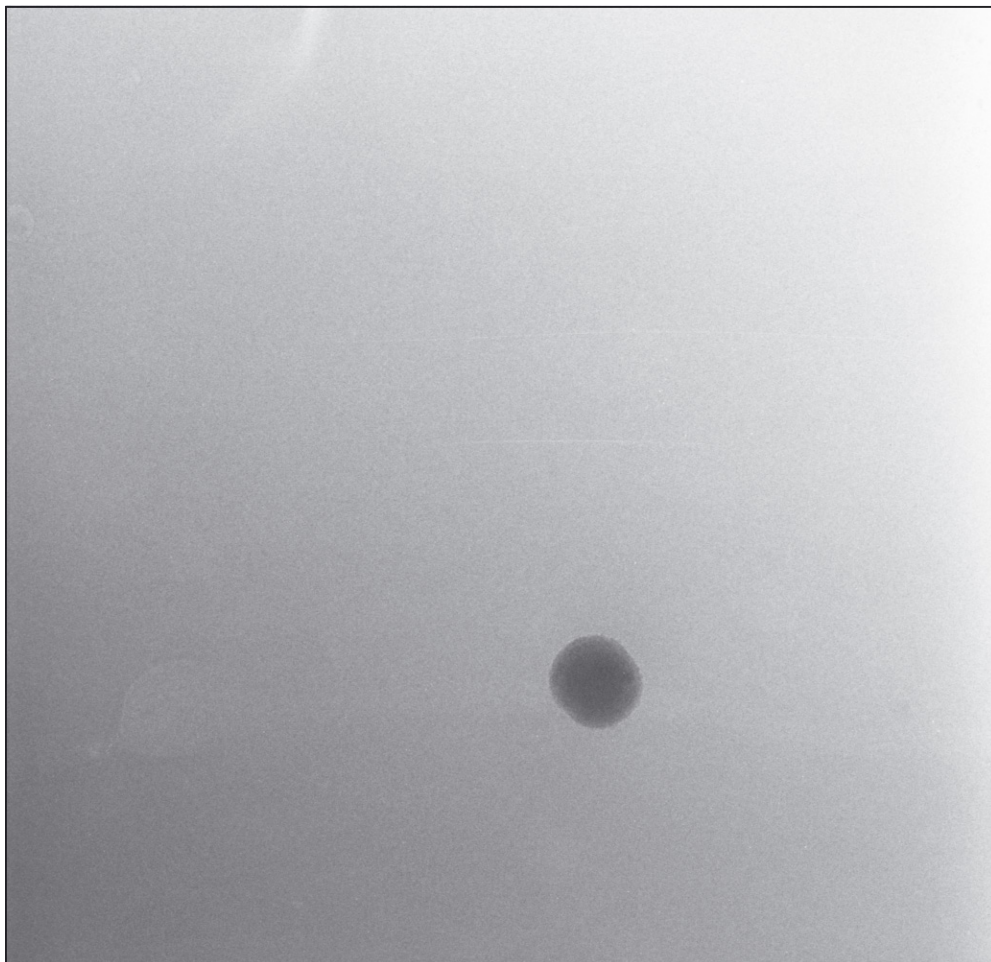


Notes on Brownian Motion



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Cover photograph: Silica sphere (radius 90 nm) arrested in glassified ethanol, imaged by cryogenic electron microscopy (courtesy P. Homan)

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Preface

These lecture notes form a primer to the study of Brownian motion by colloidal particles. The main theme is the Stokes-Einstein diffusion coefficient for a single colloidal sphere, freely diffusing in a viscous (Newtonian) fluid. These notes certainly do not form an exhaustive review of Brownian motion: main topics of current research such as effects of concentration or confinement are not addressed. The various references in these notes provide access to ample literature on many more aspects of Brownian motion.

The author is very grateful to Marina Uit de Bulten for her skill (and patience) in the preparation of these notes, and to Ingrid van Rooijen and Jan den Boesterd for figures and photography. Prof. G. Koenderink and Prof. A. Vrij are acknowledged for many enlightening discussions on Brownian motion. Dr. K. Planken and Drs. B. Kuipers are thanked for careful proof reading; any remaining errors or mistakes are, of course, the author's responsibility.

1 Introduction

A brick sinks in water by the action of gravity, whereas a very finely divided brick remains suspended in the liquid, even though its total weight remains the same. Under a microscope with sufficient resolution we would observe suspended brick particles, which perform erratic rotations and translations in arbitrary directions, with little or no effect of gravity for particles with a diameter below about one micron. Small particles, in other words, spontaneously diffuse and evolve without any external assistance towards a homogeneous distribution in a liquid. Diffusion is actually the 'thermal' transport mechanism for all components of a solution: solvent molecules and electrolyte as well as large solutes such as inorganic colloids or proteins. The diffusion coefficient is therefore a central quantity in a large set of kinetic processes, including chemical reaction kinetics of molecules, aggregation kinetics of colloids, and nucleation and growth in supersaturated solutions.

Diffusion coefficients have been intensively studied with respect to, among many other things, concentration effects or the influence of a confining medium (gel, porous material, a capillary). These effects are always compared to a well-understood reference process, namely the free diffusion of a single particle in a liquid, far away from other particles or a wall, for which the diffusion coefficient D is given by Einstein's equation¹

$$D = \frac{kT}{f}, \quad (1.1)$$

where kT is the thermal energy, k is the Boltzmann constant, and f is the friction coefficient of the particle. The simplest case is a spherical particle with radius R in a Newtonian liquid with viscosity η , for which the friction coefficient for translational motion equals the so-called Stokes friction factor:

$$f = 6\pi\eta R \quad (1.2)$$

The combined result

$$D = \frac{kT}{6\pi\eta R} \quad (1.3)$$

is called the Stokes-Einstein (SE) diffusion coefficient for translational sphere diffusion. It allows us, for example, to determine the radius of a colloidal sphere from diffusion measurements on a very dilute dispersion. Concentration effects in dense dispersions or confinement of a sphere in a small geometry lead to (sometimes drastic) deviations from eq. (1.3). These effects, however, do not concern us here. The main goal in later chapters is to derive and explain the SE equation and discuss some of its applications in colloidal kinetics.

¹ A. Pais points in his Einstein biography *Subtle is the Lord* (Oxford University Press, 1982) to the remarkable coincidence that eq. (1.3) was discovered by William Sutherland (1859-1911) at practically the same time as Einstein in 1905. See W. Sutherland, *Phil. Mag.* **9**, 781 (1905). According to Pais, (1.3) should be properly called the Sutherland-Einstein relation. Sutherland, however, can claim priority as he published eq. (1.3) already in 1904, see W. Sutherland "The measurement of large molecular masses", *Australian Association for the Advancement of Science. Report of Meeting*, 10 (Dunedin, 1904), 117-121. Firmly established naming of equations, however, is nearly impossible to change.

Brownian motion also comprises the rotational diffusion of particles, which is of importance to understand the response of colloids or molecules to external fields. The alignment of a magnetic or electric dipole moment of particles by an external field is counteracted by rotational Brownian motion which tends to randomize particle orientations, just as translational diffusion randomizes particle positions. The rotational diffusion coefficient D_{rot} has the same form as the translational coefficient, be it with a different friction factor:

$$D_r = \frac{kT}{f_r} = \frac{kT}{8\pi\eta R^3} \quad (1.4)$$

The rotational Stokes friction f_r , incidentally, is easier to derive than the translational friction factor f (see chapter 6) so there is every reason to include rotational diffusion in an introductory text.

The outline of these lecture notes is as follows. The two main topics underlying Brownian motion in a liquid are thermal diffusion and hydrodynamics which eventually appear in the diffusion coefficients (1.3) and (1.4) as, respectively, the thermal energy kT and the Stokes friction factor. The first topic rests on the general diffusion equation which is, among other things, explained in chapter 3, and applied in chapter 4 to find the quadratic displacement of Brownian particles in time. This finding is still independent of the medium in which Brownian motion takes place. Since we are interested in colloids in a liquid phase, we address in chapter 5 the second main topic, namely hydrodynamics based on the Stokes equation for viscous flow. This equation is solved in chapter 6 to obtain the friction factors for translating and rotating spheres. The now completed Stokes-Einstein diffusion coefficient is applied in chapter 7 to processes such as colloidal aggregation and diffusional growth, the kinetics of which is determined by the Brownian motion of spherical particles.

An introduction to Brownian motion would be incomplete without any attention for the historical significance of its relation in eqs. (1.3) and (1.4) to the Boltzmann constant k . Therefore we first situate in chapter 2 Brownian motion in its historical context.

2 The discovery of Brownian motion

Diffusion of colloids (*i.e.* particles with at least one dimension in the range 1-1000 nm) is often referred to as Brownian motion, and colloids are also called Brownian particles. There is no principal distinction between diffusion and Brownian motion: both denote the same thermal motion, be it of a molecule or a colloid. The adjective 'Brownian' for colloids has nevertheless stuck, for good reasons because Robert Brown's discovery ultimately became a corner stone of colloid science as we know it today. The account given below is certainly not exhaustive, but outlines some aspects of a fascinating history behind the Stokes-Einstein diffusion coefficient in which physics and chemistry came to terms with the concept of molecules in thermal motion.

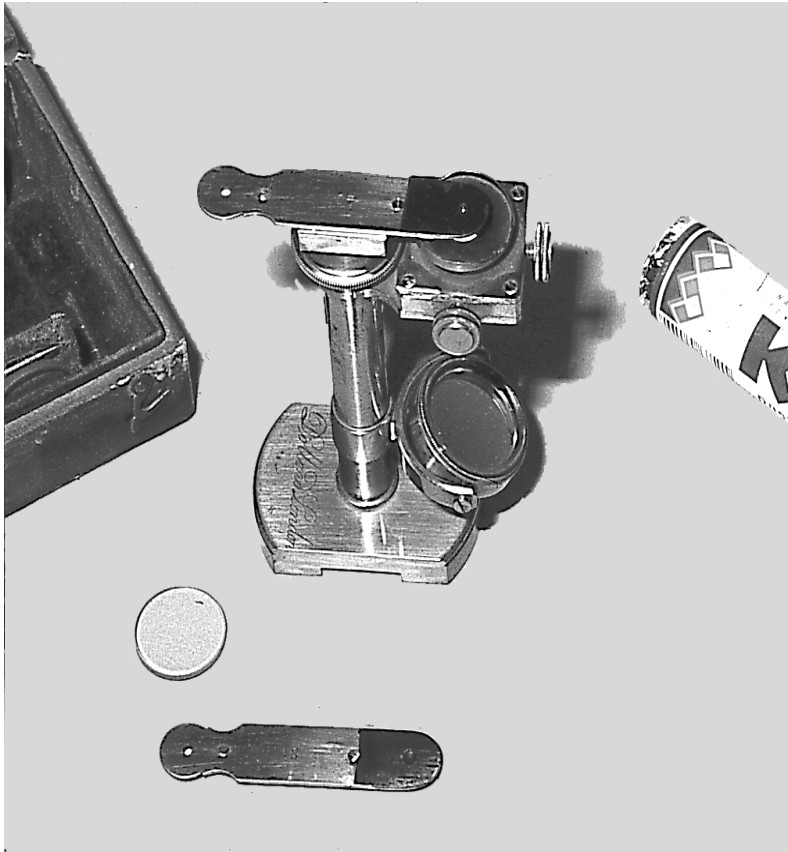


Fig. 2.1. Brown used a microscope of this type for his study of Brownian motion. This microscopic has only one lens in the form of a small glass grain.(Courtesy Dr. J. Deiman, Utrecht University Museum, photograph J. den Boesterd).

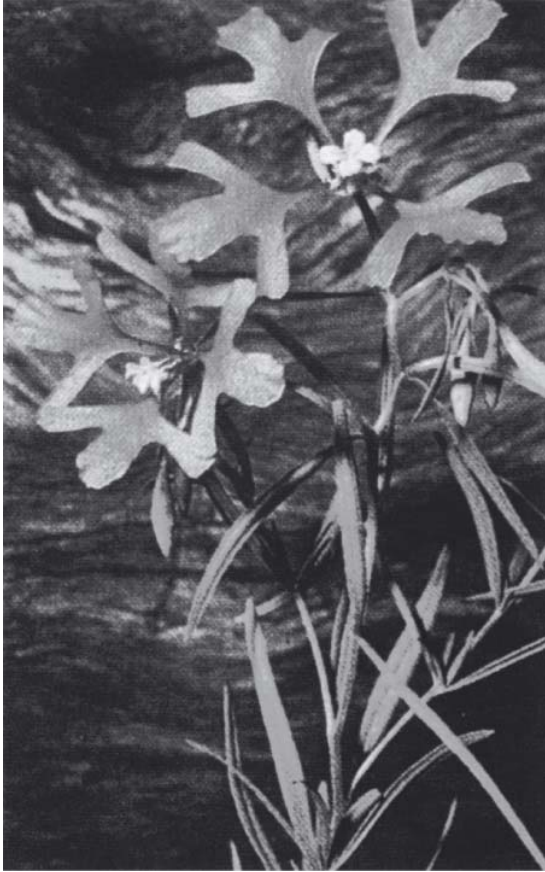


Fig. 2.2. The ornamental flower *Clarkia Pulchella* (H.W. Richett, *Wild Flowers of the United States*, vol. 6 (Mc Graw Hill, New York 1967)

A small grain of glass

The Brownian motion of visible particles suspended in a fluid led to one of the first accurate determinations of the mass of invisible molecules. The name giver of Brownian motion, however, was completely unaware of molecules in their present meaning, namely compounds of atoms from the Periodic System. The Scottish botanist Robert Brown (1773-1858) was already in his own time well-known as an expert observer with the single-lens microscope. With this modest instrument, essentially a miniature magnifying glass (fig. 2.1), Brown not only identified the cell nucleus but also studied the fertilisation process in plants, for which purpose he investigated the white pollen of the ornamental plant *Clarkia Pulchella* (fig. 2.2).

In June 1827 he observed under his microscope the zigzag motion of tiny objects in water which had escaped from the pollen grains. Such motions, of course, could be expected for small organisms which, in analogy with bacteria or spermatozoa, move in water without any external assistance. Brown decided to investigate the significance of these zigzagging organisms for the love life of *Clarkia Pulchella* in more detail. Soon, however, he started to doubt whether the tiny particles were indeed living organisms, even though their motions did not seem to stop. For Brown also scrutinized finely powdered *inorganic* substances (silica, clay, grains of sand) under his single-lens microscope and found that also inorganic particles, if sufficiently small, exhibit erratic motions when dispersed in water. Brown came to

the startling conclusion that small, dead pieces of matter *spontaneously* move in a liquid.

This conclusion was controversial for many years. Especially the spontaneity of the particle motion was contested in view of factors such as mechanical vibrations, solvent evaporation, and liquid convections, which could cause the observed motion of suspended particles. Such objections are not unreasonable; dust particles are seen to whirl around in sunlight due to airconvection, and even minute temperature gradients set up liquid flows in dispersions.

Nevertheless, an experiment by the author with the microscope in Fig. 2.1 using an aqueous dispersion of monodisperse latex spheres (diameter $1.0\ \mu\text{m}$) confirms that Brown indeed must have been able to observe Brownian motion. The irregular, diffusive movements of individual latex particles can be distinguished under the microscope of fig. 2.1, be it with some difficulty, from convective motions due to liquid flow, in which particles jointly move in the same direction. Such an experiment, of course, not only employs our modern, monodisperse latex particles in a clean solution, but is certainly also guided by what we expect to see. An unprejudiced 19th century observer trying to repeat Brown's experiments must, apart from external disturbances, have been easily confused by the complex image of moving and stagnant objects (dust, bacteria, cells, colloids of various size and shape etc.) observed in a drop of sap or water under a microscope. It is very difficult to interpret – or sometimes even to put into words – observations without sufficient guidance by expectations or theory.

This guidance developed slowly: it took nearly fifty years until Brown's observations were linked to thermal motion. The concept of molecules in thermal motion was central to the kinetic theory of gases that was developed in the 19th century. However, making a connection with Brownian motion in a liquid was anything but obvious. Christian Wiener (1826-1896) who observed Brownian motion in what we now call a colloidal silica sol, made in 1863 a first attempt to relate it to inherent fluctuations of the suspending fluid. It was, however, the Belgian Jesuit Delsaux (-) who stated in 1877 for the first time explicitly that Brownian motion results "from the interior dynamic state that the mechanical theory of heat attributes to liquids". He also notes that the Brownian motion is a remarkable confirmation of this mechanical theory. This confirmation remained qualitative, if not speculative, until statistical thermodynamics had sufficiently developed, and until it was clearly apprehended that large particles (colloids) obey the same statistical laws as molecules. This realisation was a turning point in a long-standing controversy on the status of atoms and molecules, as will be explained below.

Colloids are molecules

Proton, neutrons and electrons unite to form the atoms of the Periodic System. These atoms built molecules by covalent or ionic bonds and these molecules in turn assemble to form solids or liquids. We take this hierarchy for granted, though this certainly does not imply that the various steps in the hierarchy are easy to understand. On the contrary: why, for example, molecules form liquids and how liquids can be described in terms of molecular interactions are technically very difficult, only partly solved problems. However, we usually do not question the validity of the strategy itself, namely to explain matter in terms of its constituent

molecules. Nevertheless, even as late as 1900, the status and even the very existence of atoms and molecules were fiercely debated.

Chemists were drawing schematic diagrams, the forerunners of our chemical formulae and stoichiometric equations, at least since Dalton (1766-1844). For a critical 19th century student, however, the physical evidence that such chemical symbols might represent 'real' particles was anything but convincing. The student could point in the first place to the confusion about the nature of such particles. Were they indivisible atoms in the strict sense of the word? ('atom' derives from the ancient Greek *'α-τομος* = un-cuttable). Or were they agglomerates of such atoms? And was there only one type of atom, for example hydrogen as postulated by Prout (1785-1850), or could there be a whole family of 'chemical' atoms as advocated by Dalton? Our 19th century student could also point to the absence of any compelling evidence on the size of atoms or molecules, and that no one knew how many molecules, if they existed, went in one mole of substance.

One of the first credible estimates of molecular size was made by Loschmidt (1821-1895) using Maxwell's kinetic theory for the viscosity of a gas of hard spheres (Exercise 1). However, this result was apparently not the proof that could convince sceptics such as the physicist Ernst Mach (1838-1916), who admitted that molecules were a very useful hypothesis, but anyhow a hypothesis. Wilhelm Ostwald (1853-1932) rejected the reality of molecules, being convinced that all science should be based on phenomenological thermodynamics. We should note the consistency in this view point: the validity of the First law (total energy is conserved in any process) and the Second law (total entropy cannot decrease) does not rely on any particular molecular or microscopic model. So strict adherence to phenomenological thermodynamics is compatible with denying the existence of molecules.

Statistical thermodynamics, in contrast, is much less without engagement. It explains the Second law of thermodynamics by applying the laws of mechanics and the theory of probability to a collection of *discrete* particles in thermal motion. Ludwig Boltzmann (1844-1906), a founder of statistical mechanics, proposed in 1875 the relation between entropy S and the probability Ω

$$S = k \ln \Omega, \quad (2.1)$$

an equation carved on Boltzmann's tombstone in Vienna. Here Ω is the number of microscopic states that correspond to a certain macroscopic state with fixed total energy. Further k , the Boltzmann constant, is the ratio of the molar gas constant R_g to Avogadro's number:

$$k = \frac{R_g}{N_{Av}} = 1.38 \times 10^{23} \text{ JK}^{-1}, \quad (2.2)$$

and has the dimension of entropy. Boltzmann's entropy formula has an important consequence for the distribution of an assembly of N particles in an isolated system. According to the Second law, the entropy in an isolated system must increase until equilibrium, that is the state with maximal entropy, is reached. For the N particles the maximum of the entropy function $S = k \ln \Omega$ is reached when the particles adopt the Boltzmann distribution:

$$\frac{N_i}{N} = \frac{g_i \exp[-\varepsilon_i / kT]}{\sum_i g_i \exp[-\varepsilon_i / kT]} \quad (2.3)$$

Here N_i is the population at the energy level ε_i , with a degeneracy g_i ; the sum in the denominator over energy levels is the partition function of a particle. Such results of statistical thermodynamics are clearly only meaningful when there are really particles 'out there', which are thermally moving such that they can evolve to and remain in the equilibrium distribution of eq. (2.3).

The verification of eq. (2.3), however, presents a problem. One cannot directly count molecules in such a distribution by, for example, microscopic observations. Or so it seems, for it was realised by A. Einstein (1879-1955) and J. Perrin (1870-1942) that the Boltzmann distribution not only applies to atoms or molecules. It equally holds for the much larger particles in a colloidal suspension (see fig. 2.3), because the principle of "equipartition of energy" does not distinguish the thermal motion of a solvent molecule from that of a suspended colloid. The kinetic energy of a particle with mass m , translating with a speed v is

$$E_{kin} = \frac{1}{2} m v^2 \quad (2.4)$$

The equipartition principle guarantees that in thermal equilibrium all components of a solution (solvent molecules as well as colloids, polymers or any other particles) have the same *average* translational kinetic energy, which is fixed by the absolute temperature T :

$$\langle E_{kin} \rangle = \frac{3}{2} kT \quad (2.5)$$

Thus the root-mean-square speed of a particle is:

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}, \quad (2.6)$$

showing that at a given temperature a colloid with a large mass moves slower than a molecule. This large mass also 'compresses' the Boltzmann distribution in the earth gravity field. At a height x above the surface of the Earth at $x = 0$, the potential energy of a particle with mass m is:

$$U = mgx, \quad (2.7)$$

where g is the acceleration of gravity. The Boltzmann distribution (2.3) for colloids in the gravity field leads to an equilibrium profile of the form (exercise 2):

$$\rho(x) = \rho(x=0) \exp\left[\frac{-mgx}{kT}\right] \quad (2.8)$$

Here ρ is the colloid number density; $x = 0$ is the reference plane where $U = 0$. This exponential or 'barometric' distribution, which only holds for non-interacting particles, has a thickness characterised by the 'gravitational length':

$$l_g = \frac{kT}{mg}, \quad (2.9)$$

which is the height at which the number density has dropped to $\rho(x) = \rho(x=0) / e$. One easily verifies (exercise 2) that for oxygen molecules l_g is several kilometers, whereas colloidal spheres may adopt equilibrium profiles of only several cm or less. Since such spheres can be observed with an optical microscope, Perrin (fig. 2.3) was able to directly count the number densities predicted by eq (2.8). He determined the mass of his colloidal spheres from measurements of their Stokes sedimentation velocity (see Chapter 6). Then when $\rho(x)$ in eq. (2.8) is measured as a function of height x at a given temperature, the Boltzmann constant k remains the only unknown. Perrin thus determined experimentally k , and found in this way a reasonable value for Avogadro's number.

