Chapter 3

THEORIES OF VISCOSITY

Among the theories of viscosity (a measure of internal friction) of fluids, those related to gases are well developed compared to the situation of liquids. In a gas, momentum transfer occurs due to collisions between the molecules, while forces between the closely packed molecules cause the momentum transfer in liquids. Because of the complexities involved in the liquid momentum transfer mechanisms - including those due to dispersive and electrostatic forces - there has been no simple basis for the estimation of liquid viscosities. The simplicity of approach adopted in the kinetic theory applied to gas viscosity, which is of natural interest to the development of the theories on liquid viscosity will be dealt first in our discussion. This will be followed by the theories on the viscosities of dense gases and liquids. An account of the treatment carried out on the lean and dense gases as well as the liquid phase taken together will also be given. For a clear understanding of the theories of pure fluid and mixture viscosities, it is helpful to refer to the critical reviews like those by: Brush[1], Touloukian[2], Stephan and Lucas[3], Viswanath and Natarajan[4], Monnery et al.[5], Poling et al.[6] and Mehrotra et al.[7]

3.1 THEORIES OF GAS VISCOSITY

The case of lean gases involving momentum transfer through translatory motion with fewer collisions is described by the kinetic theory of gases. From the application of the kinetic theory of gases based on the mean free path for colliding gas molecules (as hard spheres), Maxwell deduced that the gas viscosity is independent of density and proportional to the square root of the absolute temperature. This is seen from the expression derived for the gas viscosity:

$$\eta \propto \frac{(MT)^{(1/2)}}{\sigma^2}$$

(3.1)

In Eq. (3.1), the terms M, T and σ respectively denote the molecular mass, absolute temperature in K and hard-sphere diameter (Å). Maxwell tested his theory with data on air. Hirschfelder *et al.*[8] have assigned a value of 26.69 for the proportionality constant in Eq. (3.1). Expressing the viscosity coefficient in terms of the velocity distribution function and the inter-atomic force law, Maxwell developed a more general theory. In the special case of the inverse fifth power repulsive force, the viscosity coefficient was shown to be proportional to the absolute temperature. A dimensional analysis by Rayleigh showed that, for atoms repelling with an nth power force law, viscosity varies as the $[(n+3)/(2n-2)]^{th}$ power of temperature. In the case of colliding molecules, a correction factor known as the collision integral, Ω_V, could be introduced into Eq. (3.1). The values of collision integral are reported by Chapman and Cowling[9]. For non-attracting molecules, Ω_V becomes unity. Using Hirschfelder's assignment[8] of 26.69 to the proportionality constant and introducing the term Ω_v, Eq. (3.1) can be modified as:

$$\eta_{CE} = 26.69 \frac{(MT)^{(1/2)}}{\sigma^2 \Omega_v}$$

(3.2)

Equation (3.2) is applicable to spherical monatomic gases only. Neufeld *et al.*[10] reported an empirical expression for the estimation of Ω_v in terms of the dimensionless temperature T^* $(= kT/\epsilon)$, where k is the Boltzmann constant and ϵ is the minimum pair-potential energy. Of the several potential energy functions proposed for the estimation of the collision integral, the Lennard-Jones (12-6) model[11] given by Eq. (3.3) is widely used[8].

$$\psi(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right]$$

(3.3)

In Eq. (3.3), σ denotes the value of the separation distance r at which $\psi(r)$ becomes zero. For dependable calculation of gas viscosity from Eqs. (3.2) and (3.3), the parameters σ and (ϵ/k) should be taken together from the same data compilation. Chung *et al.*[12] extended the applicability of Eq. (3.2) to polyatomic, polar and dilute gases with hydrogen bonding for the calculation of viscosity (η) by multiplying η_{CE} with a correction factor, *CF*, defined by:

$$CF = 1 - 0.2756\,\omega - 0.0509035\,\mu_R - k' \tag{3.4}$$

where, ω, μ_R, and k' are the acentric factor, reduced dipole moment and association parameter (accounting for the shape, polarity and the hydrogen bonding effects), respectively. The potential parameters σ and (ϵ/k) are determined from the critical volume and critical temperature, respectively. Using the method of Neufeld *et al.*[10] for the estimation of Ω_v and the value of k' from the regressed data on alcohols, Chung *et al.*[12] obtained viscosity estimates close to the experimental values.

