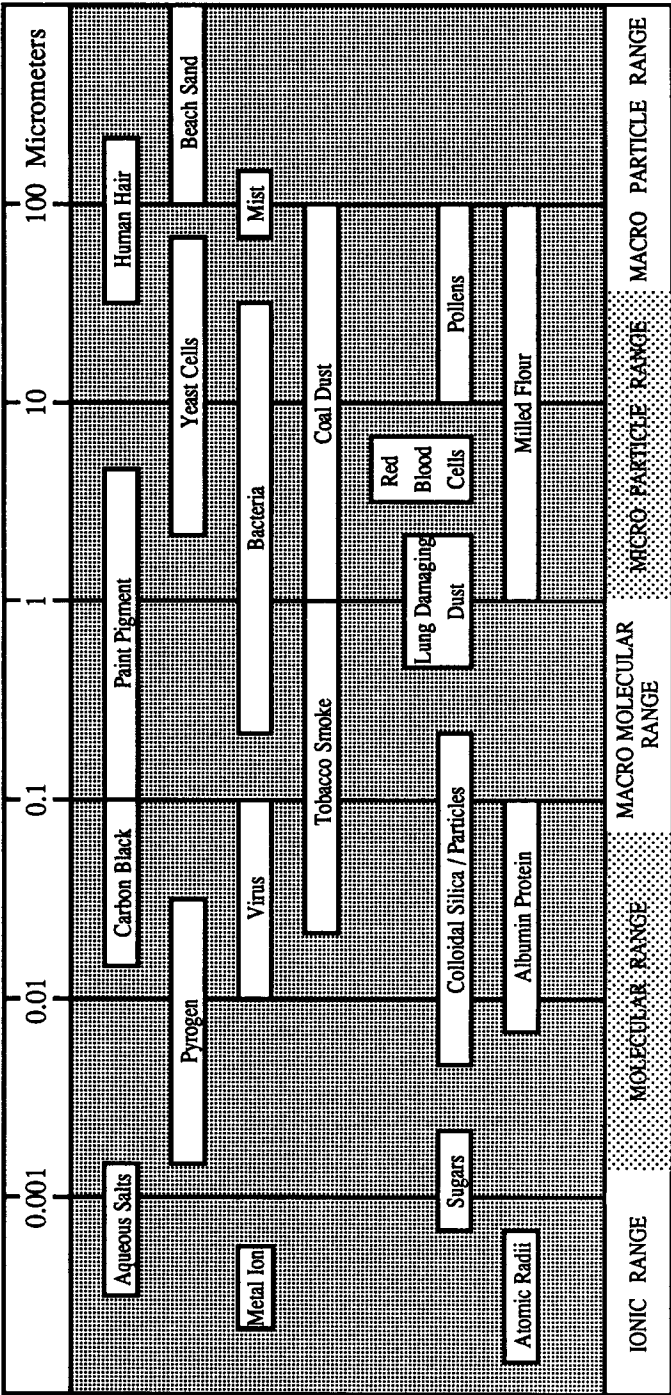
The stochastic nature of the trajectory of a single particle undergoing Brownian motion can also be modelled by using *stochastic differential equations* of the type known as the *Langevin equation*. In its simplest form, the Langevin equation incorporates the usual deterministic motion for the particle plus additional stochastic forces [15], and thus the viscous resistance of the fluid, again characterized by the mobility, is a key aspect of the computational procedure. In later chapters, we will see other subtle ways in which mobility relations and other concepts from the “standard” hydrodynamic calculations are incorporated as essential parts of the mathematical models of suspension behavior. Finally, readers interested in development of suspension simulations from a knowledge of the many-particle mobilities are directed to [7].

In Figure 1.2, we give the particle-based length scales for a number of natural and industrial particulate systems.

Going back to the central problem of relating particle motion and hydrodynamic force, we divide the task into two groups. For simple particle shapes in unbounded flow or those in flows bounded by simple container geometries, we describe a set of analytical solution techniques that enable one to relate the mobility to the key geometric parameters by elementary functions. Complex geometries for which the reader is convinced that the fine-scale details of the geometry are important can be handled by numerical methods that we describe, which are guaranteed to converge given sufficient computational power.

