Chapter 2
Phenomenological Properties and Constitutive Equations of Transport Processes

Abstract Fluid properties, flow parameters and the basic transport process laws with background theory are reviewed.

Basic fluid properties include density, viscosity, heat conductivity, diffusivity, specific heat, and compressibility. Flow properties are temperature, pressure, velocity, flux, flow rate, energy, and momentum. Further properties of the velocity field are divergence, vorticity, and turbulence. Some properties are scalar, others are vector quantities. The constitutive equations used in the mathematical models of the transport processes are relationships between properties of the fluids and flows. A property is assigned to a certain surface or volume element which may be stationary or moving with the flow of the fluid.

The property is called "extensive" if it is proportional to the surface, volume or the quantity of the fluid, e.g., flux, flow rate, energy, and momentum. Otherwise, the property is called "intensive" such as density, viscosity, heat conductivity, diffusivity, specific heat, compressibility, pressure, temperature, velocity. Note that an extensive property may be made intensive by dividing it with a reference surface area or volume.

Only a brief summary is provided in this book, referring to the detailed discussions in the technical literature of transport phenomena e.g., in Bird et al. (1960, 2007); Deen (1998); Holman (1998); Welty et al. (1984); as well as fluid mechanics and dynamics publications.

2.1 Density

The density of a substance is its quantity, m, in a unit volume. Local density, ρ, is defined as a limit value of $\Delta m/\Delta V$

$$\rho = \lim_{\Delta V \to 0} (\Delta m/\Delta V) \tag{2.1}$$

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Typical volume scale for ΔV above which a continuum approach will work must be much greater than the molecular or particle size of the fluid. In porous media, ΔV must be greater than the "representative element volume" as it is called in hydrology (Bear 1972).

The mass density is a scalar, intensive property. The usual notation for the mass density of fluid is ρ without any subscript. Other important densities to discuss are the mechanical energy density of fluid in motion; the total energy density; momentum density of flows; and partial component densities in mixtures.

The mechanical energy of m amount of fluid particles at elevation z from some base level and in volume V and at pressure p is the sum of the potential energy, mgh, the kinetic energy, $mv^2/2$, and the compression energy, Vp. Division of the sum by V gives the density of mechanical energy, ρ_M

$$\rho_M = \rho g z + \frac{\rho v^2}{2} + p \tag{2.2}$$

It must be noted that the compression energy term in Eq. (2.2) is expressed as the work done against the normal forces on the surface of the fluid mass in unit volume. Mechanical energy terms caused by friction or angular rotation are excluded from Eq. (2.2). It is prudent to consider at this point that the mechanical energy of the fluid in motion cannot be easily separated from the other elements of the thermodynamic energy, such as internal energy, the outside mechanical work done on the system, and the thermal energy exchange with the outside environment. For example, if ρ amount of fluid in a $V = 1$ unit volume is compressed isothermally and reversibly (without any loss) from a base pressure of p_o to p, the necessary external mechanical shaft work on the system is $W_s = \rho \int_{p_o}^{p} (1/\rho) \mathrm{d}p$; and the same amount of thermal energy, $Q = W_s$ must be removed from the system to satisfy the isothermal condition. Some authors use the $W_s = \rho \int_{p_o}^{p} (1/\rho) \mathrm{d}p$ term instead of p in the mechanical energy expression (e.g., Freeze and Cherry 1979). The mechanical work and thermal energy components will be discussed in detail in Chap. 6.

The internal energy of molecules, u, is associated with the random motions of the internal particles and is expressed as the product of temperature, T, and the specific heat at constant temperature, C_v for all molecules in a unit mass in ideal gas. The density of total fluid energy, ρ_E, is the sum of those of mechanical energy, ρ_M, and the integral energy, ρu

$$\rho_E = \rho g z + \frac{\rho \boldsymbol{v}^2}{2} + p + \rho u = \rho g z + \frac{\rho \boldsymbol{v}^2}{2} + \rho h = \rho g z + \frac{\rho \boldsymbol{v}^2}{2} + p + \rho C_v T \tag{2.3}$$

The $\rho g z + \frac{\rho v^2}{2} + p + \rho u$ expression in Eq. (2.3) is the general form of the energy density. The second form, $\rho g z + \frac{\rho \boldsymbol{v}^2}{2} + \rho h$, uses the enthalpy combining pressure and internal energy into one property, $h = \frac{p}{\rho} + u$. The last, $\rho g z + \frac{\rho v^2}{2} + p + \rho C_v T$ form uses the temperature to express internal energy as $u = C_v T$.

Another density of interest is that of momentum. Fluid particles of mass m moving at velocity vector $\boldsymbol{v}$ is $m\,\boldsymbol{v}$, a vector quantity. Therefore, the momentum density, $\boldsymbol{\rho}_I$, is also a vector

$$\boldsymbol{\rho}_I = \rho \boldsymbol{v} \tag{2.4}$$

2.2 Mixture Density, Concentration, Mass Fraction and Gas Law

The discussion is reduced to simple engineering properties without duplicating them with chemical properties involving mole amounts. If volume V is shared by n species with mass components m_i, the specific gas law for each component can be expressed in two different forms, either using partial volume V_i or partial pressure p_i

$$pV_i = p_i V = m_i R_i T \tag{2.5}$$

where $p = \sum p_i$, the pressure of the mixture. The partial densities may be defined as

$$\rho_i = \frac{m_i}{V} = \frac{p_i}{R_i T} \tag{2.6}$$

where p_i and R_i are partial pressure and specific gas constant of species i, and T is mixture temperature. The density of the mixture is the sum of the partial densities

$$\rho = \frac{\sum m_i}{V} = \sum \rho_i = \frac{1}{T} \sum \frac{p_i}{R_i} \tag{2.7}$$

where p_i and R_i are partial pressure and specific gas constant of species i, and T is mixture temperature.

Volumetric concentration of species i is $c_i^v = V_i/V$ that may be expressed from Eqs. (2.5) and (2.6)

$$c_i^v = \frac{V_i}{V} = \frac{p_i}{p} = \frac{\rho_i R_i T}{p} \tag{2.8}$$

Volumetric concentration is useful for representing measurement results, for example, when taking air quality samples of known volumes from the bulk flow in a working environment. However, volumetric concentration is not suitable as a driving force diffusion.

In Eq. (2.8), ρ_i is the partial mass density of species i in a mixture. The property with which species diffusion is proportional and can be used as a driving potential is

either the partial mass density or the mass fraction, $\omega_i = m_i/m$ that may be expressed from Eqs. (2.6) and (2.7)

$$\omega_i = \frac{\rho_i}{\rho} \tag{2.9}$$

Mass fractions sum up to one in mixtures, $\sum \omega_i = 1$.

Partial mass density, ρ_i, may be called mass concentration. It is analogous to molar concentration, c_i, in which the mass of species i is often measured in [g-mole], that is, c_i [g-mole] = m_i [g]/M_i where M_i is the molecular weight of component i.

The dimensionless mass fraction, ω_i, is analogous to mole fraction, often notated as x_i, calculated as $x_i = \omega_i M/M_i$ where M is the molar mean molecular weight of the mixture, M/mole.

Partial mass density is an important parameter to express the mass quantity in a given volume. Mass (or mole) fraction is an important parameter to express relative differences in densities as the driving force of molecular diffusion in mixtures. Volumetric concentration and partial mass density, on the other hand, are both only intermittent properties of mixtures.

The mass fraction can be used to formulate the gas law for mixtures based on the properties of the component gases. The summation of the partial pressures p_i and applying Eqs. (2.8) and (2.9) gives the gas law for mixtures

$$p = \rho T \sum R_i \omega_i \tag{2.10}$$

2.3 Temperature

Temperature in monatomic, dilute, ideal gas is the measure of the translational kinetic energy of a molecule of mass M^*, that is, $T \sim M^* \hat{\boldsymbol{c}}^2$, where $\hat{\boldsymbol{c}}^2$ is the root mean square (RMS) of the free molecular speed, while the gas as a whole is at rest with zero time-averaged velocity, $\bar{\boldsymbol{v}} = 0$. Recalling the universal gas law for one molecule with the Boltzmann constant K, T is related to the kinetic energy component for any gas species (Bird et al. 1960, p. 254)

$$T = \frac{1}{3K} M^* \hat{c}^2 \tag{2.11}$$

The expression of temperature in Eq. (2.11) is in excellent qualitative agreement with the result from the rigid-sphere kinetic model for molecules in which $\pi/8$ appears instead of 1/3 (Bird et al. 1960, p. 20)

$$T = \frac{\pi}{8K} M^* \hat{c}^2 \tag{2.12}$$

Suffice to say that there are other differences between theory and experimental results due to bi-atomic molecules which involve rotational as well as vibrational energy components in addition to translational kinetic energy. Nevertheless, the main point does not change, that is, the primary connection between temperature and the kinetic energy of molecules, associated with internal energy.

2.4 Pressure

In gases, pressure is related to temperature for a given volume and mass of the fluid. Substituting Eq. (2.11) into the gas law for n number of moles in volume V gives

$$pV = nRT = \frac{nRM^* \hat{c}^2}{3K} \tag{2.13}$$

Equation (2.13) can be simplified by the substitution of $nR = NK$, where N is the number of molecules in volume V

$$p = \frac{N}{3V} M^* \hat{c}^2 \tag{2.14}$$

Pressure, like temperature, is seen to be directly related to the kinetic energy of molecules. The difference between the meaning of pressure and temperature can be seen by comparing Eqs. (2.11) and (2.14). Accordingly, the number of molecules in volume V multiplies the kinetic energy of the molecules in the expression for pressure, but it does not affect the kinetic energy in the temperature expression for the same gas. This fact highlights the reason why the internal energy density, $u = C_v T$, includes only temperature; and that pressure is listed separately among the other mechanical energy components such as potential and kinetic energy terms in Eq. (2.2).

