MOMENTUM, HEAT, AND MASS TRANSPORT BY MOLECULAR DIFFUSION

By

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SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
AT
ADDIS ABABA UNIVERSITY
ADDIS ABABA,ETHIOPIA
NOVEMBER 2024

ADDIS ABABA UNIVERSITY
DEPARTMENT OF
PHYSICS

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Date: **November 2024**

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Title: **MOMENTUM, HEAT, AND MASS TRANSPORT BY MOLECULAR DIFFUSION**

Department: **Physics**

Degree: **M.Sc.** Convocation: October Year: **2024**

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Abstract

In this project we have presented a review of momentum, heat, and mass transport by molecular diffusion that takes place near interfaces and boundary layers. Specifically, we considered the thermodynamics of fluids, conductive heat and momentum transport mechanism by molecular collision, thermal conductivity and heat equation. Moreover, diffusive transport mechanisms and the associated fluxes, coupled Heat and Mass Transport by Molecular Diffusion, and the equations that describe them. Fluid flow is governed by a coupled nonlinear system of partial differential equations. However, in many practical situations, the calculation of friction or energy losses in conduits, or the heat and mass transport at interfaces can be greatly simplified by using so called transport coefficients. These coefficients, which are based on analytical solutions are typically gathered as correlations based on dimensionless numbers.

Acknowledgements

First thanks to the almighty **GOD** for his guidance and protection that keeps me always safe.

Next, I would like to express my deepest gratitude and respect to my supervisor **Dr Yitagesu Elfagd**, for his invaluable guidance, suggestions and constant support during this research. I appreciate his friendly approach and kindness.

I am grateful to my family especially **my wife Tigist**. Her awakening call everyday is just an incentive and that supports me to pass through the though times I have encountered. So her role is unforgettable.

I would like to forward my special sincere thanks to **Ato Andualem Atumo** who helped me in the resources I needed ,in the course of this project.

Finally, it is my pleasure to thank the ministry of education for sponsoring me to join the school of Graduate studies.

Chapter 1

Introduction

Molecules move continuously and this motion becomes more and more chaotic on increased thermal excitation, but is constrained due to cohesive forces between molecules. The transport by molecular diffusion is caused by the random motion of the fluid molecules. This phenomenon tends to make uniform all the fluid properties, so the fluid evolves from local to global thermodynamic equilibrium conditions.

All the mechanisms of molecular diffusion are similarly modeled, that is, by the product of a diffusivity constant (η, k, D_{AB}) times a gradient of a fluid variable. This is not by chance, but rather because all the diffusion mechanisms have the same origin: the microscopic random motion and collisions of the molecules. In particular:

Transport of momentum is translational random motion, the molecules of smaller velocity travel to areas of higher velocity, and viceversa, causing collisions which average their velocity. Viscosity is responsible for this transport phenomenon. This property creates friction between the layers of fluid because of the relative motion between the fluid particles.

Transport of heat is the temperature of a substance in an indication of its vibrational energy [1]. Collisions between molecules at different temperature tend to average the vibrational energy of all the molecules, so the temperature becomes more uniform. Heat diffusion is the mechanism of heat transport by molecular interaction.

Transport of mass causes the migration of molecules from areas of high concentration to areas of low concentrations by the molecular collision.

1.1 Background of Study

The earliest physicist, particularly bernoulli, Clausus, Maxwell, Vanderwaals and Jeans focused their attention on the gaseous state and developed a mathematical formula of the kinetic theory [1].

All materials are made up of molecules, and the same molecular motions and interactions are responsible for viscosity, thermal conductivity, and diffusion [2].

In the late seventeenth century, Isaac Newton (1642-1727) proposed that a fluids resistance to motion was proportional to a velocity gradient and proved this by a series of experiments measuring the drag force on a sphere immersed in a flowing fluid. We name the analog of Hookes law for fluids after Newton. A simpler experiment for determining the relationship between the stress on a fluid and the velocity gradient. During the late eighteenth century, James Joule (1818-1889) first classified heat as a form of energy and proved that a given amount of mechanical work done on a system was equivalent to adding heat to the system. Jean-Baptiste Biot (1771-1862), and later Jean-Baptiste Joseph Fourier (1786-1830), performed and analyzed a series of experiments finally tying the flux quantity or heat flux, to a gradient in the state variable, the temperature [3].

Long after Newtons law, and Fouriers were developed, people were still uncertain about the movement of chemical species from one location to another. Adolf Eugen Fick (1829-1901), a physiologist, performed a series of experiments tying the flux of chemical species to a gradient involving the mole/mass fraction or concentration/density of chemical species [3].

Since the days of Osborne Reynolds (1842-1912) who experimented with the motion of viscous fluids in pipes, it has been known that when the velocity of a viscous fluid exceeds a certain critical limit, the initial laminar flow breaks down into irregular turbulent eddies, resulting in a rapid mixing of the fluid elements [4].

1.2 Objectives of the Study

General objectives

To describe the aims of momentum, heat, and mass transport by molecular diffusion.

Specific objectives

To identify and examine the relation ship between thermal conductivity with mean molecular speed, density of the gas, and mean free path.

To derive the wind speed at various heights in the atmospheric boundary layer.

1.3 Out Line of the Study

This project is organized in Six chapters: Introduction, Thermodynamics of heat transfer, Thermal Conduction Transport in Fluids, Transport Phenomena by Diffusion, Conductive Heat Transfer in Boundary Layer, and Summary and Conclusion.

In the first chapter includes, Fundamentals, objectives, and basic definitions of momentum, heat, and mass transport by diffusion are introduced.

In chapter two, The laws of thermodynamics lay the framework for the science of heat transfer it includes (the first law requires that the rate of energy transfer into a system to be equal to the rate of increase of the energy of that system, and the second law requires that heat be transferred in the direction of decreasing temperature), and mechanisms of heat transfer.

In chapter three we present a general overview of the kinetic theory of fluids which is the main building block of our work. We will briefly discuss the concept of heat transport by conduction in fluids includes (heat transport equation, the general heat conduction equation, thermal conductivity of non-uniform fluids, the effect of temperature, pressure, and chemical species on the thermal conductivity of fluids, and the heat conduction velocity), and a modification of the eucken formula providing a good a agreement with exact calculations is proposed.

In chapter four, we present transport phenomena by diffusion includes momentum transport by diffusion, momentum transport equation, mass transport by binary diffusion (mass transport equation, molecular collisions and diffusion, and diffusion velocity and partial velocity), molecular interpretation of diffusion transport, and fluid flow is governed by a coupled heat, mass transport by diffusion of nonlinear system of partial differential equations are discussed.

In chapter five, we will briefly discuss the concept of boundary surfaces and present the earths land - atmosphere boundary layer, and earths ocean-atmosphere boundary layer. In chapter six, finally we will present summary and conclusions.

Chapter 2

Thermodynamics of Heat Transfer

2.1 Thermodynamics of Fluids

Thermodynamics is the study of the internal motions of many body systems. In particular, we shall be concerned with the type of motion that we normally call heat.

Heat generated by friction is transferred to the surroundings in an amount equal to the change in kinetic energy of the vehicle [3,5]. We shall try to establish what controls the flow of heat from one body to another when they are brought into thermal contact. Thermal energy is considered to be the energy associated with creating disorder in a system.

When no temperature difference exists, no spontaneous heat transfer occurs, a condition of thermal equilibrium. This is because the higher the temperature, the higher the kinetic energy of the particles of a system.

Temperature is a measure of the average kinetic energy of the particles in a system. We shall also attempt to understand the relationship between heat and mechanical work.

Entropy and temperature are the two fundamental concepts of thermodynamics [4].

2.1.1 First law of thermodynamics

The first law of thermodynamics is the law of conservation of energy for a thermodynamic system. The law says that the heat added to a system is equal to the change of the internal energy of the system plus the work done by the system [6].

A system has an internal energy (U) which is the sum of the energy of all the internal degrees of freedom that the system possesses. We can change the internal energy of the system by heating it or by doing work on it. The change in internal energy of a system can be written as

$$\Delta U = \Delta W + \Delta Q \tag{2.1.1}$$

where ΔQ is positive for heat supplied to the system and ΔQ is negative, heat is extracted from the system; ΔW is positive for work done on the system and if ΔW is negative, the system does work on its surroundings. In applying equation (2.1.1), the variables that determine Q and W will often be continuously changing. Such change can be handled by adding up very small changes of U or , more exactly, by integrating over infinitesimal changes in U. The differential form of equation (2.1.1) is

$$dU = dQ + dW \tag{2.1.2}$$

We define a thermally isolated system as a system that can not exchange heat with its surrounding $\Delta Q = 0$

$$dU = dW = -pdV \tag{2.1.3}$$

2.1.2 Second law of thermodynamics

In fact, the first law allows the cold body to become cooler and the hot body to become hotter as long as energy is conserved during the process. However, in practice this does not happen; instead, the law of nature imposes another condition on the process, a condition that stipulates the direction in which a process should take place.

To as certain the proper direction of a process, let us define a new state variable, the entropy, as follows

$$\mathrm{dS} = \frac{dq_{rev}}{T} \tag{2.1.4}$$

where S is the entropy (amount of disorder) of the system, dq_{rev} is an incremental amount of heat added reversibly to the system, and T is the system temperature. Since entropy is a state variable, it can be used in conjunction with any type of process, reversible or irreversible. The quantity dq_{rev} is just an artifice; an effective value of dq_{rev} can always be assigned to relate the initial and final states of an irreversible process, where the actual amount of heat added is dq.

$$\mathrm{ds} = \frac{dq}{T} + \mathrm{ds}_{\mathrm{irrev}} \tag{2.1.5}$$

Equation (2.1.5) applies in general to all processes. It states that the change in the entropy during any process is equal to the actual heat added, dq divided by the temperature, $\frac{dq}{T}$, plus a contribution from the irreversible dissipative phenomena of viscosity, thermal conductivity, and mass diffusion occurring with in the system, $\mathrm{ds}_{\mathrm{irrev}}$ these dissipative phenomena always cause an increase of entropy.

$$\mathrm{ds}_{\mathrm{irrev}} \geq 0 \tag{2.1.6}$$

The equals sign in the inequality (2.1.6) denotes a reversible process where, by definition, the above dissipative phenomena are absent. Hence, a combination of equation (2.1.5) and (2.1.6) yields

$$\mathrm{ds} \geq \frac{dq}{T} \tag{2.1.7}$$

If the process is adiabatic, dq=0 and (2.1.7) reduces to

$$\mathrm{ds} \geq 0 \tag{2.1.8}$$

Equations (2.1.7) and (2.1.8) are two forms of the second law of thermodynamics. The second law gives the direction in which a process will take place. Equations (2.1.7) and (2.1.8) imply that a process will always proceed in a direction such that the entropy of the system plus its surroundings always increases, or at least remains unchanged.

That is, in an adiabatic process the entropy can never decrease. If ds $>$ 0 the process is called an irreversible process, and when ds $=$ 0 the process is called a reversible process.

