CHAPTER III

THEORIES OF DIFFUSION

The theory of diffusion in solids is well defined since a solid is a well-structured form of amorphous materials or crystals. Diffusion in gases can be understood since a gas is a totally random distribution of particles. However, diffusion in liquids is difficult to describe theoretically because liquids exhibit properties of both gases and solids, with some randomness and some structure. For this reason, an accurate theory for diffusion in liquids has yet to be developed, although several theories have been proposed. This section begins with a review of the following three general classes of liquid diffusion theories; hydrodynamic theory, activated state theory, and the kinetic theory of rough hard spheres. These approaches will then be used in subsequent chapters to interpret the experimental results.

3.1 Hydrodynamic Theory

For a single particle moving in a continuum, the Nernst–Einstein equation relates the diffusivity to a frictional resistance coefficient ζ:

$$D_{12} = kT/\zeta \tag{3.1}$$

The coefficient ζ can be calculated for a sphere from classical hydrodynamics and is a function of the solvent viscosity η.

For a spherical solute of diameter σ_1 which is very large compared to the diameter of the solvent molecule, Stokes law for viscous drag on a sphere can be used. It has been shown (Sutherland, 1905) that

$$D_{12} = kT/[6\pi\eta(\sigma/2)] \tag{3.2}$$

This is called the Stokes–Einstein equation and holds for the case where there is no "slip" between the diffusing sphere and the solvent.

The other limiting case of (3.1) assumes that there would be "slip" if the diffusing molecule is of the same order in size as the solvent. In this case,

$$D_{12} = kT/[4\pi\eta(\sigma/2)] \tag{3.3}$$

Equations (3.2) and (3.3) suggest that the product $D_{12}\eta/T$ is constant.

There have been several attempts to develop a rigorous hydrodynamic approach to diffusion, but many conceptual and computational problems have been encountered (Tyrrell and Harris, 1984). For instance, for the original Stokes–Einstein formulation (which is based on Brownian motion theory), the solute must be many orders of magnitude larger than the solvent. That is not always true, and in particular it is not true for the gas and alkane systems of interest in this work. Also, if the solute is not spherically symmetrical, then there are three resistance coefficients ζ, not just one. Although the Stokes–Einstein law has been observed to hold for self-diffusion, Evans *et al.* (1981) argue that this is a fortuitous result due to the narrow density range for which the equation has been tested. Finally, Hildebrand (1971) commented that the macroscopic phenomena of viscous resistance is difficult to justify on the molecular scale, and states that any resistance coefficient is merely a fictitious quantity.

Nevertheless, the hydrodynamic approach is one of the oldest and has provided the starting point for many empirical correlations, such as the Wilke–Chang and Lusis–Ratcliff relations of chapter II (equations 2.11 and 2.12).. These are based on the observation that, within a limited temperature range, $D_{12}\eta/T$ is a constant. Other correlations such as the Sovova equation (2.9) and the Hayduk–Cheng relation (2.1) relate D_{12} to some empirical power of the viscosity. Although there is no theoretical basis for these, they follow in spirit from hydrodynamic theory, and thus most equations relating D_{12} to η are called hydrodynamic approaches.

3.2 Activated State Theory

The Eyring rate theory for diffusion is actually an extension of the absolute rate theory for chemical reactions. In the Eyring theory, diffusion occurs when a molecule attains a sufficiently high energy to overcome a potential barrier, then jumps to a new equilibrium position in the liquid. By assuming that the liquid maintains a lattice–type structure, it is possible to express the diffusion coefficient as an exponential (Glasstone *et al.*, 1941):

$$D_{12} = \frac{kT\lambda^2}{h}\exp(\frac{-\Delta G_D}{R_g T}) \tag{3.4}$$

In this equation, λ is a jump distance which is on the order of the intermolecular distance, and ΔG_D is the difference in Gibbs energy between the "normal" molecules and those in the activated state.

This approach has had success as the basis of several empirical schemes because the diffusion coefficient is observed to follow the exponential dependence of equation (3.4) over a fairly wide temperature range. This theory was used by Olander (1963) and Gainer and Metzner (1965). Akgerman and Gainer (1972 a,b) used activated state theory as the basis for equation (2.10).

However, Tyrrell and Harris (1984), Hildebrand (1971), and Alder and Hildebrand (1973) point out some conceptual difficulties with this approach. There is evidence to suggest that the potential field encountered by molecules is almost uniform, rather than there being a potential difference between activated and unactivated molecules. In addition, the activation energies observed are rather low, on the order of 10 kJ/mol. This means that a large percentage of molecules are in the activated state at any one time. This violates one feature of activated state theory which is that the proportion of molecules in the activated state should be small. Tyrrell and Harris (1984) caution that the value of the observed activation energies not be given too much physical significance.