Monnery *et al.*[5] and Poling *et al.*[6] described various empirical methods of estimating lean gas viscosities. These methods used the critical properties and the reduced dipole moment, μ_R as the inputs for viscosity estimations. Poling *et al.*[6] also listed the group contributions needed for the application of Reichenberg method[13] in addition to the critical temperature (T_C, K), critical pressure (P_C, bar) and dipole moment (μ, Debyes) for various substances. Reduced dipole moment is defined by:

$$\mu_R = 52.46\,\frac{\mu^2 P_C}{T_C^2} \tag{3.5}$$

and is to be used in calculating the correction factor (*CF*) by applying Eq. (3.4). This method is not applicable to the hydrogen bonding gases. Stiel and Thodos[14] reported empirical equations for non-polar gas viscosities as functions of reduced temperature (T_R) and a parameter (ξ) defined by:

$$\xi = \frac{T_C^{(1/6)}}{M^{(1/2)} P_C^{(2/3)}} \tag{3.6}$$

Later the authors extended the method to polar and hydrogen bonding gases[15] by introducing the critical compressibility factor (Z_C). Okeson and Rowley[16] developed a method for the estimation of non-polar gas viscosities by using the Lee-Kesler[17] approach for compressibility factor. Based on the data for 80 non-polar gases, the size/shape factor (α) was correlated by them in terms of the radius of gyration (r_g) resulting in the following equation:

$$\alpha = 7.7706 \times 10^{-4} + 0.033\,r_g + 0.01506\,r_g^{\,2} - 9.997 \times 10^{-4}\,r_g^{\,3} \tag{3.7}$$

An empirical equation for reduced viscosity of polar and quantum mechanical gases at low pressure, which is also applicable at atmospheric

pressure, was proposed by Lucas[18] that included polar and quantum correction factors F_p and F_q, respectively. The equation in terms of T_R is:

$$\eta\xi = \left[\begin{array}{c} 0.807 \ T_R^{-0.618} - 0.357 \ exp(-0.449 \ T_R) \\ + 0.34 \ exp(-4.058 \ T_R) + 0.018 \end{array} \right] F_P.F_q \qquad (3.8)$$

This equation is reported to yield deviations within a few percent from the experimental values. F_p and F_q have been expressed in terms of Z_C and T_R. The method described is not applicable to hydrogen bonding gases. Tham and Gubbins[19], from their study on dilute gas and liquid viscosities, reported that the corresponding states principle was obeyed by both the monatomic and polyatomic dilute gases.

Millat *et al.*[20] have provided explanations of the molecular theory of gas viscosity based on the kinetic theory of gases and statistical mechanics. Shan *et al.*[21] have applied a generalized correlation based on a modified Eyring's reaction rate theory for the estimation of the gas viscosities of pure oxygen, nitrogen, and argon as well as their mixtures. The same authors[22] applied Eyring's theory to trifluoromethane (R-23) for the calculation of viscosity and thermal conductivity of dilute gas and saturated vapor in addition to the supercritical and saturated liquid regions. Over the temperature range of 153-570 K, the estimated accuracy for the viscosity is 1%.

Mandal and Thakur[23] obtained reasonably good results from a modified version of a model developed by them earlier for neon, argon and helium. The modification including the effect of intermolecular forces and molecular size on the molar density can be helpful in determining the potential energy and collision diameter as well as their variation with temperature. Monnery *et al.*[5] presented a critical review of the predictive and correlative methods for pure component and mixture viscosities of dilute and dense gases as well as liquids. The chosen well-known, accepted and promising methods have been divided into the theoretical, semi-theoretical and empirical categories. The review also included the discussion on the limitations and reliability of the methods along with recommendations.

Several semi-empirical theories of gas viscosities have been reported by Partington[24]. Among the later ones, an approach is based on the method of partition functions known as the Fluctuation-Dissipation theory, using auto-correlation functions of dynamic variables. In the case of dilute gases, the auto-correlation formula was shown to reduce to Chapman-Enskog results for binary diffusion by Mori[25]. The Fluctuation-Dissipation theory is based on the concept of the tendency of an irreversible process to return to the state of equilibrium. Some of the theories developed (using mathematical techniques) subsequent to the kinetic theory of gases were reported by Massignon[26].

3.2 THEORIES OF DENSE-GAS VISCOSITY

For dilute gases, the density (at lower pressures) does not change appreciably with pressure (at lower pressures) and the gas viscosity increases with temperature only. However, at higher pressures, there will be a rapid change in the gas density resulting in a large increase in viscosity. The behavior of viscosity at high pressures is influenced by pressure, giving rise to the dense-gas situation. An account of such studies on the viscosity of dense gas, valid for hard spheres is presented here. Jager[27] proposed a correlation for the dense gas viscosity situation by taking into account the molecular finite size and represented viscosity by the formula

$$\eta = \eta_0 \left(\frac{1}{Y} + A + B\,Y \right) \tag{3.9}$$

with Y denoting the collision rate correction factor. η and η_0 are the dense gas and dilute gas viscosities. Y is determined from the equation of state:

