4.2.1 Introduction

More than half of the chemical engineering literature concerns transport phenomena. This topic deals with all those problems where a physical property, like mass, energy or momentum, is transferred from one point to another in space. For example, the study of these phenomena allow the following calculations: a) the loss of pressure in a fluid during its flow inside a pipe; b) the velocity profile of a fluid moving inside a channel; c) the length of pipe needed to heat the fluid flowing inside it to the desired temperature; d) the amount of heat dissipated from a surface in contact with a fluid stream; e) the contact area needed between two phases to transfer the desired amount of matter in a defined time.

In this chapter, only the problems of momentum, energy and matter transfer without chemical reactions will be analyzed. The interactions existing between transport phenomena and chemical reactions are analyzed in chapters 5.1 and 6.3.

The topics examined by classic thermodynamics are systems in equilibrium, while transport phenomena deal with those systems far from equilibrium conditions, where gradients of intensive properties, like velocity, temperature and concentrations, are present. From a microscopic point of view, transport phenomena are caused by the chaotic movement of molecules and their aggregates in turbulent motion, and which cause systems to evolve towards equilibrium conditions. Dissipative processes are associated with these evolutions that, from a phenomenological point of view, are identified through the resistance caused by the dissipation itself. Consequently, the phenomenological correlations developed during the years to describe the different fluxes (e.g. the amount of the considered property transferred per unit of area and time) are, in fact, correlated to these gradients with more or less complex functional forms.

The study of transport phenomena began towards the end of the Nineteenth century, with the beginning of engineering applications related to the construction of thermodynamic machines and to the building of industrial plants. Initially, the correlations developed were the macroscopic balances that deal with a finite portion of space. The origin of these macroscopic balance equations is difficult to trace; however, they are widely used, together with the assumptions and the implied approximations in their formulations, not only in chemical engineering but also in civil, mechanical and aeronautic engineering. Indeed, most of the work was done in the framework of these last three disciplines and only later were they used in a chemical context (for example, the theories on turbulence or on the velocity boundary layer, both developed Ludwig Prandtl). Once the importance of the macroscopic balance equations was ascertained, the necessity to understand the involved mechanisms emerged, together with the need to formulate operational schemes to make the application of such equations easier. Consequently, charts that describe the desired behaviour as a function of the main physical variables, grouped as dimensionless numbers, were developed. For example, it is possible to refer to the graphs for the drag coefficient as a function of the Reynolds number (adopted for the calculation of the pressure drop inside pipes) or to those equating the Sherwood number as a function of the product between the Reynolds and Schmidt numbers, each elevated to a suitable exponent (used for the estimation of the mass transfer coefficient). This treatment was developed under the physics of continuum systems and the properties of the involved fluids were identified with suitable variables introduced from a phenomenological point of view such as viscosity, thermal conductivity and diffusivity, all experimentally measurable.

At the same time, the development of kinetic molecular theories made it possible to justify the different phenomenological coefficients previously introduced, with consequent great impact on their theoretical estimation starting from the known properties of the involved molecules. For this purpose it is possible to mention the work of Chapman and Enskog on the theory of monoatomic gases and that of Chapman and Cowling (1939) on the binary gaseous mixtures, up through the extension to the multicomponent mixtures by Hirschfelder et al. (1954), whose contribution represents a milestone in the examination of molecular aspects.

Although the study of the transport of mass, of energy and of momentum were historically developed independently, today it is increasingly important to address transport phenomena as a whole for two reasons: the mechanism of transport of the different properties is often the same and, consequently, the mathemathic formalism for their description is the same.

In conclusion, the fundamentals of transport phenomena were already considered well-defined in the mid Twentieth century, as is testified by the publication by Bird et al. (1960)
of the textbook that become the ‘reference’ in the field. In the same period, the translations from the Russian of the textbooks by Landau and Lifshitz (1959) and by Levich (1962) also appeared. Today, dozens of texts dedicated to transport phenomena are available, from the introductory to those dealing with the most innovative aspects. Often the examples developed are chosen according to who the final user is and then, for example, texts specifically dedicated to chemical, metallurgical, biomedical, and so on, become available.

### 4.2.2 Macroscopic and molecular vision

From the above it emerges that, in a broad sense, the expression transport phenomena means the transfer of physical properties within a system or through its border. The properties under consideration for chemical and engineering systems are mass, momentum and energy, while the systems can evidence a greatly differentiated degree of complexity, as illustrated by some examples reported in Fig. 1. Hence, systems run from homogeneous, where a single phase is present, to heterogeneous, where multiple phases are present. Moreover, each phase can be monocOMPonent or multicomponent, depending on the number of chemical species present in it. Often, one of the phases present is a fluid in motion, thus the complexity of the problem is increased by the discontinuous changes in its behaviour, as in the case of the transition from laminar to turbulent motion or to that existing from the subsonic to the supersonic motion. Other peculiar examples of motion transitions are present, for example, in two-phase fluids, where a dozen different flow configurations are known, depending on the relative velocity between the two phases and their volumetric ratio.

A system can be analyzed at different scales, each identified by its own characteristic size. In general terms, a system, or more properly the portion being examined, is considered as a continuous medium and consequently this property is also extended to all the intensive and extensive quantities used for its description.

At the macroscopic level, the study is performed on finite dimensions, where the control volume includes the entire system and where the change in value of its properties is obtained by writing balance equations containing the input and the output quantities per unit time. As a first approximation, uniform values can be assigned to the intensive variables in the different regions of the system. This is defined as the ‘lumped’ parameters approach. From a mathematical point of view, the formulation of balances leads to the writing of algebraic equations if the system is in steady state conditions, or to ordinary differential equations if the system is transient. The characteristic length of the system coincides with one of its dimensions and thus it can span from centimetres to meters. As will be explained below, in such an approach, the transport properties can be expressed by the transfer coefficients, that state in an averaged form the contributions of the matter properties and the transport regime.

The study of the same system at an intermediate scale implies the analysis and the description of phenomena occurring at a characteristic length between a micrometre and a centimetre. Mathematically, it is appropriate to describe the involved phenomena by considering a significant elementary volume, definitely assimilated to an infinitesimal one, by an approach to the limits. Because the dimensions considered are significantly greater than those of the molecules contained in this volume, it is often correct to consider the system as a continuum. The writing of the balance equations leads to differential equations with partial derivatives with respect to the three spatial coordinates and the temporal one as independent variables. The equations obtained in this way, if integrated on the whole system, provide the fluid velocity, the temperature and the composition fields. As will be described...
below, writing the balance equations implies the knowledge of some parameters, the so-called phenomenological properties, which include the thermal conductivity, the diffusivity, the viscosity and the surface tension of the material making up the examined system. From a mathematical point of view, these properties actually reflect the use of a linear approximation in the correlations linking the local flux values of the transported properties to the corresponding gradients of the intensive variables. In a strictly phenomenological vision, the gradients are identified with the driving forces for the transport, while the fluxes in the direction opposed to them represent the effects. These phenomenological properties must be experimentally measured.

At the molecular level, it is necessary to consider the mechanisms that cause the transport on the basis of the properties of the molecules making up the examined substance. In other words, by analyzing the problem of the transport at this scale the aim is to estimate the value of the above phenomenological properties from the ultimate properties of the matter. In this case, the characteristic dimension is identified by a reasonable interval around the molecular dimensions and thus it ranges in the interval between a nanometre and a micrometre.

In the following, transport phenomena will be analyzed above all by considering a continuum system and thus deriving the expression of the differential equations at distributed parameters, the so-called microscopic balance equations (or microscopic equation of change). Until the last decade, their integration represented a tricky problem; consequently, texts dealing with transport phenomena examined a great number of simplified cases where it was possible to obtain analytical solutions, sometimes approximated. The reconstruction of the behaviour of the system was then obtained by the combination of the asymptotic trends obtained as shown above. Today, improvements in methods of calculation and especially electronic computers have permitted the use of reliable software that allow the integration of the conservation equations on complex geometric domains, also taking into consideration multiphase systems, with highly non-linear phenomenological transport laws, both for laminar and turbulent flow regimes.

Successively, the theories at the molecular level that allow the estimation of phenomenological properties, like viscosity, thermal conductivity and diffusivity will be examined.

Finally, some cases of particular interest will be examined, such as the determination of velocity profiles in channels, the study of boundary layer development for velocity, temperature and concentration for a fluid approaching a wall, temperature distribution across a composite wall, heating dynamics of a solid and diffusion through a solid or a stagnant fluid, mass transport through interfaces and some aspects of natural convection.

4.2.3 Phenomenological correlations

Physical entities like the ones examined here (mass, energy and momentum) can be transferred from one part of the system to another in two completely different ways. An example of these mechanisms is illustrated in Fig. 2. The former is linked to the macroscopic fluid movement and is called convection. The molecules of the fluid move within the system and they convey the mass, as well as all the other associated properties.

Convection can be externally induced using machines to move the fluid (stirrers, pumps, compressors); in this case the mechanism is identified as forced convection. Alternatively, as already seen, the overall fluid motion can be due to the presence of intensive variable gradients within the system. When these gradients exceed a critical value, circular motion phenomena within the fluid start and this mechanism is called natural convection. The second transport mode identifies a transfer modality to which is not associated any overall mass movement. In the energy transport this mechanism is indicated as conduction and it is associated with the presence of temperature gradients, while in the cases of mass transport, i.e. diffusion, and of momentum, it is associated with the concentration and velocity gradients, respectively.

To complete the description of the different transport modes it is also necessary to examine the way in which the motion in a fluid occurs. Using as an example, for sake of simplicity, a single-phase fluid, there can be a case where each single fluid element moves following well-defined trajectories represented by regular lines, essentially steady within the core of the fluid in motion (the so-called streamlines). If, for example, a fluid moves inside a channel, its elements move in a direction parallel to the channel walls and the velocity components at right angles to the channel axis are absent. In this case, the motion is called laminar regime. The motion can also occur following irregular, tortuous and unsteady trajectories. In this second case, the perturbation of the fluid movement is called turbulence and indicates the motion component that is superimposed on the main flow along the channel axis. Thus, at a certain instant, motion components exist both parallel to and at right angles with respect to the channel axis that identifies the main flow direction. If the system is observed for enough time the velocity components along the right angles are seen to have a zero local average value. The parallel component, on the other hand, presents an average value different from zero and is responsible for the overall fluid transport. In this case the motion is called turbulent regime.

Therefore, in the case of laminar regime motion, the transport in the direction at right angles to the main flow can happen uniquely by molecular collision and thus this last mechanism is responsible for the transports of conductive and diffusive nature. In case of turbulent motion, although the long time average of transversal velocities is zero, a very effective
transport mechanism, superimposed on the molecular one, is activated by the presence of the instantaneous fluctuations. Such a mechanism is called turbulent transport.

**Convective fluxes**

By considering a fluid element that moves uniformly with a velocity, $u$, the convective flux, $J$, indicates the amount of a given property that in the unit time flows through the reference unit surface by the effect of the transport of the entire fluid ensemble. Mathematically, this corresponds to the product of the velocity of the fluid element and an intensive variable identified by the amount of the given property contained in the unit volume. Thus, for mass, momentum and energy, the three expressions are, respectively:

1. $J = \rho \frac{\partial \rho}{\partial t}$
2. $J_p = \rho \frac{\partial u}{\partial t}$
3. $J_e = \left(U + \Phi + \frac{\omega^2}{2}\right) \frac{\partial \rho}{\partial t}$

where $\rho$, $\omega$, $U$, $\Phi$ and $\omega^2/2$ are the density, the mass fraction and the specific contributions of the unit mass for the internal, potential and kinetic energies, respectively. Although the result shown in equation [3] rigorously correspond to the total energy flux, in chemical systems the last two contributions are usually some order of magnitude lower than that of the internal energy and consequently they can be ignored. Accordingly, in the following only the contribution due to the internal energy, conveniently expressed as $U = U^\circ + \rho C_T \Delta T$, will be considered, where $^\circ$, $C_T$ and $\Delta T$ indicate the reference value, the specific heat at constant volume and the temperature difference existing between the local value and that of the reference state, respectively.

**Diffusive fluxes and constitutive equations**

To analyze the origin of the diffusive fluxes it is necessary to consider a direction at right angles to the direction of the main flow. By its intimate nature and definitions, the transport of diffusive nature in one direction should not be associated with any overall transport (i.e. convective) in the same direction. In principle, any of the different gradients present in the system, like those of composition, temperature, pressure, potential of an external force field and momentum, provide a contribution to the diffusive transport of the considered property. The simplest functional form to consider all of these contributions is a linear combination. Not all of the mentioned gradients provide a numerically significant contribution and thus, in practice, it is common to consider only the most important ones.

The expressions for the mass, energy and momentum fluxes are called ‘laws’ or more correctly, in modern terms, constitutive equations because they express the existing link between the driving force of the phenomenon and the resulting action.

For sake of simplicity, in the following the system will be assumed isotropic in order to identify through a single value any of its properties independently of the considered direction. Obviously it is easy to remove this hypothesis when non-isotropic systems are examined.