Heat Capacity

Heat as energy in transit was preceded historically by the idea that gases, liquids, and solids have capacity for heat. The smaller the temperature change caused in a substance by the transfer of a given quantity of heat, the greater its capacity. The heat capacity of an object is the amount of heat needed to raise its temperature, per degree temperature increases show equation (2.1.9).

$$C = \frac{dQ}{dT} \tag{2.1.9}$$

The heat required to a substance depends on just how that heating is conducted [7,5]. The most common ways of heating are at constant volume or at constant pressure. In general, the internal energy will be a function of temperature and volume, so that we can write $U = U(T, V)$. Hence a small change in U can be related to changes in T and V by

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.1.10}$$

Substitute equation (2.1.10) in to equation (2.1.2) we have that

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \tag{2.1.11}$$

We can divide equation (2.1.11) by dT to obtain

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT} \tag{2.1.12}$$

Which is valid for any change in T or V how ever, what we want to know is what is the amount of heat we have to add to effect a change of temperature under certain constraints. The first constraint is that a keeping the volume constants. We recall the definition of the heat capacity at constant volume C_V

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{2.1.13}$$

From equation (2.1.12) this constraint knocks out the second term and implies that

$$C_V = \left(\frac{\partial U}{\partial T}\right) V \tag{2.1.14}$$

The heat capacity at constant pressure is then using equation (2.1.12) given by

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right) + P\right] \left(\frac{\partial V}{\partial T}\right)_P \tag{2.1.15}$$

So that

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right) + P\right] \left(\frac{\partial V}{\partial T}\right)_P = R \tag{2.1.16}$$

We will use small c for the letter, known as the specific heat capacities.

$$c_V = \frac{C_V}{m}, c_P = \frac{C_P}{m} \tag{2.1.17}$$

Fluid molecules move and collide with each other, and these collisions contribute to the over all heat capacity. Each collision transfers kinetic energy between molecules.

Liquid molecules may also exhibit rotational and vibrational motion, which contributes to the total heat capacity. The total heat capacity of a liquid is a result of these combined effects, and although we don't typically break it down into "collisions heat capacity," the molecular collisions play a significant role in how energy is distributed and stored. The heat capacity of a fluid is typically measured directly and expressed as specific heat capacity or molar heat capacity.

2.2 Heat Transfer Mechanisms

Heat transfer mechanism refers to the process of transferring thermal energy from one substance to another. Heat can through three modes of energy transfer: conduction, convection, and radiation [8].

All heat-transfer processes involve one or more of these modes.

In this project you consider about heat transfer by conduction and diffusion are discussed.

When a temperature gradient exists in a body, there is an energy transfer from the high-temperature region to the low-temperature region. This type of heat transfer is called conduction heat transfer. More discussed about conduction of heat transfer in chapter 3.

Chapter 3

Thermal Conduction Transport in Fluids

3.1 The kinetic Theory of Fluids

Fluid is a substance that continually deforms under the action of shear stress and a substance that at rest cannot withstand shear stresses. The kinetic theories are available for gases, and liquid [5]. In liquids, molecules are in constant motion, but unlike gases, their movement is more constrained. Molecules in a liquid move more slowly compared to gases and are close enough to interact with each other. This results in the molecules vibrating and sliding past each other rather than moving freely.

Liquid molecules experience intermolecular forces that are stronger than those in gases. Unlike gases, which can compress or expand significantly, liquids are relatively incompressible. This is due to the relatively fixed distances between molecules, which mean the volume of a liquid is almost constant despite changes in pressure.

The kinetic theory helps explain these transitions by describing how changes in molecular motion and energy lead to different states of matter [9]. The kinetic theory of gases attempts to explain the microscopic properties of a gas in terms of the motion of its molecules. The gas is assumed to consist of a large number of identical, discrete particles called molecules, a molecule being the smallest unit having the same chemical properties as the substance [2].

Elements of kinetic theory were developed by Maxwell, Boltzmann and Clausius between 1860-1880. How ever this topic deals with kinetic theory of gases only. Postulates of kinetic theory of gases [2].

- Any gas consist large number of molecules. These molecules are identical, perfectly elastic and hard sphere.
- Gas molecules do not have preferred direction of motion, their motion is completely random.
- Gas molecules travels in straight line.
- The time interval of collision between any two gas molecules is very small.
- The collision between gas molecules and the walls of container is perfectly elastic.
- The motion of gas molecules is governed by Newton's laws of motion.
- The effect of gravity on the motion of gas molecules is negligible [2].

3.1.1 Maxwells law of distribution of velocities

This law is to find the number of molecules which have a velocity with in small interval u_x to $u_x + du_x$. The derivation of the distribution law is based on a number of assumptions. The assumptions are as follows [2].

- In the equilibrium state, the molecules have complete randomness of direction and velocity [2].
- There is no mass motion or convection current in the body of the gas. As long as there is no net force acting on the system, this assumption is quite justified [2].

- The probability of a molecule having x-velocity component, say after a large number of collisions, does not depend on y- and z velocity components. This assumptions follows from random motion of gas molecules [2].
- The probability that a molecule selected at random has velocity component in the given range is a function only of the magnitude of velocity component and the width of the interval.
- The gas molecules have no vibrational or rotational energies. This assumption is quite justified because vibrational and rotational energies remain unchanged when gas molecules under go collisions [2].

Consider a gas having N molecules enclosed in a vessel of arbitrary shape and moving randomly. We represent these molecules on a velocity diagram with u_x, u_y and u_z as the coordinate axes as shown in (Figure. 3.1). Here du_x is an infinitesimal volume element [2].

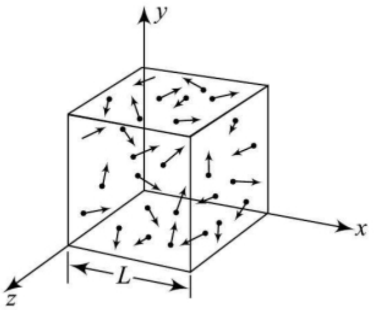

Figure 3.1: A volume element du in velocity space for a molecule of velocity u [2].

Let us denote the x, y and z components of the velocity u of a particle by u_x, u_y and

u_z. There fore, in terms of these three rectilinear components, we can write

$$u^2 = u_x^2 + u_y^2 + u_z^2 \tag{3.1.1}$$

The number of velocity vectors ending in element du=$du_x\ du_y\ du_z$ gives the average number of molecules whose velocities lie between given limits u and u+du after a large number of collisions among identical molecules. It means that we have to calculate the number of molecules simultaneously having velocity components in the range u_x to $u_x + du_x$, u_y to $u_y + du_y$ and u_z to $u_z + du_z$. Assumption stated above implies that the fraction of molecules having velocity components in the range u_x to $u_x + du_x$ is equal to $f(u_x)du_x$ that is [2]

$$dN_{u_x} = Nf(u_x)du_x \tag{3.1.2}$$

where dN_{u_x} is the number of molecules having velocity components in the range u_x and $u_x + du_x$, N is the total number of molecules and f is an unknown function, which we have to determine mathematically the ratio $\frac{dN_{u_x}}{N}$ denotes the probability of finding a molecule x-component of velocity in the range u_x and $u_x + du_x$ [2].

Let us denote it by the symbol P_x. Proceeding further, we note that existence of velocity components u_y and u_z , since these are mutually perpendicular and independent of each other. So we can write the expression for the probability that a molecule having velocity components in the range u_y to $u_y + du_y$ and u_z to $u_z + du_z$ as

$$p_y = f(u_y)du_y \tag{3.1.3}$$

$$p_z = f(u_z)du_z \tag{3.1.4}$$

We can express the probability for a molecule to simultaneously have velocity components in the range $u_x\ to\ u_x + du_x$, u_y to $u_y + du_y$ and u_z to $u_z + du_z$ using the law of the compound probabilities (According to the law of compound probabilities, the composite probability for independent events is equal to the product of the probabilities of individual events.) this gives [2]

$$\frac{d^3N_{u_xu_yu_z}}{N} = P_xP_yP_z = f(u_x)f(u_y)f(u_z)du_xdu_ydu_z \tag{3.1.5}$$

Note that all these $d^3N_{u_xu_yu_z}$ molecules lie in the small volume element $du_xdu_ydu_z$. In (figure 3.1), these molecules are depicted as velocity points (A point representing a molecule with velocity components in the three coordinate directions is called velocity point.) there fore, the density of velocity points, i.e., number density of gas molecules can be expressed as [2]

$$\rho = \frac{d^3N_{u_xu_yu_z}}{du_xdu_ydu_z} \tag{3.1.6}$$

On combining equations. (3.1.5) and (3.1.6), we can write

$$\rho = Nf(u_x)f(u_y)f(u_z) \tag{3.1.7}$$

Since the velocity space has been assumed to be isotropic, the density of velocity points can be taken to be independent of inclination of u to the axes. So we can write

$$Nf(u_x)f(u_y)f(u_z) = constant = NF(u) = NJ(u^2) \tag{3.1.8}$$

where F and J are some other function [2]

$$u^2 = u_x^2 + u_y^2 + u_z^2 = constant \tag{3.1.9}$$

Physically, it means that after a large number of collisions, the distribution will be isotropic. There fore, for fixed u, $J(u^2)$ is constant and $d[J(u^2)] = 0$ In terms of du_x , du_y and du_z, we can write [2]

$$\frac{\partial f(u_x)}{\partial u_x}du_xf(u_y)f(u_z) + f(u_x)\frac{\partial f(u_y)}{\partial u_y}f(u_z)du_y + f(u_x)f(u_y)\frac{\partial f(u_z)}{\partial u_z}du_z = 0 \tag{3.1.10}$$

On dividing equations (3.1.10) by $f(u_x)f(u_y)f(u_z)$, we obtain

$$\frac{1}{f(u_x)}\frac{\partial f(u_x)}{\partial u_x}du_x + \frac{1}{f(u_y)}\frac{\partial f(u_y)}{\partial u_y}du_y + \frac{1}{f(u_z)}\frac{\partial f(u_z)}{\partial u_z}du_z = 0 \tag{3.1.11}$$

The differential form of equation (3.1.9), which expresses the condition under which u_x,v_y and u_z can vary while u^2 remains constant is

$$u_x du_x + u_y du_y + u_z du_z = 0 \tag{3.1.12}$$

From this equation, it is clear that the differentials du_x, du_y and du_z are not mutually independent; these can take any value but must satisfy equation (3.1.12). To relax this constraint, we use lagrange's method of undetermined multipliers. In this method, the constraining relation is multiplied by a constant and the resultant expression is added to the constrained equation. In this case, we choose the undetermined multiplier to be 2B. Accordingly, on multiplying equation (3.1.12) by 2B and adding the resultant expression to the equation (3.1.11), we get

$$\left[\frac{1}{f(u_x)}\frac{\partial f(u_x)}{\partial u_x} + 2Bu_x\right]du_x + \left[\frac{1}{f(u_y)}\frac{\partial f(u_y)}{\partial u_y} + 2Bu_y\right]du_y + \left[\frac{1}{f(u_z)}\frac{\partial f(u_z)}{\partial u_z} + 2Bu_z\right]du_z = 0 \tag{3.1.13}$$

Let us choose the constant B such that

$$\frac{1}{f(u_x)}\frac{\partial f(u_x)}{\partial u_x} + 2Bu_x = 0 \tag{3.1.14}$$

Then equation (3.1.13) reduces to

$$\left[\frac{1}{f(u_y)}\frac{\partial f(u_y)}{\partial u_y} + 2Bu_y\right]du_y + \left[\frac{1}{f(u_z)}\frac{\partial f(u_z)}{\partial u_z} + 2Bu_z\right]du_z = 0 \tag{3.1.15}$$

Of the three variables du_x, du_y and du_z, we can consider any two variables as constant. So let us take du_y and du_z to be independent. Then, for finite values of du_y and du_z, equation (3.1.13) will be satisfied if the coefficients of these differentials in equation (3.1.15) vanish separately. That is

$$\frac{1}{f(u_y)}\frac{\partial f(u_y)}{\partial u_y} + 2Bu_y = 0 \tag{3.1.16}$$

and

$$\frac{1}{f(u_z)}\frac{\partial f(u_z)}{\partial u_z} + 2Bu_z = 0 \tag{3.1.17}$$

To proceed further, we rewrite equation (3.1.14) as

$$\frac{df(u_x)}{f(u_x)} = -2Bu_x du_x \tag{3.1.18}$$

This equation can be easily integrated to obtain

$$\ln f(u_x) = \frac{-2Bu_x^2}{2} + \ln A \tag{3.1.19}$$

where $\ln A$ is an integration constant. We can rewrite this result as

$$f(u_x) = A\exp[-Bu_x^2] \tag{3.1.20}$$

where A and B are unknown constants.