$$(PV/RT) = 1 + (4b/V)\,Y \tag{3.10}$$

where b is the volume occupied by spheres. A and B of Eq. (3.9) are given as $(8b/V)$ and $(16b^2/V^2)$. Enskog[28] modified Eq. (3.9) by using $A = (16b/5V)$ and $B = 0.7614\,(16b^2/V^2)$. The modified form was based on the concept that, for colliding spheres, the change in collision rate is accompanied by the momentum transfer across the finite distances. Theoretical calculations of Y over the entire range of density with reasonable accuracies are reported by Alder and Wainwright[29-31]. The viscosities of dense fluids of hard spheres given by Eq. (3.9) have been extended to a more generalized form by Davis *et al.*[32]. Livingston and Curtiss[33] modified Enskog's dense gas theory through the determination of a more accurate non-equilibrium function. Henderson[34] obtained good agreement with the experimental values of both the dense gas and liquid viscosities, by modifying the hole theory in the light of significant structures concept. The method assumed the free volume to be a linear function of the neighboring holes. In the case of dense gas hard spheres, Alder and Dymond[35] and Alder[36] assumed a faster rate of occurrence of events because of higher collision rates. Taking this increase in collision rate to be proportional to a radial distribution factor, the equation for the dense gas viscosity becomes:

$$\eta = \eta_0\,\rho b_0 \left[0.8 + \frac{1}{Z-1} + 0.761(Z-1) \right] \tag{3.11}$$

This equation could be derived in terms of the excluded volume (b_0), gas density (ρ), and compressibility factor (Z). The excluded volume, b_0, is calculated from the hard sphere diameter, σ (in Å), using the relation;

$$b_0 = (2/3)\pi N \sigma^3 \tag{3.12}$$

where N is the Avogadro number. A molecular dynamics simulation approach used by Dymond and Alder[37] predicted viscosities within 1% at densities up to 2.5 times the critical value. Further attempts by Dymond and Assael[38] and Assael et al.[39] yielded an expression for reduced viscosity (η_R) as a function of reduced volume ($V_R = V/V_0$), V_0 being the close-packed volume. η_R is expressed in terms of temperature (T, K), molar volume (V, cm^3/mol), molecular mass (M, g/mole) and a parameter (R_η) which accounts for deviations from smooth hard spheres. The values of R_η and close-packed volume (V_0) for 16 fluids are listed by Poling et al.[6]. Alle and Pomeau[40] used the Enskog and virial expansions approach to the theory of dense gases. They have computed the coefficient of the Green-Kubo integrand by means of the first Enskog approximation in the case of collisions between three particles. Their study revealed a breakdown of the Enskog expansion just beyond the Navier-Stokes range. A molecular dynamic simulation work on dense gases was carried out by Chen and Rahman[41] using a system of 500 Lennard-Jones particles. The results obtained by using the equilibrium correlation function calculated without considering the attractive part were found to be in good agreement with the hard sphere Enskog theory of dense gases at low densities. At high densities, the agreement between the simulation study and Enskog theory was not good. Collings and Evans[42] reported the calculated values of viscosity of argon ranging between (1/3) and (2/3) of the experimental data, from their study of the application of Kirkwood's molecular theory of momentum in a simple dense gas[43]. The theory, applicable to both the dense gases and liquids can be classified as a distribution function theory, wherein the momentum flux is expressed in terms of velocity distribution function. Kirkwood et al.[44] deriving an expression for viscosity in terms of a friction coefficient, calculated the viscosity of argon at 89 K as 0.127 mpa.s, compared to the experimental value of 0.239 mpa.s. Applying the distribution function theory, Kirkwood and Boggs[45] derived an integral equation for the pair distribution function for a hard sphere fluid. Frezzotti[46] used a molecular dynamics approach to the study of one-dimensional problems in the kinetic theory of dense hard sphere gases. The results obtained from this method were comparable to the Enskog theory of solutions. Some of the reviews on the theories based on non-equilibrium distribution functions are by Green[47], Bondi[48], and Rice and

Frisch[49]. Cummings and Evans[50] reviewed both the non-equilibrium and equilibrium molecular dynamic simulation approaches.

3.3 GAS AND LIQUID VISCOSITY THEORIES

Equation (3.11) applied to the hard spheres considers only the repulsions. To extend the applicability to real fluids, a term has to be included in the equation to account for the attraction between the molecules. By introducing a 'thermal pressure' term, Enskog modified Eq. (3.11) for application to real fluids. Applying the modified form to three non-polar substances (oxygen, hydrogen and argon) at temperatures below T_C, Hanley *et al.*[51] reported good agreement between the calculated and experimental viscosities (within 10-15%). Davis et al.[32] derived an expression for the viscosity of hard sphere dense fluids using a square-well intermolecular potential. Sather and Dahler[52] also reported expressions for viscosity of dense fluids of rough spheres. The square-well model developed by Davis *et al.*[32] was used by Collings and McLaughlin[53] for viscosity calculations of 14 polar and non-polar fluids. The results showed wide deviations ranging between 2 and 70%. Chung *et al.*[54] in an attempt to extend their earlier work[12] on dilute gases to dense fluids, introduced empirically correlated density and temperature-dependent functions. The extended model, tested with 37 non-polar, polar and hydrogen bonded fluids yielded average absolute deviations below 4%. Using the Enskog theory to correlate the dense fluid viscosity of argon, nitrogen and oxygen, Cohen and Sandler[55] used the equation developed by Sandler and Fizdon[63].

$$\eta = \eta_0 \, \rho b \left[0.8 + \frac{1}{y} + 0.761 \, y \right] \tag{3.13}$$

where *y* denotes the hard sphere diameter and is defined as

$$y = b \, \rho \, g(\sigma) \tag{3.14}$$

g(σ) of Eq. (3.14) is the hard sphere radial distribution function at contact. A model developed by Abdelazim[56] by multiplying the right hand side of Eq. (3.13) with an empirically determined correction factor showed good agreement with experimental data for both the dense gas and liquid phases. Application of an empirically modified square-well theory of Davis *et al.*[32] by Du and Guo[57] to 26 non-polar fluids including hydrocarbons, oxygen and nitrogen yielded an overall deviation of about 9%.