**Mass diffusive flux**

When only molecular diffusion is present, the mass transport is induced by the contributions of the ordinary diffusion $N^{(m)}$ (due to the composition gradients), of the thermal diffusion $N^{(T)}$ (due to the temperature gradients), of the diffusion by pressure $N^{(P)}$ (due to the pressure gradients) and of the diffusion by the effect of external force fields $N^{(F)}$, electromagnetic, for example, that act selectively on some species. As a first approximation, each of these is proportional to the force inducing such a flux, which can be identified through the opposite of the gradient of an examined variable by means of a coefficient that is called the diffusion coefficient. In conclusion, the mass diffusive flux is expressed by the sum of all the above contributions:

$$N^{(m)} = N^{(m)}(T) + N^{(P)} + N^{(F)}.$$

For the ordinary diffusion contribution, by far the most important, the Fick law is valid:

$$N^{(m)}(T) = -D^{(m)} \rho \nabla \omega,$$

where $D^{(m)}(T)/\rho$ is the ordinary diffusion coefficient or diffusivity of the $i$th species in the mixture, expressed in $m^2/s$. Values for the diffusion coefficients are in the range of $0.5-2 \times 10^{-5}$ $m^2/s$ for gases at atmospheric pressure and ordinary temperatures, to about $10^{-8}-10^{-9}$ $m^2/s$ for liquids at ambient temperature and to $10^{-11}-10^{-13}$ $m^2/s$ for the diffusion through solids. Obviously, for a concentration gradient to exist, the system must contains at least two chemical species and thus more correctly, it should be considered a binary diffusion coefficient. Alternatively, it is possible to refer to systems where two isotopes of the same specie are present. In that case, it is correct to refer to a self-diffusion coefficient. It is important to note that in the case of two chemical species A and B, seeing that diffusion should not give origin to an overall fluid motion, the equimolar counterdiffusion phenomena takes place. In other words, the flux of the first species through the second one is equal and opposite to that of the second species through the first one:

$$N^{(ao)}_A + N^{(ao)}_B = 0.$$

It is easy to verify that, since $\omega_g = 1 - \omega_p$, this leads to the important consequence of the equality between the two binary diffusion coefficients ($D^{(ao)}_A = D^{(ao)}_B$). Considering the dependence of diffusivity on composition in multicomponent systems complicates matters further, given that the mass fluxes of the different species are all mutually interconnected (see Section 4.2.5).

The thermal diffusion contribution, known as the Soret effect, is related to the gradient of the temperature logarithm. The temperature difference induces significant mass transport only when there are large gradients and significant molecular weight differences between the species present in the system. Its effect is to transfer the ‘heavy’ species to the colder regions and, instead, the ‘light’ ones to the hotter regions. A thermal diffusion coefficient $D^{(T)}$ is also defined in this case:

$$N^{(T)} = -D^{(T)} \rho \nabla \ln T.$$

The thermal diffusion contribution is generally negligible in common chemical systems, where the temperature gradients are modest. However, in reactors used in microelectronics for thin-film deposition technologies, it is not rare to find temperature gradients of about $30,000 \, K/m$ and thus this contribution becomes numerically important.

The pressure diffusion contribution is due to the fact that it is possible to induce the $i$th species displacement if a pressure gradient is present inside the system; it can be concisely expressed as follows:
where $D^{(P)}$ indicates the diffusion coefficient by pressure and $R$ is the universal constant of gases. However, the tendency of a mixture to separate under these conditions is indeed very small and usually this contribution is completely negligible, with the exception of the case of centrifuging where it is possible to obtain very high pressure gradients.

The diffusion contribution induced by external forces depends on the properties of the examined forces. In chemical systems, the most important contribution is that induced by the action of an electric field on the ions present in a solution:

$$N_{i}^{(e)} = - (z_i e) \zeta_{i} \omega_{0} A_{i} \nabla E$$

where $z_i$, $\zeta_{i}$, $A_{i}$ and $\nabla E$ are the electric charge of the ion, expressed in units of the electron electric charge, $e$, its ionic mobility, Avogadro’s number and the electric potential gradient, respectively. The product $eA_{i} \zeta_{i}$ corresponds to Faraday’s constant, $\mathcal{F}$. Ionic mobility, $\zeta_{i}$, is related to the ion diffusivity through the Nernst-Einstein equation:

$$\zeta_{i} = \frac{D}{RT}$$

Energy diffusive flux

As in the case of mass transport, all the previously examined contributions for the energy flux should also be taken into consideration, but actually, when, in a single-component system, selective external field forces are not present, the relevant contribution is only the one due to the temperature differences existing within the system. In a multicomponent system, the contribution induced by the presence of mass diffusion must also be considered, because every molecule is indissolubly linked to its energetic content. In the event that the mass transport is induced by a temperature gradient (thermal diffusion), the consequent energy transport is known as the Duфour effect. The energy transport by a diffusive mechanism is called conduction.

The expression for the conductive flux is thus proportional to the temperature gradient through a coefficient $k_{c}$, called thermal conductivity, expressed in W/mK; the corresponding constitutive law is known as Fourier’s law:

$$q = -k_{c} \nabla T$$

Typical values for the thermal conductivity are in the order of 10–300 W/mK for metals, 0.1–0.5 W/mK for liquids, 0.05–2 W/mK for solids and about $10^{-2}$ W/mK for gases. The origins of such diversities will be understood when the thermal conductivity is correlated to the molecular properties. It is useful to define a new quantity, related to the previous one, that assumes the same dimension as the mass diffusivity, and is analogously called thermal diffusivity:

$$\alpha = \frac{k_{c}}{\rho C_{p}}$$

where $C_{p}$ is the specific heat at constant pressure.

In multicomponent systems, the contribution of the energy transport induced by the presence of diffusive mass fluxes is given by:

$$q^{(i)} = \sum H_{i}^{r} N_{i}$$

where $H_{i}^{r}$ indicates the massive enthalpy of formation of the $i^{th}$ species.

Radiative energy flux

A material object, as a consequence of its temperature, emits electromagnetic radiation. This transmission mode does not need any medium to take place, and thus its propagation can even occur in a vacuum. By its own nature, it is a contribution relevant only at elevated temperatures. For engineering purposes, to know the flux it is sufficient to know the temperature difference existing between the two surfaces involved in the energy exchange and then to apply the Stefan-Boltzmann law. With reference to two grey bodies, the radiant flux leaving a grey body is equal to the sum of the radiant flux emitted by the body and of the reflected radiant flux. Considering that the emissivity of a body, $\varepsilon_{s}$ is equal to its absorbance, $\alpha_{s}$ it is possible to demonstrate the following expression for the radiative flux between two surfaces of area $A_{1}$ and temperature $T_{1}$, respectively:

$$q^{(rad)} = \frac{\sigma_{SB} \left( T_{1}^{4} - T_{2}^{4} \right)}{1 - \varepsilon_{1} + \frac{1}{F_{12}} \frac{E_{1} \left( 1 - \varepsilon_{1} \right)}{E_{2} \varepsilon_{2}}}$$

were $\sigma_{SB}$ and $F_{12}$ indicate the Stefan-Boltzmann constant and the view factor between the two surfaces, respectively. The latter is a geometric factor that, as illustrated in Fig. 3, expresses the projection of the first surface on the second. It is worth noticing that equation [13] does not contain any matter properties, except surface emissivity. Therefore, this contribution does not participate directly in the writing of the energy balance equation, where only volume contributions are present. However, always in principle, it is present in the boundary conditions, even if in practice it become relevant only at the higher temperatures.

Momentum diffusive flux

While for the definition of diffusive transports for mass and energy the systems can be considered indifferently in motion or at rest; for the definition of molecular momentum transport it is obviously necessary to examine a system in motion. It is to be considered, therefore, a fluid in laminar regime, where its motion in a channel develops in parallel streamlines. The momentum flux of diffusive nature is identified with the tangential stress component (shear stress).
The tangential stress component is related to the velocity gradient (shear rate) by the fundamental law of rheology which, in the simplest case where only the velocity component along the \( x \) direction exists and the momentum diffusive flux is directed along the \( y \) direction, becomes:

\[ N_{jy} = \tau_{jy} = -\mu \frac{du_j}{dy} \]

where the proportionality coefficient is a property of the fluid that assumes the name of dynamic viscosity (or simply viscosity) and it is expressed in Pa\( \cdot \)s. This equation is called Newton's law of viscosity. Although originally introduced as the simplest connection between stress and the velocity gradient, it was found to be valid for a large class of fluids, in particular for all gases and liquids with molecular weight lower than about 5,000. Accordingly, this class of fluids is called \textit{Newtonian fluids}. Conversely, the fluids not obeying this simple law are called \textit{non-Newtonian fluids}. Examples of non-Newtonian fluids are liquid polymers, solid suspensions, pastes, muds and other complex fluids. Typical values for viscosity are in the order of \( 10^{-5} \) Pa\( \cdot \)s for gases and \( 10^{-3} \) to 10 Pa\( \cdot \)s for liquids. In this case as well it is convenient to introduce a quantity homogeneous with the mass diffusivity, called kinematic viscosity (or diffusivity for the molecular momentum), defined as follows:

\[ \nu = \frac{\mu}{\rho} \]

The expression of the momentum flux derived in this way is evidently too simple to be adopted for any flow configuration, even laminar. In a generic fluid system in motion all three of the velocity components are present, each of which is a function of the three spatial coordinates. This generalization is not direct and about 150 years were needed to pass from the simple formulation suggested by Newton to the more general equation. The details of this demonstration will not be developed here, instead only the main hypothesis will be mentioned. Because each of the three velocity components depends on the three coordinates, it is evident that in total nine stress components, \( \tau_{ij} \), will be present. Moreover, in addition to the tangential stress components induced by the viscous forces, the perpendicular components, associated with pressure, \( P \), will also be present. In general terms, a molecular stress component that includes both the above mentioned contributions can be introduced, whose definition is:

\[ \pi_{ij} = P\delta_{ij} + \tau_{ij} \]

where \( \delta_{ij} \) is Kronecker's symbol, which assumes a nil value if \( i \neq j \) and unitary value if \( i = j \). The stresses with identical indexes are indicated as normal stresses, while the others are called tangential or shear stresses. Physically, \( \pi_{ij} \) can be associated with two different meanings, fully equivalent to each other. In the first case, it represents the force in direction \( j \) acting on an area at right angles to its direction. In the second, it represents the flux of the \( i^{th} \) momentum component in the \( j^{th} \) direction. The first meaning is usually adopted when the forces applied to a surface by a fluid are being analyzed, while the second is more suitable when the attention is focused on aspects of fluid motion. Mathematically, \( \pi \) and \( \tau \) are second order tensors, called \textit{tensor of molecular stresses} and \textit{tensor of viscous stresses}, respectively. In general, by assuming that any viscous stress component will be a linear function of all the velocity gradients, the resulting tensor has 81 components, which in principle give rise to 81 different viscosity coefficients. If, however, the symmetry properties are assumed valid and the fluid is considered isotropic, the expression of the tensor of viscous stresses in compact tensorial notation reduces to:

\[ \tau = -\mu \left[ \nabla u + (\nabla u)^T \right] + \frac{2}{3} \left( \mu - \kappa \right) \nabla \cdot \left[ \nabla u \right] \delta_{ij} \]

where \( \delta_{ij} \) is the unitary tensor, \( \nabla u \) is the tensor of the velocity gradient, \( (\nabla u)^T \) is its transposed counterpart and \( \nabla \cdot \left[ \nabla u \right] \) is the divergence of the velocity vector. In detail, the individual components of the tensor assume the following structure:

\[ \tau_{ij} = -\mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \left( \frac{2}{3} \mu - \kappa \right) \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \delta_{ij} \]

The generalization reported here involves two different coefficients to characterize the fluid properties. The former, \( \mu \), is the viscosity, while the latter, \( \kappa \), is the second viscosity (dilatational viscosity). Commonly, it is not strictly necessary to know this second coefficient. For ideal gases \( \kappa \) is zero, while for incompressible fluids \( \mu = 0 \), and thus the entire second term vanishes. This coefficient is important when the transmission of sound in polyatomic gases is to be described or when the fluid dynamics of liquids containing gases is to be analyzed.

**Non-Newtonian fluids**

For non-Newtonian fluids the viscosity concept, as a chemico-physical fluid property, loses its meaning because its value is not dependent only on the considered fluid and on the external conditions such as temperature and pressure, but also on fluid motion. To maintain the formalism adopted so far, an apparent viscosity \( \eta \) is then introduced which is a function also of the local stress status:

\[ \tau = -\eta(\gamma) \left[ \nabla u + (\nabla u)^T \right] = -\eta(\gamma) \gamma \]

\( \gamma \) being the so-called \textit{rate of the strain tensor} (or rate of the deformation tensor) that identifies the dissipation. As illustrated in Fig. 4, the dependence of the apparent viscosity on \( \gamma \) identifies the non-Newtonian fluids. If the apparent viscosity decreases when the viscous dissipation increases the fluid is called a \textit{pseudo-plastic fluid}, while in the opposite case it is called a \textit{dilatant fluid}. For example, liquid polymers tend to behave prevalently as pseudo-plastic fluids because when the stress status (or equivalently the velocity gradient) increases the macromolecules tend to extend and to place Fig. 4. Diagrams of the rheologic behaviour of Newtonian and non-Newtonian fluids.
themselves along the flow direction to offer as little resistance as possible to the motion. An analogous behaviour is shown by the colloidal solutions, where micelles tend to orient themselves to favour the motion. Instead, fats and starches behave like dilatant fluids because the stress to be applied to keep them in motion increases together with their velocity. For completeness, it is important to mention another class of non-Newtonian fluids, Bingham’s fluids. In these systems, to induce motion it is necessary that the applied stress exceed a critical threshold value, below which the fluid behaves as a rigid body.

To describe many of the complex behaviour patterns of non-Newtonian fluids, different models have been proposed, for example, the Bingham, the Ostwald-De Waele, the Eyring and the Reiner-Philippof models. For the sake of simplicity, following the trend in engineering, the simple Ostwald-De Waele model, better known as the power law, is commonly used to describe with satisfactory approximation their rheologic behaviour:

\[ \eta = n \frac{m}{F^{n-1}} \]

where \( m \) and \( n \) are the parameters of the fluid. It is easy to verify that if \( n = 1 \) the fluid is Newtonian and the \( m \) coefficient is identified with the viscosity \( \mu \), if \( n > 1 \) it is a dilatant fluid, and finally if \( n < 1 \) it is a pseudo-plastic fluid.