Pressure may also be interpreted using the rigid-sphere kinetic model of monatomic gas molecules filling a cube of unit volume of 1 m^3. Pressure of the gas is the force exerted on a side wall of a unit cube which is at rest and not in a force field. Pressure is caused by the presence of molecules. Each molecule moves statistically at $\hat{\boldsymbol{c}}$ RMS velocity in any direction but averages to zero mean macroscopic velocity with time. Taking one wall normal to the x-direction, the force can be expressed using the momentum theorem. The elastic collision force of one molecule traveling in x direction and hitting the wall is $F^* = 2M^* \hat{c}_x / \Delta t$, where $\Delta t = 1/\hat{c}_x$. Assuming equilibrium and that half of all molecules N in the $V = 1$ volume travels in the positive x-direction at any time instant, the total force on the side wall is $F = (N/V) M^* \hat{c}_x^2$. The three-dimensional molecular motion with three degrees of

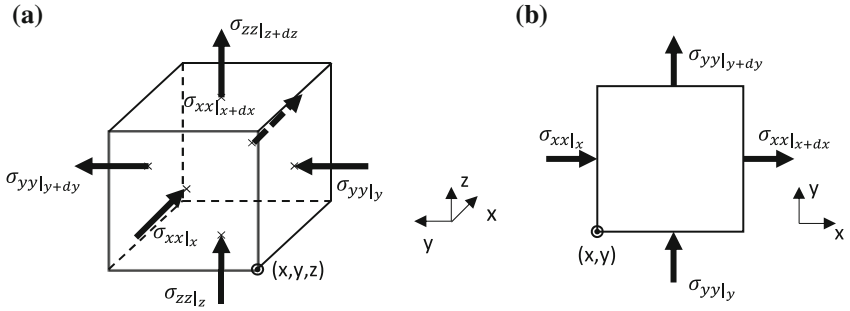


Fig. 2.1 Normal stress tensor components on a dxdydz volume element: **a** in 3-D; and **b** in 2-D

freedom statistically is $\hat{c}^2 = \hat{c}_x^2 + \hat{c}_y^2 + \hat{c}_z^2 = 3\hat{c}_x^2$, therefore, $p = F = \frac{N}{3V} M^* \hat{c}^2$ a result in perfect agreement with Eq. (2.14).

Pressure at the wall or inside the fluid space must be the same if no other force field is present following from the force balance in any control volume with one solid and one fluid wall opposite to each other. Likewise, pressure must be constant in any direction and equal to the average of normal stress components acting on a dxdydz cubic fluid volume, shown in Fig. 2.1

$$p = \frac{1}{3}\left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}\right) \tag{2.15}$$

Note that the normal stress components are assumed to be positive in Eq. (2.15) when compressing the fluid (e.g., Bird et al.) whereas it is often used in opposite sign convention with positive sign for tensile stress (e.g., Welty et al. 1984). The sign convention difference does not affect the sign of pressure.

The validity of Eq. (2.15) has been shown to hold even if the fluid is in motion and the stress tensor may include shear stress components (Bird et al. Welty et al. 1984, Deen 1998). This will be further discussed in relationship to viscous forces and the stress tensor.

2.5 Viscosity in Ideal Gases

When the fluid is in macroscopic motion with velocity differences between shear layers, molecular interactions cause shear stress. Friction stress between shear layers of solids moving at different velocities is usually independent of the velocity difference. However, in fluids, the shear stress is velocity dependent due to molecular interactions. It can be shown that viscosity, μ, in fluids is analogous to the shear modulus of elasticity in solids provided that the shear strain is replaced with the rate of shear deformation, dγ/dt of the fluid volume elements as shown in Fig. 2.2

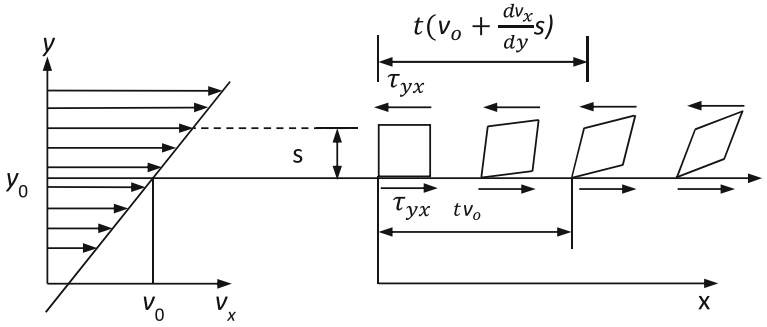


Fig. 2.2 The shear deformation in a fluid volume element assuming no vorticity

$$\tau_{yx} = -\mu \frac{\mathrm{d}\gamma}{\mathrm{d}t} = -\mu \frac{\mathrm{d}v_x}{\mathrm{d}y} \tag{2.16}$$

Equation (2.16) is intuitive recognizing that fluids have no given shape and continuous angular deformation, $\mathrm{d}\gamma/\mathrm{d}t$, with time must take place to cause deformation resistance. The kinetic theory of gases gives an insight and a more exact explanation of the molecular fluid properties involved in the expression of viscosity. Momentum transport between layers in shear flow in low density gases is pictured as exchange of impulses due to elastic collisions by crossing molecules, shown in Fig. 2.3.

The shear stress due to momentum exchange between shear layers at different velocities is

$$\tau_{yx} = m \cdot \Delta v_x \tag{2.17}$$

where m is the mass of crossing molecules over unit time with an average difference of Δv_x in macroscopic velocity. Substituting $m = M^* Z$ where Z is the number of bombardments of molecules per unit time on a unit surface; and using the values of

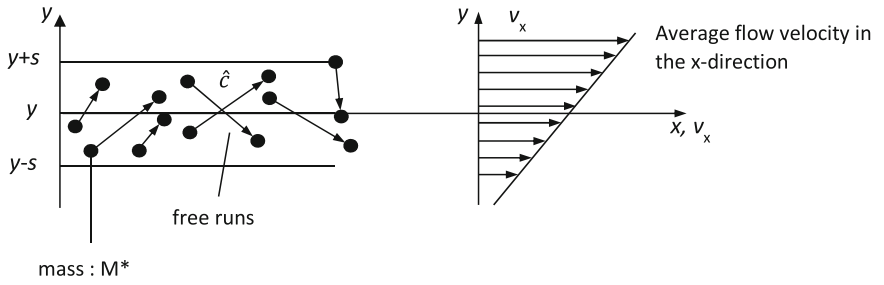


Fig. 2.3 Molecular motion in shear flow of low density gas

the velocity profile at $y_o + s$ and $y_o - s$ locations between which molecular crossing in one free run is possible, Eq. (2.17) gives

$$\tau_{yx} = M^* Z\left(v_x|_{y-s} - v_x|_{y+s}\right) \tag{2.18}$$

Considering that distance s is shorter than the mean free path of the molecules, λ, and that the macroscopic velocity profile within this small distance is approximately linear, Eq. (2.18) may be expressed with the use of the differential of v_x

$$\tau_{yx} = -2M^* Z \frac{\mathrm{d}v_x}{\mathrm{d}y} s \tag{2.19}$$

Referring to the kinetic theory of gases (Bird et al., p. 20), $Z = \frac{1}{4} N\hat{c}$; $\hat{c} = \sqrt{\frac{8KT}{\pi M^*}}$; $s = \frac{2}{3}\lambda$; and $\lambda = \frac{1}{\sqrt{2}\pi d^2 N}$ may be substituted into Eq. (2.19)

$$\tau_{yx} = -\frac{2\sqrt{M^* KT}}{3\pi^{3/2} d^2} \frac{\mathrm{d}v_x}{\mathrm{d}y} \tag{2.20}$$

Comparing Eqs. (2.16) and (2.20) gives a useful equation for viscosity for monatomic gases

$$\mu = \frac{2\sqrt{M^* KT}}{3\pi^{3/2} d^2} \tag{2.21}$$

Note that the absolute (or dynamic) viscosity for gases is increasing with the square root of the absolute temperature, $\sqrt{T}$; depends on molecular-specific properties, especially strongly on diameter, d; but does not depend on pressure.

Instead of the absolute viscosity, μ (mu) in [Pa · s], the kinematic viscosity, ν (nu) in [m^2/s], is often used in engineering

$$\nu = \frac{\mu}{\varrho} \tag{2.22}$$

2.6 Viscosity in Real Gases

The ideal gas model with billiard-ball-type molecular collisions credited to Maxwell was published in 1860. The work on fluid properties models progressed with added molecular interactions by Chapman and Enskog. The shape of the molecules with angle-dependent forces such as in water vapor was also considered together with other nonlinear effects, such as polarity and quantum behaviors;

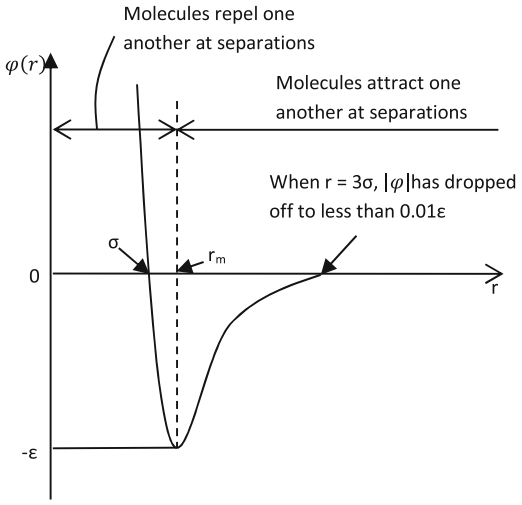


Fig. 2.4 The potential energy function for two spherical, nonpolar molecules (Bird et al. 1960)

a review may be found in Bird et al. (1960). The goal was to obtain models for interpolation between scant experimental data or for gases with no viscosity measurement available. The contemporary approach is to derive all fluid properties from Gibbson's free energy: viscosity, conductivity, specific heat, diffusivity, etc. The root of this approach is illustrated from the potential energy function, φ, known as the Lennard-Jones potential for two molecules of characteristics "collision" diameters, σ, as a function of distance, r, shown also in Fig. 2.4

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.23}$$

The potential energy has great relevance regarding the forces and thus the movement of molecules around each other. The preferred, equilibrium distance between neighboring molecules is statistically r_m, where the energy is at the characteristics value, ε, representing the minimum potential level. The viscosity model may be written with σ and ε as follows:

$$\mu = 2.6693 \times 10^{-6} \frac{\sqrt{MT}}{\sigma^2 \Omega_\mu} \tag{2.24}$$

where μ is in [Pa · s], T is in [K], σ is in Å, and Ω_μ is a nondimensional function of KT/ε (Bird et al. 1960; Welty et al. 1984) that may be considered as dimensionless temperature. The temperature dependence of viscosity according to Eq. (2.24) follows experimental data much better than using Eq. (2.21) due to Ω_μ which changes slowly with temperature.