Viscosity correlations of several investigators covering the entire phase range of dilute gas through the liquid stage are described next. Based on the observation that the residual viscosity defined as the difference between the dense fluid and dilute gas viscosities (η-η_o) is nearly independent of temperature, Jossi *et al.*[58] obtained the empirical expression for 11 non- polar fluids in the form:

$$\left(\eta - \eta_0\right)\xi = f\left(\rho_R\right) \tag{3.15}$$

where $f(\rho_R)$ is a function of the reduced density, ρ_R, valid for the range $0.1 < \rho_R < 3$. The reduced viscosity parameter (ξ) is defined by Eq. (3.6). Using a similar approach, Stiel and Thodos[59] developed the residual viscosity equations for 14 polar substances. For argon, neon, krypton and xenon, Tham and Gubbins[19] proposed a generalized corresponding states relationship;

$$\eta^*\left(T^*,V^*\right) = \frac{\eta\sigma^2}{\left(M\varepsilon\right)^{(1/2)}} \tag{3.16}$$

$$\text{where } T^* = \left(kT/\varepsilon\right), \tag{3.17}$$

$$V^* = \left(V/N\sigma^3\right), \tag{3.18}$$

in which k is the Boltzman constant, T is the absolute temperature, ε is the minimum potential energy, V is the molar volume, N is the Avogadro's number, and σ is the distance of separation between the molecules. They obtained good agreement with 6% average absolute deviation.

To extend the applicability of their approach to polyatomic fluids, Tham and Gubbins[19] modified Eq. (3.16) by multiplying the product $M\varepsilon$ with an empirically adjusting factor, α. T^* was taken as equivalent to ($kT/\varepsilon\alpha$). The modified approach, when applied to 25 non-polar substances including hydrocarbons showed errors ranging between 6% and 10%. Introducing the corrections for molecular attractions and chaos into the Enskog theory and using the values of the close-packed volumes determined from his previous work[60] , Dymond[61] correlated the viscosity data on krypton, xenon and argon within 2-5% over the entire density range, from dilute gas to liquid. A similar approach applied to C_2 - C_5 hydrocarbons[62] also yielded deviations within 2-5%, except for a few data points in the case of C_2, n-C_4 and n-C_5.

Combining a procedure of obtaining the hard sphere diameter y of the Enskog equation, Sandler and Fiszdon[63] developed the following equation.

$$\frac{\eta}{\eta_0 \, \rho b} = \left[0.8 + \frac{1}{y} + 0.761 \, y \right] \tag{3.19}$$

with the determination of the excluded volume (b_0) from the minimum of the plot of $(\eta/\eta_o b)$ vs. density (ρ), Cohen and Sandler[55] suggested a method of calculating the dense fluid viscosity, η, from the dilute gas viscosity, η_0. The method fitted the data on methane with an average deviation of 2.4%.

Lucas[64] presented a generalized viscosity phase diagram for non-polar fluids. The product of viscosity (η) and reducing factor for viscosity (ξ) defined by Eq. (3.6) is plotted as a function of the reduced temperatures (T_R), at various reduced pressures (P_R). The dilute gas state is indicated by the lower limit of the P_R-curves on the diagram. The liquid phase is simulated at higher pressures. A method developed by Ely and Hanley[65] incorporating an empirical correction to the reference fluid (methane) viscosity correlation of Hanley *et al.*[66], when tested on the data of 35 non-polar fluids, showed an *Average Absolute Deviation* (AAD) of 8.4%. However, large errors were found in the case of iso-alkanes and naphthalenes.

Modifying the Ely and Hanley model by changing the reference fluid from methane to propane, Ely[67] could bring down the AAD to 2.4%. A corresponding states approach by Pedersen *et al.*[68] for estimating the viscosity of crude oil fractions yielded an AAD of 5.0 %. The method, based on the approach of Tham and Gubbins[19], when applied to 15 non-polar fluids including carbon dioxide and hydrocarbons showed an overall deviation of 8.1%.

Modifying Ely and Hanley approach[65] using a viscosity acentric factor (ω_η) and an association parameter (k) along with the coefficients of the shape factors of Leach[69], Hwang and Whiting[70] could improve on the results obtained by Ely and Hanley[65]. For the 38 polar, hydrogen bonding and non-polar substances studied, their method showed an AAD of 5.3% compared to 17.6% of the Ely and Hanley method.