**Analogy between the diffusive transports**

Observing the three constitutive laws described so far, it can be noted that they show the same mathematical structure. The analogy among the diffusive molecular transports of mass, energy and momentum should not be surprising because these relationships find their origin in the same physical principles. To highlight this, it is useful to group the three homogeneous coefficients, diffusivity, kinematic viscosity and thermal diffusivity, into two dimensionless groups called the Prandtl and the Schmidt numbers, respectively:

\[ Sc = \frac{Dc}{\mu} = \frac{\mu}{g Dc} \]

\[ Pr = \frac{\nu}{\alpha} = \frac{\mu C_p}{k} \]

It is easy to verify that these equations represent the ratio between two characteristic times and thus identify the relative importance of the different transport mechanisms. The Schmidt number defines the relative importance of mass diffusion with respect to the momentum diffusion. The Prandtl number represents instead the relative importance of heat conduction with respect to the momentum diffusion. For gases, the long distance transport of energy, matter and momentum occurs by the same mechanism. The molecule moving within space, between one collision and the next, carries its momentum, its energy and its mass. Thus, it is reasonable to suppose that the three diffusivities assume more or less the same value \( (\nu = D = \alpha) \), and consequently \( Sc = Pr = 1 \). For liquids, it is instead important to distinguish between the ordinary liquids and the liquid metals. In fact, for the latter, the transport by conduction is particularly favoured because of the activation of the electronic mechanism, much more efficient for energy transport than collisional and the vibrational mechanisms. And so for these \( Pr \approx 1 \). For the ordinary liquids, instead, the most effective transport is momentum, while mass transport is the most inhibited. Therefore, since \( \nu > \alpha \approx D \), this means that \( Pr \approx 1 \) (with values ranging from a few dozen to \( 10^6 \) for liquid polymers) and \( Sc \approx 1 \). Evidently, for the solid systems, the two dimensionless numbers defined above have no physical meaning because it does not make sense to refer to kinematic viscosity (which assumes an infinite value when approaching the limit). It is, however, important to notice that for the solid systems \( \alpha > D \), since evidently it is easier to transfer heat instead of mass through them.

**Transfer coefficients**

In the presence of a fluid in motion, generally speaking, both transport mechanisms, diffusive and convective, are present at the same time. Moreover, the presence of the motion alters the shape of the gradient for the examined variable with respect to that of the stagnant system. Therefore, in practice, it is advisable to introduce coefficients that take into account both contributions, by expressing the driving force in linear terms in the framework of the diffusive fluxes expressions. These coefficients, called transfer coefficients, are defined as follows:

\[ N_f = -D_{j,0} \frac{\partial \omega}{\partial y} \]

\[ q = -k_f \frac{\partial T}{\partial y} \]

\[ r_{j,0} = -\frac{\partial \omega}{\partial y} \]

where \( k_f \), \( h \) and \( (j/\mu) \) are the mass, the heat and the momentum transfer coefficients, respectively. The definition of the last, compatibly with its historically development, uses the \( f \) coefficient, known as the Fanning friction factor. The superscripts \( \infty \) and \( 0 \) indicate, respectively, the function value referred to the fluid at a boundary surface, and \( 0 \) indicates the value referred to the stagnant system and the source term specific to the variable, the source term specific to the volume, and the convective flux and the diffusive flux of the same variable through the boundary surfaces.

**4.2.4 Microscopic conservation equations**

All equations of conservation or balance show the same mathematical structure. Once the volume being examined is identified, which in the considered case has infinitesimal dimensions, the change in the amount contained in such a volume of the considered variable is given by the difference between the amounts of the variable entering and leaving through the boundary surfaces in the unit time, besides any amount that could be generated inside the volume:

\[ \frac{\partial \rho}{\partial t} = -\nabla \cdot (\mathbf{J}_f + \mathbf{N}_f) + \mathbf{R}_f \]

where the symbols \( \rho \), \( R_f \), \( J_f \) and \( N_f \) are the values referred to the unit volume of the variable in question (i.e. the ‘concentration’ of the variable), the source term specific to the volume, and the convective flux and the diffusive flux of the same variable through the boundary surfaces,
FLUID MOTION

respectively. The formulation reported here examines a volume in fixed position with respect to an external reference system (i.e., the Eulerian reference system).

To write the conservation equation it is useful to identify the more suitable intensive variables. To identify the amount of matter contained within a volume, the mass concentration (or the product between the mass fraction of the \(i\)th chemical species and the density, \(\omega_i\)) is usually adopted. The corresponding ‘concentration’ for momentum is identified by the product between the density and fluid velocity, \(\rho u\).

Finally, for energy, by ignoring the contribution of mechanical energy, and thus considering only internal energy, this quantity is identified with the product \(e\), where \(U\) is the internal energy for unit mass. The term of change represents the variation in time of the amount of the variable contained in the system (i.e., the Eulerian reference system).

The source terms, \(\sum_i \omega_i\), identifies the amount of the variable, in algebraic sense, in the unit time and volume and it depends on the nature of the analyzed variable. In the case of the overall mass contained in the system, obviously the source term is absent. If a single species is considered, by the consequence of the chemical reactions such a contribution can be present if these reactions lead to the production or the consumption of the examined species. For the energy balance the source terms can originate from the dissipative effects (like the Joule effect in conductors affected by electric current or to the work performed onto a fluid by the mechanical forces acting on it). The mechanical forces acting on the system play a role in the momentum balance.

To obtain compact formulations, in the following the substantial derivative operator, defined as the sum of the time derivative and of the scalar product between the fluid velocity and the gradient of the examined variable, will be adopted:

\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla
\]

This derivative includes both the transient effects and those due to the convective transport. Thus, the terms remaining explicitly in the balance equation are all inherent to the contributions of diffusive nature.

Each of the microscopic balance equations needs to be completed with initial and boundary conditions, both typical of the system and of the problem in question. Generally, the initial condition, necessary in transient problems, coincides with the initial instant value of the examined variable within the whole integration domain. The boundary conditions can be of two different kinds. The first one assigns the value of the function on the system boundary (the Cauchy-Dirichlet condition) while the second assigns the value of the flux through the wall (the von Neumann condition). Usually, boundary conditions of this second kind are closer to physical reality.

**Microscopic balance equation for mass**

The microscopic equation for mass balance of the individual chemical species is presented in the following form:

\[
\sum_i \frac{D\omega_i}{Dt} = -\nabla \cdot N_i + M_i \dot{R}_i
\]

where \(\dot{R}_i\) is the production rate of the examined \(i\)th species (mol/m²s) due to the chemical reactions occurring in the system and where \(M_i\) and \(\omega_i\) are the molecular weight and the mass fraction of the same species, respectively. The production rate of the species is linked to the rate of the individual chemical reactions, through the relationship (see Chapter 5.1):

\[
\dot{R}_i = \sum_j \frac{v_{ij}}{r_{ij}}
\]

where \(v_{ij}\) and \(r_{ij}\) are the stoichiometric coefficient of the \(i\)th species in the \(j\)th chemical reaction and the rate of the latter, respectively. If, as often occurs, the relevant contribution to the diffusive flux is the ordinary equation [4], then equation [28] becomes:

\[
\frac{D\omega_i}{Dt} = \nabla \cdot (\rho \nabla \omega_i) + M_i \dot{R}_i
\]

Equation [28] can be written for all the species that are present. Instead of taking into account each of the mass balance equations for the individual species, in many cases, it is convenient to use the overall mass balance equation, which can be obtained by summing the balance equations for all the species that are present in the system. Considering that the ensemble of the chemical reactions does not alter the overall mass in the system \((\sum_i M_i \dot{R}_i = 0)\), just as the ensemble of the diffusive fluxes does not produce a net mass transport \((\sum_i N_i = 0)\), the following equation is then obtained, usually called a continuity equation:

\[
\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{u}
\]

**Microscopic balance equation for momentum**

The microscopic balance equation describing the motion of a fluid is well known in fluid mechanics. Together with the continuity equation it provides a system of equations that, in the case of Newtonian fluids, is commonly indicated as Navier-Stokes equations. By ignoring the stresses produced by the molecular fluxes of diffusive nature, in multicomponent systems it reduces to:

\[
\frac{D\mathbf{u}}{Dt} = \rho g - \nabla \cdot \mathbf{\tau} - \nabla P
\]

where the pressure is indicated by \(P\), while equation [17] is valid for the stress tensor, \(\mathbf{\tau}\).

**Microscopic balance equation for energy**

As already pointed out, the balance equation for energy will be written here by ignoring the mechanical energy contributions to better highlight the internal energy contribution, which is, numerically, the most important one in chemical systems:

\[
\frac{D\mathbf{U}}{Dt} = -\nabla \cdot (q + q\cdot \nabla) - P\mathbf{\nabla} \cdot \mathbf{u} + \sum_i N_i \cdot \mathbf{g}_i
\]

where the product between the pressure and the divergence of velocity represents the energy increase due to the fluid compression, while the double scalar product \(\cdot\) between the viscous stress tensor and the velocity gradient indicates the internal energy generation due to the viscous dissipations (irreversible phenomenon). Finally, the last contribution is of interest only when the possible external forces fields act differently on the species that are present, as in the case of the electrochemical systems where the electric field selectively influences the motion of the present ions. Obviously, if the only external field present is gravity, this last term vanishes.
In practice, it is more convenient to consider the state function enthalpy \((H = U + P q)\) so that, when no other external field forces besides gravity are present, equation [33] becomes:

\[ \frac{DH}{Dt} = -\nabla \cdot \left(q + q^r\right) - \tau : \nabla u + \frac{DP}{Dt} \]

If the thermal dilatations associated with the pressure changes and the heat dissipations due to viscous flow are ignored as well, it is possible to obtain an even more simplified expression, which is in any case valid for a wide range of common chemical systems. Usually, this equation is expressed directly in terms of temperature and is expressed as:

\[ \frac{q C_r}{Dt} = \sum (-H^r M R_i) + \nabla \cdot (k_i \nabla T) \]

and contains the contributions due to the chemical reactions and those due to the conductive energy transport caused by the temperature gradients.

**Dimensionless numbers deductible from microscopic balance equations**

Microscopic balance equations contain terms whose relative importance vary depending on the examined conditions. To quantify this point, it is useful to consider a suitable group of variables, known as dimensionless numbers.

By examining the momentum balance equation, it is possible to define the following dimensionless numbers:

\[ Re = \frac{ouL}{\mu} \]

\[ N_f = \frac{\Delta P}{q u' \Delta T} \]

\[ Fr = \frac{u^2}{gL} \]

\[ Gr = \frac{\rho \beta g \Delta T L^3}{\mu^2} \]

The Reynolds number, \(Re\), expresses the relative importance between the inertial forces and the viscous forces, while the ratio between the pressure originated forces and the inertial forces is expressed by the resistance number, \(N_f\), the Froude number, \(Fr\), and the Grashof number, \(Gr\), indicate the relative importance of the inertial forces with respect to the gravitational forces and that of Archimede’s forces (buoyancy) with respect to the viscous forces, respectively.

Conversely, by analyzing the microscopic balance equations for mass and energy, it is possible to single out two additional dimensionless numbers, both defined as Péclet numbers (mass and thermal, respectively), that express the ratio between the convective and the diffusive transport mechanisms:

\[ Pe_m = \frac{uL}{D_m} = Re \cdot Sc \]

\[ Pe_t = \frac{uL}{\alpha} = Re \cdot Pr \]

Finally, the contribution of the chemical reactions to the microscopic mass balance equation is quantified using the Damköhler number, \(Da\), which expresses the relative importance between these reactions and diffusive mass transport:

\[ Da = \frac{M R_k L^2}{q D_{m,0}} \]

In the event that the chemical reaction proceeds through a simple kinetics of the first order, with rate constant, \(k\), the previous equation becomes \(Da = k L^2 / D_{m,0}\).

**Dimensionless numbers linked to transfer coefficients**

The functional form of dimensionless numbers containing the various transfer coefficients, in other words the contributions originated by the linearization of the diffusive transport laws, always identifies the ratio between the transfer coefficient and the transport variable of interest. Because the exchange coefficient expresses a suitable mean value over the characteristic length where the phenomenon is examined, this last contribution also appears in the expression of the dimensionless number. Therefore, the Sherwood number, \(Sh\), and the Nusselt number, \(Nu\), are defined, which are applied to the study of the mass and the heat transport, respectively:

\[ Sh = \frac{k L}{D_m} \]

\[ Nu = \frac{h L}{k} \]

**Functional links between dimensionless numbers**

Obviously, dimensionless numbers are not all independent from each other given that they simply express ratios between variables contained in the different terms of the same balance equation. Usually, some dimensionless numbers are considered dependent on other numbers, which are independent. Among these, \(Re, Sc, Pr, Gr, Fr\) and \(Da\) can be included. Substantially, they are those numbers identifying the fluid (by means of its physical properties), the kind of motion present in the system (viscous laminar, inertial laminar, turbulent, and so on) and they are those directly definable from the terms present in the microscopic balance equations.

Consequently, typical dependent numbers are \(Sh\) and \(Nu\) which express the value of the transfer coefficients.

The links between the dimensionless numbers are usually expressed with monomial forms like the following:

\[ Nu = a Re^n Pr^c \]

\[ Sh = a Re^n Sc^c \]

which are strictly deductible only within a well-defined integral the parameters. Usually, these expressions, or a linear combination, are used as empirical expressions to state the functional links among the dimensionless numbers and they are then applied in practical engineering to estimate the mass and heat transfer coefficient values, which are necessary when the transport phenomena are analyzed at the macroscopic level.

Some relationships of this kind will be examined, together with some important typical cases, in Section 4.2.7. The use of these functional relationships to predict the transfer coefficient values, and thus of the inherent fluxes, represents the core of the practical application of the results of transport phenomena studies in engineering. Substantially, their availability makes the study of even complex systems possible at a greater scale, i.e. at the macroscopic level, thus
making all the design aspects easier. It is important to note that the exponent values do not assume a generic free value. Characteristic values typical of the existing flow regime are identified. Evidently, this is due to the existence of a well-defined chemical-physical connection between the variables contained in the dimensionless numbers. This connection is expressed by the microscopic balance equations.

4.2.5 Molecular aspects

In the following, the most reliable theories for the estimation of the phenomenological coefficients from molecular properties will be examined. The examination of transport phenomena at this level allows their most fundamental aspects to be understood. Molecular transport properties depend on the local state of the materials, liquids or solids, and thus on temperature, pressure and composition, as well as on the molecular properties like mass, molecular dimensions and their interactions (see Chapter 2.3).

As illustrated in Fig. 2, by observing systems at the molecular level, it is necessary to highlight the molecular motions of chaotic nature that superimpose themselves onto the convective ones. In these terms, the fluid velocity is given by the sum of these two contributions. Although the chaotic velocity component is not important to the convective transport, it is the one on which attention must be focused to determine the transport coefficients at the molecular level.