There is also experimental evidence suggesting that the physical basis for activated state theory may not be correct. Sun and Chen (1985b) have observed a deviation from the exponential behavior for the diffusion of aromatic hydrocarbons in cyclohexane. These deviations occurred near the cyclohexane critical temperature, in the range between above 473 K. Ruby *et al.* (1975) have calculated jump distances for an iron isotope in solution with a liquid, and have found that the average jump distance is very small, much less than a molecular diameter. Molecular dynamics simulations of diffusion confirm this (Clifford and Dickinson, 1977).

Practically there are some difficulties with using equation (3.4). One needs both the activation energy ΔG_D and the distance λ, yet there are no reliable methods for estimating these. At present, the activated approach seems best suited to extrapolation of data and not for prediction of D_{12} from first principles.

3.3 Rough Hard Sphere Theory

The rough hard sphere (RHS) approach to diffusion (and other transport properties) is one specific result in the broad field of kinetic theory. The generic approach to kinetic theory is to consider the Hamiltonian equations for a collection of a large number of molecules, and to calculate their positions and momenta as a function of time. From the time behavior of the ensemble, the transport properties can be calculated. To perform such calculations one must know the mass, shape, and size of the particles, and the dynamics of the interactions and collisions between particles. Analytical calculations are impossible except when a number of simplifying assumptions are made. Usually, one must resort to computer solutions but even these are intractable except for small numbers of particles ($\sim$ 1000) and with highly idealized assumptions.

In this section we will present the theory behind the RHS approach to diffusion. It will become evident that a number of the assumptions made will be physically unlikely for the alkane and gas systems studied. However, more realistic approaches have not yet been fully developed. In lieu of a perfect theory, one must use the available approaches as a basis for interpretation. Despite its limitations, RHS theory has been shown to be useful in interpreting diffusion data in a number of systems. Also, the physical approach to RHS theory, while imperfect, is perhaps more sound than those for hydrodynamic or activated state approaches.

In compact form, the RHS mutual diffusion coefficient is obtained as the product of four terms:

$$D_{12} = D_{12}^{RHS} = D_{12}^{HSG} \cdot \frac{1}{g(\sigma_{12})} \cdot C(\sigma_1, \sigma_2, m_1, m_2, V) \cdot A \tag{3.5}$$

The terms are listed in chronological order of their development and represent the progressive development of theory beginning with diffusion in gases and concluding with diffusion in liquids. We discuss each of the four terms separately so that the increasing complexity of the phenomena described by each term will become apparent.

The first term D_{12}^{HSG} is the mutual diffusion coefficient for a dilute (low density) collection of hard spheres, *i.e* the *hard sphere gas*. The equation for D_{12}^{HSG} was derived by Chapman and Enskog (Chapman and Cowling, 1970) with the following assumptions:

1. Molecules are spherically symmetrical and smooth (there is no exchange of angular momentum during collision).
2. The gas is "dilute"; that is, the mean free path is large compared to the diameters of the molecules.
3. Only two–body collisions occur; multiple interactions are negligible.
4. The collisions between molecules are perfectly elastic and instantaneous.
5. There are no force fields affecting the molecules on their flight between collisions.
6. Molecular chaos prevails; there is no correlation between positions and velocity vectors of molecules.

Under these conditions the mutual diffusion coefficient for a hard sphere gas is (Chapman and Cowling, 1970):

$$D_{12}^{HSG} = \frac{3}{8n\sigma_{12}^2}\left[\frac{kT}{2\pi}\frac{(m_1+m_2)}{m_1 m_2}\right]^{1/2} \tag{3.6}$$

where n is the number density (molecules/volume), $\sigma_{12} = (\sigma_1+\sigma_2)/2$ is the collision (average) diameter of the solute and solvent molecules, and m_1 and m_2 are the molecular masses.

As the density of the fluid increases, the assumptions of molecular chaos and binary collisions break down for real molecules. Enskog retained the assumption of perfectly elastic collisions, however, and for the model fluid this means that multi–body interactions are still negligibly probable since the collisions occur instantaneously. Enskog relaxed the assumption of uncorrelated positions of the molecules, but retained the assumptions for velocities. He showed analytically that (Chapman and Cowling, 1970)

$$\frac{nD_{12}}{(nD_{12}^{HSG})_0} = \frac{1}{g(\sigma_{12})} \tag{3.7}$$

where nD_{12} is the number density times the diffusivity at moderate density, while $(nD_{12})_0$ is the same quantity at low (gas-like) density, and $g(\sigma_{12})$ is the radial distribution function for hard spheres evaluated at the contact distance. The effect of $g(\sigma_{12})$ is to correct the dilute gas diffusivity for the increased frequency of collision in the denser gas.