In the category of simple particle shapes, the most important examples are spheres and ellipsoids. The latter is particularly useful because it encompasses a wide range of shapes from disks to needles. Symmetry that is naturally inherent in certain growth processes often leads to particles of high symmetry; polystyrene latexes (perfect spheres) are one such example. The simplest boundary is the plane wall, but analytical and semi-analytical methods are available for spherical and cylindrical container geometries, as well as surfaces of mild curvature and those that fit a curvilinear coordinate system in which the equations separate. These categories of problems are described in Parts II and III.

In the category of *complex particle shapes*, we include flakes (clay particles, silver halide grains) and ribbons (pulp fibers), regular polyhedra (crystals), as well as particles without any symmetry whatsoever (globular proteins). Also, by combining simple shapes we end up with complex shapes, as in the steric layer formed by rigid rods (polymers) protruding from a perfect colloidal sphere.



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Figure 1.2: The particle size spectrum of microhydrodynamics.

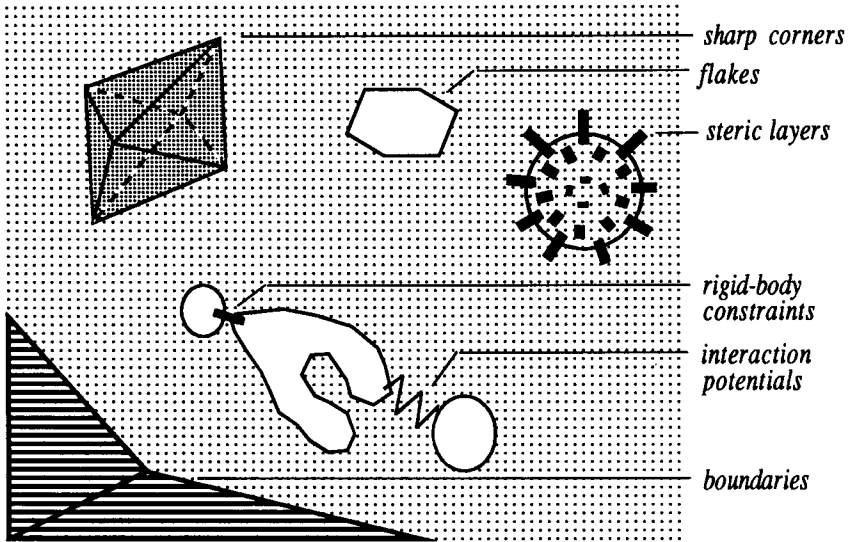


Figure 1.3: Particle shapes in microhydrodynamics.

These geometries are shown in Figure 1.3. To cite one example, the silver halide crystals or grains found in photographic emulsions are almost perfect hexagonal prisms with a thickness that is one tenth of the broadside dimensions. The analysis of the aggregation or deposition of these grains in a perfect pattern, as well as the stress distribution on a grain or aggregate, requires a local analysis with accurate hydrodynamics, especially near the sharp edges and corners. *Complex container geometries* are pervasive; examples include biological clefts and fiber mats and webs, and mathematical models that attempt to capture the geometry in a more complete manner will encounter them.

The dramatic growth in computational power over the past two decades has resulted in a similar growth in the range of problems solved in microhydrodynamics. Nevertheless, the complex geometries mentioned in the previous paragraph remain by and large outside the scope of current computational technology. These are after all three-dimensional flow problems with complex and evolving geometries (as the surfaces move relative to one another). Increased geometric resolution (a finer numerical mesh) scales into more unknowns at a quadratic to cubic growth rate and, given solution algorithms with solution times that also scale as quadratic to cubic powers of the number of unknowns, we see that even a dramatic increase (a factor of 500) corresponds only to a disappointingly small factor of two (or even smaller) increase in model complexity or resolution. Conventional supercomputers are unlikely to improve by such factors, and so the focus of Part IV is on the development of computa-

tional algorithms for parallel computers. We show how the central problem of microhydrodynamics can be split into independent concurrent streams, so that the projected growth rate in power of parallel computers can be exploited. Furthermore, the scaleup of time *vs.* number of unknowns is at the low end, approximately N^2 , so that a factor of two increase in system size results in a factor of four increase in computational time.

1.2 The Governing Equations

The equations governing fluid flow are obtained by considering first conservation equations for mass, momentum, and energy. These equations contain some quantities, in particular the stress, that must be specified by supplying constitutive equations for the fluid.