Example 2.1 Viscosity correlation for common gases
For practical applications, Eq. (2.24) may be used as a template for viscosity interpolation with changing temperature, T

$$\mu = \mu_0 \sqrt{T/T_0} \frac{\Omega_{o\mu}}{\Omega_\mu} \tag{2.25}$$

where μ_0 and $\Omega_{o\mu}$ are reference values at T_o temperature, and $\frac{\Omega_{o\mu}}{\Omega_\mu} = f(T/T_0)$ is a function that may be approximated by a polynomial expression for common gases

$$\frac{\Omega_{o\mu}}{\Omega_\mu} = -0.106\left(\frac{T}{T_0}\right)^2 + 0.4701\frac{T}{T_0} + 0.6338 \tag{2.26}$$

Combining Eqs. (2.25) and (2.26) gives a simple polynomial interpolation for viscosity with temperature variation for common gases at normal atmosphere of p = 101.33 kPa, and T = 293.3 K

$$\mu = \mu_0 \left[-0.106\left(\frac{T}{T_0}\right)^{2.5} + 0.4701\left(\frac{T}{T_0}\right)^{1.5} + 0.6338\left(\frac{T}{T_0}\right)^{0.5} \right] \tag{2.27}$$

The interpolated viscosity values at T = 250 K, T = 300 K, T = 400 K, and T = 600 K temperatures from Eq. (2.27) are given in Table 2.1 for air, N_2, O_2, CO_2, CO, and H_2, using textbook μ_0 values taken at T_o = 300 K temperature.

The interpolated values for air is within ±0.3 % for the given temperature range. The other species are also matching the textbook reference values within a few percent error range.

Table 2.1 Interpolated viscosity values in [Pa · s]

Species	$\mu_0 \times 10^5$	$\mu_{250} \times 10^5$	$\mu_{300} \times 10^5$	$\mu_{400} \times 10^5$	$\mu_{600} \times 10^5$
Air	1.8464	1.6045	1.8425	2.2859	3.0029
CO	1.7857	1.5518	1.7820	2.2107	2.9042
CO_2	1.4948	1.2990	1.4917	1.8506	2.4311
H_2	8.9630	7.7888	8.9442	11.0960	14.5769
N_2	1.7855	1.5516	1.7818	2.2105	2.9038
O_2	2.0633	1.7930	2.0590	2.5544	3.3556

2.7 Viscosity in Fluids

A liquid may be pictured as a crowd of molecules that may flow. Brownian motion in liquid shows continuous movement of molecules with runs exceeding the average distance between them even if the time-averaged velocity is zero and the mass of the liquid is at rest. This behavior may be explained by assuming a flow of individual molecules against some resistance, leading to the hydrodynamic models for viscosity. Another model approach views the liquid as a lattice arrangement of molecules with vacant holes that may migrate or allow the jump of neighboring molecules. The potential energy variation of a molecule is shown in Fig. 2.5 as a function of location. Movements of holes or molecules take place spontaneously as manifested by Brownian motion. The energy level is lower than that of the critical value for phase change by evaporation. The energy barrier must be overcome for change of location, resulting in a resistance that is proportional to the shear stress, related to the velocity gradient across the shear layers.

The frequency of jumps, f, of the molecules, affecting viscosity is related to the activation of Gibbson's free energy, $\Delta G0$, with the help of Boltzmann and Planck's constants, K and h (Bird et al. 1960)

$$f = \frac{KT}{h} e^{-\frac{\Delta \tilde{G}_0}{RT}} \tag{2.28}$$

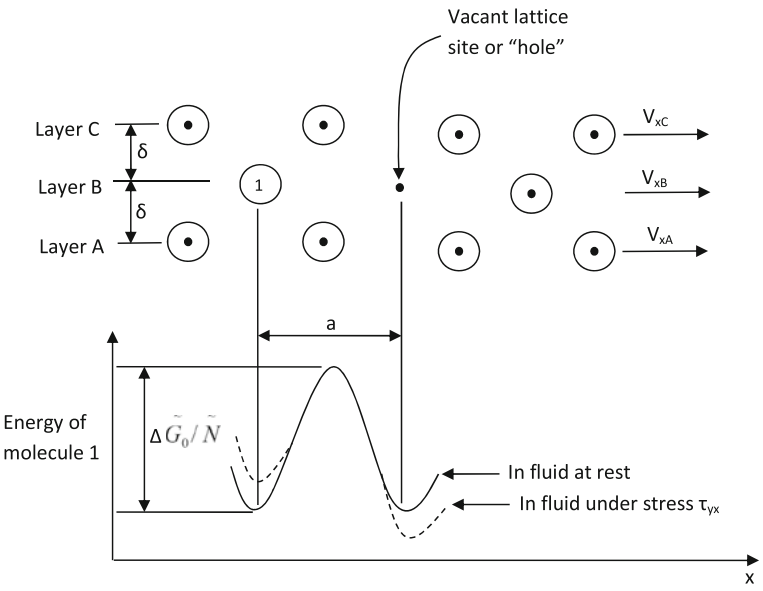


Fig. 2.5 Illustration of an escape process in flow of a liquid. Molecule 1 must pass through a "bottleneck" to reach the vacant site (after Bird et al. 1960 p. 27)

The relationship between shear stress and velocity gradient according to Newton's viscosity law involves two components. First, as shown in Fig. 2.5, the potential energy function is modified by the shear stress, τ_{yx}, and different frequencies are expected at different layers. Second, the frequency difference of the jumps of the molecules between neighboring layers is directly related to the velocity gradient. Therefore, it is possible to form a relationship between τ_{yz} and $\mathrm{d}v_x/\mathrm{d}y$ to obtain a viscosity model for liquids. A simplified model according to Bird et al. is

$$\mu = \left(\frac{\delta}{a}\right)^2 \frac{\tilde{N}h}{\tilde{V}} e^{-\frac{\Delta\tilde{G}_0}{RT}} \tag{2.29}$$

where $\tilde{N}$, $\tilde{V}$, $\Delta\tilde{G}_0$, are Avogadro's number, the volume of a mole of liquid, and the free energies of activation, respectively. Correlating the activation energy with the boiling temperature of the liquid, T_b; and further using the approximation of $\delta/a = 1$, Eq. (2.29) may be simplified

$$\mu = \frac{\tilde{N}h}{\tilde{V}} e^{3.8T_b/T} \tag{2.30}$$

As shown, the viscosity of liquids decreases with increasing temperature according to an exponential function, an opposite trend from that obtained for gases.

2.8 Typical Viscosity Variations

Equation (2.16) is often called Newton's law of viscosity. If the equation holds with a constant viscosity for a variety of shear strain rate, $\mathrm{d}v_x/\mathrm{d}y$, the fluid is called Newtonian, otherwise, the fluid is non-Newtonian. Figure 2.6 shows four typical viscosity models regarding the shear stress, $\tau_{yx} = -\mu\frac{\mathrm{d}v_x}{\mathrm{d}y}$ for various fluids such as

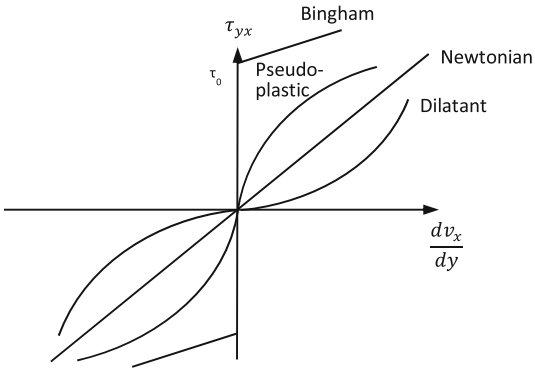


Fig. 2.6 Newtonian, dilatant, pseudo-plastic, and Bingham viscosity models

Newtonian (water, air), dilatant (corn starch, "crazy-potty,"), pseudo-plastic (concrete and most slurries), and Bingham (a simplified linearization of pseudo-plastic behavior).

2.9 Viscosity in Gas Mixtures

Viscosity in low-density gases may be calculated as the weighted average of the component viscosities. Regarding the weight factors, common sense dictates that mass fractions, ω_i, as well as molecular weights, M_i, must be involved in the weighted average calculation. Along this concept, the Chapman–Enskog theory was extended by Curtis and Hirschfelder in 1949 for the prediction of viscosity in mixtures. A simpler, empirical-based formulation is given by Wilkie, known to reproduce measured values within 2 % deviation for low density gases (Bird et al. 1960)

$$\mu_{\text{mix}} = \sum_{i=1}^{n} \frac{\omega_i \mu_i}{\sum_{j=1}^{n} \omega_j \phi_{ij}} \tag{2.31}$$

where

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \tag{2.32}$$

2.10 Viscous Stresses in Three Dimensions

Newton's law for viscosity is introduced in unidirectional flow in Eq. (2.16) in which $\boldsymbol{v} = v_x(y)\boldsymbol{e}_x$. Generalization is needed for the constitutive equations in 3-D, using Stokes' viscosity equations for Newtonian fluids (Bird et al. p. 107). Velocity changes in the 3-D space cause shear as well as normal stresses.