Note that the lagrange's method of undetermined multipliers has helped us to discover the form of the function (f); it is a decreasing exponential. But now we will have to deal with two unknown constants rather than one unknown function.

On combining this result with equation (3.1.2), we can express the number of molecules having velocity components in the range $u_x \; to \; u_x + du_x$ as

$$dN_{u_x} = NA\exp(-Bu_x^2)du_x \tag{3.1.21}$$

Proceeding further, we note that the differential equations satisfied by $f(u_y)$ and $f(u_z)$ are similar to that satisfied by $f(u_x)$, and by analogy, we can write

$$f(u_y) = Ae^{-Bu_y^2} \tag{3.1.22}$$

$$f(u_z) = Ae^{-Bu_z^2} \tag{3.1.23}$$

On combining equation (3.1.21), (3.1.22) and (3.1.23) we obtain the required expression for $d^3Nu_xu_yu_z$

$$d^3N_{u_xu_yu_z} = NA^3e^{-B(u_x^2+u_y^2+u_z^2)}du_xdu_ydu_z = NA^3e^{-Bu^2}du_xdu_ydu_z \tag{3.1.24}$$

$$\rho = NA^3\exp[-B(u_x^2+u_y^2+u_z^2)] = NA^3\exp[-Bu^2], \tag{3.1.25}$$

This is the required expression for the Maxwell's velocity distribution function.

3.1.2 The speed distribution

The number of molecules lie with in the box of volume $du_xdu_ydu_z$ whose velocity lies with in u to u+du is the same as number of molecules with in the spherical shell of inner radius u and outer radius u+du as shown in the (Figure. 3.2). The volume of the shell in velocity space will be $4\pi^2u^2du$. In view of the geometry under consideration, it is more appropriate to express the volume element in terms of spherical polar

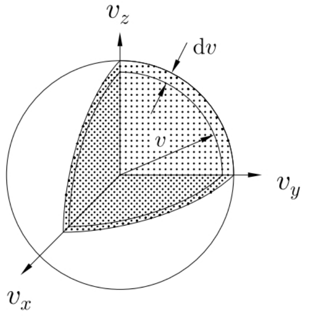

Figure 3.2: Molecules with speeds between u and u+du occupy a volume of velocity space in side a spherical shell of radius u and thickness du [2].

coordinates. The limits of integration over θ vary from 0 to π and over ϕ from 0 to 2π. This gives

$$dN_u = d^3N_{u_xu_yu_z} = \int_0^{\pi}\int_0^{2\pi} NA^3e^{-Bu^2}u^2 sin\theta d\theta d\phi du \tag{3.1.26}$$

$$dN_u = d^3N_{u_xv_yu_z} = 4\pi NA^3u^2e^{-Bu^2}du \tag{3.1.27}$$

To evaluate the unknown constants A and B , we first make use of the fact that if we integrate equation (3.1.27) for dN_u over all possible values of u from 0 to ∞, we will get the total number of molecules:

$$N = \int dN_u = 4\pi NA^3\int_0^{\infty} u^2e^{-Bu^2}du \tag{3.1.28}$$

We use the standard integral formula to integrate equation (3.1.28) by the equation $\int_0^{\infty} e^{-Bv^2}v^n dv = \frac{1}{2B^{((n+1)/2)}}\Gamma(\frac{n+1}{2})$ where $\Gamma(n)$ is gamma function. For n=2, the integral on the right hand side can be expressed in terms of the Gamma functions as $\Gamma(\frac{n+1}{2}) = \Gamma(3/2) = \frac{\sqrt{\pi}}{2}$ Using this result equation (3.1.28) for the total number of particles takes an (3.1.28).

$$N = 4\pi NA^3\frac{1}{2B^{3/2}}\Gamma(3/2) = \frac{4\pi NA^3}{2B^{3/2}}\frac{\sqrt{\pi}}{2} \tag{3.1.29}$$

On simplification and arrangement of terms in equation (3.1.29), we can express A in terms of B as

$$A = \sqrt{\frac{B}{\pi}} \tag{3.1.30}$$

We can determine B, either by calculating the average speed or the mean square speed $\overline{u^2}$ of a molecule, i.e, by relating B to the momentum or the average energy of a molecule. Here we will calculate u_{rms} and define $\overline{u^2}$ as

$$\overline{u^2} = \frac{\int_0^{\infty} u^2dN_u}{\int_0^{\infty} dN_u} \tag{3.1.31}$$

On substituting for dN_u from equation (3.1.27), we get

$$\overline{u^2} = \frac{\int_0^\infty 4\pi N A^3 e^{-Bu^2} u^2 u^2 du}{\int_0^\infty 4\pi N A^3 e^{-Bu^2} u^2 du} = \frac{\int_0^\infty u^4 e^{-Bu^2} du}{\int_0^\infty u^2 e^{-Bu^2} du} \tag{3.1.32}$$

By referring to the integral in the gamma function , you can write $\overline{u^2} = \frac{\frac{1}{2B^{5/2}}\Gamma(5/2)}{\frac{1}{2B^{3/2}}\Gamma(3/2)} = \frac{2B^{3/2}\Gamma(5/2)}{2B^{5/2}\Gamma(3/2)}$ since $\Gamma(5/2) = (3/2)\Gamma(3/2)$, we get

$$\overline{u^2} = \frac{3}{2B} \tag{3.1.33}$$

The mean kinetic energy of a gas molecule

The mean kinetic energy of a gas molecule is given by

$$< EKE >= \frac{1}{2} m < u^2 >= \frac{3}{2} K_B T \tag{3.1.34}$$

The average kinetic energy of a molecule is $\frac{3}{2}K_BT$. There fore, we can write

$$\frac{1}{2} m\overline{u^2} = \frac{3}{2} K_B T \tag{3.1.35}$$

On combining this result with equation (3.1.33) we can write

$$\frac{1}{2} m\overline{u^2} = \frac{1}{2} m \frac{3}{2B} = 3/2 K_B T \tag{3.1.36}$$

$$B = \frac{m}{2K_BT} \ and \ A = \sqrt{\frac{m}{2\pi K_B T}} \tag{3.1.37}$$

we can express the number of molecules in a maxwellian gas having speeds

$$dNu = 4\pi N \left(\frac{m}{2\pi K_B T}\right)^{3/2} u^2 \exp\left[-\left(\frac{mu^2}{2K_BT}\right)\right] du \tag{3.1.38}$$

Equation (3.1.38) tells as that distribution of molecular speeds depends on the nature of the gas as well as the temperature [2].

Average or mean speed

The average speed is the sum of all the velocities ranging from 0 to ∞ divided by total number of molecules N [7].

$$\overline{u} = \frac{\int_0^\infty u dN_u}{\int_0^\infty dN_u} = \frac{1}{N}\int_0^\infty u dN_u \tag{3.1.39}$$

On substituting for dN_u from equation (3.1.38), we get

$$\overline{u} = \frac{1}{N} 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_0^\infty u^3 e^{-\left(\frac{mu^2}{2k_B T}\right)} du \tag{3.1.40}$$

$$\overline{u} = 4\pi \left(\frac{B}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-Bu^2} u^3 du \tag{3.1.41}$$

$$\int_0^\infty e^{-Bu^2} u^3 du = \frac{1}{2B^2} \; and \; B = \frac{m}{2k_B T} \tag{3.1.42}$$

$$\overline{u} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8k_B T}{\pi \frac{M}{N_A}}} \tag{3.1.43}$$

where m is the mass of the gases molecule. If M is molecular weight which can be given by $M = mN_A$ and $R = k_B N_A$. Then the above equation becomes

$$\overline{u} = \sqrt{\frac{8RT}{\pi M}} \tag{3.1.44}$$

Root mean square speed

The *rms* speed is the square root of the sum of all the squared velocities ranging from 0 to ∞ divided by total number of molecules N is defined as $u_{rms} = \sqrt{\overline{u^2}}$ from equation (3.1.33) we recall that for a maxwellian gas, mean square speed is related to constant B. On substituting the value of B from the equation (3.1.37), we get

$\overline{u^2} = \frac{3}{2B} = \frac{3k_B T}{m}$

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3k_B T}{m}} \tag{3.1.45}$$

By comparing equation (3.1.43) and (3.1.45) for average speed and root mean square speed, respectively, you will note that $u_{rms} > \overline{u}$.

3.1.3 Mean free path

Mean free path of gas molecules is defined as the average distance traveled by a molecule between two successive collisions.

Consider a gas in container having n molecules per unit volume. Let d be the diameter of molecule (A) which is assumed to be in motion, while all other molecules are at rest. The molecule A collides with other molecules like B and C whose centers are at distance d from the center of molecule A as shown in the (Figure 3.3). If molecule moves a distance (L) with velocity u in time t, Let the number densities of these gases be n_1 and n_2. We construct a cylinder of cross-sectional area πd^2 and length , then this molecule collides with all molecules lying inside a cylinder of volume V=$\pi d^2 L$

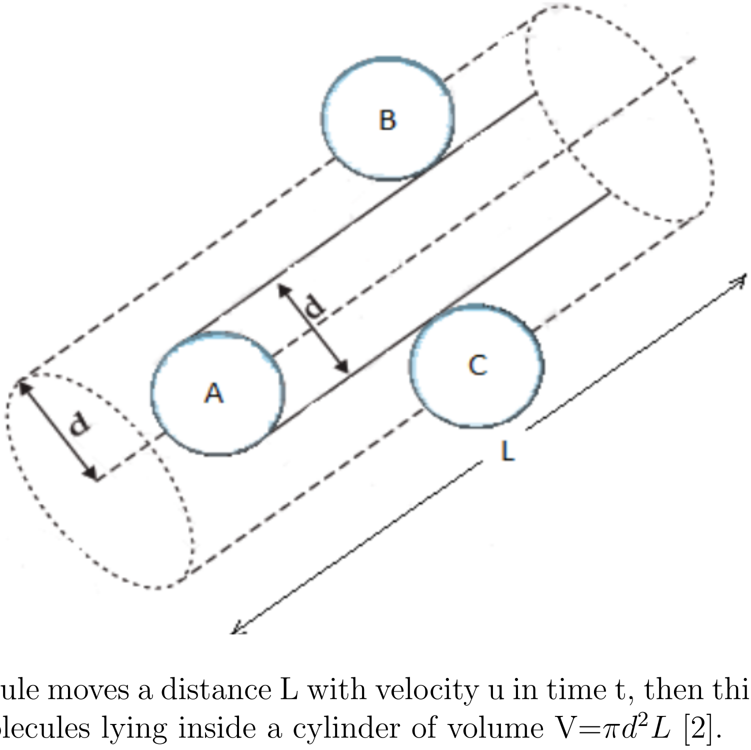

Figure 3.3: If molecule moves a distance L with velocity u in time t, then this molecule collides with all molecules lying inside a cylinder of volume V=$\pi d^2 L$ [2].