Lawal[71] developed a viscosity model similar to a cubic equation of state with four constants calculated from critical properties and two temperature-dependent functions that were evaluated from the experimental data. Tested with the data on 24 non-polar fluids at about 6700 points, the method showed an overall deviation of 5.9%.

Heyes et al.[72] fitted the expressions of Dymond *et al.*[60] to the data on shear viscosity, thermal conductivity and self-diffusion coefficient of Lennard-Jones fluid over the entire phase diagram at densities below the

solid-fluid co-existence line. A modified form of the Enskog theory is given by:

$$b_0 \, \rho \rho \, (\sigma) = \left[\frac{V}{R} \left(\frac{dP}{dT} \right)_V \right] - 1 = T \left(\frac{dZ}{dT} \right)_V + Z - 1 \qquad (3.20)$$

Equation 3.20 when combined with an equation of state like Peng and Robinson[73], can be used to obtain the hard sphere radial distribution function $g(\sigma)$. Equation (3.20) can further be utilized to obtain the excluded volume (b_0) by taking its limit as ρ and $g(\sigma)$ approach zero and unity, respectively. Using such a procedure to obtain b_0 and $g(\sigma)$ and replacing the constant 0.8 of Eq. (3.19) by an adjustable parameter (whose value is regressed), Sheng and Lu[74] calculated the viscosities for the whole phase range of five non-polar fluids with a maximum AAD of 3.7%.

Using an equation of the form

$$log(\eta^*/C) = \sum \alpha_i \left(V/V_0\right)^i \qquad (3.21)$$

with the constants α_i determined from the approach of Dymond[75] and generalizing the values of C as function of carbon number and V_0 as a function of temperature and carbon number, Assael *et al.*[76-77] obtained AADs of 2.8% for 16 non-polar fluids and less than 3% for 7 aromatic hydrocarbons. Using the same method, the authors[78] have calculated the viscosities of 6 polar and non-polar compounds with AADs ranging between 1.9 % and 4.1 %.

Hildwein and Stephan[79] developed a semi-theoretical significant structures model expressing viscosity as a function of several variables:

$$\eta = f\left(T, V, \varepsilon, r_0, d, \sigma, S, n1, a, b\right) \qquad (3.22)$$

r_0 and d in Eq. (3.22) denote the radius of Kihara potential minimum and Kihara potential hard core diameter, S is the Sutherland constant and *nl*, *a* and *b* are adjustable parameters regressed from the experimental data. For 3 polar and 14 non-polar fluids, Eq. (3.22) fitted the data with the AAD ranges of 0.2 to 1.6% for dilute gases, and 2.0 to 4.7% and 1.6 to 6.9% for saturated liquids and saturated vapors, respectively.

Introducing a cross over function between the low-pressure and high-pressure limits into Eq. (3.19), Xiang *et al.*[80] have extended its applicability to the entire fluid range. The scheme, tested with the data on 18 fluids fitted the low-pressure viscosities within 4% and high-pressure viscosities mostly within 10%.

A generalized correlation based on Eyring's significant structures theory covering the entire fluid range of the components of air and its mixtures was developed by Shan *et al.*[21]. The wide-ranging formulation explicit in viscosity and thermal conductivity as functions of temperature and density yielded satisfactory results.

Meir *et al.*[81] obtained self-diffusion coefficients and viscosities of a Lennard-Jones fluid through molecular dynamic simulations employing the Einstein plots covering the entire fluid range. The uncertainties for self-diffusion, liquid region and low-density viscosities have been 0.5%, 2.0% and 15%, respectively.

3.4 PURE-LIQUID VISCOSITY THEORIES

There has been no comprehensive theory on the viscosity of liquids so far because of its complex nature. Theoretical methods of calculating liquid viscosities like those proposed by Kirkwood *et al.*[44] and the molecular dynamic approaches reported by Cummings and Evans[50] are useful in providing valuable insights into the theory even though they result in large deviations from the measured viscosity data. In contrast, semi-empirical and empirical methods provide reasonable results but lack generality of approach. At temperatures below the normal boiling point, the logarithm of liquid viscosity varies linearly with the reciprocal of the absolute temperature as described by the model;

$$ln(\eta) = A + (B/T) \quad or \quad \eta = A exp(B/T) \tag{3.23}$$

with the constants A and B determined empirically. At temperatures above the normal boiling point, the *ln* η versus (*1/T*) relationship becomes non-linear and is described by a number of semi-empirical methods including those based on the principle of corresponding states. Among the important compilations providing liquid viscosity data are Kestin and Shankland[82], Viswanath and Natarajan[4], Daubert *et al.*[83], Perry and Green[84], Lide[85] and Dean[86]. As our primary concern in this book is liquid viscosity, in the following sections, we present the theories proposed, semi-theoretical and empirical models, for estimating liquid viscosity. More elaborate discussions about the semi-theoretical and empirical methods are presented in Chapter 4 (devoted to the correlation and estimation methods).