For gaseous systems, as illustrated in Table 1, the basic tool for approaching these problems is the kinetic theory of gases. Being, however, in its first formulation, based on the concept of mean free path and on the use of rigid elastic spheres, leads to correlations that are not fully accurate. In this framework, the mean free path, \( \lambda \), identifies the space covered by a molecule between two successive collisions, whose value can be estimated by the product of the mean velocity of the molecular motion, \( \bar{c} \), with the relaxation time, \( \tau (\lambda = \bar{c} \tau) \), while the flux of the generic function, \( \Psi \), is simply expressed by \( N_{\Psi} = -n\bar{c}d\Psi/\partial c \) (\( n \) is the molecular density).

To improve the model, it was then necessary to introduce the potentials of interaction between molecules, like the Lennard-Jones potential (see Chapter 2.3). In this approach, the path of a molecule is no longer described through a succession of linear segments because of the presence of repulsive interactions. Consequently, the concept of mean free path also become less clear. Thus, the description of the system must be conducted using a distribution function \( f(u, x, t) \) which gives the fraction of molecules that hold a defined energy value and whose shape can be estimated by integrating the Boltzmann equation. Using this approach, the estimation of viscosity, thermal conductivity and of binary diffusivity for the gases is largely improved. Accordingly, the availability of a unifying theory (the kinetic theory of gases) demonstrates the interconnection existing between the transport of different properties in the framework of the same mechanism.

The theory of liquids, based on the vacancy model allowed similar developments even if less accurate than those obtained for gases. The nature of liquids is intrinsically more complex than the nature of gases and, therefore, their theoretical description is indeed less precise. Moreover, there is an additional complication brought about by the kind of liquid under examination (ordinary liquid, liquid metal, liquid polymer) so that, in practice, different theories are formulated depending on the kind of liquid handled.

### Viscosity

The simplest system to be considered is the monoatomic ideal gas, for which it is possible to adopt the hard spheres model for a rough calculation. In this context, it is possible to demonstrate that the viscosity, \( \mu \), depends on the density, \( \varrho \), the mean free path, \( \lambda \), and the mean kinetic velocity of molecules, \( \bar{c} \):

#### Table 1. Examples of transport molecular models for diluted gases

\((f^0)\) is the distribution function of the system in equilibrium conditions

<table>
<thead>
<tr>
<th>Representation of motion</th>
<th>NON-INTERACTING massive points</th>
<th>NON-INTERACTING rigid spheres</th>
<th>INTERACTING objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecules do not have volume and do not interact with each other</td>
<td>Molecules occupy a volume and do not interact with each other</td>
<td>Molecules occupy a volume, have a generic shape, and interact with each other</td>
<td></td>
</tr>
<tr>
<td>Equation of state ( (h=\text{covolume}, a=\text{interaction parameter}) )</td>
<td>( \frac{pV}{RT} = 1 )</td>
<td>( \frac{pV}{RT} = \frac{\bar{V}}{V - b} )</td>
<td>( \frac{pV}{RT} = \frac{\bar{V}}{V - (b/T)} - \frac{a(T)}{RT\bar{V}} )</td>
</tr>
<tr>
<td>Transport model</td>
<td>( \lambda = \tau \tau )</td>
<td>( \lambda = \tau \tau )</td>
<td>( \frac{\partial f}{\partial t} + u \cdot \nabla f = \Gamma_{\text{coll}} = \frac{f - f^0}{\tau} )</td>
</tr>
<tr>
<td>Transport equation ( (\text{of the variable } \Psi \text{ in direction } z) )</td>
<td>( N_{\Psi, z} = -n\bar{c}\lambda \frac{\partial \Psi}{\partial z} )</td>
<td></td>
<td>( N_{\Psi, z} = \int f(u, x, t) u \Psi dh )</td>
</tr>
</tbody>
</table>
where \( \lambda = M Q N_0 \sqrt{2 \pi d^2} \), and \( R, N_0, M \) and \( d \) are the universal constant of gases, Avogadro’s number, the molecular weight and the molecular diameter of the examined species, respectively. In conclusion, the following equation is obtained:

\[ \mu = \frac{2 \sqrt{MRT}}{3 \pi \eta^2 N_d d^2} \]

from which it is possible to observe that the viscosity of a monoatomic ideal gas is independent, while it depends on the square root of temperature. The group \( \pi d^2 \) is called the collisional cross section of the molecule. This result, found by James Clerk Maxwell in 1860, is still essentially valid also for polyatomic gases in supercritical conditions up to a pressure of about 10 bar. Actually, the presence of intermolecular forces makes the collisions between the molecules inelastic, with the consequence that the exponent of temperature approaches a value of about 0.7.

A more rigorous kinetic theory, based on the Boltzmann equation for low density monoatomic gases, was developed by S. Chapman and D. Enskog, introducing an intermolecular potential. Today, for convenience, the Lennard-Jones expression is adopted, which assumes the following form as a function of the intermolecular distance \( r \):

\[ \phi(r) = 4 \epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \]

where \( \sigma \) and \( \epsilon \) are the collisional diameter of the molecule and its characteristic energy, respectively. They can be estimated in a semi-empirical way from the knowledge of the fluid properties (temperature and molar volume) in critical conditions, or at the normal boiling point or at melting point:

**critical conditions**

\[ \epsilon / k_B = 0.77 T_c, \quad \sigma = 0.841 \sqrt{M R T_c} \]

**boiling point**

\[ \epsilon / k_B = 1.15 T_B, \quad \sigma = 1.166 \sqrt{M R T_B} \]

**melting point**

\[ \epsilon / k_B = 1.92 T_m, \quad \sigma = 1.222 \sqrt{M R T_m} \]

where the subscripts \( c, h \), and \( m \) indicate the critical conditions, the normal boiling point, and the normal melting point, respectively. In these terms, the expression for viscosity becomes:

\[ \mu = \frac{5 \sqrt{\pi M R T}}{16 \sigma^2 N_d \Omega_h} \]

where \( \Omega_h \) indicates a dimensionless function, known as collisional integral for viscosity, which expresses the deviation of behaviour from that of rigid spheres:

\[ \Omega_h = \frac{1.16145}{T^*} + \frac{0.52487}{e^{0.77302 T^*}} + \frac{2.16178}{e^{4.50927 T^*}} \]

given that \( T^* = k_B T / \epsilon \).

The calculation of the viscosity for gaseous mixtures, in a rigorous interpretation, is based on the extension of the Chapman-Enskog theory, for convenience a semi-empirical correlation giving a so-called mixing rule can still be used:

\[ \mu_{mix} = \sum_i \sum_j \frac{x_i \mu_j}{x_i} \]

where

\[ \Psi = \left[ 1 + \frac{\mu_i}{\mu_j} \right]^{0.21} \left( \frac{M_j}{M_i} \right)^{0.19} \left( \frac{M_i}{M_j} \right)^{0.65} \]

The performed analysis is valid for low-density fluids where \( d \ll \lambda \). When the mean free path decreases, it loses its validity and thus it cannot be extended to liquids, because in that case \( d \approx \lambda \). In liquids, the viscosity decreases, not increases, with a temperature increase.

To calculate liquid viscosity a simple theory was developed by Henry Eyring. The key hypothesis of the theory is to assume that the motion of the molecules of the liquid, because the value of the mean free path is small, is substantially limited to vibration within a volume confined by the vicinal molecules that thus represent a sort of ‘cage’. In parallel, the liquid structure presents a series of ‘reticular holes’ that are continuously in motion, which can host a molecule. The transfer of one molecule from its cage to the nearest hole means that an activation barrier must be crossed. The frequency, \( \nu \), of these ‘cage’ transfers can be estimated through the following equation:

\[ \nu = \frac{k_B T}{h} e^{-\Delta G_c / RT} \]

where \( h \) and \( \Delta G_c \) are Planck’s constant and the activation free energy of the process, respectively. This last value is linked to the internal energy of vaporization in correspondence with the normal boiling point (\( \Delta G_c = 0.408 \\Delta U_{vap} \)) whose value can be estimated through the Trouton rule (\( \Delta U_{vap} = \Delta H_{vap} - RT_B = 9.4 RT_B \)). In a fluid in motion, and thus in a state of stress, this free energy value increases with respect to the value of a fluid at rest so that:

\[ v' = \frac{k_B T}{h} e^{\Delta G_{c'} / RT} \]

where \( V \), \( \alpha \), and \( \delta \) are the molar volume, the distance to be traveled during the jump toward a hole, and the distance between two molecular planes, respectively. Usually, the approximation \( \alpha = \delta \) is adopted. A positive sign indicates that the molecular jump is coherent with the stress direction and vice versa for a negative sign value. The viscosity value can be estimated by supposing that a linear variation of the fluid velocity exists between two adjacent molecular layers; by approximating the second exponential with a Taylor series truncated at the first term, the following expression is obtained because \( v' = \sqrt{2RT} \):

\[ \mu = \frac{N_0 h}{V} e^{3RT} \]

This relation agrees closely with the empirical relation usually adopted to define the dependence of the liquid viscosity on temperature (\( \mu = k_B T \)). Obviously, over the years many other empirical relationships that introduce corrective parameters to better fit the experimental data have been developed.

Unfortunately, to calculate the viscosity for liquid mixtures, the best approach is still that of performing a series of experimental measures for the mixture viscosity at different temperatures and then describing the results through an equation like [57]. An often-used mixing rule is the following:

\[ \ln \mu_{mix} = \sum_i x_i \ln \mu_i \]
In the framework of liquid systems, polymers and their mixtures obviously require more complex treatment than the preceding one because their molecular structure cannot be approximated as a sphere and this leads to non-Newtonian rheological behaviour. The final goal is to estimate the different coefficients contained in the expression of the stress tensor. The kinetic theories for polymers are substantially divided into two classes, networks and single molecule. The network theories were originally developed to describe the mechanical properties of rubber and were then extended to melted polymers and to their concentrated solutions. The single-molecule theories were originally developed to describe diluted polymeric solutions where each molecule is represented by a ‘bead-spring’ model where a system of springs is connected to some spheres, which are then free to move within a solution, where friction forces act between the fluid solvent and the spheres. The theory was then extended to concentrated solutions and to melted polymers, studying the single molecule behaviour through a mean force approximation able to represent in an effective way its surroundings. In both cases, 4 to 6 parameters are obtained, whose values must be estimated by matching the rheologic measurements.

The last cases to be examined are the heterogeneous systems, i.e. suspensions and emulsions. The easiest approach is to approximate the heterogeneous fluid as a pseudo-homogeneous system, whose viscosity depends on that of the continuum media and on the properties and the volumetric fraction of the dispersed phase. The earliest equation is the one derived in 1906 by Albert Einstein for suspensions containing rigid spheres of the same diameter:

\[ \mu_{eff} = 1 + \frac{5}{2} \phi \]

where \( \mu_{eff} \), \( \mu_0 \), and \( \phi \) are the pseudo-homogeneous fluid viscosity, the solvent viscosity and the volumetric fraction of the suspended solid, respectively. This equation was modified repeatedly to be extended to non-spherical particles and to concentrated suspensions (i.e. with \( \phi > 0.05 \)). In particular, the Mooney equation can be used for concentrated suspensions of spheres:

\[ \mu_{eff} = \exp \left( \frac{2.5 \phi}{1 - \phi} \right) \mu_0 \]

where \( \phi_{hs} \) is a constant whose value is between 0.74 and 0.52 depending on how the system of spheres is packed. In all these relationships, as well as in others not summarized here, the viscosity deviation from the solvent depends on the volumetric fraction of the solid and not on the diameter of the solid particles. For diluted emulsions, the Taylor equation implies a combination of the viscosity values for the two liquids; the subscript \( I \) adopted here is used to identify the dispersed phase:

\[ \mu_{eff} = 1 + \left( \frac{\mu_0 + 2.5 \mu_I}{\mu_0 + \mu_I} \right) \phi \]

**Thermal conductivity**

The kinetic theory for gases supplies a valid tool for the estimation of the thermal conductivity values for monoatomic ideal gases in the same way as viscosity does. In this case it is possible to demonstrate that:

\[ k_I = \frac{1}{3} \rho C_v \tau \lambda \]

\( C_v = 1.5 \) \( R/M \) being the specific heat. The simple substitution of the expressions for the mean free path and for the molecular mean velocity leads to the equation:

\[ k_I = \frac{2}{M d^2} \left( \frac{R}{\pi} \right)^{1/3} \left( \frac{T}{N_s} \right)^{1/3} = 2 \sqrt{MRT} \frac{3N_s\pi/4}{C_v} \]

from which it can be seen that the thermal conductivity of gases is independent from pressure while it depends on the square root of temperature. Even in this case the temperature dependence is underestimated because in a real system the collisions between molecules are inelastic. The Chapman-Enskog theory takes this last effect into account, leading to:

\[ k_I = \frac{25 \sqrt{MRT} / \pi}{32N_s \sigma^2 Q} \]

where the expression for the collisional integral coincides with that for viscosity [52]. Equation (64) is very similar to equation (51) for viscosity; comparing it is possible to observe that for a monoatomic gas \( k_I = 2.5 \) \( C_v \mu_t \). For polyatomic systems, besides the translational component, the rotational and vibrational components of the internal energy are also present. The theory, obviously more complex, leads to an equation that was originally empirically deduced by Arnold Thomas Eucken in 1913:

\[ k_I = \mu \left( C_v + 4 R \right) \]

Finally, the thermal conductivity for a gaseous mixture can be estimated through the following mixing rule, where the \( \psi \) coefficients have the same expression of those introduced for viscosity [54]:

\[ k_{I, mix} = \sum_i \sum_j x_i \psi_j k_{I,i,j} \]

To describe the mechanism for thermal conductivity in ordinary liquids it is useful to refer to Bridgman’s simple theory, which assumes that the molecules are arranged rigidly in a cubic lattice characterized by a reticular parameter equal to the cubic root of the molecular volume \( (\Omega/N) \) and that energy is transferred from one reticular plane to the other at the sonic velocity, \( u_s \). Starting from the expression of the thermal conductivity of gases derived through the hard spheres model [62], it is possible to obtain:

\[ k_I = \frac{1}{3} \rho C_v \tau \lambda = \frac{\rho u_s}{N_s} \left( \frac{V}{N_s} \right) \]

The specific heat for monoatomic liquids almost coincides with that of a solid at high temperature, thus it is possible to estimate its value through the Dulong and Petit equation, \( C_v = 3 \) \( R/M \), obtaining:

\[ k_I = 2.800 \frac{R}{C_v} \left( \frac{\partial P}{\partial \rho} \right) \sqrt{\frac{V}{N_s}} \]

The coefficient 3 was substituted by 2.80 to increase the agreement with the experimental data and the sonic velocity was calculated as a function of the \( C_v/C_P \) ratio and of the isothermal compressibility coefficient \( (\partial P/\partial V)_T \). To estimate the thermal conductivity of mixtures many correlations, of about the same accuracy, have been proposed.
Consequently, it is convenient to refer to the simplest one:

\[ [70] \quad k_e = AT\sigma_e \]

where \( \sigma_e \) indicates the electric conductivity. Equation [70] is valid for solid metals as well. It is important to note that the metals with the greatest electric conductivity (Al, Cu, Ag) are also those that present the greatest thermal conductivity. Instead, metal alloys have an electric conductivity lower than that of their constituting elements.