1.2.1 The Equation of Continuity

The differential equation for conservation of mass, also known as the equation of continuity, is given by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 . \quad (1.1)$$

Here $\rho(\mathbf{x}, t)$ is the fluid density and $\mathbf{v}(\mathbf{x}, t)$, the Eulerian velocity. These field variables are evaluated instantaneously at time t at the point \mathbf{x} fixed with respect to the laboratory.

Equation 1.1 can be derived by considering the mass balance over a differential volume element, as in [6], or from a balance over a macroscopic volume V fixed in space. The latter is given by

$$\frac{d}{dt} \int_V \rho dV = - \oint_S \rho \mathbf{v} \cdot \mathbf{n} dS .$$

The left side represents the time rate of change of the mass accumulated in V . Since mass is conserved, the change in this accumulation can occur only by mass entering or leaving through the bounding surface S , and that is what the right side of the equation represents. We apply the divergence theorem to obtain

$$\int_V \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) dV = 0 ,$$

and since this applies to all control volumes, the integrand must be identically zero and we obtain Equation 1.1. It is also possible to derive the equation of continuity by the use of a surface moving with the material points or *material surface* [31, 46].

The *substantial* or *material derivative* is defined by the operator equation

$$\frac{D(\cdot)}{Dt} = \frac{\partial(\cdot)}{\partial t} + \mathbf{v} \cdot \nabla(\cdot) \quad (1.2)$$

and is the result of applying the chain rule to differentiation with respect to time while following a fluid particle along its path. The equation of continuity when written in terms of the material derivative becomes

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0 . \quad (1.3)$$

If we exclude the possibility of change in the density as we follow the material so that $D\rho/Dt = 0$, then the equation of continuity reduces to the statement that the velocity field is solenoidal,

$$\nabla \cdot \mathbf{v} = 0 . \quad (1.4)$$

In practice, we shall further restrict our consideration to fluids with uniform density, *i.e.*, ρ is a constant. Sometimes this more restrictive assumption is termed *incompressibility*. The physical validity of this approximation is now estimated. For a single-component fluid, the density may be taken as a known function of temperature and pressure given by the equation of state from thermodynamics. The systems of interest in this book are all under isothermal conditions, so we focus our attention on the dependence on pressure. Whereas gas densities are quite sensitive to changes in the pressure (the most familiar example is the perfect gas law, $\rho = p/RT$), those of liquids are not. For water at room temperatures, the engineer's steam table [21] charts a change in the fourth significant figure for a 50% increase from atmospheric pressure.

1.2.2 The Momentum Balance

The equation for conservation of momentum is

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{f} . \quad (1.5)$$

Here, locally, \mathbf{v} is the velocity, ρ is the density, $\boldsymbol{\sigma}$ is the stress tensor, and \mathbf{f} is the external body force per unit mass. It is assumed that no external body couples act on the fluid. As we did earlier for the equation of continuity, this too is derived from a balance (in this case of momentum) on a macroscopic fixed control volume V ,

$$\frac{d}{dt} \int_V \rho \mathbf{v} dV = - \oint_S \rho \mathbf{v} (\mathbf{v} \cdot \mathbf{n}) dS + \oint_S \boldsymbol{\sigma} \cdot \mathbf{n} dS + \int_V \rho \mathbf{f} dV .$$

The left side represents the time rate of change of the momentum accumulated in V . Momentum can enter through the bounding surface S by virtue of material flow, and this is what the first term on the right side of the equation represents. The momentum accumulation can also change by virtue of surface and body forces acting on the fluid in V . Forces acting on the fluid in V over a differential element dS of the surface S are given by $\boldsymbol{\sigma} \cdot \mathbf{n} dS$, and the net effect is given by the surface integral over S . The action of body forces is given by the integral

over V of the product of ρ and \mathbf{f} , the force per unit mass. In the case of gravity, we will denote the body force by the gravitational acceleration, \mathbf{g} .