3.4.1 THEORIES PROPOSED

The observed fact that the liquid property values like those of density and viscosity are between those of solids and gases, led to the formulation of several theories based on gas-like, and/or, solid-like structures.

Of these, the distribution function theories favor the gas-like concept of liquids. These theories introduce a short-range pair distribution function in a disordered state of the fluid. Among the various distribution function theories applied to viscosity calculations, those by Kirkwood and associates[43-45] are already discussed in section 3.3. An expression for liquid viscosity was obtained by Born and Green[87, 88] using Kirkwood-Bogg integral[45]. Rice and Kirkwood[89] obtained an expression for viscosity coefficient of argon in terms of equilibrium properties.

The theories on liquids with solid-like structure assume the molecules to be confined within small spaces and each molecule interacts with only a few neighbors. Brush[1] referred to four types of such theories as hole, vibration, phonon (sound wave) and relaxation theories.

In hole theories, the liquid is considered as a lattice of densely populated molecules with a few holes. Jumping of molecules within the holes under the influence of a shearing stress causes the viscous flow.

Vibration theories assume that the vibration of molecules around equilibrium positions causes momentum transfer within the liquid.

Phonon theories assume that the momentum transfer within the liquid occurs due to the vibration of the lattice as a whole.

In relaxation theories, viscous flow is considered to be similar to the deformation of elastic solids. The need for sufficient data at molecular level limits their application.

The best example of the hole theory is the reaction rate theory of Eyring and co-workers[90-92], in which the viscous flow is considered as a reaction causing the molecule to acquire the activation energy, while crossing over a potential barrier. Applying Eyring's theory[90], Glasstone *et al.*[92] derived the following liquid viscosity equation in terms of the molar free energy of activation of flow (ΔF^*) and molar volume (V):

$$\eta = \frac{Nh}{V} \, exp\!\left(\Delta F * /RT\right) \tag{3.24}$$

where N is the Avogadro's number, h is the Planck's constant and R is the universal gas constant. Eq. (3.24) suggests the flow to be Newtonian in the sense that viscosity is independent of the applied force. Kincaid *et al.*[93] related ΔF^* to the energy of vaporization, ΔE_{Vap}. Plotting ΔF^* (calculated

from Eq. (3.24)) as a function of ΔE_{Vap} (expressed in terms of the enthalpy of vaporization, ΔH_{Vap}) by the equation:

$$\Delta E_{Vap} = \Delta H_{Vap} - RT_B \qquad (3.25)$$

where T_B is the normal boiling point in Kelvin, Kincaid *et al.*[93] obtained a straight line (passing through the origin) with a slope of (1/2.45) from the data of 93 organic and inorganic liquids. Their theory, based on Eq. (3.25), over-predicts experimental viscosities by 2 to 3 times[93, 94]. A brief discussion on the enthalpy of activation of several systems is given by Hirschfelder *et al.*[95].

In an extension of Eyring's theory to hydrocarbons, Moore *et al.*[96] found that the flow is largely translational at low temperatures and becomes rocking at intermediate temperatures. At high temperatures, the molecules freely rotate about their long axes. Collins[97] proposed an alternate form of Eyring's theory, making use of a constant volume temperature coefficient of viscosity instead of the isobaric temperature coefficient (employed by Ewell and Eyring) for the determination of the activation energy. The theory was reported to be in moderate agreement with the experimental viscosities of simple liquids.

Macedo and Litovitz[98] reformulated Eyring's rate theory using an expression for the probability of finding a vacant site and assessed the relative roles of the activation energy and free volume. Application of the equation developed by them to various liquids including argon, fused SiO_2, polyatomic van der Waals and H-bonded compounds provided consistent fits to both the temperature and pressure dependence of viscosity.

Shakhparonov[99] discussed the mechanism of viscous flow in monohydric alcohols and gave the reasons for the differences between the viscosity-temperature relationships of carbon disulfide, carbon tetrachloride, benzene, alcohols and normal alkanes. The solid-like and gas-like aspects of the liquid behavior, wherein a molecule vibrates about an equilibrium lattice before jumping into a neighboring vacant site are combined in the significant structures theory of Eyring *et al.* proposed in 1958[100]. The liquid viscosity (η_L) considered as the sum of contributions due to the solid-like and liquid-like behaviors can be expressed in terms of the volume fractions occupied by the solid and liquid portions as:

$$\eta_L = (V_S/V)\eta_S + \left[1 - (V_S/V)\right]\eta_G \qquad (3.26)$$

where V_S is the volume occupied by the solid portion and V is the sum of the volumes of the solid and gas portions. Application of the significant structures theory[100] by Eyring and Ree[101] to argon showed deviations from

experimental viscosities ranging up to 60%. Egelstaff[102], in a review on the structure of simple liquids, presented calculation procedures on viscosity, diffusion, and viscosity coefficients in addition to a discussion of static and dynamic structure factors.