The thermal conductivity of solids is difficult to predict because it depends on many factors (dimension of the crystal grains and their orientation, porosity, volumetric fraction of amorphous, etc.); it is, therefore, necessary to use experimental measurements. It should be noted that the nature of the solid greatly influences the conductivity value, which is very low for dry, inorganic, porous solids (which are very good insulating materials) while it is high for metals. In general, the thermal conductivity of amorphous materials is lower than that of crystalline ones. Generally, for a rough estimate, it is possible to assume a relation between electric and thermal conductivities, analogously to what was observed for metals (refractory materials are poor electric conductors too).

It is important to obtain the relationships that allow the estimation of thermal conductivity for heterogeneous systems, formed by a mixture of two different solids or by a porous system. The fundamental equation, thanks to Maxwell, is valid for systems where the inclusion of one phase into the other occupies a small volumetric fraction, \( \varphi \), of the solid:

\[ [71] \quad \frac{k_{s\varphi}}{k_{s0}} = 1 + \frac{3\varphi}{k_{s0}} + \left( \frac{k_{s0} + 2k_{\varphi}}{k_{s0} - k_{\varphi}} + \varphi \right) \]

where the subscripts 0 and 1 indicate the solid constituting the matrix and the solid representing the inclusion, respectively. For solids containing gas inclusions (porous solids) the radiative effects can be important, especially when the solid must be used at high temperatures as an insulating material. In this case, the effective thermal conductivity can be estimated through the following equation:

\[ [72] \quad \frac{k_{s\varphi}}{k_{s0}} = 1 + \frac{1 - \varphi}{\varphi k_{s0}} + \left( \frac{k_{s0} + 2k_{\varphi}}{k_{s0} - k_{\varphi}} + \varphi \right) \left( 4\sigma_{s\varphi} T^2 L \right) \]

where \( k_{s0}, L \) and \( \sigma_{s\varphi} \) are the thermal conductivity of the gas, the thickness of the material in the direction of the heat conduction and the Stefan-Boltzmann constant, respectively.

**Diffusivity**

The kinetic theory of gases allows estimations of the binary diffusivity of a gas phase within a 5% approximation when the more accurate Chapman-Enskog approach is adopted. To illustrate the main results of the theory, it is again convenient to start from the theory developed for hard-sphere systems, considering only self-diffusion phenomenon, that is the diffusion of species of the same type, such as isotopes. In this framework, the diffusion coefficient is given by:

\[ [73] \quad D_{s0} = \frac{1}{3} \pi \lambda \]

The simple substitution of the expressions for the mean free path and for the molecular mean velocity leads to the relation:

\[ [74] \quad D_{s0} = \frac{2}{3\pi^2 d_s^6} \frac{M_s RT}{d_s^6} \]

From this equation it is possible to obtain the formula for the binary coefficient by replacing the molecular weight of the species with the reduced weight \( 2/(1/M_s + 1/M_B) \) and substituting the molecular diameter with the mean arithmetic one \( 0.5(d_s + d_B) \):

\[ [75] \quad D_{AB} = \frac{2}{3\pi^2} \left( \frac{1}{M_s + 1/M_B} \right)^{-1} \frac{RT}{d_s^6} \]

From the above equation it is clear that the diffusivity depends linearly on the inverse of pressure (the density dependence of an ideal gas, \( \varrho = M/RT \)) and on temperature with exponent 1.5. However, while the dependence on pressure is correct, the dependence on temperature is underestimated because of the inelasticity of collisions between real molecules, and in practice the correct exponent is about 1.75. Using the Chapman-Enskog approach, it is possible to obtain accurate values for \( D_{AB} \) by introducing the collisional integrals \( \Omega_s \), the previous equation:

\[ [76] \quad \Omega_s = \frac{1.06036}{T^{0.15610}} + 0.19300 e^{0.657357T} + 0.13587 e^{-0.120987T} + 0.766474 e^{-0.941417T} \]

where \( T^{*} = k_BT/\epsilon \), Averaged values, such as \( \sigma_{s\varphi} = 0.5(\sigma_{s0} + \sigma_{\varphi}) \) and \( \epsilon_{s\varphi} = (\epsilon_{s0} + \epsilon_{\varphi})^{0.5} \) must be used in the calculations. Hence, the relationships for the binary diffusivity become:

\[ [77] \quad D_{AB} = \frac{3}{16} \left[ \frac{2RT(1 + \frac{1}{M_s} + \frac{1}{M_B})}{\pi} \right]^{-1} \frac{1}{P_s^{0.5} \Omega_s^{0.5}} \]

Although this equation was derived for monatomic ideal gases it can also be applied to polyatomic ones. By comparing the previous equation with the corresponding one for viscosity [51], it is possible to observe that a link between the kinematic viscosity and the self-diffusion coefficient exists for gaseous systems:

\[ [78] \quad \frac{\nu}{D_{AB}} = \frac{5}{6} \frac{\Omega_s^{0.5}}{P_s^{0.5}} \]

Because the ratio between the collisional integrals is almost constant (\( \Omega_s = 1.1 \Omega_s \)), it derives that \( D_{AB} = 1.32 \nu \), confirming that the Sc number for gases is close to 1.

The theories for diffusion in liquids do not reach a quantitative level analogous to that obtained for gaseous systems. Two models are indeed available and they can be taken as references to derive semi-empirical relationships.
correlating diffusivity to easily measured properties like viscosity or molar volumes.

The first available theory to estimate the diffusivity of a binary mixture is the hydrodynamic theory, based on the Nernst-Einstein equation [9], originally developed for the motion of particles in a stagnant fluid. This equation relates the diffusivity to the mobility, \( \xi \), the latter being the particle velocity, \( u_p \), in steady-state regime when it is subject to the action of a constant force, \( F_p \), i.e. \( \xi = u_p / F_p \). If the relative movement between the particle (whose diameter is \( d_p \)) and the fluid (whose viscosity is \( \mu_f \)) is only creep movement (Re<1), it is possible to demonstrate that:

\[
\xi = \frac{1}{3\pi\eta d_p} \left( 4\eta d_p + \eta d_p \right)
\]

where \( \eta = d_p / \mu_f \) is the sliding friction factor between particle and fluid. Two limiting solutions are possible. In the former, the fluid is supposed to adhere perfectly to the particle (non-slip conditions) and consequently \( \eta = \infty \). On the contrary, in the latter, free-slip conditions are adopted and thus \( \eta = 0 \).

Inserting equation [79] into equation [9] two limiting expressions for diffusivity are thus obtained:

\[
[80] \quad D_{\text{NS}} = \frac{1}{3\pi\eta N_d \mu_f}
\]

\[
[81] \quad D_{\text{FS}} = \frac{1}{2\pi N_d \mu_f}
\]

The first is known as the Stokes-Einstein equation and its use is recommended for the estimation of diffusivity for molecules of large dimensions in low molecular weight solvents. If in the second the molecular dimensions are estimated from the molar volume, \( d_p = (V_p / N) \frac{1}{\xi} \), it is possible to obtain an expression for self-diffusivity that was found to be reliable (uncertainty below 12%) both for ordinary (polar and non-polar) liquids and for liquid metals:

\[
[81a] \quad D_{\text{FS}} = \frac{1}{2\pi N_d \mu_f}
\]

An analogous expression can be obtained through the second model, developed by Eyring which, similarly to the estimation of the viscosity of liquids, assimilates diffusion to a monomolecular activated process:

\[
[82] \quad D_{\text{Eyring}} = \frac{1}{2\pi N_d \mu_f} \left( \frac{N_d}{V_p} \right)^{\frac{1}{3}}
\]

where \( \xi \) is a packing parameter that defines the number of molecules of the ‘nearest-neighbour’ solvent to the diffusing molecule. When examining self-diffusion, \( \xi = 2\pi \), then the Eyring formula substantially coincides with equation [81], despite the conceptual difference existing between the examined models used to derive the two equations.

Because of the limits of the two previous approaches, the estimation of diffusivity in liquid phase is usually performed by means of the Wilke and Chang empirical equation which is able to estimate the diffusion coefficients in diluted systems with an uncertainty below 10%:

\[
[83] \quad D_{\text{WC}} = 2.95 \cdot 10^{-4} \frac{M_x T}{\mu_y} \left( \frac{M_x}{M_y} \right)^{\frac{1}{6}}
\]

where \( \mu_y \) is the association parameter for the solvent, whose values are 2.6 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for benzene, ether, heptane and all the other non-polar unassociated solvents.

For solutions of electrolytes it is necessary to estimate the diffusivity of ions in a different way. It is evident that the charged species experience the effect of the electric field in their motion and thus their diffusivity is related to the electric conductivity. Therefore, by replacing the equation linking the ionic mobility to the equivalent ionic conductance of the ion \( \Lambda_i = (\varepsilon / L^2) \), the following relationship is obtained:

\[
[84] \quad D_i = \frac{RT \Lambda_i}{\varepsilon^2}
\]

Moreover, the electro-neutrality constraint imposes the coupled migration of anions and cations and thus the diffusivity of interest is that of the ionic couple inside the solvent. The property directly measurable is the equivalent conductance of the electrolyte \( \Lambda_e \), which is the sum of the conductance of the constituting ions \( \Lambda_i = \lambda_+ + \lambda_- \), linked in turn to the electric conductivity, \( \sigma_e \), of the solution through the relationship:

\[
[85] \quad \Lambda_e = \frac{\sigma_e}{z_i \nu_i C}
\]

where \( z_i \), \( \nu_i \) and \( C \) are the charge of the positive ion, its stoichiometric coefficient in the reaction of electrolytic dissociation, and the molar concentration of the salt in the solution, respectively.

An even more complex case is represented by the solution of polymers in low molecular weight solvents. For these systems a detailed theory is available which describes the polymer as an ensemble of \( N \) spheres connected through \( N-1 \) elastic springs in order to form a chain. Each sphere interacts with the solvent through a viscous interaction, thus also affecting the solvent in the environment of the nearest spheres. In terms of order of magnitude, this theory predicts that the diffusivity of polymer A in solvent B is proportional to the inverse of the square root of the polymer molecular weight:

\[
[86] \quad D_{BA} = \frac{1}{\sqrt{M_A}}
\]

For solutions of melted polymers, the theory is even more complex and the results are approximated. In general, for self-diffusion, a link with the molecular weight of the polymer is present:

\[
[87] \quad D_{BA} = \frac{1}{M_A^{\frac{n-2}{2}}}
\]

with quadratic dependence \((n=2)\) in the theoretical development, while in practice the exponent can assume even a value of 3 for some polymers.

In a liquid mixture, molecules interact in groups, and thus all the expressions reported above, valid for very dilute conditions, need to be modified to take into account the interactions present at the higher concentrations. One of the most adopted expressions is the following:

\[
[88] \quad D_{BA} = D_{BA} \left( 1 + \frac{\partial \ln \gamma_a}{\partial \phi_B} \right)
\]

where \( \gamma_a \) and \( D_{BA} \) are the activity coefficient of the species in solution and its self-diffusion coefficient, respectively.

For diffusion through solids, because of the packing of the lattice to be crossed, it is normal to find very low
diffusivity values. The reference model is similar to that of liquids, where the solute displacement from one position to another is possible only if a hole is present nearby that creates the space available for the transfer. Vacancies are common defects of crystalline solids, whose numeral density depends on thermodynamic and kinetic factors. Moreover, vacancies are mobile and they can even aggregate and give rise to defects of larger dimensions (microcavities). Analogously to the theories already seen for liquids, the resistance of the solute to moving towards a nearby vacancy is great, and so that this can happen the solute molecule must overcome a potential energy barrier. In other words, the diffusion into a solid matrix is an activated phenomena and thus the expression to be used is the following:

\[ D_{ab} = A_i \omega_i e^{-i/kT} \]

where the \( A_i \) term is connected to the vibration frequency of the atoms in the lattice (which identifies the mobility of the vacancies), while the activation energy is related to the bond energy.

To complete the analysis of molecular aspects it is also necessary to derive the equation for the estimation of diffusivity for the processes induced by temperature and pressure gradients. Because these phenomena are usually relevant only for gaseous systems, only expressions directly derived from the Chapman and Enskog theory will be addressed here. The thermal diffusion coefficient is related to the ordinary coefficient through a thermal diffusion address. The thermal diffusion coefficient is derived from the Chapman and Enskog theory will be relevant only for gaseous systems, only expressions directly.