Let as consider two molecules of masses m_1 and m_2 and diameters d_1 and d_2. When they collide, They can be considered as one body system having reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$ and the center-to-centers distance $d = \frac{d_1+d_2}{2}$.

When one molecule of the first type moves, it will collide with all the molecules of the second type contained in the cylinder. The total number of such collisions is given by

$$f_{12} = n_2 \pi d^2 \overline{u} = n_2 \pi d^2 \sqrt{\frac{8k_B T}{\pi \frac{m_1 m_2}{m_1+m_2}}} \tag{3.1.46}$$

If all the molecules are identical, We can write d_1=d_2=d, m_1=m_2=m and n_1= n_2=n. Using these in the expression for f_{12}, Which we re designate as f, we get

$$f = n\pi d^2 \sqrt{\frac{2 \times 8k_B T}{m\pi}} = \sqrt{2}\pi n d^2 \overline{u} \tag{3.1.47}$$

$$\lambda = \frac{\overline{u}}{f} = \frac{\overline{u}}{\sqrt{2}\pi n d^2 \overline{u}} = \frac{1}{\sqrt{2}\pi n d^2} \tag{3.1.48}$$

3.2 Molecular Transport Processes

Molecular transport processes in general we are concerned with the transfer or movement of a given property or entity by molecular movement through a system which can be a fluid. We know that a fluid molecule has a finite mass and is characterized by random thermal motion. There fore, it possesses momentum as well as kinetic energy. So, while moving from one part of the container to another, it is a potential carrier of physical quantities such as matter, energy or momentum. When a fluid is in equilibrium, there is no net transport of these physical quantities.

3.3 Heat Transport by Conduction in Fluids

Conduction is described by Fourier's law, which states that"the rate at which heat is transported through a medium by conduction is proportional to the temperature gradient in the direction of the flow and to the cross-sectional area A through which the heat passes" [7]. Shown in the (Figure 3.4) Fourier's law for unidirectional flow of heat in the X-direction is given by the equation (3.3.1)

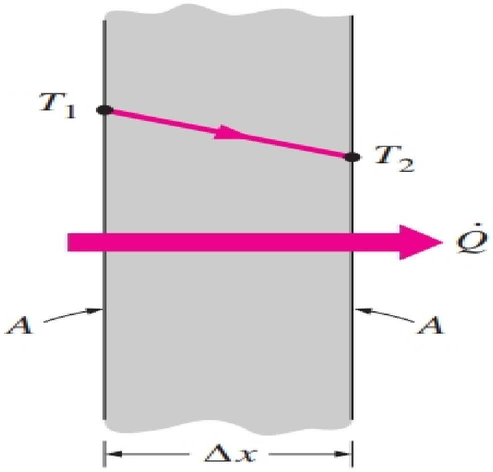

Figure 3.4: Heat conduction through a large plane wall of thickness Δx and area A [10].

$$\dot{Q} = -k \times A\frac{\Delta T}{\Delta x} \tag{3.3.1}$$

where the negative sign is because heat flows"down hill" the constant K is called the thermal conductivity of the fluids.

In general in three dimensions we can write that the heat conduction transfer is related to temperature gradient using by the given equation (3.3.2).

$$\dot{Q} = -KA\nabla T \tag{3.3.2}$$

Heat flux is defined as the rate of heat transfer per unit area through a material as a result of a temperature gradient.

$$Q_x = -K\left(\frac{\partial T}{\partial x}\right) \tag{3.3.3}$$

If the temperature varies in all three directions, then we can write an equation like (3.3.3) for each of the coordinate directions. $Q_y = \frac{\dot{Q}_y}{A_y} = -k\frac{dT}{dz}$, $Q_z = \frac{\dot{Q}_z}{A_z} = -k\frac{dT}{dz}$. If each of these equation is multiplied by the appropriate unit vector and the equations are then added vectorially, we get the equation (3.3.4) Which is the three-dimensional form of fourier's law

$$Q = -K\nabla T \tag{3.3.4}$$

When inequalities of temperature exist in a fluids, heat is transferred by molecular action from hotter regions to colder; this process is called conduction.

3.3.1 Heat transport equation

Heat is conducted through a fluid medium over time, is fundamentally governed by the heat diffusion equation or heat conduction equation. This equation is derived from Fourier's law of heat conduction and accounts for changes in temperature as heat diffuses through the fluid. In its general form, heat conduction equation in a fluid is given by using the conservation of energy principle, the rate of change of energy with in the control volume is equal to the difference between the heat in flow and out flow. Mathematically, this can be expressed as:

$$\frac{\partial}{\partial t}\left(Energy\ in\ control\ volume\right) = Heat\ in\ flow\ - Heat\ out\ flow \tag{3.3.5}$$

Since the energy stored in the control volume is related to the temperature and the material's heat capacity, we have;

$$\frac{\partial}{\partial t}\left(\rho c_p A\Delta x T\right) = -KA\left(\frac{\partial T}{\partial x}|_x - \frac{\partial T}{\partial x}|_{x+\Delta x}\right) \tag{3.3.6}$$

To simplify this, use a Taylor expansion for the temperature gradient at $x + \Delta x$:

$$\frac{\partial T}{\partial x}|_{x+\Delta x} = \frac{\partial T}{\partial x}|_x + \frac{\partial^2 T}{\partial x^2}\Delta x \tag{3.3.7}$$

Thus, the difference in heat flux becomes:

$$-k\left(\frac{\partial T}{\partial x}|_{x+\Delta x} - \frac{\partial T}{\partial x}|_x\right) = -k\frac{\partial^2 T}{\partial x^2}\Delta x \tag{3.3.8}$$

Substitute this into the energy balance equation:

$$\rho c_p A\frac{\partial T}{\partial t}\Delta x = -k\frac{\partial^2 T}{\partial x^2}\Delta x A \tag{3.3.9}$$

Dividing through by $\rho c_p A\Delta x$ gives the heat diffusion equation:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c_p}\frac{\partial^2 T}{\partial x^2} \tag{3.3.10}$$

3.3.2 The general heat conduction equation

Heat conduction is said to be multidimensional, and in this section we will develop the governing differential equation in such systems in rectangular, cylindrical, and spherical coordinate systems [10].

Rectangular Coordinates

Consider a small rectangular element of length x, width y, and height z, as shown in (Figure 3.5). An energy balance on this element during a small time interval t can

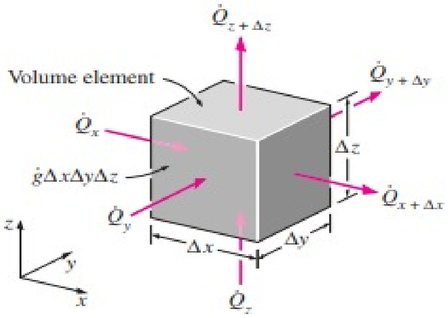

Figure 3.5: Three-dimensional heat conduction through a rectangular volume element [10].

be expressed as (Rate of heat conduction at x, y, z) - (Rate of heat conduction at $x+\Delta x, y+\Delta y, and\ z+\Delta z$)+ (Rate of heat generation in side the element) = (Rate of change of the energy content of the element) or

$$\dot{Q}_x+\dot{Q}_y+\dot{Q}_z-\dot{Q}_{x+\Delta x}-\dot{Q}_{y+\Delta y}-\dot{Q}_{z+\Delta z}+\dot{G}_{element}=\frac{\Delta E_{element}}{\Delta t} \tag{3.3.11}$$

The volume of the element is $V_{element}=\Delta x\Delta y\Delta z$ the change in the energy content of the element and the rate of heat generation with in the element can be expressed as $\Delta E_{element}=E_{t+\Delta t}-E_t=mc\left(T_{t+\Delta t}-T_t\right)=\rho c\Delta x\Delta y\Delta z\left(T_{t+\Delta t-T_t}\right)$

$\dot{G}_{element}=\dot{g}V_{element}=\dot{g}\Delta x\Delta y\Delta z$

Substituting into Eq. (3.3.11), we get

$$\dot{Q}_x+\dot{Q}_y+\dot{Q}_z-\dot{Q}_{x+\Delta x}-\dot{Q}_{y+\Delta y}-\dot{Q}_{z+\Delta z}+\dot{g}\Delta x\Delta y\Delta z=\rho c\Delta x\Delta y\Delta z\frac{T_{t+\Delta t-T_t}}{\Delta t} \tag{3.3.12}$$

Dividing by $\Delta x\Delta y\Delta z$

$$\frac{-1}{\Delta y\Delta z}\frac{\dot{Q}_{x+\Delta x}-\dot{Q}_x}{\Delta x}-\frac{1}{\Delta x\Delta z}\frac{\dot{Q}_{y+\Delta y}-\dot{Q}_y}{\Delta y}-\frac{1}{\Delta x\Delta y}\frac{\dot{Q}_{z+\Delta z}-\dot{Q}_z}{\Delta z}+\dot{g}=\rho c\frac{T_{t+\Delta t}-T_t}{\Delta t} \tag{3.3.13}$$

The heat transfer areas of the element for heat conduction in the x, y, and z directions are $A_x = \Delta y \Delta z, A_y = \Delta x \Delta z, and\ A_z = \Delta x \Delta y$, respectively, and taking the limit as $\Delta x, \Delta y, \Delta z$ and $\Delta t \longrightarrow 0$ yields

$$\frac{\partial}{\partial x}\left(\frac{k\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(\frac{k\partial T}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+\dot{g}=\rho c\frac{\partial T}{\partial t} \tag{3.3.14}$$

Equation (3.3.14) is the general heat conduction equation in rectangular coordinates. In the case of constant thermal conductivity, it the case of constant thermal conductivity, it reduces to

$$\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}+\frac{\dot{g}}{k}=\frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{3.3.15}$$

where the property $\alpha = \frac{k}{\rho c}$ is the thermal diffusivity of the material. Equation (3.3.15) is known as the fourier-Biot equation, and it reduces to these forms under specified conditions:

- Transient, no heat generation (diffusion equation)

$$\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}=\frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{3.3.16}$$

The diffusion equation is a parabolic partial differential equation. It describes the macroscopic behavior of many micro-particles in Brownian motion, resulting from the random movements and collisions of the particles.

- Steady-state (the poisson equation)

$$\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}=-\frac{\dot{g}}{k} \tag{3.3.17}$$

A Poisson distribution is a discrete probability distribution. It gives the probability of an event happening a certain number of times with in a given interval of time or space. The Poisson distribution has only one parameter, λ , which is the mean number of events. The graph below shows in (Figure 3.6) Poisson distributions with

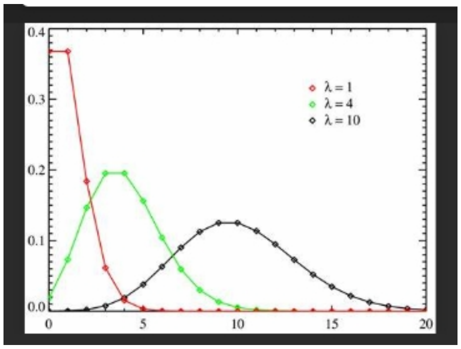

Figure 3.6: Graphical representation of a poisson distributions [10]

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different values of λ.

- Steady-state, no heat generation (laplace equation)

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = 0 \tag{3.3.18}$$

The general theory of solutions of laplace's equation is known as potential theory. The twice continuously differentiable solutions to laplace's equation are the harmonic functions, which are important to the study of heat conduction. In general, laplace's equation describes situations of equilibrium, or those that do not dependent explicitly on time.