The peculiar phenomenon of super fluidity of helium near absolute zero was attributed to the phonon excitations by Landau[103, 104]. Using density and velocity as quantum operators for describing the collective phonon excitations, Landau could predict the phenomenon of second sound (thermal waves), which was reported to have been confirmed experimentally by Peshkov in 1944 as quoted by Brush[1]. For calculating the viscosity coefficient of helium at low temperatures, Landau and Khalatnikov[105-108] introduced the concept of considering the phonon and proton excitations as quasi-particles of an ideal gas and applied the kinetic theory to compute the momentum transport.

The Landau-Khalatnikov (L-K) theory attributed the negative temperature viscosity coefficient of helium below 1.6 K to the strong temperature dependence of the phonon-phonon scattering. Further details on the application of the L-K theory can be found in Brush's review[1].

3.4.2 SEMI-THEORETICAL MODELS

In general, semi-theoretical models provide satisfactory results. Most of the theoretical models discussed involve large errors in their estimates of liquid viscosities. On the other hand, semi-theoretical methods combine theoretical principles with models based on the trends in experimental data. Semi-theoretical models generally involve coupling of a viscosity model with the density or volume prediction method. Most of these methods utilize corresponding states approaches and/or the models based on statistical mechanics like hard sphere and significant structures theory.

According to the corresponding states theory, the dimensionless property of a compound should be equal to that of a reference compound at the same reduced conditions. To calculate the viscosity of a compound, these methods need the correlations on viscosity and density of a reference liquid along with the critical properties and parameters like acentric factor and shape factors. A brief discussion of the predictive and correlative methods based on semi-theoretical approach is presented in the following section while more details particularly on applied aspects are presented in Chapter 4.

Using the square-well intermolecular potential developed by Davis *et al.*[32], Davis and Luks[109] calculated the viscosity of liquid argon. The equation for calculating liquid viscosity can be expressed as a function of the density (ρ), molar mass (M), the repulsion diameter (σ_l), intermolecular potential attractive energy (ε), ratio of attraction diameter to repulsion

diameter (R) and the radial distribution functions at repulsion diameter ($g(\sigma_1)$) and at attraction diameter ($g(\sigma_2)$) as:

$$\eta = f\left(\sigma_2, \varepsilon, R, g(\sigma_1), g(\sigma_2), \rho, M\right) \tag{3.27}$$

Obtaining the parameters: σ_1, $\in$ and R from the virial coefficient data and $g(\sigma_1)$ and $g(\sigma_2)$ by using Percus-Yevick equation along with the perturbation theory of Lowry *et al.*[110], Davis and Luks[109] predicted argon viscosities with an AAD of 6%. Letsou and Stiel[111] correlated the viscosity data for 13 liquids including hydrocarbons with an overall deviation of 3% by means of an equation of the type:

$$\eta\xi = f^{(0)}\left(T_R\right) + f^{(1)}\left(T_R\right) \tag{3.28}$$

with the parameter ξ defined by Eq. (3.6). $f^{(0)}(T_R)$ and $f^{(1)}(T_R)$ are quadratic functions in T_R, valid for the range $0.70 < T_R < 0.92$.

Fischer[112] developed an equation of state for a variety of materials including UO_2, using Eyring's significant structures theory[100]. He included a defect term in the solid-like partition function to determine the O/U ratio. The gas-like partition functions were adjusted to obtain agreement with the experimental data at the melting point. Eyring's significant structures theory[100] was also applied by Gillan[113] for deriving thermodynamic properties from the consideration of molecular structure of liquids. Liquid thermodynamic partition function is expressed as an average of the solid and gas partition functions. The three parameters contained by the liquid function are then determined from experimental data. The calculated thermodynamic properties showed good agreement with experimental data in the case of alkali metal halides and UO_2. The approach appears promising for liquid viscosity as well.

Heckenberger and Stephan[114] proposed a viscosity equation of state based on the conclusion from their earlier work[115] that a residual transport property (ΔTP) surface P-ΔTP-T corresponded better than the thermal P-ρ-T surface. Regressing the seven model parameters with experimental data, the method showed an AAD of 4.7 %. At reduced temperatures below 0.6, the deviations increased rapidly up to about 33%. The constants of Eq. (3.23) are expressed by Allan and Teja[116] in terms of carbon numbers for pure alkanes, from ethane to eicosane. Using the method, they obtained an AAD of 3% for 19 compounds. Regressing the effective carbon numbers (ECN) with an experimental value of viscosity of each compound, they could correlate the data on 50 hydrocarbons with an AAD of 2.3%. A Walther type of equation,

$$log(log\ \eta + 0.8) = b_1 + b_2\ log\ T \tag{3.29}$$

was fitted by Mehrotra[117] to the API Project 42[118] data on 273 heavy hydrocarbons with AADs ranging between 0.8 % (for n-paraffins and olefins) and 1.4% for non-fused aromatics. It this equation b_1 and b_2 are constants. Developing an empirical equation of the type given below:

$$log(log\ \eta + 0.8) = 100(0.01T)^b \tag{3.30}$$

where b is equivalent to the constant b_2 of Eq. (3.29), the optimum values of b were regressed for each compound. The method yielded an overall AAD range of 2.3 % (for branched alkanes and olefins) to 10.6 % (for fused ring naphthenes). Mehrotra[119] also correlated the data on 89 light and medium hydrocarbons by regressing the constants b_1 and b_2 of Walther equation in good agreement with experimental viscosities. Regressing the parameter b of Eq. (3.30) resulted in the AADs ranging between 6.6 % for aromatics and 12.5 % for n-alkyl cyclopentanes.