For diffusion induced by pressure in a binary system the diffusivity depends on the concentration gradient for the examined species. It is evident that in a binary system the flux of a species in one direction corresponds with the flux of the other species in the opposite direction. To account for this point in general mathematical terms the Stefan-Maxwell equations can be used for reference, through which the driving force, \( \omega_i \), or directly the effective diffusion coefficient, \( D_{ij,m} \), depends on the diffusive fluxes of all the species that are present in the system:

\[ \nabla \omega_i = \sum \frac{1}{D_{ij}} (\omega_i N_j - \omega_j N_i) \]

\[ \frac{1}{qD_{ij,m}} = \sum (U \omega_D_{ij}) \left( \omega_i N_j - \omega_j N_i \right) \]

Equation [93b] can be simplified for some cases of practical interest. For example, because one of the diffusion coefficients can be arbitrarily chosen, by assuming that \( D_{m,n} = D_{ij} \), the Blank equation can be obtained:

\[ D_{i,m} = \frac{1-\omega_i}{\sum \omega_D_{ij} D_{ij}} \]

which is often used to estimate the effective diffusion coefficient instead of the more precise, but also more computationally complex, Stefan-Maxwell equations [93]. Another relevant case is the one where a species, typically the solvent, is present in large quantities and so can be reasonably considered stagnant. In this case the diffusivity reduces to the binary coefficient:

\[ D_{i,m} = D_{i,n} \]

4.2.6 Role of turbulence

In turbulent motion, unlike laminar motion, the streamlines appear irregular and with abrupt direction changes. This fact has a strong influence on transport phenomena. Turbulence is a phenomenon analogous to phase transitions: in a fluid in laminar motion, once it has reached a critical velocity, a sharp transition towards turbulence occurs, analogously to what is observed when a liquid reaches the bubble point. A fluid in turbulent motion dissipates more energy than would be dissipated in a hypothetical laminar regime with the same Reynolds’ number.

Although in turbulent motion the local instantaneous velocity and pressure values are subject to chaotic variations, it is possible to identify some properties of time-averaged values that are well defined and significant. In other words, while the reproducibility of instantaneous values is not assured because of the chaotic nature of the motion, a
reproducibility in term of time-averaged values (long time average) is possible instead:

\[ \bar{A}(x) = \frac{1}{\Delta t} \int_{0}^{\Delta t} A(x,t) \, dt \]

where \( A \) indicates the function of interest (like velocity, concentrations, temperature and pressure) in the generic \( x \) position within the system.

Considering a fluctuating function like the one illustrated in Fig. 5, it can be observed that its instantaneous value can be expressed by adding a fluctuating contribution to the time-averaged contribution:

\[ A(x,t) = \bar{A}(x) + A'(x,t) \]

where the averaged value over a sufficiently long time of the fluctuating contribution is zero (\( A' = 0 \)). By applying this definition to the microscopic balance equations, and by introducing the function of interest (like velocity, concentrations, temperature and pressure), the examination of the original equations for laminar motion, provided that the shear stress is replaced by a contribution related to the turbulent velocity fluctuation, a common structure is obtained, presenting the common structure for expressing the fluctuating contributions to the time-averaged transport properties. To write these terms, it is generally accepted to refer to expressions with the same structure as the original ones. To write these terms, it is generally accepted to refer to expressions with the same structure as the original ones.

\[ \frac{\partial}{\partial t} \rho \overline{\mathbf{u}} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla \rho \mathbf{u} + \nabla \cdot (\tau) + \rho \mathbf{f} - \overline{\mathbf{q}} \]

Dimensional analysis and scaling effects

Experimentally, it has been observed that the intensity of turbulence, expressed as the absolute value of the fluctuating component of velocity, is proportional to the mean value of the fluid velocity itself. In particular, if the motion of a fluid in a pipe is examined, the following relationship is assumed:

\[ \eta = \sqrt{f \frac{d}{2}} \]

where \( f \) is the friction factor. This dependence can be understood through the analysis of the characteristic time and length of the turbulence. As already mentioned, beyond the Re threshold value, fluid motion destabilizes and vortices (eddies) start to form which are responsible for energy dissipation. In a vortex, because the Re number is very high (\( Re > 10^5 \)), inertial contributions are prevalent compared to viscous ones and thus the correspondent energy dissipation is negligible. Accordingly, an energy transfer with a very low dissipation from the higher dimensions vortices to the smaller ones can be hypothesized which, however, increases when the vortex dimension becomes so small that the viscous terms become important.

Based on Andrej N. Kolmogorov’s classic theory, it is useful to identify different turbulence scales, \( \lambda \), each corresponding to the average vortex dimension. Each scale is...
associated with a well-defined turbulence intensity corresponding to the vortex velocity, $u_1$. On the basis of these two variables it is then possible to define a Reynolds number typical of turbulent vortices, $Re_{\lambda}=\lambda u_1/\nu$. To each of these vortices corresponds a dissipated power per unit volume, $\epsilon$, which, by means of a dimensional analysis, can be related to the $Re_{\lambda}$ value:

$$\frac{\lambda \epsilon}{u_1} = f(Re_{\lambda})$$

where $\epsilon$ is the energy transferred per vortex. If only the asymptotic behaviour is examined, two limiting situations can be seen. In the first, where $Re\gg 1$, are contained the macrovortices, where inertial aspects are prevalent and thus the energy is transferred to the lower level vortices without dissipation. In the second, where $Re=1$, microvortices are present, where viscous aspects are prevalent, and thus where a dissipative process takes place. Thus, in the former case, the dissipated energy must be level independent, and then:

$$\frac{\lambda \epsilon}{u_1} = \text{constant}$$

where $L$ is the maximum possible dimension for the vortices that are present in the system and thus it coincides with the dimension of the apparatus generating the turbulence. It is possible to estimate the characteristic velocity of vortices at some scale beginning from the velocity at the maximum scale, $u_1$:

$$u_0 = u_1 \left(\frac{\lambda}{L}\right)^{3/3}$$

As already observed, the energy transfer between vortices stops when the viscous phenomena become prevalent, i.e. when $Re$ assumes values close to 1. Substantially, the energy transfer proceeds unaltered up to the microvortex level where it sharply decays. The characteristic dimension of microvortices, $\lambda_0$, can be estimated through the following relationship:

$$\frac{\lambda_0}{L} = \left(Re_{\lambda}\right)^{3/4}$$

Thus the aggregates whose dimensions are lower than $\lambda_0$ are not able to transfer energy but only to dissipate it. By examining the above concepts inherent to turbulent motion inside a pipe, it is possible to see that microvortices have a characteristic dimension of the order of the pipe diameter ($L=\delta$), while the turbulence intensity will correspond to about 10% of the fluid mean velocity in the channel. Numerically, for $Re=10^5$, $Re_{\lambda}=0.1 \cdot Re$, the maximum dimension of microvortices will be $\lambda_0=10^{-3} \delta$. If the pipe has a diameter of 10 cm, the microscale for turbulence is on the order of 100 $\mu m$ with a characteristic time of about 1 ms. It is to be noted that this value is bigger than the mean free path of molecules in a gas at ambient temperature (about 0.1 $\mu m$) and thus, in principle, the simulation of turbulent motion, DNS (Direct Numerical Simulation), can still be performed assuming a continuous system and by applying the Navier-Stokes equations, being careful to partition the integration domain at microvortex dimension and to use a time step of about one ms. It is clear that even with today’s computers this simulation is a difficult task.

The considerations in terms of order of magnitude like the above can in any case be used to estimate the values of turbulent diffusivities. Remembering equation [73], and by identifying the mean free path of the vortices with their dimensions, the turbulent diffusivity associated with the vortices with dimension $\lambda$ is:

$$D^{(\lambda)} = \frac{1}{3} \lambda \nu$$

and so the average value that takes into account the contributions of all vortices whose dimensions are between $\lambda_0$ and $L$ will be:

$$D^{(V)} = \nu^{(\lambda)} = \alpha^{(\lambda)} = 0.14 u_1 L$$

The direct simulation of turbulence is a problem whose solution is still highly difficult; thus alternative approaches have been developed. One of the most frequently used today is called $K$-$\epsilon$, which adds the equations for turbulent kinetic energy, $K=0.5 u^2$, and turbulent dissipation, $\epsilon$, to the averaged equations [103-105]:

$$\frac{DK}{Dt} = \nabla \left[ \left( u + C_1 \frac{K^2}{\epsilon} \right) \nabla K \right] + C_2 \frac{K^2}{\epsilon} \nabla (\nabla u)^2 - \epsilon$$

$$\frac{D\epsilon}{Dt} = \nabla \left[ \left( u + C_1 \frac{K^2}{\epsilon} \right) \nabla \epsilon \right] + C_3 C_4 K (\nabla u)^2 + C_5 \epsilon$$

where the three constants assume the values $C_1 = 0.09$, $C_2 = 1.44$ and $C_3 = 1.92$, while the turbulent diffusivity is calculated directly as a function of the variables reported above:

$$D^{(V)} = \nu^{(V)} = \alpha^{(V)} = C_0 \frac{K^2}{\epsilon}$$

### 4.2.7 Some typical problems

The theories that have been developed so far set the stage to approach in principle any problem dealing with transport phenomena. As already mentioned, it is sufficient to integrate the microscopic balance equations on have been defined, to obtain, in the most general case, the velocity, temperature and composition within the examined domain. In the framework of the mentioned approximations, by means of the computers available today, such a procedure can be adopted, both in laminar and in turbulent regimes, for any geometrical domain and even for an elevated number of chemical species. This stage has been reached gradually by the solution of a high number of simple cases for which it was possible to obtain analytical solutions, even if simplified. Substantially, a consistent fraction of the typical problems consists in the use of microscopic balance equations to obtain monomial relationships between the characteristic dimensionless numbers for the examined problem. These equations can then be applied to the solution of problems in physical terms even if with geometries that are not strictly identical. It is possible to rely on the extended similitude principle, by which the functional dependences between the dimensionless numbers are seldom influenced by the system geometry, with the exception of small adjustments of their proportionality coefficient, whose value is indeed close to one. In other words, it means that the physical phenomena underlying the
examined case are only slightly affected by geometry. Thus, for the estimation of mass and energy transfer coefficients, as well as for the friction factor for the fluid motion, it is possible to refer to equations derived for simplified geometrical configurations, or to the combination of some asymptotic behaviour. For that reason, a compilation of the most adopted relationships for the estimation of the mass transfer coefficients is summarized in Table 2.

### Table 2. Examples of some common monomial expressions between dimensionless numbers for the estimation of the mass transfer coefficient

<table>
<thead>
<tr>
<th>Flow configuration</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat horizontal wall, forced convection</td>
<td>$u^*$</td>
</tr>
<tr>
<td>Laminar:</td>
<td>$Sh_l = 0.646 Re_l^{1/2} Sc_l^{1/3}$</td>
</tr>
<tr>
<td>Turbulent:</td>
<td>$Sh_t = 0.365 Re_l^{0.8}$</td>
</tr>
<tr>
<td>Flat vertical wall, natural convection</td>
<td></td>
</tr>
<tr>
<td>Laminar:</td>
<td>$Sh_l = 0.508 Gr^{-1/4} Sc_l^{-1/2}(0.952 + Sc_l)^{-1/4}$</td>
</tr>
<tr>
<td>Turbulent:</td>
<td>$Sh_t = 0.249 Gr^{-1/4} Sc_l^{-7/12}(1 + 0.494 Sc_l^{-1/3})^{-2/5}$</td>
</tr>
<tr>
<td>Steady state flat disk</td>
<td></td>
</tr>
<tr>
<td>Laminar:</td>
<td>$Sh_l = 8/ \pi$</td>
</tr>
<tr>
<td>Turbulent:</td>
<td>$Sh_t = 0.562 Re_x^{0.508}$</td>
</tr>
<tr>
<td>Flat rotating disk</td>
<td></td>
</tr>
<tr>
<td>Laminar:</td>
<td>$Sh_l = 0.879 Re_x^{0.4} Sc_l^{1/3}$</td>
</tr>
<tr>
<td>Turbulent:</td>
<td>$Sh_t = 0.365 Re_x^{0.8}$</td>
</tr>
<tr>
<td>Flow around spheres</td>
<td></td>
</tr>
<tr>
<td>Laminar:</td>
<td>$Sh_l = 2 + 0.60 Re_x^{0.4} Sc_l^{-1/3}$</td>
</tr>
<tr>
<td>Turbulent:</td>
<td>$Sh_t = 0.347 Re_x^{0.62} Sc_l^{1/3}$</td>
</tr>
</tbody>
</table>

By considering an incompressible fluid in steady state laminar regime flowing through a circular-section pipe, it is easy to verify that the equations in [32] reduce to the single equation dealing with the uniquely present velocity component, $u_z$, that is independent from the axial coordinate because of the continuity equation [31] and from the azimuthal coordinate because of cylindrical symmetry:

\[
[116] \frac{\partial u_z}{\partial z} = - \frac{\partial P}{\partial z} + \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z}{\partial r} \right) + \frac{\partial^2 u_z}{\partial r^2} \right]
\]

\[
[117] \frac{\partial u_z}{\partial z} = 0
\]

By assigning nil velocity values in correspondence with the walls and by using the symmetry conditions in correspondence with the pipe axis, the integration of equation [116] provides the velocity profile as a function of the pressure gradient ($\Delta P/L$), of the fluid viscosity and of the channel radius $R$:

\[
[118] u_z = \frac{\Delta P}{L} r R \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
\]

which show the classic parabolic trend. It is just as easy to verify that, if instead of a Newtonian fluid a non-Newtonian fluid is considered and where the Ostwald-De Waele rheological model [20] is adopted, the integration leads to the expression (with $s=1/n$):

\[
[119] u_z = u_{z,\text{ref}} s + 3 \left( \frac{r}{R} \right)^{s+1} + \left( \frac{r}{R} \right)^{s+3}
\]

whose mean velocity value is given by:

\[
[120] u_{z,\text{ref}} = \frac{Re_x^{s+3/2} \left( \frac{\Delta P}{L} \right) \frac{R}{2}}{s + 3 \left( \frac{R}{L} \right)^{2+s}}
\]

Obviously, if $n=1/s=1$, the previous equation becomes Newtonian. It is just as important to note that the stress within the fluid, maximum at the wall and nil in the centre, is independent from the fluid rheology:

\[
[121] \tau_z = \frac{\Delta P}{L} \frac{r}{2}
\]

A comparison between the velocity profiles, at constant mean velocity, as a function of the rheologic behaviour of the fluid is illustrated in Fig. 6, from which it can be seen that pseudoplastic fluids ($n<1$) tend to a flat front profile, while

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Dilatant fluids \( (n > 1) \) tend to a linear profile. By considering equation [98], it is easy to verify that the velocity profile in turbulent regime approaches that of a pseudoplastic fluid. If a universal turbulent velocity profile is assigned, an exponent in the order of 1/7 is observed, which corresponds in the above developments to exponents \( n \) in the order of about 0.1-0.2. In particular, the velocity gradient in correspondence with the wall is even steeper, so that in practice the maximum velocity is identified by the averaged velocity (plug-like flow).