The shear stress components of the stress tensor are symmetric to the main diagonal and this necessitates a symmetrical expression with the velocity differentials

$$\left.\begin{aligned} \tau_{xy} = \tau_{yx} &= -\mu\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) \\ \tau_{yz} = \tau_{zy} &= -\mu\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \\ \tau_{zx} = \tau_{xz} &= -\mu\left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z}\right) \end{aligned}\right\} \tag{2.33}$$

While shear stress has been explained, normal stress due to viscosity and velocity differentials invites inquiry. It is caused by the rate of linear deformation,

analogous to the rate of angular deformation in the shear stress expression. Therefore, viscous stress due to the rate of linear deformation, e.g., dv_x/dx in x direction causes a viscous normal stress that is analogous to Hooke's law in solids. In 3-D, the viscous stresses in normal direction are

$$\left.\begin{aligned}\tau_{xx} &= -2\mu\frac{\partial v_x}{\partial x} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla\cdot\boldsymbol{v})\\ \tau_{yy} &= -2\mu\frac{\partial v_y}{\partial y} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla\cdot\boldsymbol{v})\\ \tau_{zz} &= -2\mu\frac{\partial v_z}{\partial z} + \left(\frac{2}{3}\mu - \kappa\right)(\nabla\cdot\boldsymbol{v})\end{aligned}\right\} \tag{2.34}$$

Note that τ is used instead of the customary σ in Eqs. (2.34) for normal stress components. It is a concession, used frequently in the literature in order to preserve σ for the diagonal elements of the full stress tensor in which pressure p is also present. A "second" viscosity term, κ, also called "bulk viscosity" in Eq. (2.34) may be needed for dilute polyatomic gases, but ignored in dense gases and liquids. The $\nabla\cdot\boldsymbol{v}$ expression, called the divergence of velocity, implies that the continuity of the flow is involved in the equation.

In steady-state flows, $\nabla\cdot\boldsymbol{v} = div(\boldsymbol{v}) = -\frac{1}{\varrho}\nabla\varrho\cdot\boldsymbol{v}$, which expresses the expansion of fluid due to tensile stress and density change. In the case of incompressible fluid, this term is zero. The full stress tensor combines Eqs. (2.33) and (2.34) with the added thermodynamic pressure term, p

$$\begin{bmatrix}\sigma_{xx} & \tau_{xy} & \tau_{xz}\\ \tau_{yx} & \sigma_{yy} & \tau_{yz}\\ \tau_{zx} & \tau_{zy} & \sigma_{zz}\end{bmatrix} = \begin{bmatrix}\tau_{xx}+p & \tau_{xy} & \tau_{xz}\\ \tau_{yx} & \tau_{yy}+p & \tau_{yz}\\ \tau_{zx} & \tau_{zy} & \tau_{zz}+p\end{bmatrix} = p\boldsymbol{I} + \boldsymbol{\tau} \tag{2.35}$$

The stress tensor elements on the left-hand side of Eq. (2.35) express the forces on the sides of a unit cube caused by the fluid at a lower distances to the fluid at greater distances along coordinate directions, the convention used, e.g., by Bird et al. The validity of Eq. (2.35) is evident from Eq. (2.15) if no viscous forces are present. The notation on the right side of Eq. (2.35) uses the 3×3 unit matrix $\boldsymbol{I}$ and the 3×3 friction tensor $\left[\tau_{i,j}\right] = \boldsymbol{\tau}$, and it will be useful for further discussions in Chaps. 6 and 7. The directions of the viscous stress components are illustrated in Fig. 2.7.

It is interesting to note that for Newtonian fluids with constant density, that is, $\nabla\cdot\boldsymbol{v} = 0$, the stress tensor τ according to Eqs. (2.33) and (2.34) can be expressed as a matrix-vector (also called tensor-vector) equation

$$\boldsymbol{\tau} = -\mu\left[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^{\mathrm{T}}\right] \tag{2.36}$$

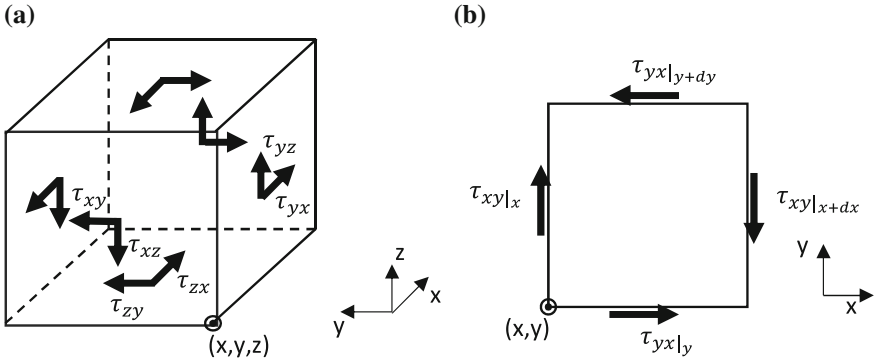


Fig. 2.7 Shear stress tensor components on a $dx \cdot dy \cdot dz$ volume element: **a** in 3-D; and **b** in 2-D

where $\nabla \boldsymbol{v}$ is the vector gradient of the velocity vector (of tensor dimension) and $(\nabla \boldsymbol{v})^{\mathrm{T}}$ is its transposed form. In Cartesian coordinates, $\nabla \boldsymbol{v}$ is the Jacobian matrix of the velocity vector, $(\nabla v)_{\xi\eta} = \frac{\partial v_\xi}{\partial \eta}$, where $\xi, \eta \in (x, y, z)$.

2.11 Viscosity and Shear Stress in Turbulent Flow

In shear turbulent flow, momentum transport takes place between the neighboring layers by exchanging "lumps" or "eddies" of the fluid due to random velocity disturbances. The instantaneous velocity profile, shown in Fig. 2.8 in 2-D is expressed as the sum of the time-averaged profile, $\bar{v}_x$, plus the time-dependent turbulent fluctuation part, v_x'

$$v_x(y,t) = \bar{v}_x(y) + v_x'(y,t) \tag{2.37}$$

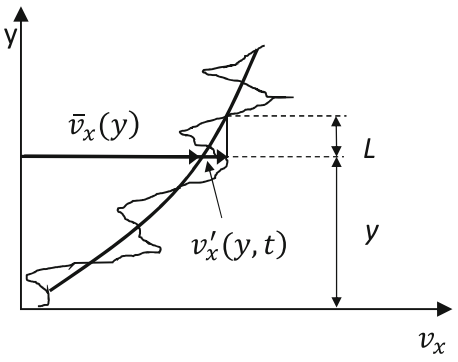


Fig. 2.8 Velocity variation with location at a time instant in turbulent flow

The time-averaged turbulent shear stress components, usually referred to as Reynold stresses, are expressed by random velocity fluctuations in the time-averaged turbulent stress tensor (Bird et al. 1960)

$$\bar{\boldsymbol{\tau}}^{(t)} = \varrho \begin{bmatrix} \overline{v_x' v_x'} & \overline{v_x' v_y'} & \overline{v_x' v_z'} \\ \overline{v_y' v_x'} & \overline{v_y' v_y'} & \overline{v_y' v_z'} \\ \overline{v_z' v_x'} & \overline{v_z' v_y'} & \overline{v_z' v_z'} \end{bmatrix} \tag{2.38}$$

The velocity fluctuations are correlated by fluid continuity, therefore, the time-averaged elements in the stress tensor are not zero, even if the average of each fluctuation component is zero, $\bar{v}_{\xi}^{'} = 0$, where $\xi \in (x, y, z)$. A rough analogy may be seen between the molecular mean free path jumps and the turbulent transport of eddies. A characteristic length, L, is introduced in the mixing length theory of Prandtl in 1925, analogous to the mean free path jumps, shown in Fig. 2.8. Using this analogy, $v_x^{'}$ can be expressed by the mean velocity derivative

$$v_x^{'} = \pm L \frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \tag{2.39}$$

Prandtl assumed that $v_x^{'} \sim -v_y^{'}$ from fluid continuity and expressed the turbulent shear stress as

$$\bar{\tau}_{yx}^{(t)} = \varrho \overline{v_x' v_y'} = -\varrho L^2 \left| \frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \right| \frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \tag{2.40}$$

Comparing Eq. (2.40) with Newton's law of viscosity in Eq. (2.16) leads to the introduction of the turbulent, or eddy diffusivity of momentum, ε_T, analogous to the kinematic viscosity in laminar flow

$$\varepsilon_T = L^2 \left| \frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \right| \tag{2.41}$$

Consequently, the turbulent shear stress is expressed similarly to laminar shear stress, following the form introduced by Boussinesq in 1877:

$$\bar{\tau}_{yx}^{(t)} = -\varrho \varepsilon_T \frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \tag{2.42}$$

The mixing length, L, is a flow and not a fluid property. Prandtl assumed that in channel flow, L is proportional to the distance from the wall, $L = Ky$. A constant value of $K = 0.4$ was found to give good agreement with measurements in pipe flow.

An improved Reynold stress model is developed by von Kármán from similarity considerations that may be presented in the form of ε_T in Eq. (2.42)

$$\varepsilon_T = K_1^2 \left| \frac{(\mathrm{d}\bar{v}_x/\mathrm{d}y)^3}{\left(\mathrm{d}^2\bar{v}_x/\mathrm{d}y^2\right)^2} \right| \tag{2.43}$$

where K_1 is a constant, to be determined for best result by experiment for a given geometry, known to be between 0.36 and 0.4 from literature.

Deissler developed an improved prediction over the models of Prandtl's and von Kármán's for flows in the neighborhood of solid surfaces. His result in the form of the turbulent momentum diffusivity, ε_T is

$$\varepsilon_T = n^2\bar{v}_x y(1 - \exp\{-n^2\bar{v}_x y/\nu\} \tag{2.44}$$

where $n = 0.124$ is an empirical constant determined by Deissler experimentally for flows in tubes in 1955 (Bird et al. 1960, p. 161).