Perrin initiated the use of 'well-defined colloids' to study molecular statistics on a spatial scale which is accessible to an optical microscope. In colloid science this 'upscaling' is still an important strategy, and one is still wrestling with the problem that also Perrin had to face: colloidal particles always have a certain distribution in shape and mass (they are 'polydisperse') whereas atoms are monodisperse – if one disregards isotopes. The distribution in eq. (2.8), however, presupposes particles with identical mass m . Perrin used fairly monodisperse latex spheres, obtained from laborious fractionation procedures on natural latex ('gamboge') solution: by repeated sedimentation a few hundred milligrams of spheres were obtained from one kilo of rubber. Nowadays well-defined colloids can be prepared by precipitation or polymerisation of insoluble substances in a solution.

The equivalence between colloids and molecules also lead Perrin to another microscopic determination of Avogadro's number. Einstein was motivated to develop arguments to support the existence of molecules and the applicability of statistical thermodynamics. In his *annus mirabilis* 1905 (in which he also first published on special relativity and the photo-electric effect) Einstein reported equations for the diffusion of a particle in a liquid. They are the expression for the diffusion coefficient in eq. (1.1) and the relation:

$$\langle r^2 \rangle = 6Dt, \tag{2.10}$$

stating that a particle with diffusion coefficient D diffuses in such a way that the average quadratic displacement $\langle r^2 \rangle$ is proportional to time t . Einstein noted - allegedly unaware of earlier literature on Brown's observations –that his work could explain Brownian motion as an observable manifestation of particles in thermal motion. Perrin verified eq. (2.10) by measuring the displacements of his colloidal latex spheres (see Fig. 4.1) under a microscope and, via the Stokes-Einstein eq. (1.1), again found a reasonable value for Avogadro's number. Perrin's experiments made quite an impact as they quantitatively confirmed that through a microscope one indeed directly observes the 'heat motion' of large molecules. Even a sceptic such as Wilhelm Ostwald accepted eventually the reality of molecules, being convinced by Perrin's experiments.

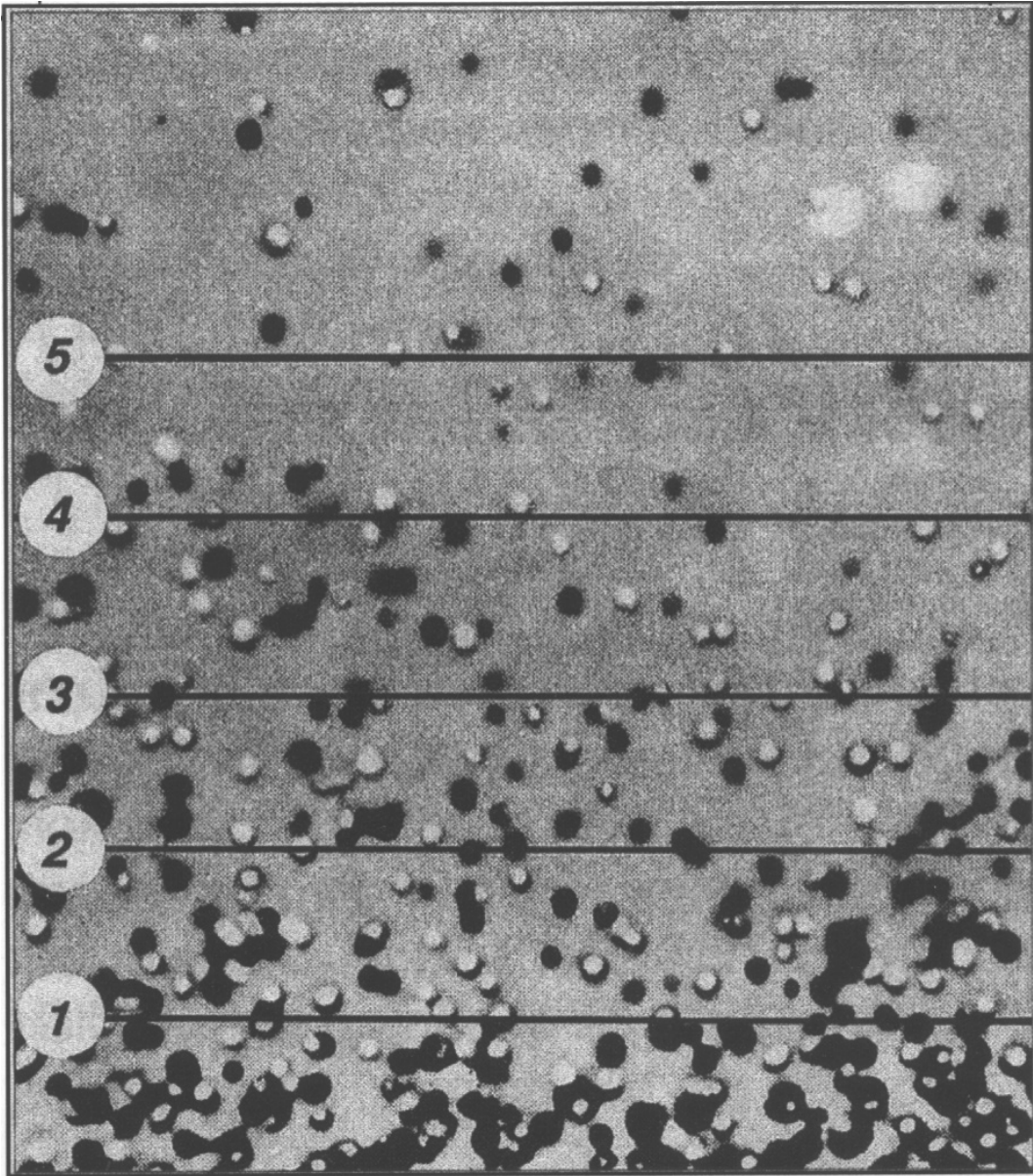


Fig. 2.3. Perrin's microscopic image of the sedimentation-diffusion equilibrium of resin spheres (diameter one micron) in water. Source: F. Randriamasy, *Revue du Palais de la Découverte* 20, no. 197, 18-27 (1992).

Does Brownian motion really demonstrate the existence of molecules? The significance of Perrin's work is the experimental demonstration that Brownian particles provide a visible example of thermal motion. Textbooks sometimes misrepresent this result by suggesting that Brownian motion is caused by 'uncompensated' collisions of solvent molecules, which kick around an otherwise totally inert colloidal particle. Consequently, if a colloid is seen to diffuse, there must be unseen solvent molecules. This inference, however, is incorrect, because each colloid has an intrinsic motion or translational kinetic energy, which has nothing to do with the surrounding liquid. Irrespective of whether a colloid is suspended in a liquid or, say, a water vapor or photon gas, it moves randomly about an equilibrium position due to its kinetic energy. Only the *distance* it moves is determined by the energy dissipation to its surroundings; a viscous damping in case of a liquid. The Stokes-Einstein diffusion coefficient in eq. (1.3) summarises this state of affairs: diffusion is driven by the thermal energy kT with no reference to the surroundings of the colloid, and damped by the Stokes friction factor which specifies that the colloid in question is suspended in a continuous fluid with viscosity η .

Exercises

1. The first estimate of a molecular diameter d in 1865 by Loschmidt is based on the proportionality:

$$d \sim \phi\lambda, \quad (2.11)$$

where λ is the mean free path length of molecules in a gas where molecules occupy a volume fraction ϕ .

- a. Verify that this proportionality is correct.
 - b. Find out how Loschmidt was able to deduce or estimate ϕ .
 - c. How would you determine ϕ for, say, nitrogen gas at $T = 298$ K and $P = 1$ bar? Could Loschmidt also have used your method?
 - d. Estimate d for this nitrogen gas using the proportionality in (2.11). Try to find the correct proportionality factor in (2.11). Does this improve your estimate of the diameter of N_2 -molecules?
 - e. Calculate Avogadro's number on the basis of your estimate of d .
2. Derive the barometric height distribution in eq.(2.8). Start with formulating the force balance on the particles in the equilibrium profile. How large is l_g for oxygen molecules, and for colloidal spheres with a radius $R = 100$ nm and mass density of 2 g cm^{-3} ? [7.9 km, respectively 50 μm , taking $T = 298$ K].
 3. Which two methods did Perrin use to determine N_{Av} ? Can you think of other methods to determine N_{Av} ?
 4. Explain in what sense Brownian motion contradicts the Second Law of Thermodynamics.

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3 The continuity equation and Fick's law

Brownian motion is a sequence of random steps in the position or orientation of a colloidal particle. Such a sequence, also called diffusion, is described by a diffusion equation which informs us how particle positions and orientations evolve in time. Diffusion belongs to the large class of transport phenomena, with other members such as the transport of heat or electricity, and also the viscous flow of liquids treated in Chapter 5. Transport phenomena obey certain *conservation* laws, which stipulate that some quantity is conserved. For example, when colloids diffuse in a closed system, their total mass will remain constant. Such a conservation of mass, charge, energy or any other quantity is conveniently expressed in the language of vector analysis (see Appendix A) by a *continuity* equation. Transport phenomena, of course, differ with respect to the substance that is displaced, and the type of force or gradient that sets the substance in motion. These distinctions are described by *constitutive* equations.

The continuity equation

Let \vec{j} be the flux density of some property f , such as the concentration of molecules or colloids in a fluid; then \vec{j} is the flux density of particles through a unit area per second. Suppose there are no 'sources' or 'sinks' for molecules in the fluid. Then f obeys a conservation law, which in vector notation is formulated as follows. Consider a surface S enclosing a region V in a fluid (Fig. 3.1), with a normal unit vector \vec{n} pointing outwards from a surface element dS .

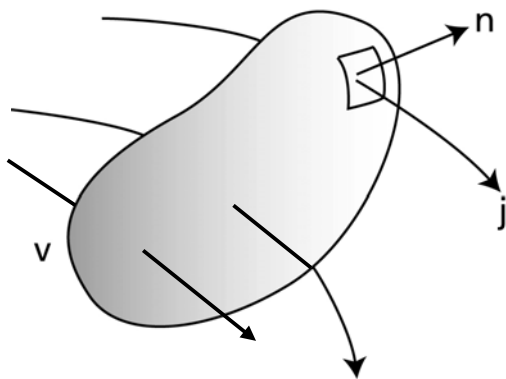


Fig. 3.1. Flux through the surface of a volume V .

The flux density component along the normal is the dot product $\vec{j} \cdot \vec{n}$ so the net amount of f flowing through the total S surface in unit time is the surface integral:

$$\int_S \vec{j} \cdot \vec{n} dS \quad (3.1)$$

Note the sign convention: in the case of a closed surface as in Fig. 3.1 the normal is pointing in the positive, outward direction and the surface integral (3.1) is positive if f is leaving the volume.

Suppose, without any loss of generality, that we consider the flow of water such that f is the local water concentration. Then at any time t the total amount of water in volume V is the volume integral:

$$\int_V f dV, \quad (3.2)$$

and the rate at which this total changes is:

$$\frac{d}{dt} \int_V f dV = \int_V \frac{\partial f}{\partial t} dV, \quad (3.3)$$

where it is assumed that $\partial f / \partial t$ is continuous such that the derivative can be moved under the integral sign. Conservation of water requires that

$$\int_S \vec{j} \cdot \vec{n} dS = - \int_V \frac{\partial f}{\partial t} dV \quad (3.4)$$

According to the divergence theorem (see Appendix A) the surface integral also equals:

$$\int_S \vec{j} \cdot \vec{n} dS = \int_V \vec{\nabla} \cdot \vec{j} dV \quad (3.5)$$

The physical significance of this theorem for water flow is as follows. The divergence $\vec{\nabla} \cdot \vec{j}$ is the net water flow, per unit volume, out of a volume element. This volume element has a positive divergence. The outgoing water enters another volume element contributing to an opposite, negative divergence. Thus in the volume-integral in eq. (3.5) all divergences cancel, except for the water leaving or entering the region V through its surface. The latter water flow is quantified by the surface integral in eq. (3.5). From eqs. (3.4) and (3.5) it follows that:

$$\int_V \left\{ \frac{\partial f}{\partial t} + \vec{\nabla} \cdot \vec{j} \right\} dV = 0, \quad (3.6)$$

The fact that the volume integral in eq. (3.6) is zero does not necessarily imply a zero integrand. One could imagine a source inside V (integrand positive) which is exactly compensated by a sink (integrand negative). However, we already excluded the existence of sources and sinks inside V so the quantity f is conserved everywhere in V . Under this assumption the integrand is always zero:

$$\frac{\partial f}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0, \quad (3.7)$$

This is the continuity equation, a basic equation both in diffusion (chapter 4) and hydro-dynamics (chapter 5), with no other physical meaning than that f is a conserved quantity. Let us apply this result to the mass flux $\vec{j} = \rho \vec{u}$ of a fluid with velocity \vec{u} and mass density ρ :

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0, \quad (3.8)$$

to find for a fluid which has everywhere the same constant mass density that:

$$\vec{\nabla} \cdot \vec{u} = 0, \quad \rho = \text{constant} \quad (3.9)$$

This is the continuity equation for an incompressible fluid. It is an important constraint on the velocity field \vec{u} around a colloid in a suspension, because the solvent usually *is* an incompressible liquid. Eq. (3.9) describes a *steady state* which by definition means that the distribution of the quantity f in (3.7) does not change in time. In a stationary flow, for example, of water in Fig. 3.1, water molecules enter and leave volume V at the same rate such that the water concentration f remains constant. Then $\partial f / \partial t = 0$ so from the continuity eq. (3.7) it follows that the steady state automatically satisfies:

$$\vec{\nabla} \cdot \vec{j} = 0 \quad (3.10)$$

In the steady state the *divergence* of the flux is zero, which should not be confused with the equilibrium state in which the flux itself is zero. The fluxes in the steady state are due to irreversible processes (diffusion, viscous flow), which produce entropy, whereas in thermodynamic equilibrium (for example the Boltzmann distribution from Chapter 2) no entropy producing transport processes can occur. One can also view equilibrium as the limiting case of a steady state in which all fluxes vanish. The concept of a steady or stationary state will be applied repeatedly in later chapters (exercise 3).

Constitutive equations; Fick's laws

The conservation eq. (3.7) has two unknowns so to find the quantity f a second relation between f and its flux \vec{j} is needed. Such a relation is the constitutive equation which specifies the transport problem and identifies the gradient that is responsible for the existence of the flux j . An example is a concentration gradient of colloids which drives *collective* diffusion. The concept of a flux driven by a gradient of an intensive variable is quite general:

Flux of	=	transport property	x	gradient in
particles		diffusivity		particle density (Fick)
charge		conductivity		potential (Ohm)
liquid		permeability		pressure (Darcy)
momentum		viscosity		momentum density (Newton)
energy		heat conductivity		temperature (Fourier)

The momentum flux will be dealt with later in Chapter 5. Liquid flow according to Darcy's law is briefly addressed in Chapter 6. Below we will formulate Fick's diffusion laws.

Brownian motion is a random motion: colloids diffuse in all directions with equal probability. Thus there is no *net* displacement of particles in a homogeneous distribution with a constant concentration of colloids. A concentration gradient, however, induces a collective displacement of colloids, also referred to as collective

or gradient diffusion. The corresponding diffusion flux is given by a constitutive equation known as Fick's first law:

$$\vec{j}_d = -D \vec{\nabla} \rho, \quad (3.11)$$

where ρ is the colloid concentration, which should not be confused with the mass density ρ in eq. (3.8). The number of colloids is conserved so the conservation law eq. (3.7) yields:

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot \vec{j}_d, \quad (3.12)$$

which is also known as Fick's second law. If there is only a particle flux due to diffusion we can substitute eq. (3.11) to obtain:

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot (-D \vec{\nabla} \rho) = D \nabla^2 \rho, \quad (3.13)$$

assuming that the diffusion coefficient D is a constant (see Appendix A for further explanation of the vector notation). This diffusion equation can be solved to give the concentration of the diffusing particles at every point in space for every time. If, for example, the particles are situated in a thin slab, the solution (exercise 2) of eq. (3.13) is a family of bell-shaped curves as depicted in Fig. 3.2.

For a steady (or stationary) diffusion process the concentration profile of diffusing particles does not change in time. Then $\partial \rho / \partial t = 0$ so the Laplacian of the concentration in eq. (3.13) is zero:

$$\nabla^2 \rho = 0 \quad (3.14)$$

This result is also known as the Laplace equation. To solve it the geometry and the boundary conditions of the diffusion problem must first be specified (Exercise 1). Often diffusion or Brownian motion is accompanied by *convection*, *i.e.* transport of particles by an external force (gravity, an electric field) or flow field. For a concentration ρ of colloids each moving with a velocity \vec{u} , the convective particle flux is:

$$\vec{j}_c = \rho \vec{u} \quad (3.15)$$

Adding a diffusive flux \vec{j}_d the continuity equation (3.7) for the colloid concentration becomes:

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot (\vec{j}_d + \vec{j}_c) = D \nabla^2 \rho - \vec{\nabla} \cdot (\rho \vec{u}) \quad (3.16)$$

This is the convection – diffusion equation which will be employed in Chapter 4 to derive the Stokes-Einstein diffusion coefficient, and in chapter 7 to analyse Brownian motion in an external force field.

Exercises

1. A vessel with constant colloid concentration C_A is connected by a tube of length L to another vessel with constant concentration $C_B \neq C_A$. Solve the diffusion equation (3.13) for diffusion in the tube.

2. a. Solve the diffusion eq. (3.13) for the case in which all particles are located at $t=0$ in a thin slab from which they start to diffuse in the positive and negative x -direction. (Hint: this problem can be solved using Laplace transformation).
b. Suppose at $t = 3$ sec, $\sqrt{\langle x^2 \rangle} = \sqrt{3}$ cm. Calculate the probability that at $t = 3$ sec a particle is found within $\sqrt{3}$ cm of the thin slab [0.68].
3. Identify where in later chapters the concept of a steady state is applied and verify that indeed eq. (3.10) has been used.
4. Re-interpret eqs. (3.1) - (3.10) for the case the flux lines in Fig. 3.1 represent an electric field \vec{E} . Rewrite these equations for the case the volume V contains a net charge density q .

References

- A pedagogical textbook on the subject matter of this chapter: R.F. Probstein, *Physicochemical Hydrodynamics; an Introduction* (2nd Edition, Wiley Europe, 1994)
- For further informal discussion of surface integrals and the divergence theorem (also applied to electrostatics) see: H.M. Schey, *Div, Grad, Curl and All That* (Norton, New York 1973)

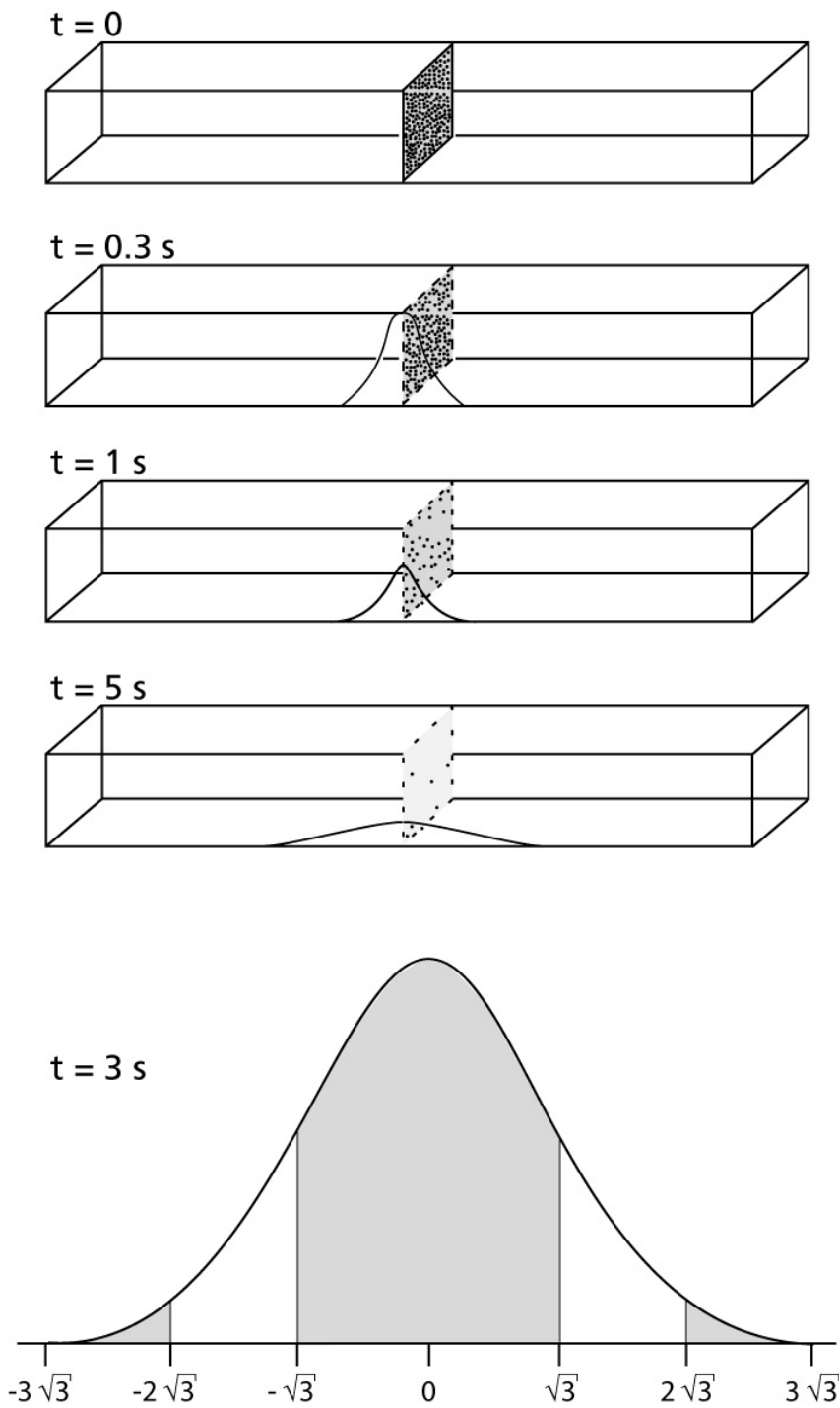


Fig. 3.2. Concentration profiles of Brownian particles which were located on a thin slab at $t=0$. The bell-shaped curve on a box represents the relative density of the particles for each point in the x -direction. The curve at the bottom illustrates the case in which the root-mean-square displacement at $t= 3$ s equals $\sqrt{3}$ cm, see exercise 2.

4 Brownian Motion

Brownian motion of colloids and the diffusion of solvent molecules are both the manifestation of translational (and rotational) kinetic energy. In thermal equilibrium this kinetic energy is on average the same for colloids and molecules. An important difference, however, arises with respect to time scales: for solvent molecules a colloidal particle is an extremely sluggish object, whereas the colloid experiences a dense swarm of molecules colliding with it at extremely high frequency. The various characteristic times are important for understanding Brownian motion and to apprehend what is actually observed when viewing the zigzagging colloids through an optical microscope (fig. 4.1). We will identify timescales below and provide typical times for the case of a standard colloidal sphere with properties listed in table 4.1.