Cylindrical coordinates

The general heat conduction equation in cylindrical coordinates can be obtained from an energy balance on a volume element in cylindrical coordinates, shown in (Figure 3.7), by following the steps just out lined.

It can also be obtained directly from Equation (3.3.14) by coordinate transformation using the following relations between the coordinates of a point in rectangular and cylindrical coordinate systems: $x = r\cos\phi$, $y = r\sin\phi$, and z=z

After lengthy manipulations, we obtain

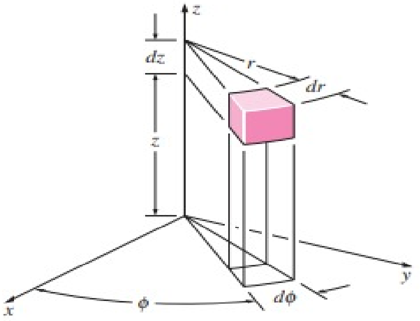


Figure 3.7: A differential volume element in cylindrical coordinates [10].

$$\frac{1}{r}\frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right)+\frac{1}{r^2}\frac{\partial}{\partial \phi}\left(kr\frac{\partial T}{\partial \phi}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+\dot{g}=\rho c\frac{\partial T}{\partial t} \tag{3.3.19}$$

The cylindrical coordinate is initially a uniform temperatur in the ϕ - direction and the temperature with in the cylindrical coordinates will change along the radial and axial distances r and z with time t, that is T=T(r,z,t). The thermal conductivity is given to be constant, and there is no heat generation in a cylindrical coordinates. There fore, the differential equation that governs the variation of the temperature in the cylindrical coordinates is obtained by the heat generation term and derivatives with respect to ϕ is equal to zero. There fore cylindrical coordinate equation (3.3.19) to simplify (3.3.20)

$$\frac{1}{r}\frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)=\rho c\frac{\partial T}{\partial t} \tag{3.3.20}$$

Spherical coordinates

The general heat conduction equations in spherical coordinates can be obtained from an energy balance on a volume element in spherical coordinates, as shown in (Figure 3.8), by following the steps outlined above. It can also be obtained directly from Equation (3.3.14) by coordinate transformation using the following relations between the coordinates of a point in rectangular and spherical coordinate systems: x=$r\cos\phi\sin\theta$, y=$r\sin\phi\sin\theta$, and z=$\cos\theta$

Again after lengthy manipulations, we obtain

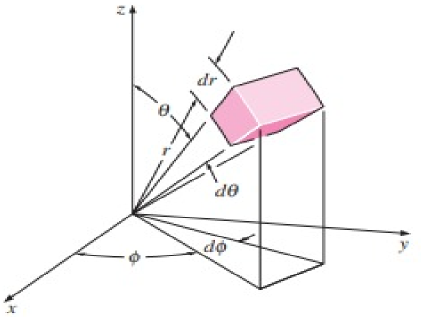


Figure 3.8: A differential volume element in spherical coordinates [10].

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(kr^2\frac{\partial T}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi}\left(k\frac{\partial T}{\partial\phi}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(k\sin\theta\frac{\partial T}{\partial\theta}\right)+\dot{g}=\rho c\frac{\partial T}{\partial t} \quad (3.3.21)$$

A spherical coordinate is initially at a uniform temperature and is cooled uniformly from the entire outer surface. Also, the temperature at any point in the spherical coordinate will change with time during cooling. There fore, this is a one - dimensional transient heat conduction problem since the temperature with in the spherical coordinate will change with the radial distance r and the time t. That is, T=T(r,t). The thermal conductivity is given to be variable, and there is no heat generation in the spherical coordinate. There fore, the differential equation that governs the variation of temperature in the spherical coordinate in this case the heat generation term equal to zero. We obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 k\frac{\partial T}{\partial r}\right) = \rho c\frac{\partial T}{\partial t} \tag{3.3.22}$$

3.3.3 Thermal conductivity of non-uniform fluids

The thermal conductivity defined by the equation (3.3.2) we consider the thermal conductivity of a gas to result from the net flux of molecular kinetic energy across a surface. The total kinetic energy per mole of the molecules of an ideal gas is simply its internal energy, which in turn equals $C_V T$. The average kinetic energy of a single molecule is there fore $C_V T$. Divided by Avogadro's number, N_a, and if we define a " molecular heat capacity" as $C_V^*{=}\frac{C_V}{N_a}$.

We assume as before that each molecule crossing the surface made its last collision at a distance $\frac{2L}{3}$ above or below the surface, and that its kinetic energy corresponds to the temperature at that distance. If T_o is the temperature at the surface the kinetic energy of a molecule at a distance $\frac{2L}{3}$ below the surface is

$$C_V^* T = C_V^*\left(T_o - \frac{2L}{3}\frac{dT}{dx}\right) \tag{3.3.23}$$

The energy transported in an down ward direction, per unit area and per unit time, is the product of this quantity and the molecular flux:

$$Q\uparrow = \frac{1}{4}n\bar{u}C_V^*\left(T_o - \frac{2L}{3}\frac{dT}{dy}\right) \tag{3.3.24}$$

In the same way, the energy transported by molecules crossing from above is

$$Q\downarrow = \frac{1}{4}n\bar{u}C_V^*\left(T_o + \frac{2L}{3}\frac{dT}{dy}\right) \tag{3.3.25}$$

The net rate of transport per unit area, which we identify with the heat current, is

$$Q = -\frac{1}{3} n\bar{u}C_V^* L \frac{dT}{dy}, \tag{3.3.26}$$

and by comparison with Eq. (3.3.2) we see that the thermal conductivity is

$$k = \frac{1}{3} n\bar{u}C_V^* L = \frac{1}{3}\frac{\bar{u}C_V^*}{\sigma} \tag{3.3.27}$$

Thus the thermal conductivity, like the viscosity, should be independent of density [24]. This is also in good agreement with experiments down to pressures so low that the mean free path becomes of the same order of magnitude as the dimensions of the container. The ratio of thermal conductivity to viscosity is

$$\frac{k}{\eta} = \frac{C_V^*}{m} = \frac{C_V}{mN_a} = \frac{C_V}{M}, \frac{kM}{\eta C_V} = 1 \tag{3.3.28}$$

where M is the molecular weight of the gas. There fore the theory predicts that for all gases this combination of experimental properties should equal unity.

3.3.4 The effect of temperature, pressure and chemical species on the thermal conductivity of fluids

The thermal conductivity is directly proportional to the density of the gas, the mean molecular speed, and the mean free path, which is the average distance traveled by an energy carrier (a molecule) before experiencing a collision [11].

$$K = \frac{1}{3} c_V \rho \bar{u} \lambda \tag{3.3.29}$$

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 p} \tag{3.3.30}$$

where K_B is Boltzmann's constant, $K_B = 1.381 \times 10^{-23} J/K$, d is the diameter of the gas molecule, and p is the pressure, representative values of which are included

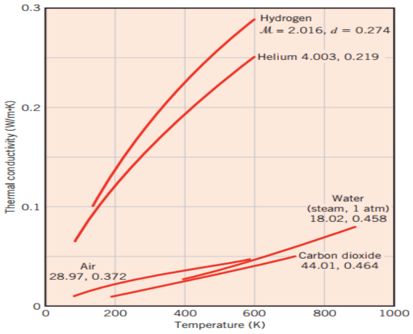


Figure 3.9: The temperature dependence of the thermal conductivity of selected gases at normal pressure molecular diameters (d) are in nm.Molecular weights of the gases are also shown [8].

in (Figure 3.9). As expected, the mean free path is small for high pressure or low temperature, which causes densely packed molecules.

The mean free path also depends on the diameter of the molecule, with larger molecules more likely to experience collisions than small molecules; in the limiting case of an infinitesimally small molecule, the molecules cannot collide, resulting in an infinite mean free path. The mean molecular speed, can be determined from the kinetic theory of gases, and Equation (3.3.29) may ultimately be expressed as

$$k = \frac{9\gamma - 5}{4} \frac{c_V}{\pi d^2} \sqrt{\frac{M k_B T}{N_A \pi}} \tag{3.3.31}$$

where the parameter γ is the ratio of specific heat capacity $\gamma = \frac{c_p}{c_V}$ equation (3.3.31) can be used to estimate the thermal conductivity of gas.

For most liquids, thermal conductivity typically increases with temperature. This is because higher temperatures generally lead to increased molecular motion, which can enhance the transfer of heat. The thermal conductivity of a liquid is highly dependent on its chemical composition. Different liquids have varying molecular structures and bonding characteristics that affect how heat is conducted.

The effect of pressure on the thermal conductivity of a liquid is less straightforward and can vary depending on the liquid. The thermal conductivity of non metallic liquids generally decreases with increasing temperature. The thermal conductivity of liquids is usually insensitive to pressure except near the thermodynamic critical point. Also, thermal conductivity generally decreases with increasing molecular weight. Values of the thermal conductivity are often tabulated as a function of temperature for the saturated state of the liquid. Liquid metals are commonly used in high heat flux applications.

3.3.5 The heat conduction velocity

The term "heat conduction velocity" in fluids is often used to refer to the thermal diffusivity of the fluid, which describes the rate at which heat spreads through the medium. This is a measure of how quickly a fluid can conduct heat compared to its ability to store thermal energy. It is defined as the ratio of thermal conductivity to the product of density and specific heat capacity at constant pressure [5]. Thermal diffusivity is formulated by the equation (3.3.32).

$$\alpha = \frac{k}{\rho c_p} \tag{3.3.32}$$

The thermal conductivity of a fluid is influenced by; the mean free path affects heat conduction as it determines how often fluid molecules collide. The relationship can be approximated by the formula.

$$\bar{u} = \frac{3k}{c_V \lambda} = \frac{3\rho c_p \alpha}{c_V} \frac{\sqrt{2}\pi d^2 p}{k_B T} \tag{3.3.33}$$

3.4 Modified Eucken Formula

Eucken proposed equation (3.4.1) for pure gases by separating the contributions due to translational and internal degrees of freedom in to separate terms:

$$\frac{kM}{\eta C_V} = \frac{1+\frac{9}{4}}{\frac{C_V}{R}} = 1 + \frac{\frac{9}{4}}{(\frac{C_p}{R}) - 1} \tag{3.4.1}$$

Eucken correlation for pure gases is indicated in equation (3.4.1). Equation (3.4.2) is often referred to as the modified eucken correlation which was used by svehla (1962) in his compilation for high-temperature gas properties [12].

$$\frac{kM}{\eta C_V} = 1.32 + \frac{1.77}{C_V/R} = 1.32 + \frac{1.77}{(C_p/R) - 1} \tag{3.4.2}$$

The modified Eucken equation (3.4.2) predicts higher values of k than those of Eucken equation (3.4.1). This difference increases when C_V increases to approximately $12.65 mol^{-1} K^{-1}$.

In the case of liquids, the situation is more complex due to stronger intermolecular forces and different molecular dynamics compared to gases. The modified Eucken equation for liquids incorporates these complexities and is expressed as

$$K = \frac{1}{3}\frac{\eta c_p}{\rho}\frac{1}{1-\frac{\alpha}{\xi}} \tag{3.4.3}$$

where ξ is a factor that accounts for molecular interactions , and η is the dynamic viscosity.