We now apply the divergence theorem to obtain¹

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{f} .$$

To complete the equations for fluid flow, we must have a model for the relation between the stress in the fluid and the state of the fluid. Naturally, we would expect this relation to vary from one material to another. If the fluid is static, the surface force acts along the surface normal, $\boldsymbol{\sigma} \cdot \mathbf{n} = -p\mathbf{n}$, where p is simply the pressure acting on the surface, and we may write $\boldsymbol{\sigma} = -p\boldsymbol{\delta}$.²

Now we consider deformation. The intuitive distinction between a solid and a fluid is that the stress in solids depends on the amount of deformation, while in fluids it depends on the *rate of deformation*. The instantaneous rate of deformation of a small material filament is characterized by the rate of strain tensor,

$$\mathbf{e} = \frac{1}{2}(\nabla \mathbf{v} + (\nabla \mathbf{v})^t) - \frac{1}{3}\boldsymbol{\delta}(\nabla \cdot \mathbf{v}) .$$

The simplest theory for a fluid is based on the hypothesis that the stress is linear with respect to \mathbf{e} , so that³

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} + 2\mu\mathbf{e} ,$$

and this equation is known as the *Newtonian constitutive equation*. Real fluids satisfying this relation to the limits of the purpose at hand are called *Newtonian fluids*. The material property μ is called the *dynamic viscosity*, and in most instances is simply referred to as the *viscosity*. The factor of two is in the constitutive relation only for historical reasons. Newton's experiments involved simple shear flow, $\mathbf{v} = \dot{\gamma}ye_x$, and μ appears as the coefficient of proportionality between the shear stress component and the shear rate $\dot{\gamma}$, i.e., $\sigma_{xy} = \mu\dot{\gamma}$. Non-Newtonian behavior is generally associated with long molecules (polymeric fluids) or fluids with microstructure (suspensions). Water and other fluids of compact molecular structure generally are Newtonian fluids [4, 5]. The methods described here can be used in the creation of mathematical models for non-Newtonian behavior of suspensions, but our main focus will be the microscale equations for the motion of a *Newtonian* solvent.

Combining the above constitutive equation with the momentum balance leads to the *Navier-Stokes equations* for an incompressible Newtonian fluid:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{f} \quad (1.6)$$

¹To be precise, we should really use the transpose of the stress tensor in the first term on the right side, i.e., use $\nabla \cdot \boldsymbol{\sigma}^t$. This distinction will soon become irrelevant because the fluids under consideration here will have symmetric stress tensors, $\boldsymbol{\sigma} = \boldsymbol{\sigma}^t$. For fluids with nonsymmetric stress tensors, see [12].

²The identity tensor $\boldsymbol{\delta}$ has Cartesian components δ_{ij} that equal one or zero according as i equals j or not. δ_{ij} is often called the Kronecker delta.

³For a compressible fluid, we add an extra term, $\kappa(\nabla \cdot \mathbf{v})$, where κ is known as the bulk viscosity.

$$\nabla \cdot \mathbf{v} = 0. \quad (1.7)$$

A more extensive discussion on the derivation of these equations may be found in many fluid mechanics texts [1, 16, 26, 27, 46, 48]. For a discussion on the kinematics of deformation and other continuum mechanical concepts, we refer the reader to Malvern [31].

1.2.3 The Stokes Equations

We note that the Navier–Stokes equations are nonlinear, since the substantial derivative contains a term that is homogeneous of order two in \mathbf{v} . Only in exceptional cases, such as steady laminar flow between parallel infinite plane walls or in an infinite circular pipe (both are called *Poiseuille flows*), will the nonlinear terms vanish from these equations.

The class of “solvable problems” is greatly expanded when we drop the nonlinear terms. The linearized Navier–Stokes equations for steady (*i.e.*, time-independent) motion are known as the *creeping motion* or (inhomogeneous) *Stokes equations*, and these are obtained by neglecting the substantial derivative of \mathbf{v} in the Navier–Stokes equations:

$$\nabla \cdot \boldsymbol{\sigma} = -\nabla p + \mu \nabla^2 \mathbf{v} = -\rho \mathbf{f} \quad (1.8)$$

$$\nabla \cdot \mathbf{v} = 0. \quad (1.9)$$

When the force field is conservative, such as gravity, it can be expressed as a gradient; then it may be lumped together with the pressure p , and this is the reason why the equations above are most often written without the force term. We shall call the equations thus obtained the *homogeneous Stokes equations* when we want to make this distinction explicitly. Actually the equations above are the *steady Stokes equations*, since sometimes the term $\rho \partial \mathbf{v} / \partial t$ is retained. To convince the reader that this linearization of a relatively complicated partial differential equations did not waste all the physical significance that the equations originally might have had, we now briefly discuss the relation between the solutions of the Stokes equations and those of the full Navier–Stokes equations.