Table 4.1 Standard colloidal sphere in water

Sphere radius	$R = 100 \text{ nm}$
Sphere mass density	$\delta = 1 \text{ g cm}^{-3}$
Temperature	$T = 298 \text{ K}$
Water viscosity	$\eta = 1 \text{ centipoise}^{1)}$ $= 10^{-3} \text{ Pa sec}$

¹⁾ 1 poise is 1 g/cm sec

Time scales

The molecular collision time τ_c

The fastest process in a colloidal dispersion, relevant for Brownian motion, is the collision of solvent molecules with each other and with a colloid. The average kinetic energy of particles with mass m with speed v equals

$$\langle E_{kin} \rangle = \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}kT \quad (4.1)$$

Thus for solvent molecules with radius a the collision time τ_c is of the order

$$\tau_c \sim \frac{a}{\sqrt{kT/m}} \quad (4.2)$$

because in a liquid the molecules are closely packed together. (The symbol ' \sim ' should be read as "is approximately equal to".) For water at room temperature $\langle v^2 \rangle^{1/2} = 370 \text{ m/sec}$ and taking $a \sim 1 \text{ \AA}$ we find $\tau_c \sim 2 \cdot 10^{-13} \text{ sec}$. Since the colloid is completely static on this time scale, τ_c is also the characteristic time for a colloid – molecule encounter. In other words, the molecules hit the colloid with a staggering frequency of $\tau_c^{-1} \sim 10^{13} \text{ sec}^{-1}$ on a colloid area of order one (\AA)². Thus on a time scale $t \gg \tau_c$ the colloid experiences a *continuous* fluid rather than a collection of discrete

molecules. In such a fluid the motion of a colloid is damped by the Stokes friction and it is this viscous damping by which a colloid 'relaxes' its momentum.

The momentum relaxation time τ_{mr}

Suppose a colloidal sphere has an initial velocity \vec{v}_0 and a momentum $\vec{p}_0 = m\vec{v}_0$ at $t = 0$. We ask for the time τ_{mr} it takes for this sphere to lose all its momentum due to viscous energy dissipation to the solvent. Bearing in mind that the viscous force on the sphere equals $f\vec{v}(t)$, we find by integrating Newton's second law

$$\frac{d\vec{p}}{dt} = -f\vec{v}(t), \text{ for } t \gg \tau_c, \quad (4.3)$$

that the instantaneous velocity $\vec{v}(t)$ decays as

$$\vec{v}(t) = \vec{v}_0 \exp[-t/\tau_{mr}], \quad (4.4)$$

with a decay time

$$\tau_{mr} = \frac{m}{f} = \frac{2}{9} \frac{\delta}{\eta} R^2, \quad (4.5)$$

for a sphere with mass $m = (4/3)\pi\delta R^3$ and friction factor $f = 6\pi\eta R$. For the standard sphere (see Table 4.1) in water $\tau_{mr} \sim (2/9)10^{-8}$ sec, which is much larger than the molecular collision time τ_c so it was indeed justified to use the Stokes friction factor in (4.3). The distance $l(t)$ travelled by the sphere during the momentum relaxation process (the 'relaxation step length') equals:

$$l(t) = \int_0^t v(t') dt' \quad (4.6)$$

$$= v_0 \tau_{mr} [1 - \exp[-t/\tau_{mr}]]; \quad v_0 \tau_{mr} \sim (mkT)^{1/2} / f$$

For the initial velocity v_0 we take the *rms*-speed from eq. (4.1) which for the reference sphere equals $\langle v^2 \rangle^{1/2} \sim 3$ cm/sec. Thus the maximum travelling distance in eq. (4.6) for the reference sphere is about $v_0 \tau_{mr} \sim 0.7 \text{ \AA}$. So in its kinetic energy exchange with the surrounding solvent, the colloid executes 'ballistic' steps which in length are comparable to those taken by solvent molecules. Due to its much larger mass, however, the colloid takes these steps at a very much lower frequency.

The diffusive or Brownian time scale $t \gg \tau_{mr}$

When the colloid has performed many 'moment-exchanging' steps it enters the diffusive time regime $t \gg \tau_{mr}$. This means that the net displacement of the colloid has become independent of its mass. This disappearance of the mass density in the diffusive regime and the appearance of the characteristic time dependence of Brownian displacements can be demonstrated as follows.

Consider a sphere on a straight line that executes 'ballistic' steps on the relaxation time scale τ_{mr} . These steps may have different lengths; eq. (4.6) suggests to consider an average displacement of order $l \sim v_0 \tau_{mr}$. The step frequency is typically $1/\tau_{mr}$ so if all steps are in the *same* direction the net displacement x at time t equals:

$$x \sim \frac{l}{\tau_{mr}} t \sim v_0 t; v_0 \sim \sqrt{3kT/m} \quad (4.7)$$

This result represents uniform, ballistic motion at a constant speed v_0 . The uniform displacement increases linearly in time and depends on the colloid mass. However, in reality the Brownian sphere does not step all the time in the same direction. The momentum exchange with the solvent is a random process: the sphere steps with equal probability either to the left (unit vector $-\hat{\delta}$) or to the right (unit vector $\hat{\delta}$). In that case the average displacement equals $\langle x \rangle = 0$, by definition. However, for the square of the displacement vector we find on average for a large number $n = t/\tau_{mr} \gg 1$ of ballistic steps:

$$\begin{aligned} \langle \vec{x} \cdot \vec{x} \rangle &\sim \left\langle \sum_{j=1}^n l \hat{\delta}_j \cdot \sum_{k=1}^n l \hat{\delta}_k \right\rangle \\ &= l^2 \frac{t}{\tau_{mr}} \langle \hat{\delta}_j \cdot \hat{\delta}_j \rangle + l^2 \sum_{j \neq k} \sum_{k=1}^n \langle \hat{\delta}_j \cdot \hat{\delta}_k \rangle \\ &= l^2 \frac{t}{\tau_{mr}} \end{aligned} \quad (4.8)$$

The average of the double-summation of cross-terms $j \neq k$ vanishes: the summation produces a sequence of dot products equal to 1 or -1 with equal probability. The colloid mass drops out in (4.8) because

$$l^2 \sim (v_0 \tau_{mr})^2 = kT \tau_{mr}^2 / m, \quad (4.9)$$

so the mean quadratic displacement is proportional to:

$$\begin{aligned} \langle x^2 \rangle &\sim \frac{kT}{m} \tau_{mr} t \\ &\sim \frac{kT}{f} t, \text{ for } t \gg \tau_{mr} \end{aligned} \quad (4.10)$$

The conclusion is that in the diffusive time regime it is the mean-squared displacement that grows linearly in time, rather than the displacement itself as for the ballistic motion in eq. (4.7). The difference is due to the fact that in the ballistic case all steps are added, whereas for Brownian motion, steps are not only added but just as frequently subtracted. We recognise in the proportionality constant in (4.10) the translational diffusion coefficient $D = kT/f$. The correct constant in (4.10) is actually $2D$, as we will show later in this chapter on the basis of the diffusion equation.

The configurational relaxation time τ_{cr}

Since the momentum relaxation steps are so small, a colloid enters the diffusive regime while its net displacement is still insignificant in comparison to its own radius. For Brownian motion to change positions of spheres (their 'configuration') significantly, we have at least to wait the time τ_{cr} needed for a sphere to diffuse across its own radius R . From eq. (4.8) we obtain:

$$\tau_{cr} \sim (R/l)^2 \tau_{mr} \quad (4.11)$$

Clearly relaxation of particle configurations is extremely slow in comparison to momentum relaxation. For the standard sphere from Table 4.1 with $R = 100 \text{ nm}$ and $l \sim 1 \text{ \AA}$, the difference is six orders of magnitude: $\tau_{cr} \sim 10^{-2} \text{ s}$. An alternative expression for τ_{cr} follows from (4.10):

$$\tau_{cr} \sim \frac{fR^2}{kT} \sim \frac{\eta R^3}{kT}, \quad (4.12)$$

which will return in our discussion of diffusion-controlled processes in chapter 7.

The angular momentum relaxation time τ_{ar}

Suppose a colloidal sphere rotates at an angular velocity $\vec{\Omega}_0$ at $t = 0$. We ask for the time τ_{ar} it takes for the sphere to dissipate all its angular momentum due to viscous friction in the solvent. First it is helpful to note the analogy between translation and angular motion:

Translational momentum $\vec{p} = m\vec{v}$	Angular momentum $\vec{J} = I\vec{\Omega}$
Force $\vec{F} = d\vec{p} / dt$	Torque $\vec{T} = d\vec{J} / dt$
Mass m	Moment of inertia I
Velocity \vec{v}	Angular velocity $\vec{\Omega}$

Newton's second law for translational motion is given by (4.3); its equivalent for rotational motion is:

$$\frac{d\vec{J}}{dt} = -f_r \vec{\Omega}(t), \quad (4.13)$$

where f_r is the rotational friction factor. The angular momentum is $\vec{J} = I\vec{\Omega}$, with I the moment of inertia. Integrating (4.13) yields for the angular particle velocity on time t :

$$\vec{\Omega}(t) = \vec{\Omega}_0 \exp[-f_r t / I] = \vec{\Omega}_0 \exp[-t / \tau_{ar}] \quad (4.14)$$

The decay time equals:

$$\tau_{ar} = \frac{I}{f_r} = \frac{1}{15} \frac{\delta}{\eta} R^2 \quad (4.15)$$

Here we have substituted the rotational friction factor $f_r = 8\pi\eta R^3$ and the moment of inertia $I = (8\pi/15)R^5\delta$ for a homogeneous sphere with mass density δ (see exercise 9). Comparing τ_{ar} to the momentum relaxation time τ_{mr} in eq. (4.5) we can conclude that translations and rotations of the sphere decay on the same time scale. Thus on the diffusive time scale both translational and angular momenta have completely relaxed. In other words, the sum of all forces and the sum of all torques on a diffusing, Brownian particle are both zero.

The rotational relaxation time τ_{RR}

When the colloidal sphere has performed many angular steps in which it exchanges angular momentum with the solvent, it enters the diffusive time regime $t \gg \tau_{ar}$.

Initially the net angular displacement θ of the sphere is still insignificant. For θ to deviate substantially from its value $\theta = 0$ at $t = 0$ we have to wait at least a time

$$\tau_{RR} = \frac{1}{D_r} \sim \frac{\eta R^3}{kT} \quad (4.16)$$

Here $D_r = kT/8\pi\eta R^3$ is the rotational diffusion coefficient that determines the decay of sphere orientation, as given by eq. (4.52). Thus the time τ_{cr} in eq. (4.12) taken by a sphere to significantly change its position coincides with the time τ_{RR} needed to significantly change its orientation.

The Brownian collision time τ_{bc}

We have already evaluated the collision time τ_c for molecules and it will come as no surprise that the collision time τ_{bc} for Brownian spheres will be *very* much larger. This collision time follows from Smoluchovski's theory for rapid coagulation in chapter 7; here we give a brief argument that leads to the same estimate for τ_{bc} .

Consider a tracer sphere with radius R diffusing in a dispersion with colloid number density ρ . The tracer diffuses an area of the order of Dt square meter in t seconds. Since spheres collide at a center-to-center distance $2R$, the tracer sweeps in t seconds a 'collision volume' $2DRt$ in which it encounters about ρDRt other spheres. Therefore, the typical time between two such encounters is of the order:

$$\tau_{bc} \sim \frac{1}{\rho DR} \quad (4.17)$$

Substituting $D = kT/6\pi\eta R$ and the volume fraction $\varphi = \rho(4/3)\pi R^3$, we can rewrite this to:

$$\tau_{bc} \sim \frac{\eta R^3}{kT\varphi} = \frac{\tau_{cr}}{\varphi}, \quad (4.18)$$

Where τ_{cr} is the configurational relaxation time from eq. (4.12). The R -dependence in (4.18) stems from the conversion of number density to volume fraction: if for a given φ we reduce the particle radius, the number density increases and particles collide at higher frequency. The time scale τ_{bc} determines the coagulation kinetics of colloids and we will return to it in Chapter 7 (see, for example, eqs. (7.14) and (7.29)).

The hydrodynamic decay time τ_{hd}

A moving colloid disturbs the surrounding fluid in two ways. First it causes a pressure wave that travels at the speed of sound. Secondly the colloid motion initiates a shear wave, namely a flow pattern of fluid layers moving at different speeds (see for example Fig. 5.1). When a liquid layer moving in the x -direction contacts a slower layer, it transfers x -momentum to the slower layer. This transfer

is further discussed in Chapter 5, where it is concluded that the time τ_{hd} needed for momentum to travel via a shear wave a distance R is, in order of magnitude:

$$\tau_{hd} \sim \frac{\rho}{\eta} R^2 \sim \tau_{mr} \quad (4.19)$$

where ρ is the fluid mass density (not to be confused with the number density ρ in (4.17)). This time is comparable to the moment relaxation time τ_{mr} , in eq. (4.5) needed for a colloid to dissipate its (translational and angular) momentum. This makes sense because viscous dissipation is primarily losing momentum via waves. Also the propagation of pressure (sound) waves occurs on a time scale similar to τ_{mr} . In water, for example, the velocity of sound is 1500 m/sec so it takes about 10^{-9} sec. for a pressure disturbance to travel a distance of $R = 100$ nm.

The important conclusion is that a hydrodynamic disturbance (either sound or shear) travels extremely fast on the diffusive time scale. When we slightly displace a sphere in a configuration of spheres, the flow field in the surrounding solvent almost instantaneously adapt itself. In other word, in the time region

$$\tau_{mr} \sim t \ll \tau_{cr} \quad (4.20)$$

colloids only experience each other (or a wall, or any other obstacle) via hydrodynamic flow fields ('hydrodynamic interactions'). Only on the timescale $t > \tau_{cr}$, the colloids encounter each other directly and experience the colloidal (or 'direct') interactions.

Quadratic displacement

The trajectory of a Brownian particle is an erratic curve with the characteristic feature that the observed *distance* in a given time interval Δt , depends on the magnification of the microscope (Fig. 4.1). Thus it is not possible to differentiate this distance unambiguously with respect to time to obtain a velocity. Einstein proposed to focus on the *displacement* of the particle, defined as the shortest distance between two positions of the colloid (Fig 4.1). Measurements of displacements yield the diffusion coefficient D of the colloid. The required relation between D and the average quadratic displacement was derived by Einstein, who also showed how D depends on the Stokes friction factor. The derivation is essentially based on the diffusion eq. (3.13). As shown below, to find the quadratic displacement no explicit solution of the diffusion equation is needed.

Consider a particle which diffuses for a time t to reach a (positive or negative) displacement x with respect to the particle position at $t = 0$. We assume that there is no external force on the colloid, so positive and negative displacements occur with equal probability. The average displacement for a large number of particles is therefore:

$$\langle x \rangle = \int_{-\infty}^{+\infty} P(x,t) x dx = 0, \quad (4.21)$$

where $P(x,t)dx$ is the probability that after t seconds, a particle displacement is in the interval between x and $x + dx$. The function $P(x,t)$ is a probability *density* (with dimension $1/m$) normalized via

$$\int_{-\infty}^{+\infty} P(x,t) dx = 1, \quad (4.22)$$

which expresses that the probability to find a particle *somewhere* equals one. The average of the quadratic displacement is calculated as follows. The probability to find a particle at a certain location x is proportional to the particle concentration $\rho(x,t)$ at that location:

$$P(x,t) = \text{constant} \times \rho(x,t) \quad (4.23)$$

This concentration is the solution of the diffusion equation (3.13), which reads for diffusion in the x -direction:

$$\frac{\partial}{\partial t} \rho(x,t) = D \frac{\partial^2}{\partial x^2} \rho(x,t) \quad (4.24)$$

where D is the diffusion coefficient. Substitution of (4.23) yields for the probability density:

$$\frac{\partial}{\partial t} P(x,t) = D \frac{\partial^2}{\partial x^2} P(x,t), \quad (4.25)$$

which allows us to evaluate the average quadratic displacement via the integration:

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} P(x,t) x^2 dx \quad (4.26)$$

We assume that the colloids have entered the diffusive time regime, i.e. the time t is much larger than the time τ_{mr} in eq. (4.5) for colloids to lose their momentum.

We are interested in the change of the average in (4.25) with time on this diffusive time scale:

$$\frac{d}{dt} \langle x^2 \rangle = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} P(x,t) x^2 dx = D \int_{-\infty}^{+\infty} \left[\frac{\partial^2}{\partial x^2} P(x,t) \right] x^2 dx \quad (4.27)$$

We now assume that $P(x,t)$ and its derivative monotonically decrease to zero for $x \rightarrow \pm \infty$. Then two integrations by parts yield (exercise 4):

$$\frac{d}{dt} \langle x^2 \rangle = 2D \quad (4.28)$$

which results in the Einstein equation for the average quadratic displacement:

$$\langle x^2 \rangle = 2Dt; \quad \text{for } t \gg \tau_{mr} \quad (4.29)$$

Note that this result has been obtained without solving the diffusion equation to find an explicit expression for $P(x,t)$, see also exercise 3. For the other Cartesian coordinates y and z the result is exactly the same. Thus the average quadratic radial displacement for a colloid diffusing in any direction \vec{r} from a central point is given by:

$$\langle r^2 \rangle = 6Dt; \quad r^2 = x^2 + y^2 + z^2 \quad (4.30)$$

Comparing eqs. (4.29) and (4.10) we must conclude that D is proportional (or possibly even equal) to kT/f . To investigate this proportionality further, it is instructive to consider colloids in an external field, again an idea due to Einstein.

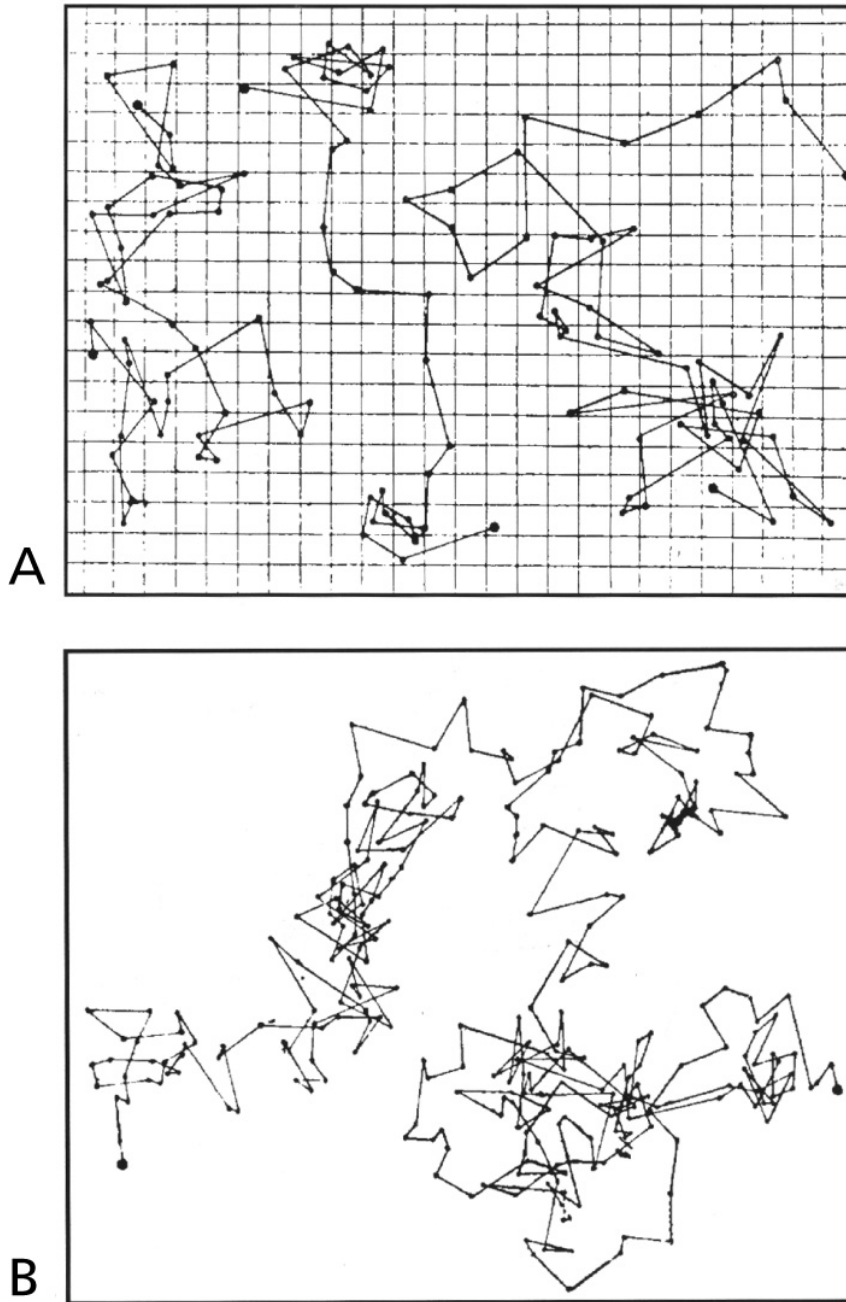


Fig.4.1. Brownian motion observed by Perrin for mastic spheres (radius $0.53 \mu\text{m}$) in water. Particle positions were marked every 30 seconds. The side of a square in A is about $3 \mu\text{m}$. Source: J. Perrin, *Atoms* (transl. D.L. Hammick), Constable & Company Ltd, London, 1916.

Translational diffusion coefficient

Suppose colloids in a dispersion experience an external force K , for example gravity or an electrical or magnetic force. The colloids accumulate in one part of the vessel (fig. 4.2). This accumulation is counteracted by diffusion which tends to homogenise the particle distribution. In equilibrium the two tendencies balance, leading to a concentration profile $\rho(x)$ which remains constant in time. This equilibrium implies that in any volume element the net flux of both momentum and colloids is zero.

The momentum flux results from two forces. The gradient in concentration produces a gradient in osmotic pressure, Π , which corresponds to a force per unit volume of dispersion, also referred to as a *force density*.

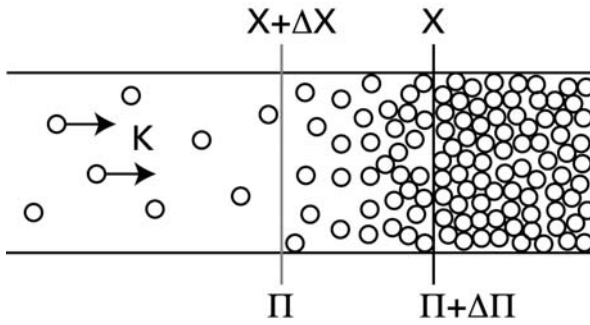


Fig 4.2. Equilibrium between osmotic pressure and an external force K

This osmotic force density is balanced by the external force which, per unit volume, equals K times the number density ρ of colloids. In equilibrium the sum of force densities (the net momentum flux) is zero:

$$\rho \vec{K} + \vec{\nabla} \Pi = 0 \quad (4.31)$$

We now assume that the colloids do not interact such that they obey Van 't Hoff's law $\Pi = \rho kT$. Then the solution of eq. (4.31) for a profile which changes only in the x -direction is:

$$\rho(x) = \rho_0 \exp[-Kx/kT], \quad (4.32)$$

where ρ_0 is the number density at $x = 0$. This is the Boltzmann distribution of non-interacting particles in an external force field. For colloids sedimenting in gravity, K can be identified as the weight of a colloid corrected for buoyancy. For that case eq.(4.32) is also called the sedimentation-diffusion equilibrium.