**Velocity, temperature and mass boundary layers**

If a Newtonian fluid approaches a wall whose linear dimension is \( L \) with a velocity, \( u_x^* \), so that \( Re = 1 \), the inertial forces are significantly greater than the viscous ones and the momentum convective flux is larger than the diffusive one. This situation is not found in proximity of the wall. As is shown in Fig. 7 A, it is possible to identify a region of space, whose thickness is \( d \), called the boundary layer and introduced for the first time by Prandtl in 1904, where the viscous forces are more prevalent than the inertial forces. Because the viscous dissipation is responsible for the resistance encountered by the fluid during its motion, the knowledge of the boundary layer features plays a paramount technological importance.

Substantially, the boundary layer thickness identifies the point where viscous and inertial forces balance. Within the boundary layer the velocity profile can be assumed linear with good approximation.

When referring to the case where the fluid approaches a flat wall placed along the direction of its movement (see again Fig. 7 A), with unperturbed velocity, \( u_x^* \), the equations for the motion reduce to two equations for the velocity components \( (u_x, u_y) \) and to the continuity equation for pressure:

\[
\rho \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) = -\frac{\partial P}{\partial x} + \mu \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} \right)
\]

\[
\rho \left( \frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right) = -\frac{\partial P}{\partial y} + \mu \left( \frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} \right)
\]

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0
\]

The boundary conditions for the velocity components are: zero velocity in correspondence with the wall \((y=0)\), velocity \( u_x^* \), unaffected and moving parallel to the wall \((u_x=0)\) at an infinite distance from the wall; analogously for pressure, \( P^* \). In correspondence with the boundary layer, by definition, the velocity value along the \( x \) direction coincides with the unaffected value \((u_x(\delta)=u_x^*)\). In terms of order of magnitude, the continuity equation [124] states that \( u_y = u_x^* \delta / \lambda \), i.e. the transverse velocity is much smaller than the longitudinal velocity, because of the small value of \( \delta \), and that the order of magnitude of the longitudinal coordinate approaches the wall length. Comparing equations [122] and [123] it is possible to observe that:

---

**Fig. 6.** Velocity profile for a fluid in a circular pipe in steady-state conditions and as a function of the rheologic fluid behaviour.

**Fig. 7.** Graphs of the boundary layer developments during a fluid-wall interaction:
A, velocity boundary layer; B, thermal boundary layer; C, composition boundary layer.
and thus it is possible to ignore the pressure variation along the transversal coordinate and thus the pressure value in any point within the boundary layer is equal to that in the unperturbed zone outside the layer. By examining again equation [122] it is easy to identify that the two left hand side convective terms are of the same order of magnitude, while the first one of the two viscous terms in the right hand side is much smaller than the second one. Thus, by imposing the balance of the convective term with the viscous one (boundary layer definition) it follows that:

\[ \frac{\mu}{x} \frac{d}{dx} \left( \frac{u_x^2}{x} \right) = \mu \frac{d}{dy} \left( \frac{u_y^2}{y} \right) \]

or in other words:

\[ \frac{\delta}{x} \left( Re \right)^{0.5} \]

having established that \( Re_y = \rho u_x^2 x / \mu \). If the transverse velocity gradient \( (\partial u_x / \partial y) \) is estimated, it is possible to obtain the stress \( \tau_y = -\mu (\partial u_x / \partial y) \), and thus to derive the expression for the friction factor:

\[ f = \frac{2 \tau_y}{\rho u_x^2} = \left( Re \right)^{-0.5} \]

Four years after the publication of Prandtl’s paper, the problem was reconsidered in a more rigorous way by Heinrich Blasius, who determined more accurately \( f = 0.64 Re^{-0.5} \).

If the system is not isothermal, it is necessary to add the energy balance to equations [122-124]:

\[ u_x \frac{\partial T}{\partial x} + u_y \frac{\partial T}{\partial y} = \alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \]

with boundary values for temperature \( T^o \) in correspondence with the wall and \( T^\circ \) in the zone that is not disturbed. In this case it is also possible to identify a region in space whose extension is small compared to the dimensions of the wall inside which all the temperature variations occur, the so-called thermal boundary layer as illustrated in Fig. 7 B. To calculate the order of magnitude of the thermal boundary layer, \( \delta_t \), the approach developed above can be followed. Two cases can be distinguished as a function of the value of the Reynolds number, \( Re \geq 1 \) and \( Re < 1 \).

In the first case there is the development of two independent boundary layers, the velocity layer and the thermal layer, which can be either inside or outside velocity layer depending on the value of the Prandtl number. In particular, \( \delta_t > \delta \) if \( Pr < 1 \) and vice versa if \( Pr > 1 \). For small \( Pr \) values, which is the case for liquid metals, it can be found that the phenomenon is controlled by the thermal Péclet number \( (Pe_T = Re / Pr) \):

\[ \frac{\delta_t}{L} = \left( Re \cdot Pr \right)^{-0.5} \]

\[ Nu = \frac{L}{\delta_t} \approx \left( Re \cdot Pr \right)^{0.5} \]

If instead \( Pr > 1 \), which is the case for ordinary liquids, the exponents for \( Re \) and \( Pr \) are different:

\[ \frac{\delta_t}{L} \approx \left( Re \cdot Pr \right)^{-1/3} \]

\[ Nu = \left( Re \cdot Pr \right)^{1/3} \]

In practice, these trends remain valid for gases as well, where \( Pr = 1 \). Thus, the \( Nu \) trend (and consequently that of the heat transfer coefficient) follows the combination of profiles shown in Fig. 8 A.

If \( Re < 1 \), the velocity boundary layer does not develop and thus the only boundary layer present is the temperature layer. If \( Pe_T \) is small as well, which means that convection can be ignored with respect conduction, \( Nu \) is constant and its value is close to one. If instead \( Pe_T \) is great, a dependence with respect to its value is found:

\[ Nu \approx \left( Re \cdot Pr \right)^{1/3} \]

Thus, the \( Nu \) trend for \( Re < 1 \) follows the combination of profiles illustrated in Fig. 8 B.

Because the mass balance equation [30] assumes the same shape of the energy balance equation [129], the only difference being the substitution of the thermal diffusivity with mass diffusivity, the previous information can also be
applied to the examination of mass transport. In this case, a mass boundary layer is defined, shown in Fig. 7 C, whose trends are exactly those illustrated in Fig. 8, substituting $Sh$ for $Nu$ and $Sc$ for $Pr$. Naturally, the same substitution is applied to equations [130-135].

This shows that if $Re=1$ there is an analogy between heat and mass transport and transport of momentum. This fact is stated by the Chilton and Colburn analogy, which calculates the transfer coefficient using the knowledge of either of the other two:

\[ \text{Nu} = 0.5 f Re \cdot Pr^{1/3} \]

\[ \text{Sh} = 0.5 f Re \cdot Sc^{1/3} \]

The previous results can be verified through the integration of the balance equations. The development of the boundary layers is in fact clearly shown in Fig. 9, where the details of the velocity, temperature and composition fields are reported for the case of a fluid approaching a flat plane, in analogy with the above examined cases.

The analysis above can also be repeated in turbulent regime because the structure of the balance equations, when the averaged variables are considered, is identical to that of the laminar case. Moreover, it must be remembered that ‘diffusive’ transport is entirely due to turbulence and that the value of the three turbulent diffusivities is the same. Accordingly, the boundary layer analysis for velocity leads to the following expression for the friction factor:

\[ f = 0.791 Re^{-0.25} \]

from which, by applying the Chilton and Colburn analogy, the expressions for $Nu$ and $Sh$ can be obtained:

\[ \text{Nu} = 0.5 f Re \cdot Pr \]

\[ \text{Sh} = 0.5 f Re \cdot Sc \]

From this it follows that in turbulent regime the exponent for $Pr$ and $Sc$ is one, differently to what happens in laminar regime, where its value is 1/3.

**Temperature distribution within solids**

In steady state conditions, as shown in Fig. 10, inside a flat slab of finite thickness, a linear temperature profile is observed and the heat flux through the slab by conductive mechanism is $q = kA\Delta T/s$. In this case the divergence of the flux is nil in the energy balance equation [35], in other words $kA\sqrt{T} = 0$. In the case of composite walls in contact with two fluids, in practice, it is common to define an overall heat transfer coefficient that accounts for all the ‘resistances’ present in the heat transport from one fluid to the other:

\[ q = U(T_{hot} - T_{cold}) \]

\[ \frac{1}{U} = \frac{1}{h_1} + \sum s_j \left( \frac{1}{k_j} \right) + \frac{1}{h_2} \]

where $h_1$ and $h_2$ are the heat transport coefficients of the two fluids, while $k_j$ are the thermal conductivities of the solid materials making up the wall, each one of thickness $s_j$. To justify the two previous equations it is sufficient to equate the expressions for the heat flux through any phase and to impose the temperature continuity for the walls in contact.

In a wall formed by a single material it is important to verify the relative importance between the external heat transfer by convection and the internal one by conduction. This ratio is given by the Biot number:

\[ Bi = \frac{h_1}{k} \]

Another interesting case, illustrated in Fig. 11, deals with heat conduction in transient conditions. For a semi-infinite slab, the analytical integration of the energy balance equation gives the following expression:

\[ \frac{T - T_0}{T_1 - T_0} = \text{erf} \left( \frac{y}{\sqrt{4at}} \right) \]

where $T_1$ and $T_0$ indicate the ‘skin’ temperature of the slab and the initial temperature (constant at every point of the slab) and $y$ is the internal coordinate along the slab. It is of interest to estimate the penetration thickness for heat, $\delta_T$, that identifies the point where the temperature assumes 99% of its asymptotic value. By inverting equation [144] $\delta_T = 4\sqrt{at}$ is
obtained, from which can be derived, for example, the thickness of a solid that can be assumed to be semi-infinite if the phenomenon is observed for times lower than $t$.

**Mass transport through interphase**

Because the mass balance equation in absence of chemical reaction is identical to that of energy balance, equation (144) also describes the penetration of a chemical species through a solid or through a stagnant fluid, when temperatures are substituted by concentrations (or by mass fractions) and the thermal diffusivity is substituted by the mass diffusivity:

$$[145]$$

In steady state conditions, as shown in Fig. 12, when the mass transfer occurs through an interface or through an interface between two different phases, its presence induces a discontinuity in the composition profile. It is usually assumed that at the interface thermodynamic equilibrium conditions are established. A typical example is the gas-liquid mass transfer. In steady-state conditions, the mass flux from the 'gas side' must be equal to the corresponding flux on the 'liquid side':

$$[146] \quad N_i = k_{i,G} \left( \omega_{i,G} - \omega_{i,L} \right) = k_{i,L} \left( \omega_{i,L} - \omega_{i,G} \right)$$

where the subscripts $L$ and $G$ indicate the liquid and gaseous phases, while the asterisk identifies the interfacial conditions. Moreover, by considering the equilibrium condition at the interface, synthetically expressed by means of the partition constant $K_i$:

$$[147] \quad \omega_{i,G} = K_i \omega_{i,L}$$

it is possible to obtain the following expression for the mass flux:

$$[148] \quad N_i = \omega_0 k_{i,L}^{\text{eff}} \left( \omega_{i,G} / K_i - \omega_{i,L} \right)$$

where, analogously to the heat transfer, an overall mass transport coefficient is defined:

$$[149] \quad 1 / k_{i,L}^{\text{eff}} = 1 / k_{i,L} + \omega_0 / K_i \omega_0 / \rho_0$$

Because the mass transport coefficient in liquid phase is significantly smaller than that in gaseous phase (see the ratio of the two diffusivities $D_{i,L}/D_{i,G} = 0.001$), often $k_{i,L}^{\text{eff}} = k_{i,L}$ is assumed.

**Natural convection**

In natural convection, fluid motion is induced by the presence of density gradients that can originate both from temperature and concentration gradients. In principle and with the computational facilities available today, to solve these problems only an equation of state expressing fluid density as a function of temperature and composition is necessary. It is possible to obtain approximated analytical solutions of this problem through a linearization of the equation of state, as proposed by Boussinesq:

$$[150] \quad q = \frac{\rho_0}{\rho_0} \left[ 1 + \beta_r (T - T_0) + \sum \frac{\partial \rho}{\partial \omega_i} (\omega_i - \omega_{i,0}) \right]$$

where $\beta_r$ is the thermal dilatation coefficient for the fluid and the subscript 0 indicates the reference conditions. It is necessary to indicate that in the presence of temperature gradients, the first term is usually the dominant one. Its substitution within the balance equations allows the definition of the Grashof thermal number [39] and of the homologous number for the concentration. It is important to note that natural convection initiates only for values greater than a critical threshold. An example is evidenced by the heating of a fluid through a hot wall underneath. When the heat flux is small (and consequently the density and temperature gradients are limited) the fluid remains at rest. Once the threshold value is surpassed it can be observed that fluid motion starts with the formation of natural convection.

![Fig. 12. Chemical composition profile during the mass transfer through an interface where thermodynamic equilibrium conditions are reached.](image)

![Fig. 13. Vortices caused by natural convection for different geometric configurations of the tank holding the fluid (fluid heated from below).](image)
cells (Benard’s cells). The extension and the number of these cells depends on the ratio between the vertical and horizontal dimensions for the tank holding the fluid. As illustrated in Fig. 13, if the vertical dimension is prevalent, either a single cell, whose extension covers the whole fluid, or two counter-rotating cells are present. Vice versa, if the horizontal dimension prevails, the formation of a great number of cells takes place, because the maximum vortex extension is vertical.