Note that the turbulent momentum diffusivity, ε_T, in Eq. (2.44) is a property of the flow field and is applicable to any gas or liquid irrespective of the molecular viscosity of the particular fluid in turbulent motion that is characterized by the Reynolds number. The reason for listing ε_T in this chapter is that ε_T virtually replaces the molecular fluid property, ν, in turbulent flow and that it is necessary to include it in the constitutive equation for momentum transport

$$\bar{\tau}_{yx} = -\varrho(\nu + \varepsilon_T)\frac{\mathrm{d}\bar{v}_x}{\mathrm{d}y} \tag{2.45}$$

2.12 Molecular Thermal Conductivity in Gases

The kinetic theory can be used once again to introduce the explanatory model for thermal conductivities in low density, monatomic gases. Unlike in the viscosity model, the gas is assumed to be stationary with zero mean, macroscopic velocity, $\bar{v}_x(t) = 0$. However, the individual molecules are at random motion with the mean molecular speed of $\hat{c}$. The energy transport, q_y, is the averaged exchange of kinetic energy between the layers of gas carried out by Z crossings of molecules, depicted in Fig. 2.9

$$q_y = \frac{1}{2}Z(M^*\hat{c}^2\big|_{y-s} - M^*\hat{c}^2\big|_{y+s}) \tag{2.46}$$

Substituting Eq. (2.11) and expressing the temperature difference between the gas layers by the first derivative of the temperature profile gives

$$q_y = \frac{3}{2}KZ\left(T\big|_{y-s} - T\big|_{y+s}\right) = -3KZ\frac{\mathrm{d}T}{\mathrm{d}y}s \tag{2.47}$$

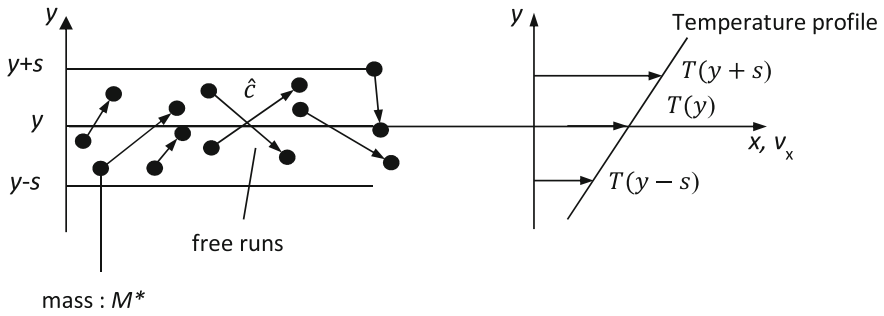


Fig. 2.9 Kinetic energy transport by molecular motion in low density gas

Further substitution of $Z = \frac{1}{4}N\hat{c}$; and $s = \frac{2}{3}\lambda$ from the kinetic theory of gases (Bird et al. p. 20) into Eq. (2.47) yields

$$q_y = -\frac{1}{2}NK\hat{c}\lambda\frac{\mathrm{d}T}{\mathrm{d}y} = -k\frac{\mathrm{d}T}{\mathrm{d}y} \tag{2.48}$$

The constant in front of the first derivative of the temperature profile is recognized as the thermal conductivity, k; and with this notation Eq. (2.48) corresponds to Fourier's law of heat conduction. Further substitution of $\lambda = \frac{1}{\sqrt{2}\pi d^2 N}$ and $\hat{c} = \sqrt{\frac{8KT}{\pi M^*}}$ from the literature (Bird et al. 1960, p. 20) gives an expression for thermal conductivity in ideal, dilute, monatomic gases

$$k = \frac{1}{d^2}\sqrt{\frac{K^3 T}{\pi^3 M^*}} \tag{2.49}$$

A more accurate formula for k is given by the Chapman–Enskog theory, similar to that for viscosity in Eq. (2.24)

$$k = 0.0829\frac{\sqrt{T/M}}{\sigma^2\Omega_k} \tag{2.50}$$

where k is in [W/(mK)]; M is molecular weight; T is in [K]; σ is in Å; and $\Omega_k = \Omega_\mu$ is Lennard-Jones collision integral, a non-dimensional function of KT/ε (Bird et al. 1960; Welty et al. 1984) that may be considered as dimensionless temperature. The temperature dependence of conductivity for gases according to Eq. (2.50) follows experimental data better than that from Eq. (2.49).

The thermal conductivity can also be expressed by the heat capacity of the crossing molecules, $\hat{C}_V$ from the change of the internal energy between gas layers of different temperatures (Bird et al. 2007, p. 275)

$$k = \frac{1}{2} NK\hat{c}\lambda = \frac{1}{3}\rho \hat{C}_V \hat{c}\lambda \tag{2.51}$$

where $\hat{C}_V$ is the heat capacity of one molecule at constant volume, expressed with the gas constant

$$\hat{C}_V = \left(\frac{\partial \widetilde{U}}{\partial T}\right)_V = \widetilde{N}\frac{\mathrm{d}\left(\frac{1}{2}M^*\hat{C}^2\right)}{\mathrm{d}T} = \widetilde{N}\frac{\mathrm{d}\left(\frac{3}{2}KT\right)}{\mathrm{d}T} = \frac{3}{2}\widetilde{N}K = \frac{3}{2}R \tag{2.52}$$

Thermal conductivity, specific heat taken at constant pressure, C_p (in [J/kg-K] unit), and viscosity can be combined into a non-dimensional parameter called the Prandtl number, Pr. It is a material constant that shows small variation over a wide variety of gas species

$$Pr = \frac{C_p \mu}{k} \tag{2.53}$$

For ideal gas, $C_p = C_v + R$ (discussed in detail in Sect. 2.21), whereas for liquids and solids with low compressibility, $C_p \approx C_v$ (Bird et al. 1960). A more common form of the Prandtl number is expressed with the molecular thermal diffusivity, a

$$Pr = \frac{v}{a} \tag{2.54}$$

where

$$a = \frac{k}{C_p \varrho} \tag{2.55}$$

The ratio of v/a in Eq. (2.54) suggests that the Prandtl number may be considered a similarity parameter between momentum and heat transport. For monatomic ideal gas, the kinetic theory predicts $Pr = 2/3$ (Bird et al. 2007, p. 861) that is within the range of 0.66 through 0.94, that is, the Prandtl number found for common gases at atmospheric pressure. The thermal conductivity may be predicted from the viscosity, the specific heat at constant pressure, and the Prandtl number

$$k = \frac{C_p \mu}{Pr} \tag{2.56}$$

Example 2.2 Thermal conductivity correlation for common gases
For practical applications, Eq. (2.50) may be used for conductivity interpolation with changing temperature, T

$$k = k_0\sqrt{T/T_0}\frac{\Omega_{ok}}{\Omega_k} \tag{2.57}$$

where k_0 and Ω_{ok} are reference values at T_0 temperature, and $\frac{\Omega_{ok}}{\Omega_k} = f(T/T_0)$ is a function that may be approximated by a polynomial expression for common gases

$$\frac{\Omega_{ok}}{\Omega_k} = -0.1259\left(\frac{T}{T_0}\right)^2 + 0.6303\frac{T}{T_0} + 0.4942 \tag{2.58}$$

The constants in Eq. (2.58) are slightly different from those in Eq. (2.26) obtained for $\Omega_{o\mu}/\Omega_\mu$. Combining Eqs. (2.50) and (2.58) gives a simple polynomial interpolation for thermal conductivity with temperature variation for common gases at normal atmosphere of p = 101.33 kPa, and T = 293.3 K

$$k = k_0\left[-0.1259\left(\frac{T}{T_0}\right)^{2.5} + 0.6303\left(\frac{T}{T_0}\right)^{1.5} + 0.4942\left(\frac{T}{T_0}\right)^{0.5}\right] \tag{2.59}$$

The interpolated thermal conductivity values at T = 250 K, T = 300 K, T = 400 K, and T = 600 K temperatures from Eq. (2.59) are given in Table 2.2 for air, N_2, O_2, CO_2, CO, and H_2, using textbook k_0 values taken at T_0 = 300 K temperature.

The interpolated values for all species except for CO_2 match the textbook reference values within a few percent error range. The error for CO_2 is higher, changing from +9 % at T = 250 K to −31 % at T = 600 K monotonously.

Table 2.2 Interpolated thermal conductivity values in [W/(mK)]

Species	$k_0 \times 10^2$	$k_{250} \times 10^2$	$k_{300} \times 10^2$	$k_{400} \times 10^2$	$k_{600} \times 10^2$
Air	2.6240	2.2325	2.6203	3.3656	4.6431
CO	2.5242	2.2269	2.5206	3.3651	4.6430
CO_2	1.6572	1.4100	1.6549	2.1256	2.9324
H_2	18.2000	15.4848	18.175	23.3436	32.2042
N_2	2.6052	2.2165	2.6016	3.3415	4.6098
O_2	2.6760	2.2768	2.6723	3.4323	4.7351

2.13 Thermal Conductivity in Gas Mixtures

The thermal conductivity in low density gas mixtures may be calculated similarly to that of viscosity given by Eq. (2.31):

$$k_{\text{mix}} = \sum_{i=1}^{n} \frac{\omega_i k_i}{\sum_{j=1}^{n} \omega_j \phi_{ij}} \tag{2.60}$$

where ϕ_{ij} is identical to that in Eq. (2.32) in which the viscosity, instead of conductivity ratios appear. The Prandtl number can be used to provide linkage between viscosity and thermal conductivity using Eq. (2.54): $\mu_i/\mu_j = \left(k_i Pr_i c_{Pj}\right)/\left(k_j Pr_j c_{Pi}\right)$. Considering that the specific heat and the Prandtl number both changes very moderately with temperature, the approximation of $\mu_i/\mu_j = k_i/k_j$ may be used in ϕ_{ij} in Eq. (2.60)