We can also describe equilibrium in terms of the particle flux \vec{j} which appears in the continuity equation

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot \vec{j} \quad (4.33)$$

Suppose the external force K propels particles at a stationary, constant velocity u . The corresponding convective flux ρu has to be added to the diffusive flux due to Brownian motion. Hence for convection and diffusion in the x -direction eq. (4.33) becomes:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x} \left[\rho u + D \frac{\partial \rho}{\partial x} \right] \quad (4.34)$$

In a stationary state the concentration ρ is independent of time t :

$$0 = -\frac{d}{dx} \left[\rho u + D \frac{d\rho}{dx} \right], \quad (4.35)$$

implying that the total flux is a constant, independent of x . In equilibrium this constant must be zero:

$$\rho u + D \frac{d\rho}{dx} = 0, \quad (4.36)$$

which can be integrated to yield:

$$\rho(x) = \rho_0 \exp[-ux/D] \quad (4.37)$$

This equilibrium profile must be the same profile as in eq. (4.32), which requires that the diffusion coefficient D equals:

$$D = \mu kT \quad (4.38)$$

Here the mobility coefficient μ is defined as the stationary velocity per unit of applied force:

$$u = \mu K \quad (4.39)$$

This mobility links two at first sight quite distinct transport processes, namely the drift velocity u of particles due to an external force and, secondly, the random spreading of particles or diffusion due to the thermal energy kT . For both processes the response of particles to the driving force is determined by the same mobility coefficient μ . Einstein's result eq. (4.38) is very general: the external force K remains unspecified and may be arbitrary small, just as the concentration gradient $d\rho/dx$. Further, no assumption has been made about the shape or size of the Brownian particles or the nature of the medium in which diffusion takes place: eq. (4.38) applies to the diffusion of DNA molecules in a porous gel, as well as to colloidal silica spheres in water. For each case, of course, the mobility coefficient has to be specified.

Colloids with a stationary velocity u in a viscous fluid experience a frictional force fu , where f is the Stokes friction factor. Thus $K = fu$ and, consequently, the mobility equals $\mu = 1/f$. Therefore the translational diffusion coefficient in (4.38) for colloid diffusion in a viscous fluid becomes:

$$D = \frac{kT}{f} \quad (4.40)$$

For spheres of radius R in a liquid of viscosity η we will derive in chapter 6 that

$$f = 6\pi\eta R \quad (4.41)$$

From eqs. (4.29), (4.40) and (4.41), incidently, we find the relation between the displacement of a colloidal sphere and Avogadro's number:

$$\langle x^2 \rangle = \frac{2kT}{6\pi\eta R} t = \frac{2R_g T}{6\pi\eta R N_{Av}} t, \quad (4.42)$$

in which R_g is the gasconstant. This is the relation which Perrin used in 1908 to determine N_{Av} by tracking the trajectories of diffusing colloids with an optical microscope, as mentioned in Chapter 2.

Quadratic angular displacement

The time dependence of angular Brownian displacements we employ here a derivation that is similar to that of (4.29). Consider a label diffusing on the surface of a unit sphere with radius $R = 1$ (see Fig. 4.3). The unit vector $\hat{u}(t)$ denotes the position of the label or, equivalently, the orientation of an axis through the label and the sphere centre. The angular displacement of the label at time t is defined by the vector $\hat{u}(t) - \hat{u}_0$, where \hat{u}_0 marks the label position at $t = 0$. For a large number of independently diffusing labels the average of the squared modulus of the displacement vector is:

$$\langle |\hat{u}(t) - \hat{u}_0|^2 \rangle = 2 - 2 \langle \cos \theta \rangle, \text{ for } t \gg \tau_{ar} \quad (4.43)$$

Here θ is the angle between the unit vectors $\hat{u}(t)$ and \hat{u}_0 . Note that (4.43) is only valid on the diffusional timescale, i.e. time t is much larger than the time τ_{ar} for the angular momentum to relax, see. Eq. (4.15). At $t = 0$ all labels have the same orientation \hat{u}_0 such that $\langle \cos \theta \rangle = 1$. By rotational diffusion the orientations gradually randomize until $\langle \cos \theta \rangle = 0$, signifying that all orientations occur with equal probability. This 'relaxation' of the initially non-uniform distribution of orientations is described by the distribution function $P(\theta, t)$. Analogous to the case of translational diffusion, the time dependence of the quadratic displacement in (4.43) can be found without solving the diffusion equation

$$\frac{\partial}{\partial t} P(\theta, t) = D_r \nabla^2 P(\theta, t) \quad (4.44)$$

Here D_r is the rotational diffusion coefficient, actually a frequency with dimension 1/sec. Note that $P(\theta, t)$, a probability density with dimension m^{-2} , does not depend on the angle ϕ (see also Fig. 4.4) so for a unit sphere with radius $R = 1$ the normalization condition is:

$$2\pi \int_{\theta=0}^{\pi} P(\theta, t) \sin \theta d\theta = 1 \quad (4.45)$$

The average of the cosine in eq. (4.43) follows from:

$$\langle \cos \theta \rangle = 2\pi \int_{\theta=0}^{\pi} P \sin \theta \cos \theta d\theta; \quad P = P(\theta, t) \quad (4.46)$$

For the time-derivative we can write, making use of the diffusion equation (4.44)

$$\begin{aligned} \frac{d}{dt} \langle \cos \theta \rangle &= 2\pi \int_{\theta=0}^{\pi} \frac{\partial P}{\partial t} \sin \theta \cos \theta d\theta \\ &= 2\pi D_r \int_{\theta=0}^{\pi} \frac{1}{\sin \theta} \left[\frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial P}{\partial \theta} \right) \right] \sin \theta \cos \theta d\theta \end{aligned} \quad (4.47)$$

Note that we only need the θ -dependent part of the Laplace operator in spherical coordinates (see Appendix A). Partial integration of the integral in (4.47) yields:

$$\left[\cos \theta \sin \theta \frac{\partial P}{\partial \theta} \right]_{\theta=0}^{\pi} - \int_{\theta=0}^{\pi} \sin \theta \frac{\partial P}{\partial \theta} d(\cos \theta) \quad (4.48)$$

The bracket term equals zero and the remaining integral, after a second partial integration, turns out to equal:

$$-2 \int_{\theta=0}^{\pi} P \sin \theta \cos \theta d\theta = -\frac{1}{\pi} \langle \cos \theta \rangle \quad (4.49)$$

The time-derivative in (4.47) therefore becomes

$$\frac{d}{dt} \langle \cos \theta \rangle = -2D_r \langle \cos \theta \rangle \quad (4.50)$$

with the solution

$$\langle \cos \theta \rangle = \exp[-t/\tau_{RR}]; \quad \tau_{RR} = \frac{1}{2D_r} \quad (4.51)$$

Thus the orientation of initially aligned, non-interacting anisometric particles decays exponentially in time. The rotational relaxation time τ_{RR} is determined by the rotational diffusion coefficient of the particles in question (spheres, rods, platelets, magnetic dipoles etc.). The angular displacement (4.43) can be rewritten as:

$$\langle |\hat{u}(t) - \hat{u}_0|^2 \rangle = 2(1 - \exp[-2D_r t]), \quad \text{for } t \gg \tau_{ar} \quad (4.52)$$

This expression has time limits that reveal an interesting resemblance, and a characteristic difference, to the case of translational Brownian motion. At short times such that $D_r t \ll 1$ and, consequently, small angular displacement such that $\cos \theta \sim 1 - \theta^2/2$, eq. (4.52) simplifies to:

$$\langle \theta^2 \rangle = 4D_r t, \quad \text{for } D_r t \ll 1 \quad (4.53)$$

This is equivalent to translational diffusion on a two dimensional plane for which $\langle z^2 \rangle = 4Dt$, where z is a two-dimensional displacement. Indeed, at short times the diffusive label has not probed the curvature of the sphere surface yet. Gradually, however, the label discovers it is diffusing on a sphere instead of on a flat plane. In the flat plane the quadratic displacement keeps on growing in time, whereas the angular displacement on a sphere surface is bounded by a maximum achieved when $\langle \cos \theta \rangle \sim 0$:

$$\langle |\hat{u}(t) - \hat{u}_0|^2 \rangle \sim 2; \quad \langle \hat{u}(t) \cdot \hat{u}_0 \rangle = 0, \quad \text{for } D_r t \gg 1 \quad (4.54)$$

This upper bound signifies that for a label the displacement θ and $\theta + 2\pi$ represent the same physical situation.

Rotational diffusion coefficient

The coefficient $D = kT/f$ for translational Brownian motion was found from the distribution of particle *positions* resulting from the equilibrium between diffusion and an external *force*. The rotational diffusion coefficient D_r can be derived in a very

similar manner from the distribution of particle *orientations* in response to an external *torque*. To this end we consider a collection of independent direction vectors as in fig. 4.4, each representing an orientation angle θ with respect to the axis at $\theta = 0$. The vectors rotate with the same angular velocity

$$\Omega = \frac{d\theta}{dt} [\text{rad sec}^{-1}], \quad (4.55)$$

towards $\theta = 0$. This rotation is caused by a torque T_0 , the physical nature of which we do not have to specify. One can choose a rotating external magnetic field acting on magnetic dipoles, or a shear flow aligning rods but for the argumentation here this choice is irrelevant. All we ask from the torque is to sustain a constant angular velocity, which is given by:

$$\Omega = \mu_r T_0 \quad (4.56)$$

Here μ_r is the rotational mobility defined as the steady angular velocity per unit of applied torque; note the analogy between μ_r and the translational mobility μ in eq. (4.39). The convective angular flux, that is, the number of vectors rotating by per second is:

$$j_\omega(\theta) = -\Omega \rho(\theta) = -\mu_r T_0 \rho(\theta), \quad (4.57)$$

in which $\rho(\theta)$ represents an orientation density, *i.e.* the number of direction vectors per unit angle. Due to this angular flux, vectors accumulate near $\theta = 0$ so a gradient $d\rho(\theta)/d\theta$ is formed which attempts to relax by rotational diffusion. The corresponding diffusive flux

$$j(\theta) = -D_r \frac{d\rho(\theta)}{d\theta}, \quad (4.58)$$

defines the rotational diffusion coefficient D_r of the independent, freely moving vectors. At equilibrium $j + j_\omega = 0$, and after integration we find the orientational equilibrium profile:

$$\rho(\theta) = \rho(\theta = 0) \exp[-\mu_r T_0 \theta / D_r], \quad (4.59)$$

which is the equivalent of (4.37) for the distribution of particle positions. The work done by the torque to achieve an angular displacement θ starting from $\theta=0$ equals

$$w(\theta) = \int_0^\theta T_0 d\theta' = T_0 \theta ; T_0 = \text{constant} \quad (4.60)$$

The Boltzmann distribution of the orientations is therefore:

$$\rho(\theta) = \rho(\theta = 0) \exp[-w(\theta) / kT] = \rho(\theta = 0) \exp[-T_0 \theta / kT] \quad (4.61)$$

The distributions (4.59) and (4.61) are identical only if the rotational diffusion coefficient satisfies:

$$D_r = \mu_r kT \quad (4.62)$$

This result is still independent of the medium in which a particle is rotating. When the medium is a viscous fluid the mobility is the inverse of the Stokes friction factor f_r :

$$D_r = \frac{kT}{f_r} \quad (4.63)$$

The analogy between the translational and the rotational diffusion coefficient is complete: they manifest a random spreading of, respectively, positions and orientations, driven by the thermal energy kT which is resisted by the same Stokes friction that also opposes, respectively, linear and angular drift in an external field.

Colloidal gases

Exercises

1. Calculate how far a marble with radius $r = 1$ cm diffuses in water in a century. ($T = 298$ K).
2. a) Calculate using equipartition the *rms* velocity of a colloidal sphere with radius 100 nm and mass density $\delta = 1$ g cm⁻³ at $T = 298$ K. [5.4 cm/sec]
 b) How large is the distance the sphere would traverse in one second with this velocity in uninterrupted linear motion?
 c) How large is the *rms* displacement in one second in case of Brownian motion of the sphere? (Explain any difference with b). [2.1×10^{-6} m]
3. Use the solution of the diffusion equation from exercise 2 in chapter 3, to verify that the law for quadratic displacement in eq. (4.29) is indeed correct.
4. Evaluate the integral in eq.(4.27). Which assumptions do you have to make for $P(x, t)$? Why are they physically plausible?
5. Where in the derivation of the diffusion coefficient eq. (4.40) it is assumed that the particles do not interact?
6. Estimate the time it would take oxygen molecules to diffuse in water ($D = 18 \times 10^{-6}$ cm²/sec) at room temperature a distance equal to 1) the typical thickness of a bacteria; 2) the typical thickness of a human being. Verify that diffusive transport of oxygen from the environment to the lungs is not an alternative to oxygen transport by red blood cells. Do you expect that an oxygen molecule in air diffuses much slower or much faster than in water? See for example S. Vogel *"Life's Devices; the physical world of animals and plants"* (Princeton University Press, 1988).
7. Discuss the validity of the rotational diffusion coefficient in eq. (4.63) for non-spherical particles.
8. Surprisingly often one finds in the literature the incorrect assertion that Brown observed 'Brownian motion' of pollen grains themselves. What is a typical pollen

grain size, and how far would such a grain diffuse in an observation time of , say , 10 sec? Conclusion?

9. Calculate I for a homogeneous sphere with radius R and mass density δ (see eq. (4.15)).

References

- An English translation of Einstein's work on Brownian motion can be found in: A. Einstein, *Investigations on the Theory of the Brownian Motion*, (Ed. by R. Fürth, Dover 1956). The editor gives a brief historical survey starting with the work of Robert Brown.
- Indispensable scientific biography of Albert Einstein, including an elucidating analysis of Einstein's papers on Brownian motion: A. Pais, *Subtle is the Lord* (Oxford University Press, 1982)
- For an instructive analysis of Brownian motion see *The Feynman Lectures on Physics* Vol. I (Addison-Wesley, Reading, 1977).
- An advanced treatment of Brownian motion can be found in: W.B. Russel, D.A. Saville and W.R. Schowalter, *Colloidal Dispersions* (Cambridge, 1995). J.K.G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier, Amsterdam, 1996).
- Brownian motion in its wider context of stochastic processes is treated in: N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, (North Holland, 1981). S. Chandrasekhar, *Stochastic Problems in Physics and Astronomy*, Rev. Mod. Phys. 15, 1 (1993).
- Rotational diffusion is treated by Debye in his classic *Polar Molecules* (Dover Publication, reprint of the 1929 Reinhold edition).

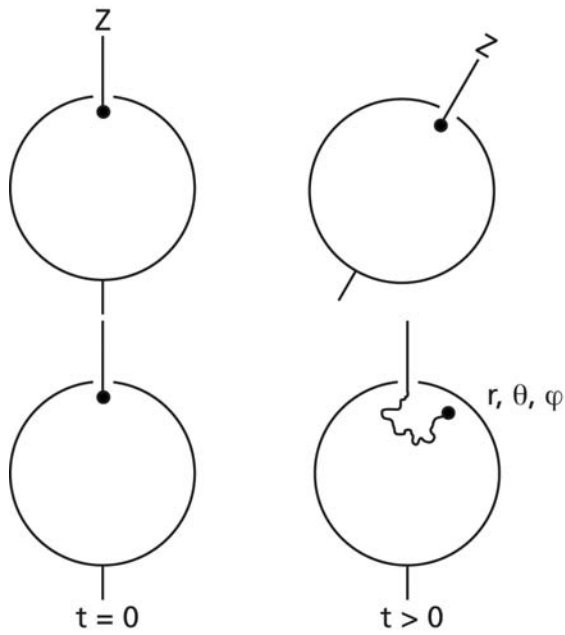


Fig. 4.3 Due to Brownian motion the direction of the z-axis (fixed to the spheres) fluctuates in time, which may be represented by a label that diffuses on the sphere surface from its initial position on the z-axis to a position (r, θ, ϕ) at time t .

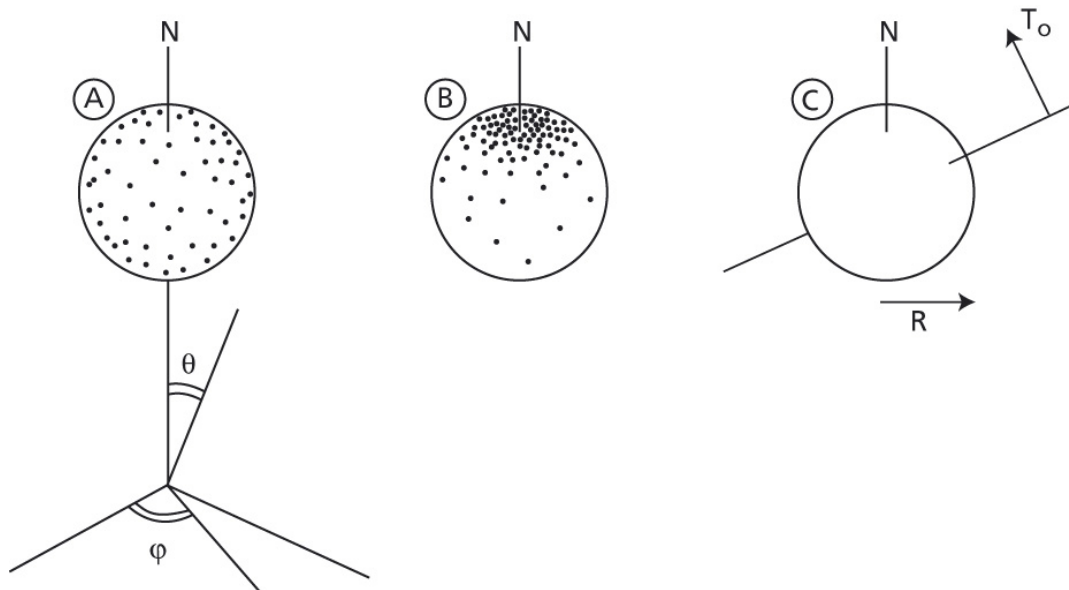


Fig. 4.4 Diffusing labels on a sphere surface (A) accumulate at the north pole (B) since all labels represents an axis subjected to the same constant torque T_0 as indicated in (C). Rotational diffusion tends to randomize axis orientations and counteracts the angular convection due to T_0 . In equilibrium the distribution of labels is given by eq. (4.59) or (4.61)

5 Stokes flow

Brownian motion of colloids usually takes place in a liquid medium, though there are notable exceptions such as colloids in a gas (aerosol), or the inorganic colloids which in vast numbers inhabit interstellar dust clouds. Thus we have to specify the mobility μ in the diffusion coefficient $D = \mu kT$ (in eq. 4.62) as a *hydrodynamic* mobility or its inverse, a hydrodynamic friction factor. This factor depends on the shape and size of the colloidal particle. The simplest case is a smooth, undeformable solid sphere. In this chapter we will introduce hydrodynamics to the level required to eventually calculate in chapter 6 the friction factor for such a solid sphere. We begin with a general description of fluid flow.

Fluid flow

The flow velocity \vec{u} in a fluid at position vector $\vec{r} = [x, y, z]$ and time t

$$\vec{u} = \vec{u}(\vec{r}, t) \quad (5.1)$$

has three Cartesian components u , v and w . Thus eq. (5.1) is a shorthand for the vector function:

$$\vec{u} = [u(x, y, z, t), v(x, y, z, t), w(x, y, z, t)] \quad (5.2)$$

Finding eq. (5.1) is the main task in a flow problem, because the velocity field \vec{u} tells us what all elements of the fluid are doing at any time. A simplification is a *steady flow* in which both magnitude and direction of \vec{u} are constant at any fixed point in space. Thus

$$\frac{\partial \vec{u}}{\partial t} = 0, \quad (5.3)$$

defines steady flow. Further, in many flow problems of interest (such as flow in a tube or past a sphere) \vec{u} is independent of one or two spatial coordinates. For example, *two-dimensional steady flow* has the form:

$$\vec{u} = [u(x, y), v(x, y), 0] \quad (5.4)$$

A *streamline* is a curve which at any point has the same direction as \vec{u} . For a steady flow the streamline pattern is the same at all times. Nevertheless, even though \vec{u} is constant at a fixed point in space, the flow velocity may change for a particular fluid element traveling along its streamline.

It is important to clearly distinguish the fate of a blob of fluid which 'follows the flow' from what happens in a volume element fixed in space. This distinction also appears in the notation for derivatives of fluid properties. Let $f = f(x, y, z, t)$ denote some property of the moving fluid such as its mass density or a component of \vec{u} . According to the chain rule:

$$df = \frac{\partial f}{\partial t} dt + \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz \quad (5.5)$$

The total rate of change in f is therefore:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} + \frac{\partial f}{\partial z} \frac{dz}{dt} \quad (5.6)$$

Suppose we measure f in a volume element rigidly attached to our boat, which is located at a position x, y, z . If this position is fixed then, according to eq. (5.6), $\partial f / \partial t$ is the change of f in time. However, if we tour around in the fluid the rate of change in f also depends on the components dx/dt etc. of the boat velocity. Only if the boat (engine switched off) passively follows a streamline these components equal the components of the flow velocity \vec{u} :

$$dx/dt = u, \quad dy/dt = v, \quad dz/dt = w \quad (5.7)$$

For this particular case of 'following the fluid' the notation D/Dt is used instead of d/dt :

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} + v \frac{\partial f}{\partial y} + w \frac{\partial f}{\partial z} = \frac{\partial f}{\partial t} + (\vec{u} \cdot \vec{\nabla})f \quad (5.8)$$

The derivative

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u} \cdot \vec{\nabla} \quad (5.9)$$

is known as the *material* or *substantial* derivative. Note that in eq. (5.8) the term $(\vec{u} \cdot \vec{\nabla})f$ is the contribution to the change in f in a blob of fluid due to its convection along a streamline. Consequently whenever

$$(\vec{u} \cdot \vec{\nabla})f = 0, \quad (5.10)$$

f is constant along a streamline; then f is called *stream function*, because its value generates a streamline. (Note that f might be a different constant on different streamlines, just as isobars in the weather forecast represent different but constant pressures). Stream functions will be needed later to analyse viscous flow past a translating sphere. By applying eq. (5.8) to the components u , v and w of the fluid velocity the *acceleration* of a fluid element at position \vec{r} is found to be:

$$\frac{D\vec{u}}{Dt} = \frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla})\vec{u} \quad (5.11)$$

Here $(\vec{u} \cdot \vec{\nabla})\vec{u}$ is a vector (see Appendix A) describing changes in \vec{u} for a fluid blob traveling along a streamline. The acceleration in eq. (5.11) is due to forces on the blob which will be identified below.