Another interesting case, where it is possible to obtain an analytical solution, is that of a fluid contained between two parallel infinite vertical walls at different temperatures. In this case, the channel being infinite in length, only one velocity component $u(x)$ exists, whose direction is parallel to the channel axis and whose value depends on the transversal coordinate. Analogously, the fluid temperature $T(x)$ also depends uniquely on the same coordinate. It is easy to verify that the energy balance reduces to the Laplace equation, in other words $k \frac{\partial^2 T}{\partial x^2} = 0$, thus leading to a linear temperature profile between the two walls. The integration of the momentum balance equation for the uniquely present velocity component leads to the following expression for the velocity profile, which is the sum of a zero average value velocity component (component due to natural convection) and of a Poiseuille’s parabolic profile (component due to forced convection):

$$[151] \quad \frac{u(x)h}{v} = G_r \left[ \frac{1}{12} \left( \frac{h}{x} \right)^3 - \frac{1}{3} \left( \frac{x}{b} \right) \right] + \frac{2 \cdot Re}{3} \left[ \frac{1}{12} \left( \frac{h}{x} \right)^3 - 1 \right]$$

where $Re$ is calculated by means of the averaged fluid velocity due to the forced convection and $b$ is the semi-distance between the two walls. The fact that the velocity profile is the sum of two profiles should not be surprising, seeing that the starting equations are linear. When forced convection is absent ($Re=0$), the velocity profile becomes at zero mean value, because the rising flow rate in half of the channel is exactly equal to the descending flow rate in the other half.

### 4.2.8 Conclusions and future developments

Research dealing with transport phenomena is at present focusing on molecular aspects, thanks to the availability of molecular dynamic software that simulates fluid behaviour in conditions closely approaching real conditions. In particular, the formulation of a reliable model for liquid polymers surely represents one of the frontiers in the study of transport phenomena, while considering that a molecular theory for heat transport in polymers has not been yet formulated. In addition, fast computers are of great importance for the study of turbulent flow systems, because they allow the direct simulation of the flow (direct numerical simulations) and thus permit, with time averaging techniques (long time average), to evidence the turbulence features that later can be adopted to formulate adequate turbulence models. The application of transport phenomena to small systems (micro-channels) produces surface phenomena which must be included in the balance equations. Although such a correction is known, fundamental theories on the interface interaction (fluid-solid interaction, surface wetting), are presently still incomplete. Finally, the application to biological systems makes it necessary to include transport mechanisms reflecting the particular nature of the membranes present in the cellular organisms, for which the simple description through permeability coefficients is greatly over simplified.

### Bibliography


### References


### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>area of the $i^{th}$ surface</td>
</tr>
<tr>
<td>$a$</td>
<td>lattice parameter of the crystal</td>
</tr>
<tr>
<td>$a_i$</td>
<td>molecular interaction parameter</td>
</tr>
<tr>
<td>$b$</td>
<td>covolume</td>
</tr>
<tr>
<td>$C_i$</td>
<td>molar concentration of $i^{th}$ species</td>
</tr>
<tr>
<td>$C_T$</td>
<td>specific heat at constant volume</td>
</tr>
<tr>
<td>$C_R$</td>
<td>specific heat at constant pressure</td>
</tr>
<tr>
<td>$c$</td>
<td>velocity module of molecular chaotic motions</td>
</tr>
<tr>
<td>$D_{ab}$</td>
<td>binary diffusion coefficient</td>
</tr>
<tr>
<td>$D_{om}$</td>
<td>ordinary diffusion coefficient of $i^{th}$ species in the mixture</td>
</tr>
<tr>
<td>$D_{i}^{OL}$</td>
<td>thermal diffusion coefficient</td>
</tr>
<tr>
<td>$D_{i}^{P}$</td>
<td>diffusion coefficient by pressure</td>
</tr>
<tr>
<td>$d$</td>
<td>molecular diameter</td>
</tr>
<tr>
<td>$E$</td>
<td>electric potential</td>
</tr>
<tr>
<td>$e$</td>
<td>absolute value of the electron electric charge, $1.602 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>$e_i$</td>
<td>emissivity of $i^{th}$ surface</td>
</tr>
<tr>
<td>$F_{12}$</td>
<td>view factor between two surfaces</td>
</tr>
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### Fluid Motion

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathcal{J} )</td>
<td>Faraday's constant, 96.485 C/mol</td>
</tr>
<tr>
<td>( f )</td>
<td>Fanning's friction factor</td>
</tr>
<tr>
<td>( g )</td>
<td>gravity acceleration</td>
</tr>
<tr>
<td>( h )</td>
<td>heat transfer coefficient</td>
</tr>
<tr>
<td>( h )</td>
<td>Planck's constant, 6.626 ( \times ) 10(^{-34} ) m(^2) kg/s</td>
</tr>
<tr>
<td>( J_i )</td>
<td>mass convective flux of ( i )-th species</td>
</tr>
<tr>
<td>( J_p )</td>
<td>momentum convective flux</td>
</tr>
<tr>
<td>( J_E )</td>
<td>energy convective flux</td>
</tr>
<tr>
<td>( J_X )</td>
<td>convective flux of variable ( X ) through the boundary surfaces</td>
</tr>
<tr>
<td>( K )</td>
<td>kinetic energy by unit mass</td>
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<tr>
<td>( k_B )</td>
<td>Boltzmann's constant, 1.38 ( \times ) 10(^{-23} ) J/K</td>
</tr>
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<td>( k_T )</td>
<td>thermal conductivity of the media</td>
</tr>
<tr>
<td>( k_c )</td>
<td>mass transport coefficient</td>
</tr>
<tr>
<td>( L )</td>
<td>characteristic length</td>
</tr>
<tr>
<td>( M_i )</td>
<td>molecular mass of ( i )-th species</td>
</tr>
<tr>
<td>( m, n )</td>
<td>parameters for equation [20] – non-Newtonian fluid rheologic model</td>
</tr>
<tr>
<td>( N_A )</td>
<td>Avogadro's number, 6.023 ( \times ) 10(^{23} ) molecules/mol</td>
</tr>
<tr>
<td>( N_i^{(1)} )</td>
<td>overall diffusive mass flux of ( i )-th species</td>
</tr>
<tr>
<td>( N_i^{(2)} )</td>
<td>diffusive mass flux of ( i )-th species induced by the ordinary diffusion</td>
</tr>
<tr>
<td>( N_i^{(3)} )</td>
<td>diffusive mass flux of ( i )-th species induced by the thermal diffusion</td>
</tr>
<tr>
<td>( N_i^{(4)} )</td>
<td>diffusive mass flux of ( i )-th species induced by the pressure gradient</td>
</tr>
<tr>
<td>( N_i^{(5)} )</td>
<td>diffusive mass flux of ( i )-th species induced by the external forces field</td>
</tr>
<tr>
<td>( N_X )</td>
<td>diffusive flux for the ( X ) variable through the boundary surfaces</td>
</tr>
<tr>
<td>( P )</td>
<td>pressure</td>
</tr>
<tr>
<td>( q )</td>
<td>diffusive energy flux</td>
</tr>
<tr>
<td>( q^{(s)} )</td>
<td>diffusive energy flux due to the presence of matter diffusive fluxes</td>
</tr>
<tr>
<td>( q^{(rad)} )</td>
<td>radiative energy flux</td>
</tr>
<tr>
<td>( R )</td>
<td>universal gas constant, 8.313 J/mol-K</td>
</tr>
<tr>
<td>( R_i )</td>
<td>production rate of ( i )-th species by the effect of chemical reactions</td>
</tr>
<tr>
<td>( R_X )</td>
<td>source term for the generic ( X ) variable specific to the volume</td>
</tr>
<tr>
<td>( r )</td>
<td>intermolecular distance</td>
</tr>
<tr>
<td>( r_i )</td>
<td>rate of the ( i )-th chemical reaction</td>
</tr>
<tr>
<td>( s )</td>
<td>wall thickness</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( T_b )</td>
<td>normal boiling point for a liquid</td>
</tr>
<tr>
<td>( U )</td>
<td>internal energy for unit mass</td>
</tr>
<tr>
<td>( U )</td>
<td>overall heat transfer coefficient</td>
</tr>
<tr>
<td>( u )</td>
<td>fluid velocity vector</td>
</tr>
<tr>
<td>( u_i )</td>
<td>component of velocity in the ( i )-th direction</td>
</tr>
<tr>
<td>( u_s )</td>
<td>speed of sound</td>
</tr>
<tr>
<td>( u_l )</td>
<td>velocity of the turbulent vortex</td>
</tr>
<tr>
<td>( \bar{V} )</td>
<td>molar volume</td>
</tr>
<tr>
<td>( X )</td>
<td>specific value with respect to volume for the examined variable</td>
</tr>
<tr>
<td>( x, y, z )</td>
<td>Cartesian coordinates</td>
</tr>
<tr>
<td>( x_i )</td>
<td>mole fraction for ( i )-th species</td>
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<tr>
<td>( z_i )</td>
<td>electric charge for ( i )-th ion</td>
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### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>thermal diffusivity</td>
</tr>
<tr>
<td>( \alpha ^{(1)} )</td>
<td>thermal diffusion factor</td>
</tr>
<tr>
<td>( \hat{\beta}_T )</td>
<td>volumetric dilatation coefficient</td>
</tr>
<tr>
<td>( \beta_{ij} )</td>
<td>sliding friction coefficient between fluid and particle</td>
</tr>
<tr>
<td>( I_{coll} )</td>
<td>collisional dissipation integral</td>
</tr>
<tr>
<td>( \gamma_i )</td>
<td>activity coefficient for ( i )-th species in solution</td>
</tr>
<tr>
<td>( \Upsilon )</td>
<td>rate of strain tensor</td>
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<tr>
<td>( \Delta G_i^\circ )</td>
<td>free energy variation associated to the ('\text{cage-vacancy}') transfer in liquids</td>
</tr>
<tr>
<td>( \Delta H_{vap} )</td>
<td>enthalpy variation associated to the vaporization of a liquid</td>
</tr>
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<td>( \Delta T )</td>
<td>temperature difference</td>
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<tr>
<td>( \Delta U_{vap} )</td>
<td>internal energy variation associated to the vaporization of a liquid</td>
</tr>
<tr>
<td>( \delta )</td>
<td>distance between two molecular planes</td>
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<td>( \delta )</td>
<td>thickness of the velocity boundary layer</td>
</tr>
<tr>
<td>( \delta_C )</td>
<td>thickness of the concentration boundary layer</td>
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<tr>
<td>( \delta_T )</td>
<td>thickness of the temperature boundary layer</td>
</tr>
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<td>( \delta_{ij} )</td>
<td>component of the Kroneker operator</td>
</tr>
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<td>( \varepsilon_L )</td>
<td>energy transferred by a turbulent vortex</td>
</tr>
<tr>
<td>( \eta )</td>
<td>ionic mobility</td>
</tr>
<tr>
<td>( \eta )</td>
<td>apparent viscosity</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>dilatational viscosity or second viscosity</td>
</tr>
<tr>
<td>( \Lambda )</td>
<td>Lorentz's constant (value dependent by the considered metal within a limited interval)</td>
</tr>
<tr>
<td>( \Lambda_{e})</td>
<td>equivalent conductance for the electrolyte</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>free mean path of molecules</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>turbulence scale</td>
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<tr>
<td>( \lambda_+), ( \lambda_- )</td>
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<td>( \mu )</td>
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<td>( \nu )</td>
<td>vibration frequency</td>
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<td>( \nu_i )</td>
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<tr>
<td>( \xi_i )</td>
<td>packing parameter, see equation [82]</td>
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<td>( \psi )</td>
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<td>volumetric fraction of a solid in a suspension</td>
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<td>( \pi_{ij} )</td>
<td>molecular stresses tensor component</td>
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<td>mass density</td>
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<td>( \sigma_e )</td>
<td>electric conductivity</td>
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<td>( \sigma_{SB} )</td>
<td>Stefan-Boltzmann constant, 5.67 ( \times ) 10(^{-8} ) W/m(^2) K(^4)</td>
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<td>( \tau )</td>
<td>relaxation time of the system</td>
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<td>( \tau )</td>
<td>viscous stresses tensor</td>
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<tr>
<td>( \tau_{ij} )</td>
<td>viscous stresses tensor component</td>
</tr>
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<td>kinematic viscosity of the fluid</td>
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<td>( \psi_{ab} )</td>
<td>association parameter for the solvent, see equation [83]</td>
</tr>
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<td>mixing rules parameters</td>
</tr>
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<td>( \Omega_k )</td>
<td>collisional integral for the ( k )-th variable</td>
</tr>
<tr>
<td>( \omega_i )</td>
<td>mass fraction for ( i )-th species</td>
</tr>
</tbody>
</table>

### Superscripts and Subscripts

- \( ^o \) | reference value |
- \( ^t \) | transposed vector or matrix |
- \( ^\circ \) | unperturbed value |
- \( ^\prime \) | fluctuant quantity |
- \( ^\ast \) | average quantity |
equilibrium conditions

eff effective value

**Subscripts**
G gaseous phase
L liquid phase
i i\textsuperscript{th} species
W value referred to the wall

**Dimensionless numbers**

\( Bi = \frac{h_s}{k_r} \) Biot number

\( Da = \frac{M R L^2}{\rho D_{i,s} \mu} \) Damkohler number

\( Fr = \frac{u^2}{gL} \) Froude number

\( Gr = \frac{g^2 \beta L \Delta TL^1}{\mu^2} \) Grashof number

\( Nu = \frac{hL}{k_r} \) Nusselt number

\( Pe_i = \frac{uL}{D_{i,s}} = Re \cdot Sc \) mass Péclet number

\( Pe_i = \frac{uL}{\alpha} = Re \cdot Pr \) thermal Péclet number

\( Pr = \frac{\mu C_p}{k_r} \) Prandtl number

\( Re = \frac{u L}{\mu} \) Reynolds number

\( Sc = \frac{\mu}{\rho D_{i,s}} \) Schmidt number

\( Sh = \frac{k_r L}{D_{i,s}} \) Sherwood number

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