The Stokes solutions provide a good approximation to the flow field near a particle when the *Reynolds number* defined by

$$\text{Re} = \rho V L / \mu \quad (1.10)$$

is small. Here V and L are representative values of the speed (magnitude of the velocity) of the flow and the particle dimensions, respectively. As Proudman and Pearson [36] showed (for a sphere explicitly), matched asymptotic expansions may be used to correct the Stokes solution to that of the full equations, the correction being $O(\text{Re})$ in the vicinity of the particle boundary, actually for distances up to $O(1/\text{Re})$. Considering ρ and μ fixed, we see that the Stokes solutions require less correction, as either the particle size or the characteristic speed of the flow is reduced. The article by Brenner and Cox [11] demonstrates that these ideas apply to particles of arbitrary shape. Using the length scales from

Figure 1.2 and the properties of water (density of 1 gram per cubic centimeter and viscosity of 1 centipoise), and creeping motions ranging from microns to millimeters per second, we see that the Reynolds numbers range from 10^{-6} to 10^{-4} . Henceforth, the Stokes equations will be considered as the mathematical model to be used for particles in the realm of microhydrodynamics, or viewed in another way, microhydrodynamics is defined as such, but the tautology is physically relevant since many important systems fall into this category. In any case, an *a posteriori* check of the size of the neglected inertial terms could be made after a Stokes solution is obtained.

Even though a problem might be unsteady, in the sense that the geometric configuration of the boundaries will change with time, we shall continue to use the steady Stokes equations by making the assumption of quasi-steady flow, meaning that we assume the terms related to time dependence to be negligible. We will examine this in more detail in Chapter 6, the essential conclusion being that for the scales mentioned above, the quasi-steady approximation gives the correct behavior in the leading order with a small error proportional to $O(\text{Re}^{1/2})$.

Modelling with Stokes equations has the following assets over the use of full Navier–Stokes equations. Firstly since the Stokes equations are linear, solutions may be superposed to get new solutions. Secondly, since inertial terms are neglected anyway, we need not restrict our coordinate frames to just the inertial ones; using, say, coordinates fixed to a rotating sphere will not give rise to any fictitious force field in the equations.

In spite of the simplifications indicated above, the number of analytical solutions known is still very small. A fairly comprehensive list can be obtained from Lamb's *Hydrodynamics* [25], Oseen's *Hydrodynamik* [35], Villat's *Leçons sur les Fluides Visqueux* [44], and Happel and Brenner [16]. Chapter 1 of the last reference gives an excellent historical perspective to the low-Reynolds-number hydrodynamics literature from antiquity to the 1960s, including the first three of the preceding list. The 1930 paper by Odqvist [34] provides existence and uniqueness theorems for integral representation solutions of the Stokes equations. Although his work is in German, the main ideas and results are accessible in English in the monograph, *The Mathematical Theory of Viscous Incompressible Flow*, by Ladyzhenskaya [24].

1.2.4 Boundary Conditions for Fluid Flows

At the interface between a fluid and another inert medium (rigid solid or another fluid), the normal component of the velocity (in the frame moving with the boundary) vanishes identically; this is a kinematic condition that must be satisfied if the interface is to have an identity of its own. The conditions for the tangential component of the velocity are on less firm grounds. At a boundary with a solid, it is customary to use the *no-slip boundary condition*, based on empirical evidence. As the name implies, we assume that there is no slipping between the fluid and the boundary so that the tangential fluid velocities match those of the solid. Slip occurs for polymeric liquids and rarefied gases. In both

cases the mechanism of interaction between the fluid molecules and those in the solid wall differs from that for compact molecules, such as water and the solid wall.

At the interface between two immiscible fluids, the tangential components of the velocity and tractions must match.⁴ The normal component of the surface tractions jumps from one side to the other, with the jump balanced by the surface tension γ times the surface curvature. More explicitly, if the stresses on the two sides of the interface are σ' and σ'' , then

$$\sigma' \cdot \mathbf{n} - \sigma'' \cdot \mathbf{n} = -\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \mathbf{n} ,$$

with the surface normal pointing into the concave side where σ'' prevails. For charged interfaces, these equations must be modified by inclusion of surface charges and electric stresses into the balance [32].