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{k_i}{k_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \tag{2.61}$$

2.14 Thermal Conductivity in Liquids and Solids

Heat conduction is far more complex in liquids than in gases and there are no simple molecular models for useful estimates from theoretical basis. The simple theory of Bridgman starts with rigid-sphere heat flux expression of Eq. (2.52). The derivation further assumes that the heat capacity of the molecules equals $\hat{C}_V = 3K/M^*$ from empirical observations for solids (Bird et al. 2007, p. 279); the speed of the energy exchange is by the sonic velocity, v_s; and that travel distance of energy exchange equals the average lattice spacing, $(\tilde{N}/\tilde{V})^{1/3}$

$$k = \frac{1}{3}\rho \hat{C}_V \hat{c} \lambda = 3(\tilde{N}/\tilde{V})^{2/3} K v_s \tag{2.62}$$

It is interesting that Eq. (2.62) needs only a small adjustment, that is, a change from 3 to 2.8 in the constant multiplier to match experimental data for even polyatomic liquids. Substituting the formula for the sound velocity $v_s = \sqrt{\frac{C_P}{C_V}\left(\frac{\partial P}{\partial \varrho}\right)_T}$ in liquids and adjusting the constant to 2.8 yields

$$k = 2.8(\tilde{N}/\tilde{V})^{2/3} K \sqrt{\frac{C_P}{C_V}\left(\frac{\partial P}{\partial \varrho}\right)_T} \tag{2.63}$$

The C_P/C_V fraction in Eq. (2.63) is the ratio of the specific heat at constant pressure, C_P, to that of at constant volume, C_v, a number closed to unity in fluids. This ratio is further reviewed in Sect. 2.21. The sound velocity may be obtained by direct measurement or calculated from compressibility measurement of the liquid.

Thermal conductivity of solids depends on many more factors than that for gases and liquids even in homogeneous and heterogeneous materials, such as crystalline structures. Consider the example of carbon in the form of four structures: amorphous, graphite, diamond, and the two-dimensional graphene with very different thermal conductivities. The monocrystalline diamond has the highest thermal conductivity of all known solid material, 3320 W/(mK) at room temperature whereas the conductivity of graphite is only around 130 W/(mK). Considering that diamond is an excellent electrical insulator, unlike graphite that is a good conductor, it is obvious that thermal and electrical conductivities of nonmetals are not related to the movement of electrons. For pure metals, however, an approximate relation is expressed by the Wiedemann, Franz and Lorenz equation (Bird et al. 1960, p. 262)

$$\frac{k}{k_e T} = L \tag{2.64}$$

where k_e is the electrical conductivity, T is absolute temperature and L is the Lorenz number that varies between 22×10^{-9} and 29×10^{-9} in $[V^2/K^2]$ units at 273 K temperature from metal to metal. Equation (2.64) implies that the free electrons carry the thermal energy in pure metals which become superconductors for electricity near absolute zero temperature. However, even pure metals do not show superconductor behavior for heat at low temperature and L strongly varies with temperature in this range.

2.15 Thermal Conductivity and Diffusivity in Turbulent Flow

In shear turbulent flow, energy transport takes place between the neighboring layers by exchanging "eddies" of the fluid due to random velocity disturbances. Heat flux driven by the temperature variation between layers is vastly enhanced by the random molecular motion similarly to the enhancement of the momentum flux driven by velocity variation in turbulent flow. Fourier's law for heat conduction is thus expressed analogously to Newton's law for momentum transport according to Eq. (2.45)

$$\bar{q}_y = -(k + k_T)\frac{\mathrm{d}\bar{T}}{\mathrm{d}y} \tag{2.65}$$

Substituting the molecular conductivity k using Eq. (2.55); and the turbulent conductivity, k_T, applying Eq. (2.56) with the turbulent Prandtl number, Pr_T, and turbulent kinematic viscosity, v_T, Eq. (2.65) yields

$$\bar{q}_y = -\varrho C_p \left(a + \frac{v_T}{Pr_T} \right) \frac{\mathrm{d}\bar{T}}{\mathrm{d}y} \tag{2.66}$$

It must be noted that the turbulent Prandtl number, defined using constant pressure properties in Eq. (2.66), is expected to be close to unit value. The assumption of $Pr_T = 1$ has been widely used in the derivation of transport models based on the similarity between heat transport and momentum transport, and proven by experimental verifications (Schlichting 1979, pp. 706–712). Therefore, the turbulent thermal diffusivity may be estimated equal to the value of the turbulent kinematic viscosity.

2.16 Mass Diffusivity in Gases

Diffusion may be caused by various potential differences such as pressure, temperature, or mass concentration gradients. Knudsen diffusion (Bird et al. 1960) may involve only one, low-density gas component diffusing from one tank to another through a capillary tube kept at different temperatures and pressures at either end. Diffusion in most applications is the transport of molecules in the space typically occupied by at least two different types of species. The simplest process to consider is self-diffusion that may happen in a large volume of gas having two types of molecules A and A^*, distinguishable only by name but possessing the same properties such as mass, shape, and size. Mass transport by diffusion under mass fraction difference can be pictured by the random motion and statistical exchange of molecules A and A^*, depicted in Fig. 2.10, in an analogous way to the transport of momentum and heat shown in Figs. 2.3 and 2.9, respectively.

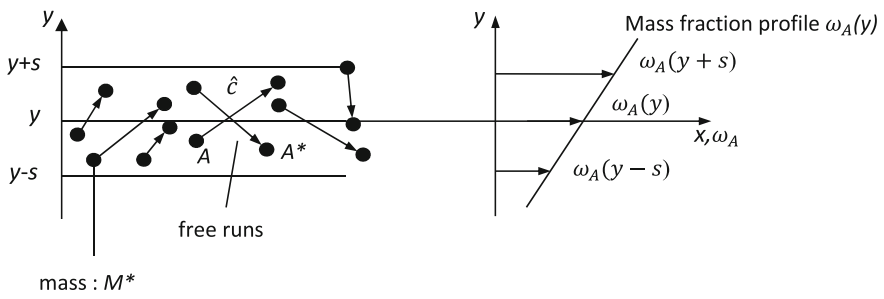


Fig. 2.10 Molecular transport of species A by molecular motion in low density gas

The molecular mass flux, j_{Ay}, of species A across a unit surface of a plane at y is the net difference between the mass of A moving in the positive and the negative directions (Bird et al. 2007, p. 525)

$$j_{Ay} = \left(\frac{1}{4}\varrho\omega_A\hat{c}\right)\Big|_{y-s} - \left(\frac{1}{4}\varrho\omega_A\hat{c}\right)\Big|_{y+s} \tag{2.67}$$

The molecular mass flux in Eq. (2.67) does not take into consideration the advective transport caused by the macroscopic motion of the gas mixture. Molecular diffusion is pictured as a superimposed transport mechanism on the advective component that will be the subject of a different transport phenomenon. Assuming that ρ and $\hat{c}$ are constants and the change in ω_A can be approximated with the first derivative, Eq. (2.67) can be simplified

$$j_{Ay} = -\frac{1}{2}\varrho\hat{c}s\frac{\mathrm{d}\omega_A}{\mathrm{d}y} \tag{2.68}$$

Using properties for $\hat{c}$ and s from the kinetic theory of gases (Bird et al. p. 20) as $\hat{c} = \sqrt{\frac{8KT}{\pi M^*}}$; $s = \frac{2}{3}\lambda$; $\lambda = \frac{1}{\sqrt{2}\pi d^2 N}$; and $\varrho = M^* N$, Eq. (2.69) yields

$$j_{Ay} = -\frac{1}{3}\varrho\hat{c}\lambda\frac{\mathrm{d}\omega_A}{\mathrm{d}y} = -\frac{2}{3d^2}\sqrt{\frac{M^*KT}{\pi^3}}\frac{\mathrm{d}\omega_A}{\mathrm{d}y} \tag{2.69}$$

Fick postulated molecular diffusion by analogy to heat conduction in 1855. The analogous diffusion equation to Fourier's first law for conduction is called Fick's first law and written as follows:

$$j_{Ay} = -\rho D_{AB}\frac{\mathrm{d}\omega_A}{\mathrm{d}y} \tag{2.70}$$

Comparison of Eqs. (2.69) and (2.70) gives the expression for the coefficient of self-diffusion

$$D_{AA^*} = \frac{2}{3\mathrm{d}^2\varrho}\sqrt{\frac{M^*KT}{\pi^3}} \tag{2.71}$$

The problem with the analogy between conduction and diffusion is that at least two different species, often very different in molecular masses and diameters, must take place in diffusion. For example, for two ideal gases A and B, binary diffusion coefficient according to the Chapman and Enskog formula is

$$D_{AB} = \frac{0.018583\sqrt{T^3\left(\frac{1}{M_A} + \frac{1}{M_B}\right)}}{p\sigma_{AB}^2\Omega_{D,AB}} \tag{2.72}$$

where D_{AB} is in [m^2/s]; T is temperature in [K]; M_A and M_B are molecular weights of A and B; p is pressure in [Pa]; σ_{AB} is the collision diameter in Å, taken as $\sigma_{AB} = \sigma_A + \sigma_B$; and $\Omega_{D,AB}$ is the collision integral for diffusion for the A, B pairs. It is of particular and practical interest that $\Omega_{D,AB}$ is only slightly dependent on the dimensionless temperature, KT/ε_{AB}, where $\varepsilon_{AB} = (\varepsilon_A\ \varepsilon_B)^{1/2}$ (Bird et al. 1960, Welty et al. 1984). The same has been shown for the analogous collision integrals for viscosity and thermal conductivity. Therefore, Eq. (2.72) can once be conveniently used for interpolating the diffusion coefficient from a reference value of $D_{0,AB}$ given at p_0 and T_0. Using an empirical correlation function for $\frac{\Omega_{0,AB}}{\Omega_{AB}} = f_\Omega(T/T_0)$ similar to those for $\Omega_{o\mu}/\Omega_\mu$ and $\Omega_{ok}/'\Omega_k$, Eq. (2.72) yields

$$D_{AB} = D_{0,AB}\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{3/2}\frac{\Omega_{0,AB}}{\Omega_{AB}} \tag{2.73}$$

The $f_\Omega(T/T_0)$ function may be determined from the tabulated values of the collision integral (Bird et al. 1960, p. 746).