The Navier-Stokes equation

Consider a surface S enclosing a region V in the fluid, with a normal unit vector \vec{n} pointing outwards. The flow velocity component along the normal is $\vec{u} \cdot \vec{n}$ so the net fluid volume leaving V in unit time is

$$\int_S \vec{u} \cdot \vec{n} dS \quad (5.12)$$

For an incompressible fluid this integral must be zero because there can be no net gain or loss of fluid volume. Using the divergence theorem we find

$$\int_V \vec{\nabla} \cdot \vec{u} dV = 0, \quad (5.13)$$

which implies that

$$\vec{\nabla} \cdot \vec{u} = 0 \quad (5.14)$$

anywhere in the fluid: the divergence of the flow is zero for any volume element in V . Note that (5.14) is the continuity equation for an incompressible fluid which we already encountered in eq. (3.9). Next we consider the effect of the pressure $p=p(x,y,z,t)$ in the fluid. This pressure is a scalar function, independent of \vec{n} , so the force on a surface element δS is:

$$-p\vec{n}\delta S, \quad (5.15)$$

with a minus sign because \vec{n} points out of the region V . The net pressure force on the region is, using the divergence theorem:

$$-\int_S p\vec{n} dS = -\int_V \vec{\nabla} p dV \quad (5.16)$$

If $\vec{\nabla} p$ is continuous it will be almost constant over a sufficiently small blob of volume δV . The net pressure force on the blob due to the surrounding fluid is therefore $-\vec{\nabla} p \delta V$. The gravitational force on the blob with mass density ρ is $\rho \vec{g} \delta V$. The sum of forces must equal the product of the blob's mass $\rho \delta V$ and its acceleration, so we obtain:

$$\rho \frac{D\vec{u}}{Dt} = -\vec{\nabla} p + \rho \vec{g} \quad ; \quad \vec{\nabla} \cdot \vec{u} = 0 \quad (5.17)$$

This is the so-called *Euler equation* for the motion of a *non-viscous*, incompressible fluid. It turns out, however, that viscous forces in a colloidal suspension are important, if not dominating, so eq. (5.17) must be extended with the viscous stress on the blob. This stress is related to viscous transport of momentum as can be explained with reference to the sliding fluid layers in Fig. (5.1).

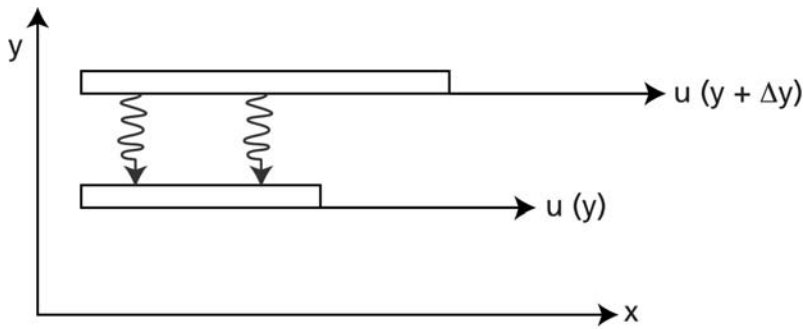


Fig. 5.1. Momentum transport from a fast fluid layer to a slower fluid layer.

We illustrate the origin of viscous forces in a sheared fluid for the simple case of a steady flow of an incompressible fluid described by:

$$\vec{u} = [u(y), 0, 0] ; \vec{\nabla} \cdot \vec{u} = \frac{\partial u(y)}{\partial x} = 0 \quad (5.18)$$

Thus the velocity component in the x -direction depends only on y . The momentum \vec{p} (not to be confused with pressure p) carried by this flow field is

$$\vec{p} = [p_x, p_y, p_z] = [mu(y), 0, 0] \quad (5.19)$$

For the change in momentum we can write, in general (see eq. (5.5))

$$d\vec{p} = \frac{\partial \vec{p}}{\partial t} dt + \frac{\partial \vec{p}}{\partial x} dx + \frac{\partial \vec{p}}{\partial y} dy + \frac{\partial \vec{p}}{\partial z} dz \quad (5.20)$$

In the present case all partial derivatives are zero, except the one with respect to y , and (5.20) simplifies to:

$$\frac{dp_x}{dt} = \frac{\partial p_x}{\partial y} \frac{dy}{dt} = \frac{dy}{dt} \frac{\partial mu(y)}{\partial y} \quad (5.21)$$

This equation describes a *shear force* in the x -direction acting on a fluid area at position y . In other words: x -directed momentum is transported in the y -direction: a slowly moving fluid layer at y receives momentum from a faster layer at $y+dy$. The *shear stress* τ is defined as the shear force divided by the area A on which it is working:

$$\tau = \frac{dy}{A dt} \frac{\partial mu(y)}{\partial y} = L \frac{dy}{dt} \frac{\partial \rho u(y)}{\partial y} \quad (5.22)$$

Here ρ is the mass density of the fluid, and L a length over which x -momentum diffuses in the y -direction. The kinematic viscosity ν is the ratio of the stress τ and the gradient in the moment density:

$$\tau = \nu \frac{\partial \rho u(y)}{\partial y} ; \nu = \frac{\eta}{\rho}, \quad (5.23)$$

where η is the *shear viscosity* of fluid. Before proceeding to Newton's law in (5.27) we look at the analogy between (5.23) and Fick's law for the diffusion flux of particles.

The flux of momentum, τ , is proportional to the gradient in momentum concentration, just as the flux of particles is proportional to the gradient in particle concentration. The coefficient ν in (5.23) is indeed a diffusion coefficient with dimension m^2/sec – consistent also with (5.22). Furthermore, for the case the momentum diffuses a distance L we find from (5.22) and (5.23)

$$L \int_0^L dy = \nu \int_0^t dt , \quad (5.24)$$

which leads to an instance of Einstein's law for quadratic displacement (see also eq. (4.30):

$$L^2 \sim \nu t , \quad (5.25)$$

where ν is a 'momentum diffusion coefficient'. Thus the time τ_h (not to be confused with the stress τ in (5.23)) needed for momentum to propagate a sphere radius R is of the order:

$$\tau_h \sim \frac{R^2}{\nu} = \frac{R^2 \rho}{\eta} \quad (5.26)$$

This is the hydrodynamic timescale already anticipated in Chapter 4, see eq. (4.18). The analogy between diffusion of momentum and diffusion of particles is somewhat veiled when for a liquid of constant mass density ρ , eq.(5.22) is rewritten to its usual form:

$$\tau_{yx} = -\eta \frac{\partial u(y)}{\partial y} \quad (5.27)$$

which is known as *Newton's viscosity law*. Though we obtained this law from the simple flow of eq. (5.18), it is valid for the general flow pattern described by eq. (5.1). Note the convention of indices; τ_{yx} is the x -directed shear stress on a fluid layer at y . Alternatively one can say that τ_{yx} is the flux of x -momentum in the y -direction. The latter interpretation makes the minus sign in eq. (5.27) easier to visualise: it is needed to give the flux in fig. 5.1 the right direction.

In rectangular coordinates nine stress components as in eq. (5.27) may be written down: τ_{yx} , τ_{yy} , τ_{yz} etc. Consider a volume element in a flow field (fig. 5.2). The stress component τ_{yx} works on the surface elements $\Delta x \Delta z$ so the corresponding viscous force component on the volume element is:

$$\Delta x \Delta z \left\{ \tau_{yx} \Big|_y - \tau_{yx} \Big|_{y+\Delta y} \right\} \quad (5.28)$$

Per unit volume this force equals

$$-\frac{\partial \tau_{yx}}{\partial y} = \eta \frac{\partial^2 u}{\partial y^2} \quad (5.29)$$

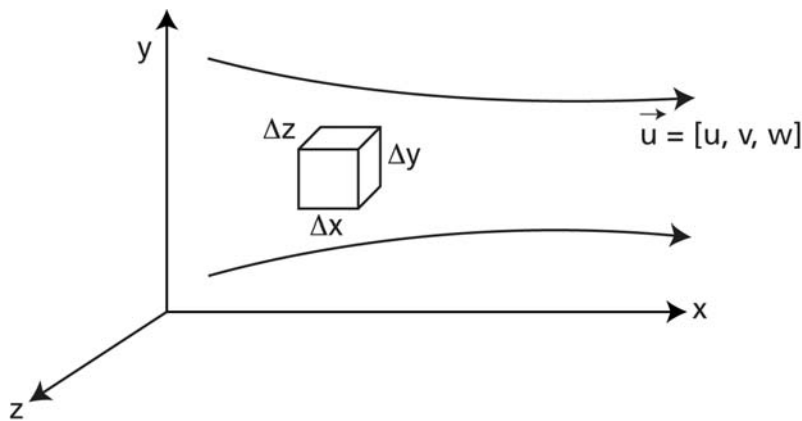


Fig. 5.2. Flow field exerts viscous forces on a volume element.



Fig. 5.3. Examples of turbulent flow of liquid water (top) and purely viscous flow of frozen water (bottom). Note the well-defined stream lines of the glacier, in contrast to the chaotic patterns in the breakers.

Considering all nine stress components the total viscous force per volume is

$$\eta \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) [u, v, w] = \eta \nabla^2 \vec{u} \quad (5.30)$$

The Laplacian ∇^2 is here expressed in rectangular co-ordinates x, y, z . The more general form of the Laplacian in Appendix A also applies to curvilinear co-ordinates. Adding eq. (5.30) to Eulers equations (5.17) we find:

$$\rho \frac{D\vec{u}}{Dt} = -\vec{\nabla}p + \rho\vec{g} + \eta\nabla^2\vec{u} ; \nabla \cdot \vec{u} = 0 \quad (5.31)$$

This is the *Navier-Stokes* equation for an incompressible fluid with constant viscosity η and constant mass density ρ .

The number of solutions of the complete Navier-Stokes equation are few. A serious difficulty arises at high velocities when chaotic turbulent flow occurs, in which the velocity and pressure are no longer unique functions of space and time coordinates. Turbulent flow can be observed everywhere (fig. 5.3) and common as it may be, its theoretical description is extremely complicated.

A sufficiently slow, *steady flow* is stable against the occurrence of turbulence. For a steady flow $\partial u / \partial t = 0$ in the material derivative D/Dt of eq. (5.9) so the equation of motion becomes:

$$\rho(\vec{u} \cdot \vec{\nabla})\vec{u} = -\vec{\nabla}p + \rho\vec{g} + \eta\nabla^2\vec{u} \quad (5.32)$$

A further simplification involves the omission of the inertial terms $\rho(\vec{u} \cdot \vec{\nabla})\vec{u}$ resulting in the so-called *Stokes* equation. This simplification is fortunately justified for the small-scale flow patterns involving colloidal particles for reasons explained in the next section.

Stokes flow

The example of flow in a curved tube (fig. 5.4) illustrates the physical meaning of the various terms in eq. (5.32). The hydrostatic pressure $\rho\vec{g}z$, which has a gradient in the vertical z -direction, induces liquid flow \vec{u} and the concomitant pressure distribution p . If the flow is steady nothing changes in time in any fixed volume element. Following a streamline we notice that the flow velocity changes direction which is 'resisted' by inertia: the $\rho(\vec{u} \cdot \vec{\nabla})\vec{u}$ term in eq. (5.32). In a cross section of the tube a velocity gradient is present leading to the viscous term $\eta\nabla^2\vec{u}$. The relative contributions from inertia and viscosity are estimated from the *Reynolds number* Re :

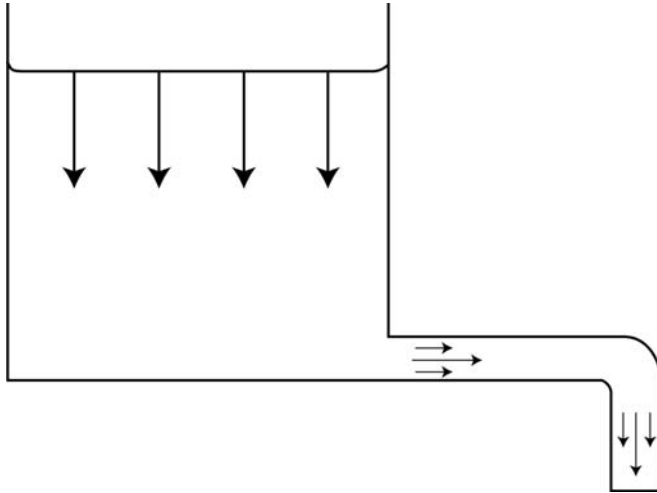


Fig. 5.4. Flow from a large reservoir into a curved tube.

$$Re = \rho \frac{UL}{\eta}, \quad (5.33)$$

in which U is a typical flow speed and L a characteristic length scale of the flow; in fig. 5.4 U may be the average flow velocity and L the diameter or length of the tube. The viscous term will dominate inertia if $Re \ll 1$. To understand the origin of this inequality we note that derivatives of velocity components such as $\partial u / \partial x$ are of order U/L , whereas second derivatives are of order U/L^2 . This gives the order of magnitude estimates:

$$\begin{aligned} |(\vec{u} \cdot \vec{\nabla})\vec{u}| &\sim U^2 / L \\ |\nabla^2 \vec{u}| &\sim U / L^2 \end{aligned} \quad (5.34)$$

The ratio of the two terms in eq. (5.32) is therefore:

$$\frac{\text{inertia term}}{\text{viscous term}} \sim \frac{\rho U^2 / L}{\eta U / L^2} = \rho \frac{UL}{\eta}; \quad (5.35)$$

which equals the Reynolds number in eq. (5.33). For colloidal particles typical values of UL are small enough to ensure that $Re \ll 1$ (Exercise 1). Then we may neglect the inertia term in eq. (5.32) to obtain (for $\vec{g} = 0$):

$$0 = -\vec{\nabla}p + \eta \nabla^2 \vec{u}; \quad \nabla \cdot \vec{u} = 0 \quad (5.36)$$

This is the *creeping flow* equation for purely viscous flow of an incompressible, Newtonian fluid, also known as *Stokes flow*. The term 'creeping' may be misleading; it denotes a flow rate U which is small enough such that $Re \ll 1$. On the colloidal scale (L in the submicron range) this rate may be actually quite high: rapidly sedimenting colloids and swimming microbes experience low-Reynolds number flow. Humans will only have this experience in a bath of very viscous syrup.

This is not the place to further elaborate on hydrodynamics, for which we refer to references at the end of Chapters 5 and 6. One final point here is the assessment that hydrodynamics for a diffusing colloid is quite different from what we observe

on a macroscopic scale when shaking or stirring a liquid. One surprising feature of creeping flow is its *reversibility* which can be demonstrated (in a famous experiment by G.I. Taylor) as follows. Fill the gap of a Couette geometry (two concentric cylinders) with viscous oil and insert a dyed blob of oil with a syringe. The blob is greatly sheared by slowly rotating one cylinder a few revolutions. However, if the cylinder is rotated back to its original position, the blob will return almost exactly to its original shape.

The reversibility of purely viscous flow has an interesting biological consequence: a microbe which tries to swim by flapping its tail to and fro makes no progress, because the effect of one flap is undone by the opposite flap. We are all living evidence of the fact that spermatozoa use their tail in a more efficient manner to swim in viscous biofluids.

Exercises

1. Estimate the Reynolds number for the sedimentation (due to gravity) of a colloidal sphere with a mass density of 2 g cm^{-3} , for a sphere radius $R = 100 \text{ nm}$ and $R = 1 \text{ }\mu\text{m}$.
2. a) A force F moves a very large flat plate with constant speed $u(D)$, at a distance $y = D$ from a parallel wall in water. Derive the velocity profile $u(y)$ from the Stokes equations (5.36), and give an expression for the average flow velocity $\langle u \rangle$.
b) Show that $u(y)$ is a stream function, and that it satisfies the continuity equation.
c) Suppose $u(D) = 1 \text{ mm sec}^{-1}$; $D = 1 \text{ mm}$ and $\eta = 10^{-3} \text{ Pa sec}$. How large is F (per unit area)? [10^{-3} Pa]

References

- For a more extensive treatment of the Navier-Stokes equation and Stokes flow see R. Bird, W. Stewart and E. Lightfoot, *Transport Phenomena* (New York, Wiley, 2002), and D.J. Acheson, *Elementary Fluid Dynamics*, (Oxford, Clarendon Press, 1992).
- More discussion on the viscosity dominated world of micro organisms and colloids is given in: E.M. Purcell, *Life at low Reynolds number*, Am. J. Physics 45 (1977) 3-11.

6 Stokes friction factor

Flow problems in colloidal systems either concern flow in channels or flow around submerged particles. Channel flow, also known as Poiseuille flow, occurs for example for colloidal dispersions in the Couette geometry of a viscosimeter and in the capillary for electrophoresis or electro-osmosis. Flow around particles occurs for colloids undergoing sedimentation or Brownian motion. Though our primary goal is the hydrodynamic friction factor for flow past a sphere, we will first, as a warming-up, solve the Stokes equations for viscous flow in channels with a simple geometry.

Viscous flow in simple geometries

Flow between flat plates

Consider two flat parallel plates as in fig. 6.1 at a distance d , and a flow of the form:

$$\vec{u} = [u(y), 0, 0] \quad (6.1)$$

This *plane parallel flow* satisfies $\vec{\nabla} \cdot \vec{u} = 0$, because $u(y)$ is independent of x . For this flow eq. (5.36) becomes:

$$\frac{\partial p}{\partial x} = \eta \frac{\partial^2 u}{\partial y^2}, \quad \frac{\partial p}{\partial y} = \frac{\partial p}{\partial z} = 0 \quad (6.2)$$

Since $\partial p / \partial x$ is constant in the y -direction, $\partial^2 u / \partial y^2 = \text{constant}$ so u must be a quadratic function of y . Integrating twice indeed yields the parabola:

$$u = \frac{1}{2\eta} \frac{dp}{dx} y(y-d), \quad (6.3)$$

a solution which satisfies the *stick boundary* or no-slip condition

$$u(y=0) = u(y=d) = 0, \quad (6.4)$$

stating that at the surface of the plates the fluid is in rest relative to the plates. The flow velocity averaged over the volume in the gap between the two plates is:

$$\langle u \rangle = \frac{\int_0^d \int_0^L u \, dx \, dy}{\int_0^d \int_0^L dx \, dy} = \frac{d^2}{12\eta} \frac{\Delta P}{L} \quad (6.5)$$

Here ΔP is the total pressure drop going from $x=0$ to $x=L$. The form of eq. (6.5) could have been guessed from a dimensionless form of the Stokes equation as follows.

Suppose $\langle u \rangle$ is the velocity averaged in the y -direction over a length d , and ΔP is the pressure drop over a characteristic length L . Introducing dimensionless parameters $\tilde{p}, \tilde{x}, \tilde{u}$ and \tilde{y} defined as:

$$p = \tilde{p} \Delta P, \quad x = \tilde{x} L, \quad u = \tilde{u} \langle u \rangle, \quad y = \tilde{y} d, \quad (6.6)$$

the Stokes equation becomes:

$$\frac{\Delta P}{L} \frac{\partial \tilde{p}}{\partial \tilde{x}} = \frac{\eta}{d^2} \langle u \rangle \frac{\partial^2 \tilde{u}}{\partial \tilde{y}^2} \quad (6.7)$$

Since the two derivatives only contain dimension-less quantities we can write:

$$\langle u \rangle = \frac{d^2}{\eta} \frac{\Delta P}{L} \times \text{numerical factor} \quad (6.8)$$

So we can expect that Stokes flow in another geometry will have an average fluid velocity with the same functional forms as the result for flat-plates in eq. (6.5). We will verify this expectation for flow in a capillary with a circular cross-section.

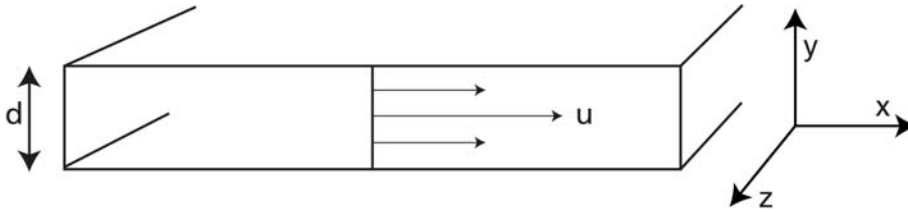


Fig. 6.1. Viscous flow between two parallel plates, with the parabolic liquid flow velocity profile given by eq. (6.3).

Flow in a circular tube

The flow velocity \vec{u} for *axial flow* in a tube of radius R , parallel to the z -axis (see fig. 6.2) has the components:

$$\vec{u} = [u_r, u_\theta, u_z] = [0, 0, u_z(r)] \quad (6.9)$$

Here we use cylindrical coordinates (r, θ, z) ; note that velocity components in the θ and r direction are zero. The Stokes equation for this type of flow is:

$$\frac{1}{\eta} \frac{\partial p}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} u_z \right) + \frac{\partial^2}{\partial z^2} u_z \quad (6.10)$$

$$\vec{\nabla} \cdot \vec{u} = \frac{\partial u_z}{\partial z} = 0$$

The zero-divergence of \vec{u} implies that u_z is constant in the z -direction, as expected for an incompressible liquid. Clearly then also $\partial^2 u_z / \partial z^2$ is zero:

$$\frac{1}{\eta} \frac{dp}{dz} = \frac{1}{r} \frac{d}{dr} \left(r \frac{d}{dr} u_z \right) \quad (6.11)$$

Integrating once yields the velocity gradient:

$$\frac{du_z}{dr} = \frac{1}{2\eta} \frac{dp}{dz} r + \frac{C}{r}; \quad C = 0 \quad (6.12)$$

The constant C must be zero, because otherwise this gradient is infinite at $r = 0$, which would imply an infinite stress. From this velocity gradient we obtain the viscous stress

$$\tau_{rz} = -\eta \frac{du_z}{dr}, \quad (6.13)$$

which can be used to calculate the total viscous force on the inner wall of the tube (exercise 2). The second boundary condition, in addition to the absence of an infinite stress at $r = 0$, is the no-slip boundary at the wall of the tube:

$$u_z(r = R) = 0 \quad (6.14)$$

The solution for eq. (6.12) which also satisfies this second condition is:

$$u_z = \frac{1}{4\eta} \frac{dp}{dz} (r^2 - R^2), \quad (6.15)$$

The average velocity in the tube is:

$$\langle u \rangle = \frac{\int_0^L \int_0^R u_z r dr dz}{\int_0^L \int_0^R r dr dz} = \frac{R^2}{8\eta} \frac{\Delta P}{L} \quad (6.16)$$

The similarity to the flat plate result in eq. (6.5) is clear; the different geometry only changes the numerical factor in eq. (6.8). Note that the volume rate of flow Q

$$Q = \langle u \rangle \pi R^2 = \frac{\pi R^4}{8\eta} \frac{\Delta P}{L} \quad (6.17)$$

strongly depends on the tube radius R . This result, called the *Hagen-Poiseuille law*, is the basis of viscosity measurements on (Newtonian) dispersions from flow rates in a tube.