Chapter 4

Transport Phenomena by Diffusion

4.1 Momentum Transport by Diffusion

Momentum conduction involves the transfer of momentum due to molecular collisions and interactions. When fluid molecules move and collide with each other, momentum is transferred from one molecule to another, leading to the over all conduction of momentum through the fluids [13, 14]. We know that the property by virtue of which a fluid opposes the relative motion between the adjacent layers is known as viscosity. It is quantitatively expressed in terms of the coefficient of viscosity, which is defined as the tangential force (F) per area when a unit velocity gradient exists in a direction perpendicular to the direction of motion. Mathematically, for small velocity gradient is given by the equation (4.1.1).

$$\frac{F}{A} = \tau_{xy} = -\eta \frac{du_x}{dy} \tag{4.1.1}$$

where τ_{xy} is denotes molecular momentum diffusion flux and $\frac{du_x}{dy}$ is the velocity gradient along the positive y-direction [25]. The negative sign signifies that the viscous force is directed against the velocity gradient.

4.2 Momentum Transport Equation

For the general three-dimensional situation, the viscous stresses acting on an element of fluid are shown in (Figure 4.1). We find that the diffusive momentum flux is given by τ, where τ is the stress tenser.

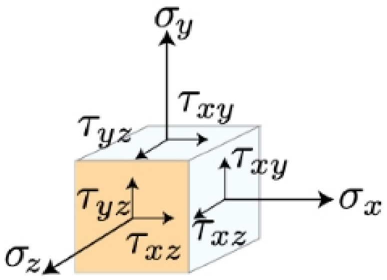


Figure 4.1: Three dimensional stress state [25].

$$\tau = \begin{pmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{pmatrix} \tag{4.2.1}$$

The stress tenser is a 3x3 matrix. The component τ_{ij} of the stress tensor is the stress that acts on the plane perpendicular to the axis i and in the direction of the axis j for foreground faces and in the opposite direction for background faces. Foreground faces are those where the normal vector is aligned to a coordinate axis and background faces those where the normal vector is in the opposite direction to a coordinate axis [15]. Normal stresses are those perpendicular to the face upon which they act, i.e. $\tau_{xx} = \sigma_x$, $\tau_{yy} = \sigma_y$ and $\tau_{zz} = \sigma_z$ and shear or tangential stresses are those tangent to the surface upon which they act, i.e. τ_{xy}, τ_{xz}, τ_{yx}, τ_{yz}, τ_{zx} and τ_{zy}. For a general three-dimensional flow equation(4.1.1) generalizes.

$$\tau_{ij} = \eta \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \delta_{ij} \mu \overrightarrow{\nabla} \cdot \overrightarrow{u} \tag{4.2.2}$$

where μ the second viscosity coefficient. Expanding equation (4.2.2) to

$$\tau = \eta \begin{pmatrix} 2\frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} & \frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1} \\ \frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_2} & 2\frac{\partial u_2}{\partial x_2} & \frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} \\ \frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3} & \frac{\partial u_3}{\partial x_2} + \frac{\partial u_2}{\partial x_3} & 2\frac{\partial u_3}{\partial x_3} \end{pmatrix} + \mu \overrightarrow{\nabla} \cdot \overrightarrow{u} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.2.3}$$

where i and j are indices that represents the x, y, or z- directions, δ_{ij} is the kronecker delta ($\delta_{ij} = 0$) if $i \neq j$, and $\delta_{ij} = 1$ if i=j, and μ is the longitudinal viscosity. For most fluids, $\mu = -\frac{2\eta}{3}$. This value implies that spherically symmetric expansion and contraction processes are frictionless. The kinetic viscosity ν is defined as the ratio between viscosity to density of the fluid ($\frac{\eta}{\rho}$). The deformation or strain rate **S** is the symmetric part of the velocity gradient tensor,

$$\mathbf{S} = \frac{1}{2} \left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right] \tag{4.2.4}$$

The rate of deformation represents how fast the fluid particle deforms. The deformation is expressed as change of angles and change of unitary volume per unit time of a fluid particle. Using the strain rate, the Navier-Poission constitute equation (4.2.2) can be written as

$$\tau = 2\eta \mathbf{S} + \mu \overrightarrow{\nabla} \cdot \overrightarrow{u} \delta_{ij} \tag{4.2.5}$$

For the most frequently encountered substances, such as water and air, the viscosity depends only on thermodynamic variables, like the temperature, and is independent on the velocity gradient or deformation rate. These fluids are called Newtonian and the constitutive relation between the viscous stress and the deformation rate is linear. The second law of thermodynamics dictates that $\eta \geq 0$ and $\mu + \frac{2}{3}\eta \geq 0$.

4.3 Mass Transport by Binary Diffusion

The movement of chemical species A through a binary mixture of A and B to the concentration gradient of A. Ficks law of diffusion is the mass transfer analog of Newtons law of viscosity for momentum transport, and Fouriers law of heat conduction for energy transport [13].

Suppose, in a binary mixture of A and B, that A is diffusing to the left and B to the right, this molecular transport of one substance relative to another is known as diffusion (also known as mass diffusion, and concentration diffusion) (see Figure 4.2). The rate equation for mass diffusion is known as Ficks law, and for the transfer of species A in a binary mixture of A and B, it may be expressed in vector form as

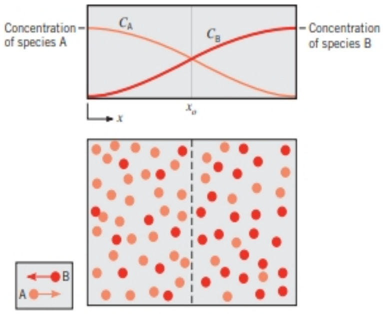


Figure 4.2: Mass transfer by diffusion in a binary mixture [28].

$$\frac{\omega_{Ay}}{A} = j_{Ay} = -\rho D_{AB}\frac{d\omega_A}{dy} \tag{4.3.1}$$

where $\frac{\omega_{Ay}}{A}$ is the diffusive mass flow rate of species A per unit area (or diffusive mass flux) is proportional to the mass fraction difference divided by the plate thickness, ρ is the density of the species A and B, and proportionality factor D_{AB} is the diffusivity of the species A and B [28].

For a mixture of two chemical species, the local mass average velocity v is defined as

$$v = \frac{\rho_A v_A + \rho_B v_B}{\rho_A + \rho_B} = \frac{\rho_A v_A + \rho_B v_B}{\rho} = \omega_A v_A + \omega_B v_B \tag{4.3.2}$$

j_{Ay} is defined as the mass flux relative to the mass average velocity of the mixture v_y is defined as

$$v_y = \omega_A v_{Ay} + \omega_B v_{By} \tag{4.3.3}$$

Equation (4.3.1) relates the diffusive mass flux to the concentration gradient, The y component of the diffusive mass flux is

$$j_{Ay} = \rho\omega_A \left(v_{Ay} - v_y\right) \tag{4.3.4}$$

This is the flux relative to a coordinate system moving with the mass average velocity v. The diffusive mass flux of B is defined analogously.

As the two chemical species interdiffuse, there is, locally, a shifting of the center of mass in the y direction if the molecular weights of A and B different [26]. The mass fluxes j_{Ay} and j_{By} are so defined that $j_{Ay} + j_{By} = 0$.

When equations similar to Equation (4.3.1) are written for diffusion in the x and z directions, and the three equations added vectorially, we then get the vector form of Ficks law for the diffusive mass flux vector of species A:

$$j_A = -\rho D_{AB} \nabla \omega_A \tag{4.3.5}$$

A similar relation can be written down for the diffusive mass flux vector of species B:

$$j_B = -\rho D_{BA} \nabla \omega_B \tag{4.3.6}$$

$$j_A + j_B = 0 \tag{4.3.7}$$

If Equations (4.3.5) and (4.3.6) are substituted into Equation (4.3.7), and it is recognized that $\nabla\omega_A = -\nabla\omega_B$, since $\omega_A + \omega_B = 1$ for a binary mixture, it follows that

$$D_{AB} = D_{BA} \tag{4.3.8}$$

The molar flow rate of species A at steady state is

$$J_{Ay} = \frac{W_{Ay}}{A} = -cD_{AB}\frac{dX_A}{dy} \tag{4.3.9}$$

where W_{Ay} is the number of moles of species A transported in the y direction per unit time, c is the total molar concentration of the species A and B, and x_A is the mole fraction of species A.

For a mixture of two chemical species, the local molar average velocity v^* is defined as

$$v^* = \frac{c_A v_A + c_B v_B}{c_A + c_B} = \frac{c_A v_A + c_B v_B}{c} = X_A v_A + X_B v_B \tag{4.3.10}$$

J_{Ay} is defined as the molar flux relative to the local molar average velocity the mixture v_y^* is defined as

$$v_y^* = X_A v_{Ay} + X_B v_{By} \tag{4.3.11}$$

$$J_{Ay} = cX_A\left(v_{Ay} - v_y^*\right) \tag{4.3.12}$$

A similar relation for the diffusive mass flux vector of species B:

For diffusion in three dimensions, the vector form of Fick's law for the diffusive molar flux vectors are written for species A and B as

$$J_A = -cD_{AB}\nabla X_A \tag{4.3.13}$$

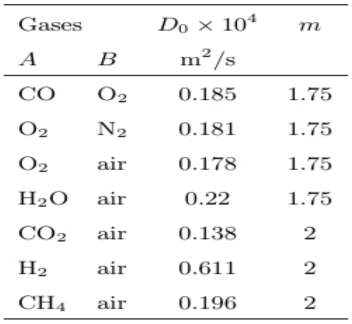
$$J_B = -cD_{BA}\nabla X_B \tag{4.3.14}$$

If Equations (4.3.13) and (4.3.14) are substituted to give equation (4.3.15).

$$J_A + J_B = 0 \tag{4.3.15}$$

where again $D_{AB} = D_{BA}$. To predicting the mass diffusivity D_{AB} for the binary mixture of two gases, A and B. Assuming ideal gas behavior, kinetic theory may be used to show that

$$D_{AB} \approx \frac{1}{3}\overline{u}\lambda \sim p^{-1}T^{\frac{3}{2}} \tag{4.3.16}$$



Gases		$D_0 \times 10^4$	m
A	B	m^2/s	
CO	O_2	0.185	1.75
O_2	N_2	0.181	1.75
O_2	air	0.178	1.75
H_2O	air	0.22	1.75
CO_2	air	0.138	2
H_2	air	0.611	2
CH_4	air	0.196	2

Table 4.1: Coefficients for the mass diffusivity of binary mixtures of gases at $p_0 =$ 101300 Pa and $T_0 = 273$ K [13].

where $\overline{u}$ increases with increasing temperature and decreasing molecular weight, and therefore the mass diffusivity increases with increasing temperature and decreasing molecular weight. Because λ is inversely proportional to gas pressure, the mass diffusivity decreases with increasing pressure. This relation applies for restricted pressure and temperature ranges and is useful for estimating values of the mass diffusivity at conditions other than those for which data are available [27].

For binary liquid solution the small concentrations of A (the solute) in B (the solvent), D_{AB} is known to increase with increasing temperature.

The mass diffusion coefficients typically depend on the temperature, the chemical composition and the pressure. For gases, a good approximation is

$$D = D_0 \left(\frac{T}{T_0} \right) \frac{p_0}{p} \tag{4.3.17}$$

which reflects that the diffusion coefficient D increases with temperature but decreases with pressure and the molar mass. See Table 4.1.

For liquids, the diffusion coefficient increases with temperature.