1.2.5 The Energy Balance

We can derive the expression for the time rate of change of the total internal and kinetic energy in the control volume V by following the same procedure as that employed for the mass and the momentum balance. The end result is

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) = \rho \mathbf{v} \cdot \mathbf{f} + \nabla \cdot (\sigma \cdot \mathbf{v}) + \nabla \cdot (k \nabla T) . \quad (1.11)$$

Here \hat{U} is the internal energy per unit mass (the hat reminds us that it is per unit mass), k is the thermal conductivity of the fluid, and T is temperature. The heat flux \mathbf{q} is given by Fourier's law as $\mathbf{q} = -k \nabla T$.

An expression for the time rate of change of the kinetic energy may be obtained from the momentum balance by taking the dot product of that equation with \mathbf{v} , and when this expression is subtracted from the energy balance we obtain the result

$$\rho \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \hat{U} = 2\mu \mathbf{e} : \mathbf{e} + \nabla \cdot (k \nabla T) . \quad (1.12)$$

The first term on the right is always positive, unless \mathbf{e} is identically zero; it represents the rate of production of internal energy by irreversible dissipation of kinetic energy. Under steady conditions, $\partial \hat{U} / \partial t = 0$, and the energy that is dissipated is either convected or conducted away from the material element. Thus the dissipation results in a raised temperature. For laminar viscous flows with velocity scale V , dimensional analysis reveals that this temperature increase scales as $\mu V^2 / k$. In our problems in microhydrodynamics, the relative velocity is sufficiently small that we may neglect the temperature increase and assume that the system is under isothermal conditions.

⁴A tangential stress difference results if there are surface tension gradients on the interface, giving rise to the so-called Marangoni effect.

1.3 Colloidal Forces on Particles

Repulsion between small particles is governed by electrostatic forces, while attraction is governed primarily by London–van der Waals forces, also known as dispersion forces, and to a lesser extent, electrostatic forces. The relative importance of these to the hydrodynamic drag depends on two length scales: the size of the particles and the separation between the surfaces. The colloidal forces are quite short range in nature, and their range for a particle in the colloidal size range is tens to hundreds of angstroms ($100 \text{ \AA} = 10^{-8} \text{ m} = 0.01 \text{ }\mu\text{m}$). For problems involving aggregation and capture phenomena of larger particles, this suggests that colloidal forces can be neglected altogether for most of the particle trajectory, suggesting that the trajectory should be determined from hydrodynamic considerations, with colloidal forces appearing in the form of a sticking boundary condition below a critical particle-particle separation. On the other hand, the breakup of aggregates requires a careful analysis of the fairly difficult hydrodynamic calculation of stresses in flow past nearly touching particles, initially all moving in tandem as a rigid body. We show how to handle these situations in Part III (for the simple aggregate formed by two spheres) and Part IV (more general particle shapes).

The London–van der Waals attraction between a sphere of radius a and a plane wall may be quantified as [43]

$$F = \frac{A}{6} \frac{a}{h^2} ,$$

where A is Hamaker's constant. As the particle size a tends to 0, the attractive force decreases proportionally to a , while, for example, the gravitational forces decrease faster, as a^3 . Hamaker's constant has units of energy and is commonly scaled with respect to the thermal energy scale kT . The values range from 0 to $20kT$, depending on the nature of the surface. A more rigorous foundation for the calculation of the dispersion force is given in the monograph by Mahanty and Ninham [30]. The review article by Kim and Lawrence [23] tabulates the relative importance of the attractive and hydrodynamic forces for a number of different sphere-plane interactions in air and water.

A charged surface in an aqueous environment attracts a layer (or cloud) of ions of the opposite charge (the counter-ions). Thus the electrostatic repulsion between two surfaces immersed in an aqueous medium is coulombic in nature, but is modified by the screening effect of the counter-ions. The calculation of this repulsive force in a flowing system thus requires the solution of a simultaneous system of partial differential equations governing the flow of the fluid (and the ions), as well as Maxwell's equations. The hydrodynamic and electrostatic forces are then obtained by surface integration of the hydrodynamic and Maxwell stresses, respectively. In Part II, we encounter the simplest example of this in the electrophoresis problem. A comprehensive treatment of both attractive and repulsive forces may be found in books on colloidal phenomena [19, 37, 39].