Example 2.3 Binary diffusion coefficient correlation for common gases in air

For practical applications, approximation of $\Omega_{o,AB}/\Omega_{AB}$ may be used by a second-order polynomial for a temperature range from 250 to 600 K as follows, adjusted for the binary pairs of common gas components of N_2, O_2, CO_2, CO, and H_2 (as A) air (as B):

$$\frac{\Omega_{0,AB}}{\Omega_{AB}} = -0.1038\left(\frac{T}{T_0}\right)^2 + 0.5323\frac{T}{T_0} + 0.5685 \tag{2.74}$$

The constants in Eq. (2.74) are slightly different from those in Eqs. (2.26) and (2.58) obtained for $\Omega_{o\mu}/\Omega_\mu$ and Ω_{ok}/Ω_k. Combining Eqs. (2.73) and (2.74) gives a simple polynomial interpolation for $\Omega_{D,AB}$ with T and p

$$D_{AB} = D_{0,AB}\left(\frac{p_0}{p}\right)\left[-0.1038\left(\frac{T}{T_0}\right)^{3.5} + 0.5323\left(\frac{T}{T_0}\right)^{2.5} + 0.5685\left(\frac{T}{T_0}\right)^{1.5}\right] \tag{2.75}$$

For example, using $D_{AB} = 1.378 \times 10^{-5}$ [m^2/s] as reference value for the CO_2-air pair at 273 K temperature, the interpolation equation of Eq. (2.75) gives $D_{AB} = 1.563 \times 10^{-5}$ at 293 K temperature which is within 1 % error from the correct value published from experimental result.

2.17 Mass Diffusivity in Gas Mixtures

An example of mass diffusivity in gas mixture is D_{AB} for the binary pair of CO_2 as species A and air as mixture B. It is possible to predict theoretically the outcome of D_{AB} from the diffusivities of the single binary pairs of CO_2 as species A and each of the air mixture components N_2, O_2, plus contaminants listed as B_1, B_2,… B_n. In general, C.R. Wilke proved and published an approximation relation according to which D_{AB} for species A diffusing in a mixture of B_1,..., B_n is

$$D_{AB} = \frac{1}{\sum_{i=1}^{n} \varpi_i D_{AB_i}} \tag{2.76}$$

where ϖ_i are the mole fractions that can be expressed by the mass fractions, ω_{B_i}, and molecular weights, M_{B_i}, of species B_i in the gas mixture excluding species A

$$\varpi_i = \frac{\omega_{B_i}/M_{B_i}}{\sum_{i=1}^{n} \omega_{B_i}/M_{B_i}} \tag{2.77}$$

The Schmidt number, Sc, relates molecular viscosity to diffusivity, an analogous dimensionless similarity parameter to Prandtl number that relates viscosity and thermal conductivity

$$Sc_{AB} = \frac{\mu_{AB}}{\varrho_{AB} D_{AB}} = \frac{\nu_{AB}}{D_{AB}} \tag{2.78}$$

Although the binary diffusion coefficient varies significantly with composition in gas mixtures, it is interesting to note that the Schmidt number is found between 0.2 and 5 for most gas pairs (Bird et al. 1960, p. 512), allowing to roughly estimate diffusivity from viscosity.

2.18 Mass Diffusivity in Liquids

Molecular diffusivity models from theoretical basis follow either a hydrodynamic flow concept of creeping spherical particles A in stationary liquid B; or Eyring's activated-state molecular lattice model analogous for estimating liquid viscosity (Bird et al. 2007). In spite of generous simplification, the models provide comparable estimates for dilute solvents even for colloidal suspensions.

Only two model results are recalled of each approach, starting with the Stokes–Einstein equation that approximates well the diffusion of large spherical molecules A in solvents of B of low molecular weight

$$D_{AB} = \frac{KT}{6\pi\mu_B R_A} \tag{2.79}$$

where K is Boltzmann's constant, T is temperature, μ_B is solvent viscosity and R_A is the radius of the solute particle. The model was published by Einstein on investigating the theory of Brownian motion in 1905 and is shown to agree with recent solutions to the Langevin equation for the stochastic motion of colloid particles (Bird et al. 2007, pp. 528–532). The Stokes–Einstein model assumes no-slip condition between the surface of the spherical molecules A and solvent B. If the derivation assumes complete slip condition, the diffusivity expression in Eq. (2.79) is modified only by a multiplication factor of 1.5. If the molecules A and solvent B are identical, as in the so-called self-diffusion, and assuming that the adjacent molecules are just touching each other in the cubic lattice with freedom to complete slip, then Eq. (2.79) can be rewritten with the substitution of $2R_A = \left(\widetilde{N}_A/\tilde{V}_A\right)^{1/3}$

$$D_{AA} = \frac{KT}{2\pi\mu_A}\left(\frac{\widetilde{N}_A}{\widetilde{V}_A}\right)^{1/3} \tag{2.80}$$

where $\widetilde{N}_A$ and $\tilde{V}_A$ are the number of molecules and the molar volume, respectively.

The Eyring model is postulated in a very similar form of Eq. (2.80) for traces of A in solvent B

$$D_{AB} = \frac{KT}{\xi\mu_B}\left(\frac{\widetilde{N}_A}{\widetilde{V}_A}\right)^{1/3} \tag{2.81}$$

where parameter ξ represents the number of nearest neighbors of the solvent molecule. For self-diffusion, parameter ξ is close to 2π, giving an excellent agreement with the Stokes–Einstein equation assuming complete slip condition.

2.19 Mass Diffusivity in Solids

It is of general and particular interest to formulate the constitutive equations for diffusion of gases and liquids in the pores and fractures of solid material in ordinary transport problems. Interdiffusion of solid atoms in a solid substrate is another type of phenomenon, the main interest of the metallurgists. There are three types of diffusion in pores and fractures: Knudsen diffusion when the molecular mean free path is comparable or greater than the connecting channel size; surface diffusion; and Fick-type diffusion. The main interest is in the latter in which the mass flux density, $\boldsymbol{q_A}$ of species A is driven by the gradient of the mass fraction, $\nabla\omega_A$ measured within the pore space of solid B

$$\boldsymbol{q}_A = -\varrho D_{A,eff}\nabla\omega_A \tag{2.82}$$

The effective diffusivity, $D_{A,\text{eff}}$, is the combination of the diffusivity, D_{AB}, of species A in substrate B with its catalytic effect, the fractional void space called porosity, Φ, and tortuosity, Ψ, that is the ratio between the actual path length of diffusion relative to the nominal length of the porous media (Scatterfield 1980)

$$D_{A,\text{eff}} = \frac{D_{AB}\Phi}{\Psi} \tag{2.83}$$

It must be noted that beside the Fick-type, many other mass flux components may be present in transport processes, such as those driven by pressure, temperature, magnetic, electrical, or other potential fields. These mass flux components, however, belong to the phenomena of coupled and other cross effects, described by the Onsager relations (Bird et al. 1960, p. 565).

The pressure-driven component of mass diffusion in porous and fractured media is of special importance in earth science and engineering transport problems in subsurface applications. Mass diffusion, caused by the pressure gradient belongs to macroscopic, creeping flow against viscous flow resistance. The mass flow rate per unit area is formulated

$$\boldsymbol{q} = -\frac{k}{\mu}\nabla p \tag{2.84}$$

where k, μ, and ∇p are the permeability of the porous solid in [m^2], absolute viscosity of the fluid, and the driving pressure gradient, respectively. Equation (2.84) is a special form of Darcy's law, originated from laboratory experiments on the flow through a sand-packed column in 1856. Written in one dimension for the velocity, v, and using the hydraulic conductivity, K, and the hydraulic gradient, dh/dl, Darcy's equation is as follows (Bear 1972):

$$v = -K\frac{\mathrm{d}h}{\mathrm{d}l} \tag{2.85}$$

where $K = k\rho g/\mu$, and its unit is [m/s].

2.20 Diffusivity in Turbulent Flow

Diffusivity in turbulent flow may be simplified and considered as dispersion of one species into the mixture of the bulk flow by turbulent eddies. An analogy with turbulent heat conduction may be applied by linking turbulent mass diffusivity to turbulent viscosity. Recalling that turbulent thermal conductivity was linked to turbulent viscosity through the use of the turbulent Prandtl number, Pr_T in Eq. (2.66), an analogous equation can be written for turbulent diffusion flux density of species A in mixture B with the turbulent Schmidt number, $Sc_{T,AB}$

$$\bar{j}_{Ay} = -\varrho\left(D_{AB} + \frac{\varepsilon_T}{Sc_{T,AB}}\right)\frac{\mathrm{d}\bar{\omega}_A}{\mathrm{dy}} \tag{2.86}$$

The turbulent Schmidt number, similar to the turbulent Prandtl number varies very moderately with molecular properties of the species and is in the order of single digits for turbulent flows (Bird et al. 1960). Lacking empirical correlations or measurement data, estimating $Sc_{T,AB}$ allows for estimating the turbulent diffusivity from turbulent viscosity. However, the validity of these approximations is limited to simple flow geometry and breaks down in three dimensions (Kays 1994).