Aasberg-Petersen *et al.*[120] developed a method using the Teja-Rice[121] type of model for estimating liquid viscosities. The equation is given by:

$$ln(\eta\xi) = ln(\eta\xi)^{R1} + \frac{(\omega - \omega^{R1})}{(\omega^{R2} - \omega^{R1})}\left[ln(\eta\xi)^{R2} - ln(\eta\xi)^{R1}\right] \tag{3.31}$$

where *R1* and *R2* refer to the two chosen reference fluids and ξ is defined by Eq. (3.6). Aasberg-Petersen employed molecular mass (*M*) instead of the acentric factor (ω) as the characteristic property. Testing of Eq. (3.31) for 6 aromatics and 12 alkanes at pressures up to 70 MPa, yielded deviations ranging between 5% and 39%.

Cao *et al.*[122] developed a viscosity model for pure liquids and mixtures on the basis of Eyring's absolute rate theory, statistical thermodynamics and local compositions. The model, used to describe the viscosity-temperature relationship of 314 pure liquids showed a mean relative standard deviation (MRSD) of 1.1%. All the four parameters were regressed for the calculation of viscosities. The liquids studied include hydrocarbons, alcohols, ethers, acetates, amines, aldehydes, ketones and water. Mehrotra[123] proposed a method that predicted viscosities of 70 liquid hydrocarbons with an AAD of 5% by employing Eq. (3.30) along with the expression for b in the equivalent carbon number, *ECN*

$$b = -5.745 - (40.468\ /\ ECN) + 0.616\ ln(ECN) \tag{3.32}$$

Other methods include those of Mehrotra[123], Monnery et al.[5], Sauder and Orbey[124], and Lei et al.[125]. Monnery *et al.*[5] presented a review on theoretical, semi-theoretical and empirical categories of methods for dilute and dense gases, liquids and mixtures and included many references. They have also discussed the limitations and reliability of various methods. The gaps in viscosity prediction/correlation methods were also identified. Sandler and Orbey[124] reviewed the methods of prediction and correlation of the viscosity of liquid hydrocarbons and their mixtures with regard to the changes in pressure, temperature and composition. Mehrotra[7] reviewed semi-theoretical and empirical methods used for prediction or correlation of pure liquid hydrocarbons, petroleum fractions and their mixtures. The review also summarized the results obtained from various calculation methods for the selected set of compounds and their mixtures mentioned earlier. Lei *et al.*[125] presented a two-parameter model based on Eyring's absolute rate theory for the calculation of pure liquid viscosities over a wide temperature range. The model parameters were determined using the viscosity data and from knowledge of the vapor pressure, saturated liquid volume and heat of vaporization. The overall average deviation was reported as 1.5% for 106 compounds (including non-polar, polar, organic and inorganic liquids) for 1473 data points.

3.4.3 EMPIRICAL METHODS

Finding relationships between viscosity and other properties, by means of mathematical expressions that provide the best fit of the experimental data, is a common practice among investigators. Partington[24] presented some of the empirical methods proposed and tested on several liquids by various experimenters in addition to providing a state of the art assessment of the literature. The models included two, three and multi-constant equations. A number of such equations involve temperature, pressure, molecular mass and properties like surface tension, vapor pressure, heat of vaporization, normal boiling point and refractive-index. Some of the important and commonly used correlation and estimation methods including those dependent on group contributions are discussed in detail in Chapter 4.

3.5 SUMMARY

Well understood theories of liquid viscosity have not been developed, probably because liquid state is an intermediate state of matter between gas and solid, and not easy to represent in terms of different characteristic properties of substances. Often attempts have been made to describe liquid

as having solid-like and/or liquid-like structure. Therefore an attempt has been made to describe theories of dilute gas viscosity and dense gas viscosity in the first two sections of this chapter. The next two sections describe the theories for the understanding gas and liquid viscosity and liquid viscosity (exclusively). The discussion under pure liquid viscosity is sub-divided into theories proposed, semi-theoretical models and empirical methods.

In all the sections, an attempt has been made to present a review of the salient features, application aspects like requirements of input data, average absolute deviation in applying the theory/method, etc., to the extent possible. It is expected that the information provided will be useful in developing relations for liquid viscosity based on the theoretical concepts/ideas presented, to the situation of one's interest and type of accuracies required.

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