4.3.1 Mass transport equation

Mass can not be created or destroyed, so there is no generation term in the balance equation [18]. The differential equation of mass conservation, called the continuity equation, is obtained

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \tag{4.3.18}$$

Using indicial notation, and for cartesian coordinates,

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i), i = 0 \tag{4.3.19}$$

Noting that

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + u \cdot \nabla \rho \tag{4.3.20}$$

The continuity equation can also be written as

$$\frac{1}{\rho} \frac{D\rho}{Dt} = -\nabla \cdot u \tag{4.3.21}$$

For an incompressible fluid or a liquid, the density is constant and the continuity equation simplifies to

$$\nabla \cdot u = 0 \tag{4.3.22}$$

In indicial notation and for Cartesian coordinates it can be written in the more compact form

$$u_i, i = 0 \tag{4.3.23}$$

Recall that the divergence of the velocity is the unit dilatation per unit time of an infinitesimal volume of fluid Vol (i.e. the rate of change of the volume of a fluid particle per unit volume),

$$div(u) = \nabla \cdot u = \frac{1}{Vol}\frac{dVol}{dt} \tag{4.3.24}$$

For a liquid, since the volume of a fluid particle (or a small fluid volume) is constant, the dilatation is zero. Thus the divergence of the velocity in an incompressible velocity field is zero.

4.3.2 Molecular collisions and diffusion

Molecular collisions are the underlying mechanism that drives diffusion. As molecules collide and interact, they move from areas of high concentration to low concentration, leading to the spreading out of substances this processes is called diffusion. Diffusion is the transport of material due to concentration gradients or more precisely due to gradients in the chemical potential [16].

4.3.3 Diffusion velocity and partial velocity

In a multi component system the various species will normally move at different velocities; accordingly, an evaluation of a velocity for the gas mixture requires the averaging of the velocities of each species present [16,17]. The mass-average velocity for a multi component mixture is defined in terms of the mass densities and velocities of all components by

$$\mathbf{v} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v_i}}{\sum_{i=1}^{n} \rho_i} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v_i}}{\rho} \tag{4.3.25}$$

where $\mathbf{v}_i$, denotes the absolute velocity of species i relative to stationary coordinate axes.

The molar-average velocity for a multi component mixture is defined in terms of the molar concentrations of all components by

$$\mathbf{v}^* = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{\sum_{i=1}^{n} c_i} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{c} \tag{4.3.26}$$

The velocity of a particular species relative to the mass-average or molar average velocity is termed a diffusion velocity. We can define two different diffusion velocities.

$\mathbf{v}_i - \mathbf{v}$, the diffusion velocity of species i relative to the mass-average velocity.

$\mathbf{v}_i - \mathbf{v}^*$, the diffusion velocity of species i relative to the molar-velocity average.

According to Fick's law, a species can have a velocity relative to the mass or molar average velocity only the gradients in the concentration [2].

If partial velocity typically refers to the velocity component of a particular species with in a mixture or multi-component system. Each component in a mixture can have its own partial velocity. Which describes how fast that particular component is moving. In a gas mixture, for instance, the partial velocity of a gas component i, can be related to the over all velocity of mixture and the relative motion of that component i $\mathbf{v_i} = v - u_i$, where $\mathbf{v_i}$ is the partial velocity of component i v is the velocity of the over all gases mixture and u_i is the velocity of component i relative to the mixture.

4.4 Molecular Interpretation of Diffusion Transport

The diffusivity coefficients can be estimated for gases at low densities by the kinetic theory of gases. In this theory, the gas molecules are considered rigid spheres of mass m, which neither repel nor attract. Let us assume that the density of molecules is N and that the molecules transport the property Γ. Γ represents the velocity u for momentum transport, specific enthalpy (h) for heat transport and chemical concentration for mass transport of the species A. According to the lattice model for gases, at equilibrium the relative velocity of the molecules with respect to the fluid velocity is stochastically distributed in all spatial directions. We want to calculate the net flux of property Γ to the right across the surface [13]. Thus,

$$\Psi = net\ flux = \Psi_{left} - \Psi_{right} \tag{4.4.1}$$

$= \frac{1}{6}Nm\overline{u}\Gamma(left) - \frac{1}{6}Nm\overline{u}\Gamma(right)$
$= \frac{1}{6}Nm\overline{u}(\Gamma(left) - \Gamma(right))$

$$\frac{1}{6}Nm\overline{u}(\Gamma(x-\frac{l}{2}) - \Gamma(x+\frac{l}{2}) \tag{4.4.2}$$

The coefficient $\frac{1}{6}$ stems from distributing the molecules randomly in all three Cartesian axes and, for each axis, in the two directions. Applying Taylor series around x,

$$\Gamma(x-\frac{l}{2}) = \Gamma(x) - \frac{d\Gamma(x)}{dx}\frac{l}{2} + \frac{d^2\Gamma(x)}{dx^2}\frac{l^2}{4} - - - - - - - \tag{4.4.3}$$

$$\Gamma(x+\frac{l}{2}) = \Gamma(x) + \frac{d\Gamma(x)}{dx}\frac{l}{2} + \frac{d^2\Gamma(x)}{dx^2}\frac{l^2}{4} - - - - - - - \tag{4.4.4}$$

and subtracting $\Gamma(x-\frac{l}{2}) - \Gamma(x+\frac{l}{2}) \approx \frac{d\Gamma(x)}{dx}l$ The length l is related to the distance that the molecules travel between collisions in direction x and is proportional to the mean-free path. Thus,

$$\Psi = \frac{-1}{6} N m \overline{u} l \frac{d\Gamma(x)}{dx} \tag{4.4.5}$$

$$D = \frac{1}{6} N m \overline{u} l \tag{4.4.6}$$

$\Psi = \tau, q, and J_A$ and D=$\mu, k, and\ D_{AA}$. Therefore, for a gas at low pressures, the following relation between the diffusion transport coefficients can be derived,

$$\mu \approx \frac{k}{c_p} \approx D_{AA} \tag{4.4.7}$$

where D_{AA} is the self-diffusion parameter.

4.5 Coupled Heat, Mass Transport by Molecular Diffusion

The concentration gradients can induce heat transport and, vice versa, temperature gradients can cause mass transport. Heat transport by diffusion can be caused by three effects: temperature gradients, mass diffusion and concentration gradients,

$$\dot{Q} = \dot{Q}^T + \dot{Q}^m + \dot{Q}^{Dufour} \tag{4.5.1}$$

The first term, $\dot{Q}^T$, due to temperature gradients, is given by Fouriers law of conduction, $\dot{Q}^m$ is the heat transport due to mass diffusion, and $\dot{Q}^{Dufour}$ is the Dufour or diffusion-thermo effect,

$$\dot{Q}^m = \sum_{A=1}^{n_{esp}} h_A j_A \tag{4.5.2}$$

$h_A = e + \frac{p}{\rho}$ is specific enthalpy of species A.

$$\dot{Q}^{Dufour} = RT \sum_{A=1}^{n_{esp}} \sum_{B=1}^{n_{esp}} \frac{x_B D_A^T}{m_A D_{AB}} \left(\frac{j_A}{\rho_A} - \frac{j_B}{\rho_B} \right) \tag{4.5.3}$$

where R is the universal gas constant, and D_A^T are the thermal diffusion coefficients. Mass transport by diffusion can be produced by concentration gradients, temperature gradients, pressure gradients for each chemical species,

$$j_A = j_A^m + j_A^T + j_A^p \tag{4.5.4}$$

For binary systems ($1 \leq A, B \leq 2$), mass transport can be simplified to

$$j_A = -\rho D_{AB} \nabla \omega_A - D_A^T \nabla (\ln T) + \frac{m_A m_B D_{AB} \omega_A}{\rho} \nabla p \tag{4.5.5}$$

Coupled heat and mass transport through molecular diffusion involves the simultaneous movement of heat and mass in a medium due to concentration and temperature gradients.

Chapter 5

Conductive Heat Transfer in Boundary Layer

5.1 Conductive Heat Transfer at Boundary Surfaces

As for the flow field, boundary layers can be laminar or turbulent. Laminar flow is typically orderly, predictable and deterministic. Turbulent flow is always three-dimensional, unsteady and chaotic. In turbulence flow, there are random fluctuations of the fluid field transport properties [19].

Turbulent involves rapid fluctuations in time of the velocity at any point as the sum of a time-averaged component and fluctuation. The transition from laminar to turbulent flow in pipes was first described quantitatively by Reynolds in 1883. The number that governs the transition from laminar to turbulent flow is the transition Reynolds number(Re), which depends on the geometry of the flow among other factors such as the free-stream turbulence and surface roughness [20, 21]. The dimensionless parameter is given by the equation (5.1.1)

$$R_e = \frac{D\rho u}{\eta} \tag{5.1.1}$$

Taking into account the qualitative structure of the boundary layer, the transport equations can be simplified within interfaces. This is known as Prandtls boundary layer theory (1904), which states that for high Reynolds numbers, the boundary layer thickness δ at a position x = L from the beginning of the boundary layer is much smaller than L, i.e. $\delta \leq L$, the local Reynolds number is defined as

$$R_{eL} = \frac{Lu\rho}{\eta} \tag{5.1.2}$$

5.2 Earth's Ocean - Atmosphere Boundary Layer

In the atmosphere, the boundary layer may be defined as the thin layer extending from the earths surface up ward in which the airflow strongly experiences the effect of the earths surface friction [22]. Carrying the analogy of molecular diffusion to turbulent transport in the atmosphere, we can express the fluxes of momentum, heat, and moisture(E) in terms of gradients in the vertical direction z;

$$\tau = -\mathbf{K_m}\rho\frac{\partial\overline{u_x}}{\partial z} \tag{5.2.1}$$

$$Q = -\mathbf{K_h}\rho c_p\frac{\partial\overline{\theta}}{\partial z} \tag{5.2.2}$$

$$E = -\mathbf{K_q}\rho\frac{\partial\overline{q}}{\partial z} \tag{5.2.3}$$

where $\mathbf{K_m}, \mathbf{K_h}$, and $\mathbf{K_q}$ are the turbulent exchange coefficients for momentum, heat, and moisture; $\overline{u_x}, \overline{\theta}$, and $\overline{q}$ are the mean stream wise wind component, mean potential temperature, and mean specific humidity. The extension of that concept to turbulent exchange in the atmosphere is known as **K**-theory.

We start with definition of velocity components u_x, u_y, and u_z along right handed coordinate axes x, y, and z, respectively these velocity and scalars such as θ and q can each be separated in to mean component denoted by an over bar and an eddy component denoted by a prime; $u_x = \overline{u}_x + u'_x$, $u_y = \overline{u}_y + u'_y$, $u_z = \overline{u}_z + u'_z$, $\theta = \overline{\theta} + \theta'$, and $q = \overline{q} + q'$ By definition, we have $\overline{u'}_x = \overline{u'}_y = \overline{u'}_z = \overline{\theta'} = \overline{q'} = 0$. If the x-axis is defined in the direction of the mean flow, $\overline{u}_y = \overline{u}_z = 0$; only $\overline{u}_x \neq 0$. Over a flat, level, homogeneous surface, we take x and y to be horizontal and z to be vertical and positive up wards.