2.21 Specific Heat

The "total specific heat" may be obtained from the "specific total energy" (Welty et al. 1984, p. 80) that is, from the total energy of unit mass $\omega_E = \rho_E/\rho$ (the energy fraction) of the fluid as it relates to its temperature, $\partial\omega_E/\partial T$. Using Eq. (2.3) for the expression of ω_E, the partial derivative for constant z and v gives the definition of the total specific heat, C

$$C = \frac{\partial\left(\frac{p}{\rho} + u\right)}{\partial T} = \frac{1}{\rho}\frac{\partial p}{\partial T} - \frac{p}{\rho^2}\frac{\partial \rho}{\partial T} + \frac{\partial u}{\partial T} \tag{2.87}$$

The specific heat for constant pressure, C_p is obtained from Eq. (2.87) for $\partial p/\partial T = 0$

$$C_p = -\frac{p}{\rho^2}\frac{\partial \rho}{\partial T} + \frac{\partial u}{\partial T} \tag{2.88}$$

A simpler expression for C_p may be obtained for an ideal gas. Using the gas law of $p/\rho = RT$ with the specific gas constant R for a given gas; and with the definition of the internal energy, $u = C_v T$ where C_v is the specific heat for constant volume for the species, the specific heat for constant pressure is as follows:

$$C_p = R + C_v \tag{2.89}$$

As seen from Eqs. (2.87) through (2.89), the most basic specific heat is C_v, determined for a thermal process in a constant volume. The specific heat property C_p is specified at constant pressure and it includes C_v. Both C_v and C_p can be determined from measurements, but neither property measures the total specific heat, C.

The ratio between C_p and C_v is related to the compressibility of the fluid. For ideal gas, it is called the adiabatic index, $\kappa = C_p/C_v$. While both C_p and C_v are temperature dependent, index κ, shows moderate temperature dependency and can

be approximated by a low-order polynomial of the absolute temperature. After evaluating κ, C_v can be calculated as follows:

$$C_v = \frac{R}{\kappa - 1} \tag{2.90}$$

Example 2.4 Adiabatic index, κ, for air
For practical applications, approximation of κ/κ_0 may be given by a second-order polynomial for a temperature range from 273 to 773 K from best fit to published data for air (Blevins 1984)

$$\frac{\kappa}{\kappa_0} = -0.0049095\left(\frac{T}{T_0}\right)^2 + 0.0008908\frac{T}{T_0} + 1.0047724 \tag{2.91}$$

where κ_0 = 1.401 is taken at $T_0 = 273.3$ K. The value of κ over 500 °C temperature range changes only moderately from 1.4 to 1.36, therefore, there is no need to use higher than a second-order polynomial approximation.

2.22 Compressibility of Gas and Liquid

Compressibility number of fluids may be defined in general as $\beta = \partial\rho/\partial p$. For ideal gas, β can be calculated from the gas law

$$\beta = \frac{\partial\rho}{\partial p} = \frac{1}{RT} = \frac{\rho}{p} \tag{2.92}$$

The compressibility number for gas is a variable of temperature and the specific gas constant. For most common gases at room temperature the value of β is lower than 1×10^{-5} [kg/J].

For liquids, compressibility is related to the bulk modulus of volumetric elasticity, E_v, defined as $E_v = -V\partial p/\partial V$, giving $\partial p = -E_v\partial V/V$. Assuming that the mass of liquid in volume V during compression does not change, $\partial m = \partial(\rho V) = \partial\rho V + \rho\partial V = 0$, giving $\partial\rho = -\rho\partial V/V$. Substituting ∂p and ∂V for liquid to the definition given in Eq. (2.92) gives

$$\beta = \frac{\partial\rho}{\partial p} = \frac{-\rho\partial V/V}{-E_v\partial V/V} = \frac{\rho}{E_v} \tag{2.93}$$

For most common liquids, the compressibility number is constant and less than 1×10^{-6} [kg/J]. For water at room temperature and normal atmospheric pressure, $\beta = 4.65 \times 10^{-7}$ [kg/J].

2.23 Corollary of the Elements of Transport Processes

Advection. Advection transport of an extensive is considered when the substance is carried by velocity, determining the direction of the flux. The majority of the technical literature calls this transport mode convection, while at the same time, uses convection also for transport in the flow in direction other than that of the velocity, caused by concentration, mass fraction, or pressure difference of the scalar substance. Distinction between advection and convection is therefore warranted.

The surface flux density of a scalar substance e by *advection* is expressed with the carrying velocity, $\boldsymbol{v}$

$$\boldsymbol{q}_a = \rho_e \boldsymbol{v} = \rho \omega_e \boldsymbol{v}, \tag{2.94}$$

where $\boldsymbol{q}_a$ is in [ext/(m^{2}s)]; ρ_e is the substance density, [ext/ m^3]; ρ is the bulk flow density in [kg/m^3]; and ω_e is the substance mass fraction, [ext/kg], relative to the mass of the substance in the same volume.

The density is a vector for the vector extensive of momentum, $\boldsymbol{\rho}_e = m\boldsymbol{v}$. Momentum transport by *advection* is also a tensor quantity expressed by the dyadic product of two vectors, $\boldsymbol{\rho}_e$ and $\boldsymbol{v}$ as

$$\boldsymbol{q}_a = \boldsymbol{\rho}_{\mathrm{e}} \circ \boldsymbol{v} \tag{2.95}$$

where $\boldsymbol{\rho}_{\mathrm{e}}$ is the momentum density vector and $\boldsymbol{v}$ is velocity. In matrix-vector notation, $\boldsymbol{q}_a = \boldsymbol{\rho}_{\mathrm{e}} \boldsymbol{v}^T$.

Diffusion. Diffusion is a microscopic, molecular-scale, random process, infinite in speed by abstraction, and does not involve any macroscopic carrying velocity that has a nonzero mean value. Diffusion transport is the movement of the substance driven by potential difference. For example, mass fraction or temperature differences induce mass or energy transports in the direction of the gradients.

Dispersion. Dispersion is the displacement of the substance by a combination of advection and diffusion. Dispersion may be viewed as an equivalent, apparent diffusion, driven by concentration differences within a flow field. Dispersion depends on the carrying velocity field, but the advection component is statistically averaged in all directions and thus the process can be modeled as an enhancement upon diffusion. For example, in turbulent flow, the eddy diffusivity is used which may be three or more orders of magnitude higher than molecular diffusivity. Since diffusion and dispersion are both modeled as concentration-driven transport processes, diffusion will stand for dispersion as a proxy in the mathematical formulations.

The surface flux density of substance e by *diffusion or dispersion* is expressed with the gradient of partial density of e, $\text{grad}(\rho\omega_e) = \nabla(\rho\omega_e)$, multiplied by some diffusion or dispersion coefficient, D

$$\boldsymbol{q}_d = -D\nabla(\rho\omega_e) \tag{2.96}$$

The unit of D is [m^2/s].

Convection. Convection transport is the transversal movement of the substance through a velocity field in a complex way that involves a combination of advection in the flow direction and diffusion or dispersion across the velocity field simultaneously. The driving force for convection is potential difference whereas the transport resistance is affected by the velocity field. A typical example is convective heat transfer across a slow-moving boundary layer in a flow over a flat plate.

The surface flux density of substance e by *convection* is expressed as follows between a unit surface element at ω_e and the moving fluid at $\omega_{e,\infty}$ at the outside of the boundary layer marked with the symbol ∞

$$\boldsymbol{q}_c = -\alpha(\omega_e - \omega_{e,\infty})\boldsymbol{n} \tag{2.97}$$

where α is the convective transport coefficient defined for driving extensive flux density, $\boldsymbol{q}_c$, by some extensive fraction difference. The unit of α is [kg/(m^{2}s)].

One fundamental difference between $\boldsymbol{q}_a$ and $\boldsymbol{q}_c$ in spite of the fact that both are related to the velocity field is that the directions of $\boldsymbol{q}_a$ and $\boldsymbol{v}$ are the same, whereas the direction of $\boldsymbol{q}_c$ is normal to that of velocity $\boldsymbol{v}$, i.e., $\boldsymbol{v} \cdot \boldsymbol{q}_c = 0$. Another reason for using a different name for *advection* and distinguish it from *convection* is the difference in their driving mechanism.

Heat radiation. Heat exchange by radiation takes place between solid surfaces, as well as between solid surfaces and the surrounding fluids other than to and from monatomic gases. According to Stefan–Boltzmann law, the radiation heat flux from a black body at T absolute temperature to an infinite, absorbing space at zero temperature is $q_r = 5.669 \times 10^{-8} \times T^4$ [W/m^2]. Heat exchange by radiation can be conveniently expressed as a difference between counter-radiations involving two surfaces or SF network nodes. The heat flux density by *radiation* between a unit surface element at T_w and another ambient surface or absorbing fluid element at T_a may be written analogous to flux density of convective transport

$$q_r = -\alpha_r(T_w - T_a) \tag{2.98}$$

where α_r is the radiative transport coefficient defined for driving flux density, q_r, (a loss if $T_w < T_a$) by the temperature difference. The direction of the heat flux depends on the relative position vector between the heat exchanging elements. The unit of α_r is [W/(m^{2}K)], specific to thermal radiation. The value of α_r includes the Stefan–Boltzmann constant; and depends on the emissivity of the surfaces and/or materials; a combination of temperatures according to $(T_w + T_a)(T_w^2 + T_a^2)$; as well as on the geometry, involving the radiation view angle.

SF network models are especially advantageous for solving radiation heat transport between multiple bodies.

Accumulation or discharge. This transport term represents the storage or depletion of the substance in a fixed control volume by changing the density of the species with time at the instantaneous location during motion.

The flux of substance e from *accumulation or discharge* in 1 m^3 volume is

$$Q = \frac{\partial(\rho\omega_e)}{\partial t} \tag{2.99}$$

Source or sink. The introduction or removal of the substance is a transport term affecting the balance of a species in a control volume. This transport term may represent phase change, for example, evaporation or condensation; chemical reaction; or any transport other than the ones listed in the foregoing.

The flux of substance e from a *source or sink* f_e, relative to the mass in 1 m^3 volume is

$$Q = \rho f_e \tag{2.100}$$

where f_e is the relative rate of source of extensive.

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