Darcy's law

We note here in passing Darcy's law for viscous flow in a porous medium which states that the average flow velocity $\langle u \rangle$ is proportional to the average pressure gradient that drives the flow:

$$\langle u \rangle = -\frac{k}{\eta} \langle \vec{\nabla} p \rangle \quad (6.18)$$

Here k is the so-called *liquid permeability* of the porous medium. For one-dimensional flow in a medium of length L Darcy's law becomes:

$$\langle u \rangle = -\frac{k}{\eta} \frac{\Delta P}{L}, \quad (6.19)$$

where ΔP is the total pressure drop over the length L . The permeability depends on the geometry of the medium and can only be calculated for simple cases. We have, in fact, already made this calculation for flow in tubes and between parallel plates. So Darcy's law in its integrated form (6.19) is just an instance of eq. (6.8), with all geometrical details 'hidden' in the numerical factor. The liquid permeability k is

proportional to the square of a typical 'pore diameter' d , a proportionality which also holds for more complicated pore geometries, as further discussed in Scheidegger's book quoted at the end of this chapter.

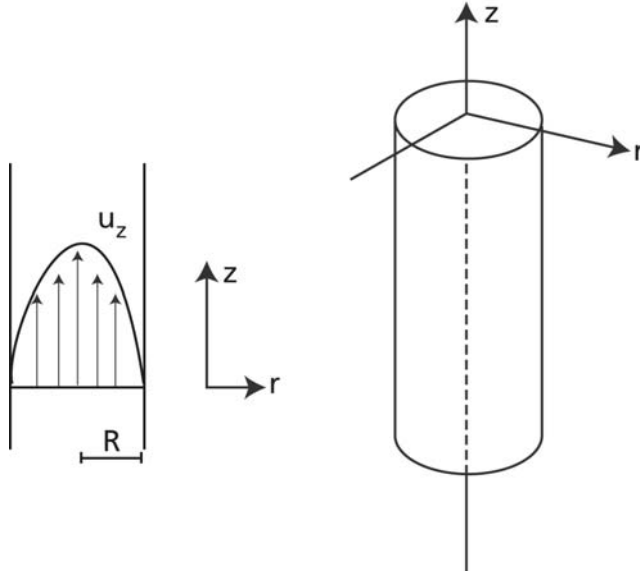


Fig. 6.2. Axial flow in a straight tube; the velocity profile is given by eq. (6.15).

Viscous flow past a sphere

In the previous examples of flow through a channel the total viscous force on the inner wall of the channel equals the external force (i.e. the pressure drop ΔP) which drives the flow (exercise 2). The analogous force balance for viscous flow past a colloidal particle defines the Stokes friction factor f :

$$K = fu \tag{6.20}$$

Here u is the constant liquid velocity relative to the particle and fu is the total viscous force which balances the external force on the colloid. For a rotating particle we have to read K as a torque and u as an angular velocity, see eq. (6.21). We will first calculate the rotational friction factor which involves a simpler flow field than for translational friction.

Rotational friction factor

Consider a solid sphere of radius R that slowly rotates at a constant angular velocity Ω around the z -axis in a large volume of quiescent fluid (see Fig. 6.3). We ask for the torque T_z required to maintain the sphere rotation, which defines the rotational friction factor f_r via

$$T_z = f_r \Omega \tag{6.21}$$

In terms of spherical coordinates (r, θ, ϕ) , the flow field near the sphere will be of the form:

$$\vec{u} = [u_r, u_\theta, u_\phi] = [0, 0, u_\phi(r, \theta)], \tag{6.22}$$

This field is symmetric about the z-axis of rotation so there is no dependence on the angle ϕ . The pressure P will be of the form $P = P(r, \theta)$, again without any ϕ dependence. The Stokes equation (5.36) therefore adopts the form:

$$\eta[\nabla^2 \vec{u}]_\phi = [\vec{\nabla} p]_\phi = 0 \quad (6.23)$$

From the ϕ -component of $\nabla^2 \vec{u}$, the Laplacian for spherical co-ordinates (see Appendix), we only need the derivatives that depend on θ and r . Thus the Stokes equation becomes:

$$0 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u_\phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (u_\phi \sin \theta) \right) \quad (6.24)$$

Since there is no distinction between 'up' and 'down' in the flow field, the substitution $\theta \rightarrow \pi - \theta$ should not change the flow velocity, which suggests that u_ϕ is proportional to $\sin \theta = \sin(\pi - \theta)$. As a trial solution for the flow field we therefore choose: $u_\phi = f(r) \sin \theta$. Insertion of this trial solution in eq. (6.24) leads to the following differential equation for $f(r)$:

$$\frac{d}{dr} \left(r^2 \frac{df}{dr} \right) - 2f = 0 \quad (6.25)$$

Here the trial solution is $f = r^n$, which on substitution in eq. (6.25) gives $n = 1$ and $n = -2$. Thus the flow field becomes:

$$u_\phi(r, \theta) = \left(C_1 r + \frac{C_2}{r^2} \right) \sin \theta \quad (6.26)$$

To determine the constants C_1 and C_2 we note that at infinity all velocity components are zero, and that on the sphere surface the liquid rotates with the same velocity as the sphere (stick boundary):

$$\begin{aligned} u_\phi &\rightarrow 0 && \text{as } r \rightarrow \infty \\ u_\phi &\rightarrow R\Omega \sin \theta && \text{as } r = R \end{aligned} \quad (6.27)$$

Here $R \sin \theta$ is the shortest distance of a point on the sphere surface to the rotation axis z . The point traverses a circle with circumference $2\pi R \sin \theta$ with velocity $R\Omega \sin \theta$. Application of these boundary conditions shows that $C_1 = 0$ and $C_2 = \Omega R^3$. Therefore the final expression for the flow field induced by the rotating sphere is:

$$u_\phi = \Omega R \left(\frac{R}{r} \right)^2 \sin \theta = u_\phi(r=R) \left(\frac{R}{r} \right)^2 \quad (6.28)$$

The relevant component of the stress is (see Appendix A):

$$\tau_{r\phi} = -\eta r \frac{\partial}{\partial r} \left(\frac{u_\phi}{r} \right) \quad (6.29)$$

To find the total torque we need to integrate the tangential force $\tau_{r\phi}(r=R) dS$ exerted on the fluid by a solid surface element dS , multiplying each element by its lever arm $R \sin \theta$ with respect to the rotation axis:

$$\begin{aligned}
T_z &= \int \tau_{r\phi}(r=R)R \sin \theta dS \\
&= \int_0^{2\pi} \int_0^\pi (3\eta\Omega \sin \theta)(R \sin \theta)R^2 \sin \theta d\theta d\phi = 6\pi\eta R^3 \Omega \int_0^\pi \sin^3 \theta d\theta \\
&= 8\pi\eta R^3 \Omega
\end{aligned} \tag{6.30}$$

By comparison with eq. (6.21) we conclude that the rotational friction factor for a sphere in a pure viscous fluid is given by:

$$f_r = 8\pi\eta R^3 \quad , \tag{6.31}$$

so the rotational diffusion coefficient of the sphere in eq. (4.63) equals:

$$D_r = \frac{kT}{8\pi\eta R^3} \tag{6.32}$$

Perhaps we expected the friction factor to be proportional to R^2 , namely the surface area between the rotating sphere and the surrounding fluid. However, f_r is proportional to the sphere *volume* because instead of the total viscous force ($\sim R^2$) we need to in (6.30) evaluate the viscous torque, which entails an additional R -term in the lever arm.

Sphere in a cavity

The rotational friction factor in (6.31) has been derived for a sphere in an unbounded fluid, far away from a confining wall or other spheres. For one particular confinement the friction factor can be easily corrected. Suppose the sphere is rotating in a spherical cavity with radius $(1+\delta)R$, with $\delta \geq 0$. If the cavity represents a stick boundary which is at rest with respect to the rotation axis, we have instead of (6.27) the boundary conditions:

$$\begin{aligned}
u_\phi &\rightarrow 0 & \text{as } r &\rightarrow (1+\delta)R \\
u_\phi &\rightarrow R\Omega \sin \theta & \text{as } r &= R
\end{aligned} \tag{6.33}$$

Evaluating the constants C_1 and C_2 in eq. (6.26), we find the flow field:

$$\frac{u_\phi}{\Omega R \sin \theta} = \frac{(1+\delta)^3 (R/r)^2 - (r/R)}{(1+\delta)^3 - 1} \tag{6.34}$$

Substitution of this flow field in the stress component $\tau_{r\phi}$ from eq. (6.29) we again obtain the torque T_z , to find eventually for the rotational friction factor:

$$f_r = 8\pi\eta R^3 \frac{(1+\delta)^3}{(1+\delta)^3 - 1} \tag{6.35}$$

Note that this result reduces to $8\pi\eta R^3$ in the limit $\delta \rightarrow \infty$, as it should. The rotational diffusion coefficient of the sphere in the cavity is accordingly:

$$D_r = \frac{kT}{8\pi\eta R^3} \left[1 - (1+\delta)^{-3} \right] \tag{6.36}$$

This simple extension of the rotational diffusion coefficient is also relevant for a sphere rotating in a complex fluid (such as a polymer solution) instead of a continuous solvent.²

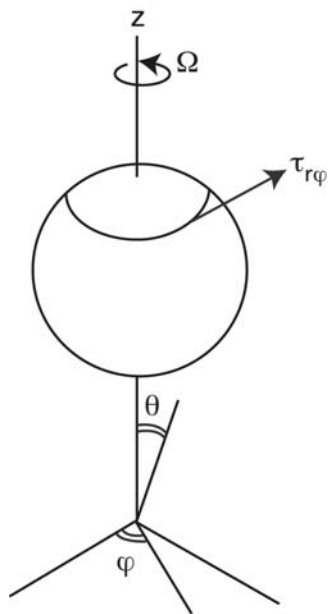


Fig.6.3. A solid sphere rotates at constant angular velocity. The sphere exerts a stress - $\tau_{r\varphi}$ in the φ -direction on the fluid.

² See for example: G.H. Koenderink, S. Sacanna, D.G.A.L. Aarts and A.P. Philipse, *Rotational and translational diffusion of fluorocarbon tracer spheres in semidilute xanthan solutions*, Phys. Rev. E (2004) 69 021804-1-12

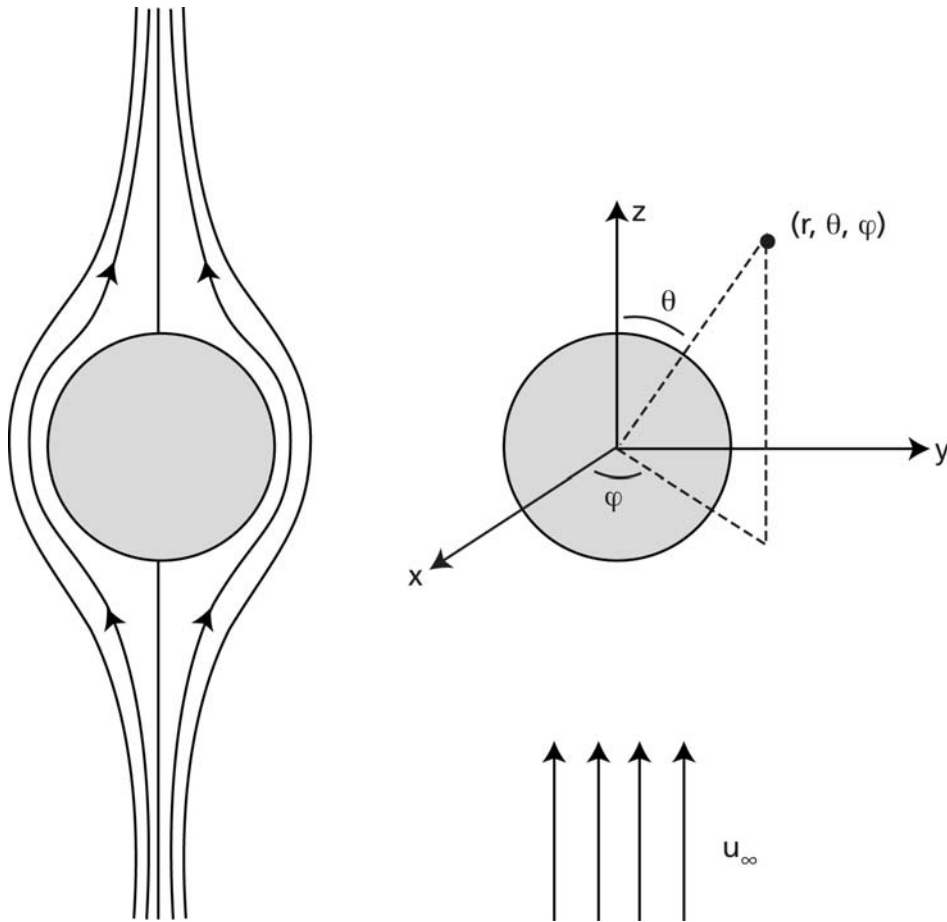


Fig. 6.4. Creeping flow past a fixed sphere.

Translational friction factor

We now determine the solution of the Stokes equations for creeping flow past a translating sphere. The non-rotating sphere in fig. 6.4 is fixed in a fluid which has a uniform speed u_∞ far away from the sphere. Using spherical coordinates (r, θ, ϕ) , the flow near the sphere is of the form:

$$\vec{u} = [u_r(r, \theta), u_\theta(r, \theta), 0] \quad (6.37)$$

This is a two-dimensional 'axisymmetric' flow: the fluid approaches from the z -direction so if we observe the flow in a plane perpendicular to the z -axis at a fixed distance r the pattern is the same for every angle ϕ ; the velocity component u_ϕ in eq. (6.37) is zero. In contrast to Poiseuille flow in a straight tube streamlines are now curved, which makes the creeping flow equation more difficult to solve directly for the components of \vec{u} . One option is to simplify the Stokes equation by rewriting them in terms of a stream function ψ instead of \vec{u} .

Stokes stream function

A stream function has a constant value along a streamline. According to eq. (5.10) ψ is a stream function if

$$(\vec{u} \cdot \vec{\nabla})\psi = 0 \quad (6.38)$$

In the case of plane parallel flow in eq. (6.1), the velocity component $u(y)$ is itself a stream function:

$$(\vec{u} \cdot \vec{\nabla})u(y) = u \frac{\partial u(y)}{\partial x} = 0 \quad (6.39)$$

Along the curved streamlines past a sphere, however, velocity components are not constant. The components are actually derivatives of a stream function:

$$u_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta}, \quad u_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \quad (6.40)$$

These equations define the *Stokes stream function* ψ , which is indeed a stream function because

$$(\vec{u} \cdot \vec{\nabla})\psi = u_r \frac{\partial \psi}{\partial r} + \frac{u_\theta}{r} \frac{\partial \psi}{\partial \theta} = 0 \quad (6.41)$$

For the velocity components in eq.(6.40) it is also the case that

$$\vec{\nabla} \cdot \vec{u} = 0 \quad (6.42)$$

This is the trick of Stokes' stream function: if we find ψ , the velocity \vec{u} in eq. (6.37) immediately follows while we automatically satisfy $\vec{\nabla} \cdot \vec{u} = 0$. So from the creeping flow eq. (5.32) we only need: (see Appendix A, eq. (A.12)):

$$\vec{\nabla} p = \eta \nabla^2 \vec{u} = -\eta \vec{\nabla} \times (\vec{\nabla} \times \vec{u}), \quad (6.43)$$

where we have substituted the Laplacian from eq. A12 in Appendix A. The curl of \vec{u} in terms of the stream function in eq. (6.40) is the vector:

$$\vec{\nabla} \times \vec{u} = \left[0, 0, -\frac{1}{r \sin \theta} E^2 \psi \right], \quad (6.44)$$

where E^2 is the differential operator

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \quad (6.45)$$

Substitution of (6.44) in eq. (6.43) yields:

$$\frac{\partial p}{\partial r} = \frac{\eta}{r^2 \sin \theta} \frac{\partial}{\partial \theta} E^2 \psi ; \quad \frac{1}{r} \frac{\partial p}{\partial \theta} = \frac{-\eta}{r \sin \theta} \frac{\partial}{\partial r} E^2 \psi \quad (6.46)$$

Next we note that the pressure $p=p(r,\theta)$ is a state function (dp is an exact differential). Then by definition the order of differentiation may be reversed:

$$\frac{\partial}{\partial \theta} \frac{\partial p}{\partial r} = \frac{\partial}{\partial r} \frac{\partial p}{\partial \theta} \quad (6.47)$$

The pressure can now be eliminated by combining (6.46) and (6.47) to obtain

$$E^2 (E^2 \psi) = 0, \quad (6.48)$$

which on substitution of (6.45) can be rewritten to:

$$\left[\frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \right) \right]^2 \psi = 0 \quad (6.49)$$

This is the simplified version of the differential equation (6.43) for \vec{u} . We now have to guess a form of ψ which satisfies (6.49). A suitable form suggests itself by the 'infinity condition': at $r \rightarrow \infty$ the flow becomes uniform with speed u_∞ (see fig. 6.4) in the z -direction:

$$u_r \sim u_\infty \cos\theta, \quad u_\theta \sim -u_\infty \sin\theta, \quad \text{as } r \rightarrow \infty \quad (6.50)$$

For the stream function in eq. (6.40) this implies:

$$\psi \sim \frac{1}{2} u_\infty r^2 \sin^2\theta, \quad \text{as } r \rightarrow \infty, \quad (6.51)$$

which suggests a solution to eq. (6.49) of the form

$$\psi = f(r) \sin^2\theta \quad (6.52)$$

Substitution of this trial solution in eq. (6.49) shows that $f(r)$ follows from the differential equation:

$$\left(\frac{d^2}{dr^2} - \frac{2}{r^2} \right) f(r) = 0 \quad (6.53)$$

We now try solutions of the form $f = r^\alpha$, which indeed satisfy eq. (6.53) provided that:

$$[(\alpha - 2)(\alpha - 3) - 2][\alpha(\alpha - 1) - 2] = 0, \quad (6.54)$$

which is the case for $\alpha = -1, 1, 2, 4$. Therefore:

$$f(r) = \frac{A}{r} + Br + Cr^2 + Dr^4, \quad (6.55)$$

where A, B, C and D are arbitrary constants. The condition of uniform flow at infinity in eq. (6.51) can only be fulfilled if $C = \frac{1}{2} u_\infty$ and $D = 0$. The stick-boundary condition that u_θ and u_r in eq. (6.40) are both zero on the sphere surface implies

$$-\frac{\partial \psi}{\partial r} = \frac{1}{r} \frac{\partial \psi}{\partial \theta} = 0 \quad \text{on } r = R, \quad (6.56)$$

which reduces to $(1/R)f(R) = f'(R) = 0$. This determines the constants $A = u_\infty R^3/4$ and $B = -3u_\infty R/4$. The Stokes stream function finally turns out to be:

$$\psi = \frac{1}{4} u_\infty \left(2r^2 + \frac{R^3}{r} - 3Rr \right) \sin^2\theta \quad (6.57)$$

Streamlines as sketched in fig. 6.4 correspond to certain values of ψ . For example $\psi = 0$ generates the streamline which satisfies either $r = R$ or $\theta = 0, \pi$. Note in fig. 6.4 that the flow pattern has 'for-aft' symmetry: the streamlines will remain the same if the flow u_∞ is reversed. This is another example of the reversibility of

creeping flow referred to at the end of section 5.3. By substituting ψ we can compute the velocity components in eq. (6.40):

$$\frac{u_r}{u_\infty} = \left[1 - \frac{3}{2} \left(\frac{R}{r} \right) + \frac{1}{2} \left(\frac{R}{r} \right)^3 \right] \cos \theta \quad (6.58)$$

$$\frac{u_\theta}{u_\infty} = - \left[1 - \frac{3}{4} \left(\frac{R}{r} \right) - \frac{1}{4} \left(\frac{R}{r} \right)^3 \right] \sin \theta$$

One striking feature of this velocity profile of a translating sphere is its long range due to the R/r term (cf the flow field around a rotating sphere in (6.28)). So a diffusing or sedimenting colloidal sphere causes a disturbance of a uniform flow which extends over many sphere diameters. Therefore these solutions to the Stokes equation for a single sphere are only valid if the sphere is far away from other spheres or a wall.

The radial pressure gradient in eq. (6.46) turns out to be:

$$\frac{\partial p}{\partial r} = 3u_\infty \eta R r^{-3} \cos \theta \quad (6.59)$$

At infinity the pressure in the uniform flow is p_∞ :

$$p = p_\infty - \frac{3}{2} u_\infty \eta \frac{R}{r^2} \cos \theta \quad (6.60)$$

As expected the pressure is larger than the bulk pressure p_∞ at the sphere side which receives the flow. For a colloidal sphere sedimenting or diffusing in a liquid we are interested in the net force which is exerted on the sphere in fig. 6.4. The relevant viscous stress component is

$$\tau_{r\theta} = -\eta r \frac{\partial}{\partial r} \left(\frac{u_\theta}{r} \right) \quad (6.61)$$

namely the stress tangential to the sphere surface due to the velocity gradient perpendicular to the surface. For the velocity component u_θ in eq. (6.58) we obtain for the stress on the sphere surface:

$$\tau_{r\theta} = \eta \frac{3}{2} \frac{u_\infty}{R} \sin \theta, \quad \text{at } r = R \quad (6.62)$$

Further, the pressure on the surface is:

$$p = p_\infty - \eta \frac{3}{2} \frac{u_\infty}{R} \cos \theta, \quad \text{at } r = R \quad (6.63)$$

By symmetry the net force on the sphere will be in the z-direction, parallel to the uniform flow (fig. 6.4). The relevant components of p and $\tau_{r\theta}$ on the sphere surface are

$$t = \tau_{r\theta} \sin \theta - p \cos \theta = \frac{3}{2} \frac{\eta u_\infty}{R} - p_\infty \cos \theta \quad (6.64)$$

The total force F on the sphere is the integral of t over the whole sphere surface:

$$\begin{aligned}
F &= \int_0^{2\pi} \int_0^{\pi} tR^2 \sin\theta d\theta d\varphi \\
&= 6\pi\eta u_{\infty} R
\end{aligned}
\tag{6.65}$$

Note that the term $\rho_{\infty} \cos\theta$ in eq. (6.64) does not contribute to this total force, because the isotropic bulk pressure p_{∞} can have no net effect on the sphere. Thus the stress in eq. (6.64) on the sphere surface is everywhere the same, a surprising result in view of the velocity profile in Fig. 6.4. The proportionality factor between the uniform flow velocity u_{∞} far away from the sphere and the drag force is:

$$f = 6\pi\eta R, \tag{6.66}$$

the well-known Stokes friction factor for the translational motion of a spherical particle in a viscous fluid.

One application of the Stokes friction factor in (6.66) concerns a sedimenting sphere which accelerates downwards in a fluid until a constant velocity U_0 is achieved. Then the drag force exactly balances the weight of the sphere, corrected for buoyancy:

$$6\pi\eta U_0 R = \frac{4}{3} \pi R^3 (\rho_{\text{sphere}} - \rho_{\text{fluid}}) g, \tag{6.67}$$

where ρ is a mass density. The stationary sedimentation velocity

$$U_0 = \frac{2R^2}{9\eta} (\rho_{\text{sphere}} - \rho_{\text{fluid}}) g, \tag{6.68}$$

also called the Stokes velocity, of course only applies if all assumptions underlying the Stokes friction factor ($Re \ll 1$, no-slip boundaries etc.) are justified. The same applies of course for the Stokes-Einstein diffusion coefficient for the sphere (see also eq. (4.40)):

$$D = \frac{kT}{6\pi\eta R} \tag{6.69}$$

One assumption has not been addressed explicitly, namely that the fluid surrounding the sphere is a continuum. For a colloidal micron-sphere diffusing or sedimenting in a low-molecular solvent this is certainly the case: on its diffusive time scale the sphere experiences macroscopic hydrodynamics (see the discussion on time scales in Chapter 4). For an ion, however, one would expect that the continuum hypothesis fails. Nevertheless, the Stokes friction factor eq. (6.66) is widely used in the Stokes-Einstein diffusion coefficient of small solute molecules, and in many cases appears to work well.