The fluxes can now be written as

$$\tau'_{zx} = -\rho\overline{u'_x u'_z} \tag{5.2.4}$$

$$Q = -\rho c_p \overline{u'_z \theta'} \tag{5.2.5}$$

$$E = -\rho\overline{u'_z q'} \tag{5.2.6}$$

Prandtl hypothesized that turbulent fluctuations can be parameterized in terms of the mean field variables if we postulate a characteristic mixing length l' for the eddy motion somewhat like the mean free path in molecular motion. According to this hypothesis a parcel of air at level z which is displaced vertically through a height interval l' carries the mean momentum of the original level to the new level where it mixes with the air at the new level to cause a fluctuation in the mean momentum of the new level. The extent of the fluctuation will depend upon the magnitude of the mixing length and the vertical gradient of the mean velocity. Thus, for the u_x-components $u'_x = -l'\partial\overline{u}_x/\partial z$. Since $\partial\overline{u}_x/\partial z$ is usually positive in the boundary layer, l' is positive for down ward displacement($u'_z < 0$) and negative for up ward displacement($u'_z > 0$). We may, therefore, write

$$\tau'_{zx} = -\rho\overline{u'_x u'_z} \tag{5.2.7}$$

$u'_z = l'\frac{\partial \overline{u}_x}{\partial z}$, since u'_x and l' are opposite sign by the above-mentioned convention of sign. Thus,

$$\tau'_{zx} = \rho \mathbf{K_m} \left(\frac{\partial \overline{u}_x}{\partial z} \right) \tag{5.2.8}$$

where l_x is the mean mixing- length and $\mathbf{K_m} = l_x^2 \left(\frac{\partial \overline{u}_x}{\partial z} \right)$, is called the coefficient of eddy vicosity for the vertical transport of x- momentum. Hence, we may write (5.2.8) in the form

$$\frac{\tau_o}{\rho} = \mathbf{K_m} \frac{\partial \overline{u}_x}{\partial z} \tag{5.2.9}$$

where $\frac{\tau_o}{\rho}$ has the dimension of velocity- squared and is written as u_x^{*2}, where u_x^* is called the friction velocity [29].

The logical choice is the friction velocity for the velocity and a length proportional to height z above the surface. This means that we put $\mathbf{K_m} = \kappa z u_x^*$, where κ, the constant of proportionality is vonkarman constant ($\kappa = 0.4$). Making the substitutions in equation (5.2.9) and simplifying we obtain,

$$\frac{\partial \overline{u}_x}{\partial z} = \frac{u_x^*}{\kappa z} \tag{5.2.10}$$

Integrating (5.2.10) with respect to z, we get the logarithmic velocity profile,

$$\overline{u}_x = \left(\frac{u_x^*}{\kappa} \right) \ln \left(\frac{z}{z_o} \right) \tag{5.2.11}$$

where z_o, which is called the roughness length, is the constant of integration chosen so that u_x=0 at z=z_o. The logarithmic wind profile is strictly valid only for the neutral atmosphere.

As the atmosphere becomes more stable or unstable, the profile departs from being logarithmic (Figure 5.1). For most applications very close to the ground (i.e.,$z < 10m$),however, the wind profile can be assumed to be almost always logarithmic.

This allows us to use the relation ships in (5.2.1), (5.2.2), and (5.2.3) to compute the fluxes from gradient measurement of properties in the layer. Thus, if $\overline{u}_{x1}$ and $\overline{u}_{x2}$ are the mean winds measured at two heights z_1 and z_2, we have

$$\overline{u}_{x2} - \overline{u}_{x1} = \frac{u_x^*}{\kappa} \ln\left(\frac{z_2}{z_1}\right) \tag{5.2.12}$$

$$\mathbf{K_m} = \kappa z_r u_x^* = \frac{\kappa^2 z_r}{\ln(z_2/z_1)}(\overline{u}_{x2} - \overline{u}_{x1}) \tag{5.2.13}$$

Substituting for u_x^* from (5.2.9). If the reference height z_r is the geometric mean of

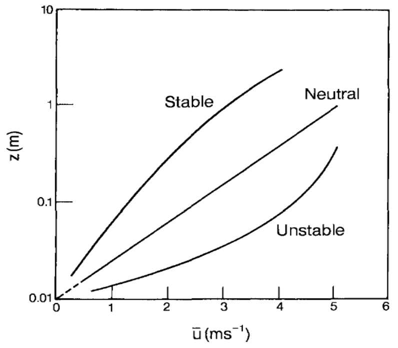


Figure 5.1: Wind profile in stable, neutral, and unstable air [29].

z_1 and z_2, that is $(z_1 z_2)^{\frac{1}{2}}$ then at z=z_r the mean wind speed is equal to $(\overline{u}_{x1} + \overline{u}_{x2})/2$. Now, if we assume that close to the ground K_m=K_h= K_q, all we need for computing the vertical fluxes are the mean values of θ and q measured at the same heights at which $\overline{u}_{x1}$ and $\overline{u}_{x2}$ are observed [29]. The fluxes of momentum, heat, and moisture assume the form

$$\frac{\tau}{\rho} = -\left(\frac{\kappa}{\ln(z_2/z_1)}\right)^2 (\overline{u}_{x2} - \overline{u}_{x1})^2 \tag{5.2.14}$$

$$\frac{Q}{\rho c_p} = -\left(\frac{\kappa}{\ln(z_2/z_1)}\right)^2 (\overline{u}_{x2} - \overline{u}_{x1})(\overline{\theta}_2 - \overline{\theta}_1) \tag{5.2.15}$$

$$\frac{E}{\rho} = \left(\frac{\kappa}{\ln(z_2/z_1)}\right)^2 (\overline{u}_{x2} - \overline{u}_{x1})(\overline{q}_2 - \overline{q}_1) \tag{5.2.16}$$

Estimation of fluxes from profiles is subject to several constraints. We require the fluxes to be constant with height, which implies uniform flat terrain and observing heights well within the surface layer. The logarithmic law applies strictly to neutral surface layers; the estimates become less reliable as the stability departs from neutral and the profiles deviate more and more from logarithmic.

5.3 Earth's Land - Atmosphere Boundary Layer

The land surface and the atmospheric boundary layer (ABL) are crucial components of Earth's climate system and play significant roles in weather and climate dynamics [20,21]. The roughness length varies widely with the physical characteristics of the surface and the average height of the obstacles to airflow. When z_o is very large as over dense vegetation, a modified logarithmic wind profile as given below has been found to represent the observations some what better.

$$\overline{u}_x = \left(\frac{u_x^*}{\kappa}\right) \ln\left\{\frac{z-d}{z_o}\right\} \tag{5.3.1}$$

where d is called the datum-level displacement [23]. Corresponding expressions for heat and humidity, assuming the same d for both are

$$\overline{\theta}_z - \overline{\theta}_0 = \frac{T^*}{\kappa} \ln\left(\frac{z-d}{z_h}\right) \tag{5.3.2}$$

$$\overline{q}_z - \overline{q}_0 = \frac{q^*}{\kappa} \ln\left(\frac{z-d}{z_q}\right) \tag{5.3.3}$$

where z_h and z_q are new roughness lengths for heat and humidity (analogous to z_0) q^* is the humidity scale analogous to T^* defined

$$q^* = -\frac{\overline{u_z' q'}}{u_x^*} \tag{5.3.4}$$

The traditional nondirectional surface layer functions become

$$\phi_m = \frac{\kappa(z-d)}{u_x^*}\frac{\partial \overline{u}_x}{\partial z}, \tag{5.3.5}$$

$$\phi_h = \frac{\kappa(z-d)}{T_x^*}\frac{\partial \overline{\theta}}{\partial z}, \tag{5.3.6}$$

$$\phi_q = \frac{\kappa(z-d)}{q^*}\frac{\partial \overline{q}}{\partial z} \tag{5.3.7}$$

where ϕ_m, ϕ_h, and ϕ_q are functions now of (z-d) in steady of z. It is readily seen that (5.3.5), (5.3.6), and (5.3.7) are equivalent to flux- gradient expressions [29].

$$\frac{\tau}{\rho} = u_x^{*2} = -\left[\kappa(z-d)u_x^*\phi_m^{-1}\right]\frac{\partial \overline{u}_x}{\partial z} = \mathbf{K}_m\frac{\partial \overline{u}_x}{\partial z} \tag{5.3.8}$$

$$\frac{Q}{\rho c_p} = u_x^* T^* = -\left[\kappa(z-d)u_x^*\phi_h^{-1}\right]\frac{\partial \overline{\theta}}{\partial z} = -\mathbf{K}_h\frac{\partial \overline{\theta}}{\partial z} \tag{5.3.9}$$

$$\frac{E}{\rho} = u_x^* q^* = -\left[\kappa(z-d)u_x^*\phi_q^{-1}\right]\frac{\partial \overline{q}}{\partial z} = -\mathbf{K}_q\frac{\partial \overline{q}}{\partial z} \tag{5.3.10}$$

In neutral conditions, $\mathbf{K_m}= \mathbf{K_h}= \mathbf{K_q}=\kappa(z-d)u_x^*$.

The modified logarithmic profiles for humidity and temperature provide a useful framework for understanding how these variables vary with height in the atmosphere. They can be tailored to account for surface characteristics, atmospheric stability, and interactions between heat and moisture.

Chapter 6

Summary and Conclusion

Transport properties are based on the law of conservation of energy for a thermodynamic system ($dU = dQ + dW$). In the thermally isolated system that can not exchange heat with its surrounding ($dQ = 0$).

In the second law of thermodynamics or entropy ($ds = \frac{dq_{rev}}{T} + ds_{irrev}$) in this concept a molecular collision causes molecules in a substance moving and vibrating randomly. This movement is a result of the thermal energy they possess, which causes them to move in various directions at different speeds. The average kinetic energy of the molecules is directly related to the temperature of the substance ($\frac{3}{2}K_BT$).

Heat is transferred by molecular action from hotter regions to colder; this process is called conduction. The heat conduction is described by fourier's law. It is fundamentally governed by the heat diffusion equation or multi dimensional heat differential equation.

The proportionality constant in the heat conduction equation is called thermal conductivity. It is directly proportional to the density of the gas, the mean molecular speed, and the mean free path. The ratio of thermal conductivity to the product of density and specific heat capacity at constant pressure is called thermal diffusivity.

Eucken proposed that $(\frac{kM}{\eta C_V})$ be modified for polyatomic gases by separating the contributions due to translational and internal degrees of freedom into separate terms. Newtons law of viscosity describes the momentum transport by conduction involves the transfer of momentum due to molecular collisions and interactions is governed by the general three-dimensional flow equation: $\left(\tau_{ij} = \eta\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \delta_{ij}\mu\vec{\nabla}\cdot\vec{u}\right]\right)$.
Fick's law describes the movement of mass from higher concentration to lower concentration, which is called diffusion. The governing differential equation of mass conservation is called continuity equation and a species can have a velocity relative to the mass or molar average velocity only the gradients in the concentrations. The concentration gradients can transport heat and temperature gradients can cause mass transport.

The boundary layer is the lowest 1-2 km of the atmosphere, the region most directly influenced by the exchange of momentum, heat, and water vapor and other chemical species at the earth's surface. The boundary layer, describing the surface layer over flat grounds, can be laminar or turbulent. The mean velocity profile in the surface layer under neutral stability conditions is described by the logarithmic function $\left[\overline{u}_x = \left(\frac{u_x^*}{\kappa}\right)\ln\left(\frac{z}{z_o}\right)\right]$.

The roughness length varies widely with the physical characteristics of the surface and the average height of the obstacles to airflow. When z_o is very large as over dense vegetation, a modified logarithmic wind profile $\left[\overline{u}_x = \left(\frac{u_x^*}{\kappa}\right)\ln\left\{\frac{z-d}{z_o}\right\}\right]$.

Finally, we applied the energy conservation principle to the turbulent fluctuations of air molecule to the surface layer of earth's-atmospheric boundary. The fluctuating air molecule is calculated by using time-average velocity logarithmic profile to predict the weather/climate condition is neutral, unstable or stable.

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