Stick versus slip

The Stokes-Einstein diffusion coefficients for sphere translation and rotation are widely applied, often without attention being paid to the crucial assumption of a stick boundary condition. The derivation of the Stokes friction factors relies on fluid mechanics of a sphere suspended in a continuum whereas the occurrence of 'stick' or 'slip' at the solid-liquid interface involves molecular details. In the derivation of (6.66) the stick boundary is primarily a mathematical convenience and it is not at all certain that it holds for a particular particle in a particular liquid.

Indeed, an important advantage of the stick boundary condition is that only the sphere radius R and the solvent viscosity η enter into the Stokes friction factors. Slip, however, leads to an additional parameter β whose value is not a priori known, because when the solid surface and the adjacent fluid move at different speeds the resulting frictional force may differ from one solid-liquid combination to another. The parameter β can be defined as the constant of proportionality between the tangential stress τ and the relative solid-liquid speed u , at the sphere surface:

$$\tau = \beta u, \quad \text{at } r = R \quad (6.70)$$

Note the analogy with eq. (6.20): β has the dimension of a friction factor per unit area. For the tangential velocity component u_ϕ on a rotating sphere this boundary condition adopts the form

$$\beta(R\Omega \sin \theta - u_\phi) = \tau_{r\phi} = -\eta r \frac{\partial}{\partial r} \left(\frac{u_\phi}{r} \right), \quad \text{at } r = R \quad (6.71)$$

bearing in mind that u_ϕ is the velocity relative to the z -axis of rotation (see fig. 6.3). The flow field is (cf eq. (6.26))

$$u_\phi = \frac{C}{r^2} \sin \theta, \quad (6.72)$$

which on substitution in eq. (6.71) determines the constant C with the result:

$$u_\phi = \Omega R \left(\frac{R}{r} \right)^2 \sin \theta \frac{1}{1+3S}; \quad S = \frac{\eta}{\beta R} \quad (6.73)$$

Where S is a dimensionless parameter, which measures the 'amount' of slip at the sphere surface. The term $1/1+3S$ multiplies the flow field from eq. (6.28) and obviously also the total torque T_z on the sphere in eq. (6.30), so the rotational friction factor modifies to

$$f_r = \frac{8\pi\eta R^3}{1+3S} \quad (6.74)$$

The stick boundary condition is the limit $S \rightarrow 0$, where we recover our earlier result $f_r = 8\pi\eta R^3$. The pure slip boundary condition $S \rightarrow \infty$ (i.e. zero tangential stress on the sphere surface) reduces the Stokes factor to $f_r = 0$. In this limit the rotating sphere does *not* displace any liquid; no steady state rotation can occur because there is no friction to balance the external torque. For the translational friction factor one can show (exercise 4) that the boundary condition (6.70) leads to:

$$f = 6\pi\eta R \frac{1+2S}{1+3S} \quad (6.75)$$

In this case the pure slip limit yields

$$f = 4\pi\eta R, \quad \text{for } S \rightarrow \infty \quad (6.76)$$

So we may conclude that for spheres in a continuous fluid the incorporation of slip effects in friction factors is possible on the basis of the plausible boundary condition of eq. (6.70). Nevertheless, the issue of 'slip versus stick' is far from resolved. For further discussion we refer to the literature cited below.

Exercises

1. Give the equation for the volume rate of flow Q for the flat plates in fig. 6.1.
2. Sketch the profile of the viscous stress τ_{rz} and show that the total viscous force on the inner wall of the tube in fig. 6.2 equals $\pi R^2 \Delta P$.
3. Derive the Stokes friction factor (per unit length) for the rotation of a very long cylinder with radius R around its long axis (cf. fig. 6.3). Answer: $f_r = 4\pi\eta R^2$.
4. Eq. (6.74) seems not to have been reported earlier. Formula (6.75), however, can be found in a somewhat different notation in J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Englewood Cliffs, NJ: Prentice-Hall, 1965). Verify that the formula is correct.
5. Re-examine the Poiseuille flow in simple geometries with a "pure-slip" boundary condition. Conclusion?

References

- The derivation of the translational Stokes friction factor is adapted from: D.J. Acheson, *Elementary Fluid Dynamics*, (Oxford, Clarendon Press 1992).
- The derivation by Stokes himself can be found in: G.C. Stokes, *Mathematical and Physical Papers*, Vol III, (Cambridge, Cambridge University Press, 1901).
- The treatment of the rotational friction factor is adapted from a classic textbook with many practical transport problems:
R. Bird, W. Stewart and E. Lightfoot, *Transport Phenomena*, (New York, Wiley, 2002).
- For flow in porous media and Darcy's law, see for example: Scheidegger, *Physics of Flow in Porous Media* (Toronto, University of Toronto Press, 1974).
- An entrance to literature on 'stick versus slip' is S. Granick, Y. Zhu and H. Lee, *Slippery questions about complex fluids flowing past solids*, Nature Mat. 2 (2003) 221.
- For experiments on rotational and translational diffusion of colloids and discussions on the validity of the Stokes-Einstein equation for Brownian motion in 'discrete' host solutions, see G.H. Koenderink, *Rotational and translational diffusion in colloidal mixtures*, PhD thesis, Utrecht University, 2003.

7. Brownian encounters

In a quiescent solution, in absence of any external fields, Brownian motion is the only transport mechanism for (non-living) colloidal particles to encounter each other. To get an idea of the time scale involved we compute the time τ taken by a sphere of radius R to diffuse a mean-square-displacement equal to R^2 . This is the configurational relaxation time τ_{cr} from eq. (4.11). For spheres in water at room temperature:

R = 10	nm	$\tau_{cr} = 2.4 \cdot 10^{-7}$	sec
100	nm	$2.4 \cdot 10^{-4}$	sec
1000	nm	$2.4 \cdot 10^{-1}$	sec
10	μm	$2.4 \cdot 10^2$	sec

Clearly for small colloidal particles, Brownian motion on their own colloidal length scale is fairly rapid, whereas for radii much larger than one micron, diffusion is a hopelessly inefficient transport vehicle. This inefficiency also applies to small colloids that have to cross over distances of micron's or more. In these cases convective transport must take over: we stir to homogenize a solution rather than waiting for diffusion to do the mixing.

On the other hand, convection becomes an inadequate transport vehicle close to a surface, or in sufficiently narrow geometries, where the viscous drag is very large. (It is left as an exercise to the reader to calculate the diameter of a capillary below which diffusion is faster than Poiseuille flow). So for small particles or molecules that have to react with a surface – or penetrate a biological cell – the combination of convection to cross large distances, plus Brownian motion for the final 'sub-micron step' is a profitable strategy. Of the many examples in nature we mention viruses that are convected on a (literary) global scale by their hosts in aero planes but that eventually have to locate suitable receptors on a new target cell via Brownian motion on a sub-micron scale.

Diffusion to a spherical target

Brownian collisions on a spherical target will be analysed in more detail below because it captures the essential kinetics of many processes including coagulation of colloids, diffusional growth and diffusion-controlled chemical reactions.

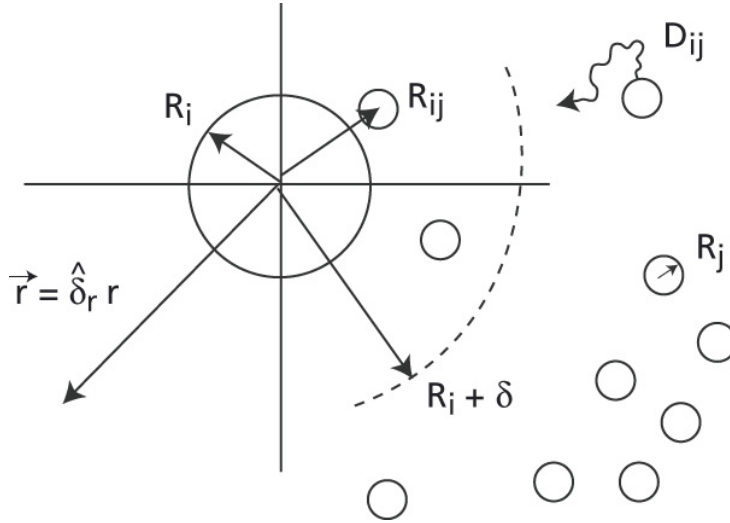


Fig. 7.1. Spheres j diffuse from a bulk (with number concentration $c_{j,\infty}$) at a distance $R_i + \delta$ towards a diffusing tracer sphere with radius R_i which acts as an infinite sink.

We consider a collection of Brownian spheres with radius R_j , diffusing in the vicinity of a target sphere with radius R_i centered at the origin (fig. 7.1). The frequency of collisions of j -spheres on the target sphere can be found (following Smoluchovski) via a stationary diffusion model as follows.

Imagine that every j -sphere that hits the target sphere is removed from the solution while simultaneously a new j -sphere is added to the bulk far away from the target. In this way a steady diffusion of j -spheres from the bulk to the target will be established. Alternatively one can also remove j -spheres by incorporating them in the target i -sphere which, consequently, will grow in time (see the later text on diffusional growth). In the latter case the bulk should be large enough to ensure a constant bulk concentration of j -spheres. The continuity equation for the number concentration c_j of j -spheres is (see chapter 3):

$$\frac{\partial c_j}{\partial t} = -\vec{\nabla} \cdot \vec{j}_d, \quad (7.1)$$

which together with Fick's first law

$$\vec{j}_d = -D_{ij} \vec{\nabla} c_j \quad (7.2)$$

leads to the diffusion equation which we already encountered in slightly different notation in eq. (3.13):

$$\frac{\partial c_j}{\partial t} = D_{ij} \nabla^2 c_j \quad (7.3)$$

Here D_{ij} is the diffusion coefficient of the j -spheres *relative* to the centre of the target sphere which itself also exhibits Brownian motion. The concentration profile of j -spheres reached a steady state when $\partial c_j / \partial t = 0$. Then (7.3) reduces to the Laplace equation:

$$\nabla^2 c_j = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_j}{\partial r} \right) = 0, \quad (7.4)$$

with the solution:

$$c_j(r) = \frac{A}{r} + B, \quad (7.5)$$

in which A and B are constants. The boundary conditions are a constant bulk concentration $c_{j,\infty}$ beyond some distance $R_i + \delta$ from the origin, and zero-concentration of (free) j -spheres at the target surface:

$$c_j(r = R_i + \delta) = c_{j,\infty}; \quad c_j(r = R_{ij}) = 0 \quad (7.6)$$

Note that the zero-concentration actually occurs at the 'collision distance' R_{ij} , i.e. the center-to-center distance at which the i - and j -sphere touch. After evaluating A and B from the boundary conditions in (7.6), the steady-state profile turns out to be:

$$\frac{c_j(r)}{c_{j,\infty}} = \left(1 - \frac{R_{ij}}{r} \right) \frac{R_i + \delta}{R_i + \delta - R_{ij}} \quad (7.7)$$

The question now is which value we have to take for the 'diffusion-zone thickness' δ , in other words, where in Fig. 7.1 does the bulk begin? Fortunately, for a single target sphere in a sufficiently large container of j -particles, we do not have to specify δ any further than that it is much larger than R_{ij} . Thus for the steady-state profile we can take the limit:

$$\lim_{\delta \rightarrow \infty} \frac{c_j(r)}{c_{j,\infty}} = 1 - \frac{R_{ij}}{r} \quad (7.8)$$

In what follows we will only employ this concentration profile. We note here that the simple, asymptotic result in (7.8) is a fortunate consequence of Brownian motion in *three* dimensions: diffusion in a two-dimensional plane involves an undetermined δ (exercise 1).

The steady diffusion flux of j -spheres in radial direction (unit vector $\vec{\delta}_r$) towards the target follows from substitution of (7.8) in Fick's first law (7.2):

$$\vec{j}_d = -D_{ij} \vec{\delta}_r \frac{dc_j}{dr} = -\frac{\vec{\delta}_r}{r^2} D_{ij} R_{ij} c_{j,\infty} \quad (7.9)$$

This is a flux of particles (per unit area per second) which decreases with increasing r . However, because of mass conservation the *total* flux J through a spherical envelope of with surface area $4\pi r^2$ must be independent of r . This also follows from the steady-state condition $\vec{\nabla} \cdot \vec{j}_d = 0$. Thus the collision-frequency of j -particles on the target sphere can be equated to this total flux, evaluated at $r = R_{ij}$:

$$J(j \rightarrow i) = 4\pi R_{ij}^2 \left| \vec{j}_d(r = R_{ij}) \right| = 4\pi D_{ij} R_{ij} c_{j,\infty} \quad (7.10)$$

Next we note that for solid spheres the collision radius equals $R_{ij} = R_i + R_j$, and that for independently diffusing spheres their relative diffusion coefficient equals (exercise 2):

$$D_{ij} = D_i + D_j = \frac{kT}{6\pi\eta} \left(\frac{1}{R_i} + \frac{1}{R_j} \right) \quad (7.11)$$

Consequently eq. (7.10) becomes:

$$J(j \rightarrow i) = \frac{2}{3} \frac{kT}{\eta} \left(2 + \frac{R_i}{R_j} + \frac{R_j}{R_i} \right) c_{j,\infty} \quad (7.12)$$

It is instructive to rewrite this expression in terms of the volume fraction $\phi_j = (4/3)\pi R_j^3 c_{j,\infty}$ of j -spheres:

$$J(j \rightarrow i) = \left(2 + \frac{R_i}{R_j} + \frac{R_j}{R_i} \right) \frac{\phi_j}{2\pi\tau_{cr}}; \quad \tau_{cr} = \eta R_j^3 / kT \quad (7.13)$$

This form shows that, for a give volume fraction, it is the configuration relaxation time τ_{cr} from eq. (4.11) that largely determines the collision frequency of j -spheres on the target.

An at first sight curious feature of the diffusion flux $J(j \rightarrow i)$ is its minimum for spheres of identical size (exercise 3):

$$J(j \rightarrow i) = \frac{2\phi_j}{\pi\tau_{cr}}; \quad R_i = R_j \quad (7.14)$$

In other words, for a given volume fraction, polydispersity always accelerates encounters due to Brownian motion in comparison to monodisperse spheres. The minimal value of (7.14) can be qualitatively understood by noting that if, in a monodisperse system, we shrink all spheres except the target sphere, the collision frequency increases due to the enhanced diffusion of the shrunk spheres. If, on the other hand, only the target sphere is reduced to a point-like particle, it will rattle around rapidly in a collection of static j -spheres which also increases the diffusion flux $J(j \rightarrow i)$.

To get an idea of the collision frequencies involved, imagine the fate of a target sphere with radius $R_i = 1 \mu\text{m}$ immersed in an aqueous host dispersion with a particle volume fraction $\phi_j = 0.01$. According to eq. (7.13) the collision frequency on this target is in order of magnitude:

$R_j = 10 \text{ nm}$	$J(j \rightarrow i) = 68 \times 10^2 \text{ sec}^{-1}$
100 nm	$80 \times 10^{-2} \text{ sec}^{-1}$
1000 nm	$26 \times 10^{-3} \text{ sec}^{-1}$

Thus the micron-size target is bombarded quite frantically by the Brownian motion when the hosts are nano-particles, whereas for an equal volume fraction of micron-size hosts the target has to wait for more than half a minute for the next Brownian encounter.

Diffusional growth

Eq. (7.10) is also useful to estimate the growth rate of a colloidal sphere in a supersaturated solution of reactive molecules or of monomers (j -particles). In this case $D_j \gg D_i$ and $R_j \approx R_i$ so the collision frequency on the sphere is approximately:

$$J(j \rightarrow i) \approx 4\pi D_j R_i c_{j,\infty} \quad (7.15)$$

Suppose each j -particle contributes a volume v_j to the volume V_i of the growing target:

$$\frac{dV_i}{dt} = J(j \rightarrow i)v_j; \quad V_i = (4/3)\pi R_i^3 \quad (7.16)$$

Substitution of (7.15) and integration yields for the radius R_i at time t :

$$R_i^2(t) - R_i^2(t_0) = 2D_j\phi_j(t-t_0); \quad \phi_j \approx c_{j,\infty}v_j \quad (7.17)$$

The volume fraction ϕ_j is actually larger than the true volume fraction of j -particles because the volume contribution v_j to the the growing sphere volume is larger than the volume of sphere j itself. Note in (7.17) the scaling $R \sim t^{1/2}$ which is characteristic for diffusion-controlled growth. The growth equation (7.17) is indeed an instance of Einstein's law for quadratic displacement (see eq. 4.29) due to an 'effective' diffusion coefficient $D_j\phi_j$.

Diffusion coefficients of small molecules or ions in water are typically $D_j \sim 10^{-5}$ cm²sec⁻¹ so for a volume fraction $\phi_j = 0.01$, the growth rate of the sphere from (7.17) is about $dR_j^2/dt \cong 20$ μm²/sec. This is quite fast; growth of colloidal spheres by precipitation in a supersaturated solution is often much slower. Retarding factors include exhaustion of the bulk (decrease of ϕ_j in time) or a slow chemical process that generates the particles j .

Flocculation kinetics

By flocculation or aggregation we refer to the sticking together of colloids which keep their 'identity', in contrast to droplets which merge together in a coalescence process. When the colloids strongly attract each other such that each Brownian encounter leads to a permanent aggregate, we speak of *fast flocculation*. Its kinetics can be treated as an irreversible 'bi-molecular reaction' between species i and j :

$$\frac{dc_i}{dt} = \frac{dc_j}{dt} = -k_{ij}c_i c_j \quad (7.18)$$

Here c_i and c_j are bulk number concentrations of species i and j (the subscript ∞ denoting bulk values has been dropped). The rate constant k_{ij} of this second order reaction directly follows from the flux in eq. (7.10), because the total collision frequency between particles i and j equals $J(j \rightarrow i)c_i$. Since every collision removes a free i and j particle we have:

$$\frac{dc_i}{dt} = \frac{dc_j}{dt} = -J(j \rightarrow i)c_i, \quad (7.19)$$

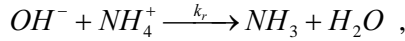
which implies for the rate constant:

$$k_{ij} = J(j \rightarrow i) / c_j = 4\pi D_{ij} R_{ij} , \quad (7.20)$$

where we have substituted the diffusive flux $J(j \rightarrow i)$ from eq. (7.10). This rate constant (first derived by Smoluchowski) has the remarkable feature that for monodisperse particles it is independent of particle size, for if we substitute $R_{ij} = 2R_1$ and $D_{ij} = 2D_1$ it turns out that:

$$k_{11} = 8kT / 3\eta \quad (7.21)$$

This size independence suggests that k_{11} should also give a reasonable estimate for diffusion-controlled reactions between small molecules or ions. For example, for



the rate constant is $k_r = 5.6 \times 10^{-17} \text{ m}^3/\text{sec}$. From (7.21) we obtain for water ($\eta = 0.84 \text{ m Pa sec}$) at 298 K: $k_{11} = 1.2 \times 10^{-17} \text{ m}^3/\text{sec}$, which is indeed correct in order of magnitude. Eventhough the rate constant is independent of particle size, the particle number density due to flocculation decreases in time at a rate that strongly depends on the sphere radius R , as can be seen as follows.

Consider the initial stage of flocculation in which only doublets of spheres are formed. Integration of eq. (7.18) for identical spheres shows that in this initial stage the concentration $c(t)$ of free singlet spheres decreases as

$$c(t) = c_0 / (1 + (t/t_{1/2})) \quad (7.22)$$

Here $t_{1/2}$ is the half-life of the singlet spheres and c_0 the singlet number density at $t=0$. For a starting volume fraction $\phi_0 = c_0(4/3)\pi R^3$ the half-life equals:

$$t_{1/2} = \frac{1}{k_{11}c_0} = \frac{\pi\tau_{cr}}{2\phi_0}; \quad \tau_{cr} = \eta R^3 / kT \quad (7.23)$$

Here τ_{cr} is the configurational relaxation time from eq. (4.11), note that $t_{1/2}$ approximately equals the Brownian collision time τ_{bc} in (4.17). The half-life also turns out to be the reciprocal of the flux in (7.14). It is evident that for a given volume fraction, colloids in the micron size range flocculate relatively slowly. For nano-particles at a volume fraction of say $\phi = 0.01$, rapid flocculation occurs within a split of a second.

Flocculation in a later stage involves the formation of triplets, quadruplets etc. which also collide by Brownian motion to form large clusters. Smoluchowski showed that this – at first sight hopelessly complicated – kinetic problem can be approximately solved as follows.

Consider the concentration c_α of aggregates containing α spheres. Such α -mers are formed by the encounters of smaller aggregates, and disappear by the uptake of any other particle or aggregate. The change of α -mer concentration in time is therefore:

$$\frac{dc_\alpha}{dt} = \frac{1}{2} \sum_{i=1}^{\alpha-1} k_{i,\alpha-i} c_i c_{\alpha-i} - \sum_{i=1}^{\infty} k_{i\alpha} c_i c_\alpha \quad (7.24)$$

This equation can be solved easily if we neglect any difference between reaction rate constants k_{ij} and consequently substitute $k_{ij} = k_{11}$:

$$\frac{dc_\alpha}{dt} = \frac{1}{2}k_{11} \sum_{i=1}^{\alpha-1} c_i c_{\alpha-i} - k_{11} c_\alpha \sum_{i=1}^{\infty} c_i \quad (7.25)$$

In terms of the total number density

$$c(t) = \sum_{i=1}^{\infty} c_i, \quad (7.26)$$

eq. (7.25) can be written as:

$$\frac{dc_{tot}}{dt} = -\frac{1}{2}k_{11}c_{tot}^2, \quad (7.27)$$

with the solution

$$c(t) = \frac{c_0}{1 + t/t_{1/2}} \quad (7.28)$$

Here the half – life equals

$$t_{1/2} = \frac{\pi\tau_{cr}}{\phi_0}, \quad (7.29)$$

which is twice the half-life of singlet spheres in eq.(7.23). Apart from the total particle number density, we can also evaluate the concentration all the various particle species (α -mers) in time. From eq. (7.24):

$$\begin{aligned} \frac{dc_1}{dt} &= -k_{11} \sum_{i=1}^{\infty} c_i c_1 \\ \frac{dc_2}{dt} &= \frac{1}{2}k_{11}c_1^2 - k_{11} \sum_{i=1}^{\infty} c_i c_2 \end{aligned} \quad (7.30)$$

etc.

Again all rate constants are equal: $k_{ij} = k_{11}$. This leads to the concentrations of the various species in fig. 7.2. The assumption that all rate constants equal k_{11} seems drastic. It implies, for example, that the rate constant for *irregular* aggregates of, say, 10 particles equals that of one single sphere. Note, however, that the diffusion coefficient D of a cluster is inversely proportional to the typical cluster size R_c . This implies that the rate constant $k \sim DR_c$ is indeed fairly insensitive to the shape and size of the aggregates that form in the flocculation process.

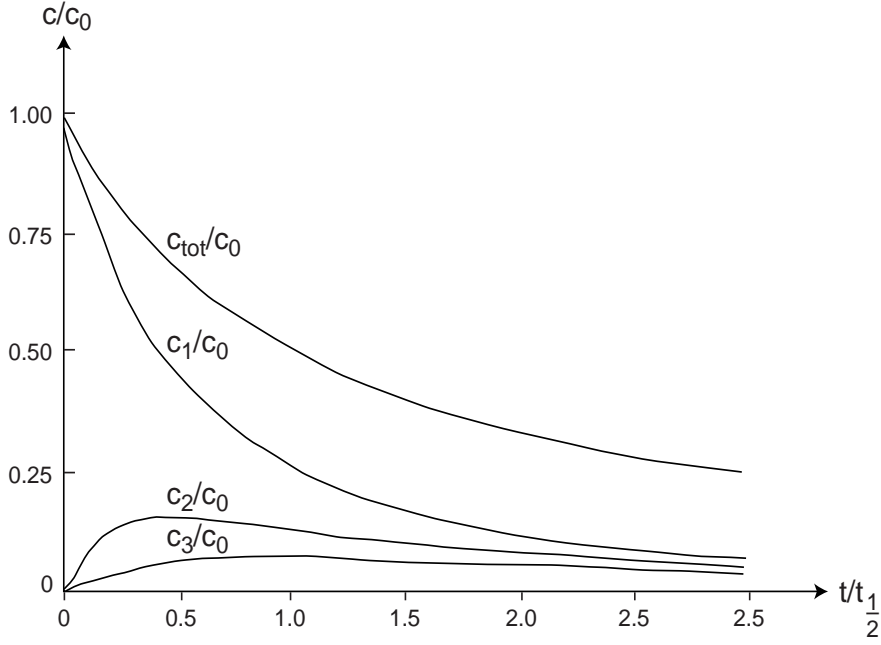


Fig. 7.2. Change in species concentration in time according to eqs. (7.30).

Effect of shear flow

Shear forces (flow, stirring) increase the flocculation rate, because the velocity gradient in the suspension increases the collision frequency of the colloids. Suppose a constant velocity gradient $\dot{\gamma} = dv/dz$ is present in the z -direction (see fig. 7.3). Then the flux of particles j at height z in the direction of sphere i centered at $z = 0$ is:

$$c_j v(z) 2 \sqrt{R_{ij}^2 - z^2} dz ; v(z) = \dot{\gamma} z \quad (7.31)$$

Integration of this expression (see also fig. 7.4) gives the total flux of j -particles to the i -sphere:

$$J = (j \rightarrow i) = 4c_j \dot{\gamma} \int_0^{R_{ij}} z \sqrt{R_{ij}^2 - z^2} dz = \frac{4}{3} \dot{\gamma} R_{ij}^3 c_j \quad (7.32)$$

The corresponding rate constant is:

$$k_{ij} = \frac{4}{3} \dot{\gamma} R_{ij}^3 \quad (7.33)$$

We compare this 'shear-induced' rate constant to the purely diffusional rate constant in eq. (7.20):

$$\frac{(k_{ij})_{shear}}{(k_{ij})_{diff}} = \frac{\dot{\gamma} R_{ij}^2}{3\pi D_{ij}} \approx \frac{4R^3 \eta \dot{\gamma}}{kT} = 4\tau_{cr} \dot{\gamma} \quad (7.34)$$

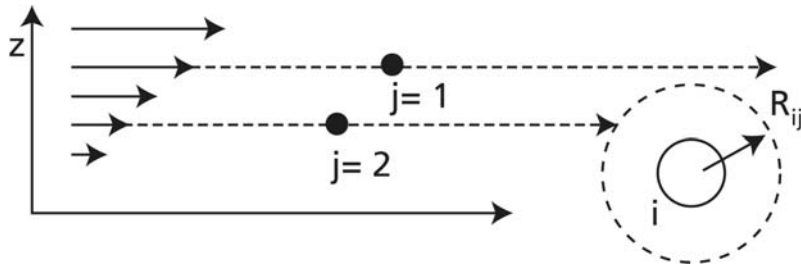


Fig. 7.3. Centra of particles j move in a shear flow towards particle i .

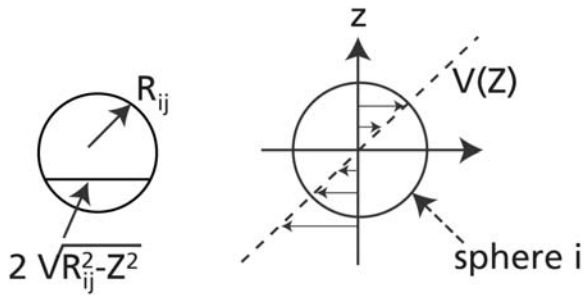


Fig.7.4. Sketch accompanying eq. (7.32)

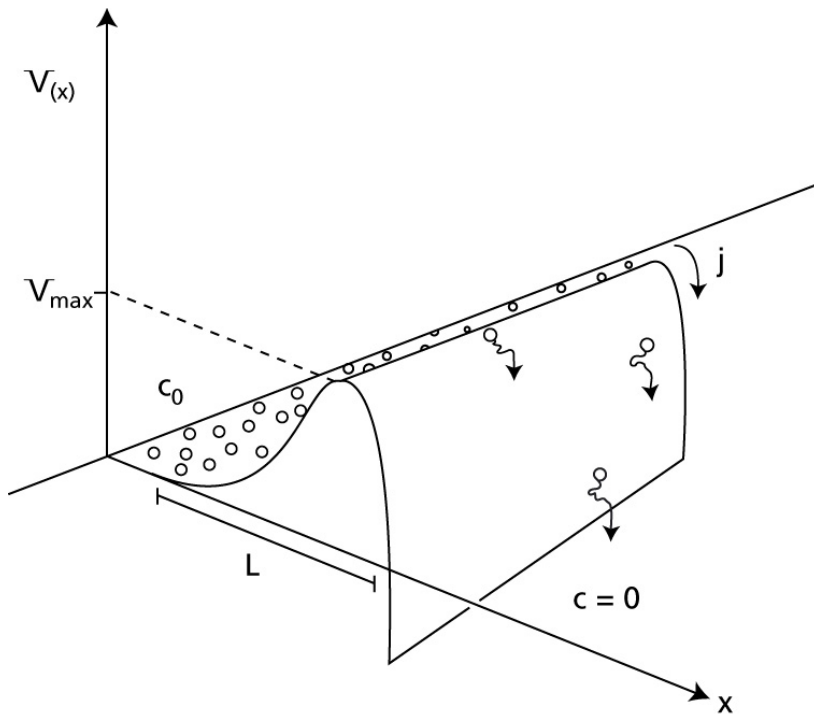


Fig. 7.5: Colloids diffuse across a potential barrier of width L into a sink with zero-concentration. The sink may be a strong Van der Waals attraction, in which case V_{max} is the repulsive barrier in the DLVO-potential.

Clearly for large particles ($R > 1 \mu\text{m}$) shear-induced flocculation becomes important. In practice, this type of flocculation appears to have an autocatalytic character; once flocculation has started (either by diffusion or stirring) further stirring strongly accelerates the process. This is because of the R^3 -dependence in eq.(7.34); the

larger the aggregate or floc the more rapid it will catch other aggregates in the stirred suspension.

Brownian motion in an external field

In our treatment of Brownian kinetics we have ignored colloidal interactions, apart from a strong attraction at particle contact responsible for 'fast flocculation'. Additional long-range Van der Waals attractions will accelerate particle aggregation whereas a repulsive barrier (as in the DLVO-potential between charged colloids) decreases the frequency at which colloids collide by Brownian motion.

To analyse the effect of a potential (either due to the colloids themselves or an external field) on colloidal kinetics, we consider the Brownian motion of particles from a source with concentration ρ_0 at $x = a$ to a sink with concentration $\rho = 0$ at $x = a + L$ (see fig. 7.5). In absence of a potential, the diffusion flux and the concentration gradient in the steady state are:

$$j_d = D \frac{\rho_0}{L} \quad ; \quad \rho(x) = \rho_0 \left(1 - \frac{x}{L}\right) \quad (7.35)$$

A potential $V(x)$ produces a convective flux due to the force $K = -dV(x)/dx$ on each particle:

$$j_c = -\rho(x) u = -\frac{\rho(x)}{f} \frac{dV(x)}{dx} \quad (7.36)$$

Thus the total steady-state flux $j = j_d + j_c$ is given by

$$j = -D \left[\frac{d\rho(x)}{dx} + \frac{\rho(x)}{kT} \frac{dV(x)}{dx} \right] = \text{constant} \quad (7.37)$$

In thermodynamic equilibrium ($j = 0$) the solution of (7.37) is

$$\rho_{ev}(x) = \rho_0 \exp[-V(x)/kT] \quad , \quad (7.38)$$

which is the same Boltzmann distribution as in (4.23). To find the concentration profile in the non-equilibrium steady-state ($j \neq 0$), Debye proposed to substitute in eq. (7.37) the trial solution

$$\rho_{ev}(x) = \gamma(x) \exp[-V(x)/kT] \quad , \quad (7.39)$$

to find that $\gamma(x)$ is given by the differential equation:

$$\exp[-V(x)/kT] \frac{d\gamma(x)}{dx} = \frac{-j}{D} \quad (7.40)$$

In view of the boundary condition $\gamma(x = a) = \rho_0$, eq. (7.40) yields:

$$\gamma(x) = \rho_0 - \frac{j}{D} \int_a^x \exp[V(x')/kT] dx' \quad (7.41)$$

The magnitude of the steady-state flux follows from the second boundary condition, namely that $\gamma(x = a + L) = 0$:

$$j = \frac{Dc_0}{\int_a^{a+L} \exp[V(x)/kT] dx} \quad (7.42)$$

The steady-state concentration profile is obtained by substitution of (7.41) and (7.42) in (7.39):

$$\frac{\rho(x)}{\rho_{ev}(x)} = 1 - \frac{\int_a^x \exp[V(x')/kT] dx'}{\int_a^{a+L} \exp[V(x)/kT] dx} \quad (7.43)$$

Here $\rho_{ev}(x)$ is the equilibrium distribution from (7.38). Note that for $V(x) = 0$ we recover the flux and the linear concentration profile from (7.35). With respect to kinetics, the essential point is that the effect of a potential is equivalent to a rescaling of the diffusion coefficient. We can rewrite (7.42) as:

$$j = D_{eff} \frac{\rho_0}{L} \quad (7.44)$$

in which

$$D_{eff} = \frac{D}{\frac{1}{L} \int_a^{a+L} \exp[V(x)/kT] dx}, \quad (7.45)$$

is an effective diffusion coefficient that accounts for the retardation or acceleration of particle transport due to the external potential. So, in principle, all foregoing results for the kinetics of Brownian encounters remain valid, provided the appropriate effective diffusion coefficient is substituted. Eq. (7.45) applies to one-dimensional diffusion problems; for the case of three-dimensional spheres, see exercise 5.

To make an estimate of D_{eff} we note that for a high repulsive barrier V_{max} (see fig. 7.5), the integral in (7.42) approximately equals $(L/2) \exp[V_{max}/kT]$. Thus:

$$D_{eff} \approx 2D \exp[-V_{max}/kT], \text{ for } V_{max} \gg kT, \quad (7.46)$$

This result reminds of the Arrhenius equation in chemical reaction kinetics, where reaction rates are exponentially retarded by an activation energy barrier. Eqs. (7.46) informs us that, independent of the detailed shape of the potential $V(x)$, a repulsive barrier in the range 5-10 kT suffices to practically eliminate Brownian encounters. This is the principal idea underlying the DLVO-theory of colloidal stability: a barrier due to an electrical double-layer repulsion strongly reduces the frequency at which particles 'fall' into each others deeply attractive Van der Waals well. Addition of salt lowers V_{max} which accelerates flocculation in a exponential fashion.

Flocs and particle clusters, of course, may also fall apart due to thermal motion provided the attractive well is not too deep. We can estimate the life time of a doublet from the time it takes for a particle to diffuse out of a well with depth V_{max} and a width comparable to its own radius:

$$\tau \sim \frac{R^2}{D_{eff}} \sim \frac{\eta R^3}{kT} \exp[V_{max}/kT] = \tau_{cr} \exp[V_{max}/kT], \quad (7.47)$$

where τ_{cr} is the configurational relaxation time for the colloids in absence of any force field. This scaling relation also gives an indication for the temporal stability of larger clusters or aggregates or particle gels. Such non-equilibrium structures are

practically permanent if τ exceeds the characteristic observation time τ_{obs} , which is about $\tau_{obs} \sim 10^{-2} - 10^{-3}$ sec. for dynamic light scattering and seconds to minutes for visual microscopy.

Exercises

1. Derive the equivalent of (7.10) for Brownian motion on a flat plane, for discs with radius R_j towards a target disc with radius R_i . Consider the limit $\delta \rightarrow \infty$. Conclusion(s)?
2. Show that (7.11) is indeed correct for spheres that diffuse independently from each other.
3. Show that (7.14) is the minimum of (7.13).
4. Calculate the half-life for the flocculation of identical spheres in the initial stage, for $\phi = 0.01$ and $R = 10$ nm, respectively, $R = 10$ μm . [3.8×10^{-5} , 3.8×10^3 sec]
5. Derive the effective diffusion coefficient D_{eff} for colloids diffusing in a radial potential $V(r)$. Start with formulating the total steady-state flux.

References

- For the original work of Smoluchowski on his diffusion model for coagulation see M.von Smoluchowski, Phys. Z. 17 (1917) 557; 585 (1916); Z. Phys. Chem. 92 (1917) 129.
- Brownian motion in a force field is treated in:
P. Debye, *Molecular Forces*, Wiley 1967
N. Fuchs, Z. Phys. 89 (1934) 736.
H.A. Kramers, *Brownian motion in a field of force and the diffusion model of chemical reactions*, Physica VII (4), 284 (1940).

Appendix A

Summary vector notation

The following summary only relates to results needed in these notes. A vector \vec{v} may be represented as

$$\vec{v} = [v_1, v_2, v_3], \quad (\text{A.1})$$

where v_i is the component of the vector along axis i . An alternative, convenient notation is:

$$\vec{v} = \sum_i \vec{\delta}_i v_i \quad ; \quad i = 1, 2, 3 \quad (\text{A.2})$$

Here $\vec{\delta}_1, \vec{\delta}_2$ and $\vec{\delta}_3$ are unit vectors in the direction of, respectively, axes 1, 2 and 3. The scalar (or dot) product of two vectors is:

$$\vec{v} \cdot \vec{w} = \sum_i v_i w_i, \quad (\text{A.3})$$

as follows from the dot product of the unit vectors

$$\vec{\delta}_i \cdot \vec{\delta}_j = \delta_{ij}, \quad (\text{A.4})$$

in which δ_{ij} is the Kronecker delta; $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$. The vector (or cross) product of \vec{v} and \vec{w} is also a vector, with components given by the determinant:

$$\vec{v} \times \vec{w} = \begin{vmatrix} \vec{\delta}_1 & \vec{\delta}_2 & \vec{\delta}_3 \\ v_1 & v_2 & v_3 \\ w_1 & w_2 & w_3 \end{vmatrix} \quad (\text{A.5})$$

The vector *differential operator* $\vec{\nabla}$ ('del') is defined in Cartesian coordinates as:

$$\vec{\nabla} = \sum_i \vec{\delta}_i \frac{\partial}{\partial x_i} \quad (\text{A.6})$$

If s is a scalar function of x_1, x_2 and x_3 then its *gradient* ('grad') is:

$$\vec{\nabla} s = \sum_i \vec{\delta}_i \frac{\partial s}{\partial x_i} \quad (\text{A.7})$$

If \vec{v} is a function of the coordinates x_i then its *divergence* ('div') is the dot product:

$$\vec{\nabla} \cdot \vec{v} = \sum_i \frac{\partial v_i}{\partial x_i} \quad (\text{A.8})$$

The *curl* of the vector is the cross product

$$\vec{\nabla} \times \vec{v} = \begin{vmatrix} \vec{\delta}_1 & \vec{\delta}_2 & \vec{\delta}_3 \\ \frac{\partial}{\partial x_1} & \frac{\partial}{\partial x_2} & \frac{\partial}{\partial x_3} \\ v_1 & v_2 & v_3 \end{vmatrix} \quad (\text{A.9})$$

For example, the component of curl \vec{v} in the direction of $\vec{\delta}_1$ is:

$$[\vec{\nabla} \times \vec{v}]_1 = \frac{\partial v_3}{\partial x_2} - \frac{\partial v_2}{\partial x_3}$$

The *Laplacian* of a *scalar* s is the divergence of its gradient:

$$\vec{\nabla} \cdot \vec{\nabla} s = \sum_i \frac{\partial^2}{\partial x_i^2} s = \nabla^2 s, \quad (\text{A.10})$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \quad (\text{A.11})$$

is the Laplacian (read: 'del squared') in Cartesian coordinates. The Laplacian of a *vector field* \vec{v} is defined as:

$$\nabla^2 \vec{v} = \vec{\nabla}(\vec{\nabla} \cdot \vec{v}) - [\vec{\nabla} \times [\vec{\nabla} \times \vec{v}]] \quad (\text{A.12})$$

The definition is valid for curvilinear as well as rectangular coordinates.

The divergence theorem

Let S be a surface (with unit outward normal \vec{n}), which encloses a region with volume V . Then

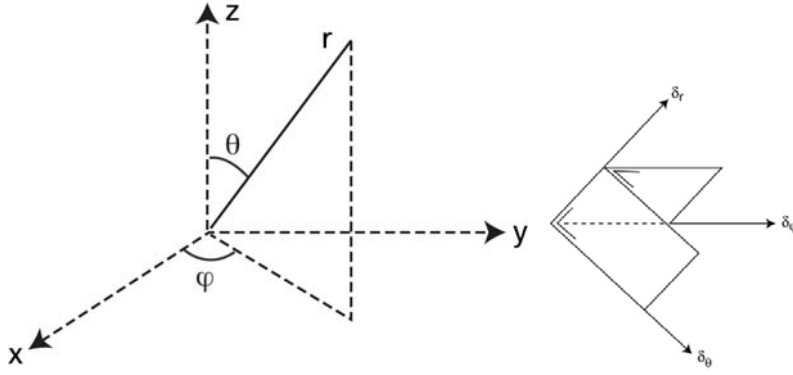
$$\int_S \vec{F} \cdot \vec{n} dS = \int_V \vec{\nabla} \cdot \vec{F} dV \quad (\text{A.13})$$

A similar identity is:

$$\int_S p \vec{n} dS = \int_V \vec{\nabla} p dV \quad (\text{A.14})$$

where p is a scalar function.

Spherical coordinates (r, θ, ϕ)



$$\bar{\nabla} p = \frac{\partial p}{\partial r} \bar{\delta}_r + \frac{1}{r} \frac{\partial p}{\partial \theta} \bar{\delta}_\theta + \frac{1}{r \sin \theta} \frac{\partial p}{\partial \phi} \bar{\delta}_\phi \quad (\text{A.15})$$

$$\bar{\nabla} = \bar{\delta}_r \frac{\partial}{\partial r} + \bar{\delta}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \bar{\delta}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad (\text{A.16})$$

$$\bar{\nabla} \cdot \bar{u} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (u_\theta \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial u_\phi}{\partial \phi} \quad (\text{A.17})$$

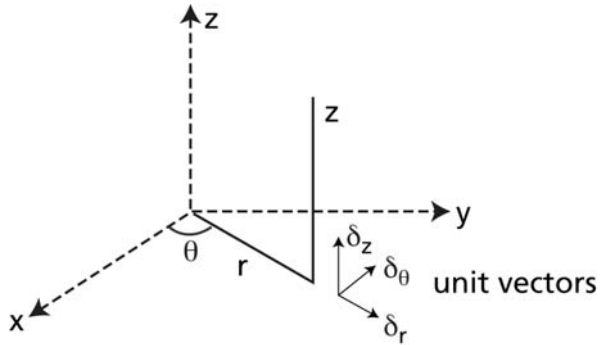
$$\nabla^2 p = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial p}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial p}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 p}{\partial \phi^2} \quad (\text{A.18})$$

$$\bar{\nabla} \times \bar{u} = \frac{1}{r^2 \sin \theta} \begin{vmatrix} \bar{\delta} & r \bar{\delta}_\theta & r \sin \theta \bar{\delta}_\phi \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \\ u_r & r u_\theta & r \sin \theta u_\phi \end{vmatrix} \quad (\text{A.19})$$

$$\begin{aligned} [\nabla^2 \bar{u}]_\phi &= \phi\text{-component of the Laplacian of } \bar{u} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial u_\phi}{\partial r} \right] + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left[\frac{1}{\sin \theta} \frac{\partial u_\phi \sin \theta}{\partial \theta} \right] + \text{derivatives with respect to } \phi \end{aligned} \quad (\text{A.20})$$

$$\begin{aligned} \tau_{r\phi} &= r\phi\text{-component of the stress in Newton's law} \\ &= -\eta r \frac{\partial}{\partial r} \left[\frac{u_\phi}{r} \right] + \text{derivative to } \phi \end{aligned} \quad (\text{A.21})$$

Cylindrical coordinates (r, θ, z)



$$\vec{\nabla} p = \frac{\partial p}{\partial r} \vec{\delta}_r + \frac{1}{r} \frac{\partial p}{\partial \theta} \vec{\delta}_\theta + \frac{\partial p}{\partial z} \vec{\delta}_z \quad (\text{A.22})$$

$$\vec{\nabla} \cdot \vec{u} = \frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{\partial u_z}{\partial z} \quad (\text{A.23})$$

$$\nabla^2 p = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 p}{\partial \theta^2} + \frac{\partial^2 p}{\partial z^2} \quad (\text{A.24})$$

$[\nabla^2 \vec{u}]_z = z$ – component of the Laplacian of \vec{u}

$$= \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial u_z}{\partial r} \right] + \frac{1}{r^2} \frac{\partial^2 u_z}{\partial \theta^2} + \frac{\partial^2 u_z}{\partial z^2} \quad (\text{A.25})$$

$\tau_{rz} = rz$ – component of the stress in Newton's law

$$= -\eta \left[\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right] \quad (\text{A.26})$$

References

- An extensive summary of vector (and tensor) notation can be found in:
R. Bird, W. Stewart and E. Lightfoot, *Transport Phenomena* (Wiley, New York 2001)
- An informal text which emphasizes the physical significance of vector calculus is:
H.M. Schey, *Div, Grad, Curl, and All That*, (Norton, New York 1973)
- For more details on vector analysis see for example:
M.L. Boas, *Mathematical Methods in the Physical Sciences*, (Wiley, New York, 1983).