The function $g(\sigma_{12})$ can then be thought of (in this context) as a correction term relating diffusivity in dilute gas to that in moderately dense gas (the distinction between dilute and moderately dense being unimportant to the present discussion). The radial distribution function depends on the composition and molar volume of the mixture and on the diameters of the constituent molecules. For an infinitely dilute solution, $g(\sigma_{12})$ can be calculated as follows (Evans *et al.*, 1981; Alder *et al.*, 1974):

$$g(\sigma_{12}) = \frac{1}{1-\xi} + \frac{3\xi\sigma_1}{(1-\xi)^2(\sigma_1+\sigma_2)} + \frac{\xi^2\sigma_1}{2(1-\xi)^3\sigma_2} \qquad (3.8)$$

where ξ is the packing factor for hard sphere assemblies. For the infinitely dilute case $(n_1 = 0)$

$$\xi = \frac{\pi n_2 \sigma_2^3}{6} \qquad (3.9)$$

This expression is based on the Percus–Yevick equation of state for hard spheres (Leibowitz, 1964). It may not be valid for values of σ_1/σ_2 far from unity.

At liquid densities, it is found that the assumption of uncorrelated velocities breaks down completely. The diffusion coefficients calculated from the first two terms of equation (3.5) were found to differ widely from experimental values and from those calculated from computer simulation (Dymond, 1972; Alder *et al.*, 1970). The deviation from Chapman–Enskog theory is due to two phenomena, backscattering and vortex motion. At high densities (greater than 1.5 to 2 times the critical density ρ_c) and for low solute to solvent mass ratios, the diffusion coefficient is decreased by backscattering, or the multiple successive collision of the solute with its neighbor molecules. The solute is temporarily trapped in a "cage" for a time corresponding to several collisions before it can move on. The phenomena of backscattering has been found from computer simulations to increase with decreasing mass ratio m_1/m_2. At somewhat lower liquid densities ($\rho < 1.5\rho_c$) and for higher solute to solvent mass ratios, it has been shown (Alder and Wainwright, 1970) that a *vortex* of neighbor molecules forms around the diffusing molecule, acting to increase its velocity (and diffusion coefficient) above that predicted by Chapman–Enskog theory.

The term $C(\sigma_1, \sigma_2, m_1, m_2, V)$ in equation (3.5) corrects the Enskog theory in the region of liquid densities for backscattering and vortex formation. The correction cannot be obtained analytically; rather, computer calculations are performed to obtain the actual diffusivity, and the results are expressed as a ratio of the actual (computer) diffusivity D^{HS} to the Enskog diffusivity. The factor C is defined thus:

$$C(\sigma_1, \sigma_2, m_1, m_2, V) = \frac{D^{HS}}{(D^{HSG}/g(\sigma_{12}))} \tag{3.10}$$

The extreme complexity of the calculations prohibits using the computer to calculate a diffusivity for every system of interest. Rather, the few available results are given as a function of $\sigma_1/\sigma_2, m_1/m_2$, and V/V_0, where V_0 is the close–packed hard sphere volume

$$V_0 = N\sigma_2^3/\sqrt{2} \tag{3.11}$$

Chen (1981) recently compiled and graphed the machine calculations from Alder *et al.* (1974), Herman and Alder (1972), Shelton (1981), and Alder *et al.*, (1970). Czworniak *et al.* (1975) expressed C as a polynomial function of $m_1/m_2, \sigma_1/\sigma_2$, and ξ. It should be noted that the accuracy of the calculations by Alder *et al.* (1974) has been questioned by Esteal *et al.* (1983) based on their more recent calculations.

In collisions between polyatomic molecules, it is possible that kinetic and rotational energy can be exchanged, violating the smoothness assumption of Enskog theory. Chandler (1975) has discussed this phenomenon and has shown that a roughness factor A (the fourth term in equation 3.5) should be introduced to account for this. The effect of coupling between rotational and kinetic energy is to reduce the diffusion coefficient, so

$$0 \leq A \leq 1 \tag{3.12}$$

A is a constant essentially independent of density and temperature. Values of 0.54 and 0.59 for A have been found to explain intradiffusion in carbon tetrachloride (Chandler, 1975) and tetramethylsilane (Parkhurst and Jonas, 1975), respectively. Baleiko and Davis (1974) calculated A for rough spheres from geometric considerations and concluded that, theoretically, $0.71 < A \leq 1$. Evans *et al.* (1981) fitted several sets of diffusion data using values of A equal to either 1, 0.78, of 0.7, depending on the constituents of the system. Bertucci and Flygare (1975) similarly fitted data and found values of A between 0.44 and 0.552.

To summarize, the rough hard sphere theory for liquids is a modification of the hard sphere theory for gases. The hard sphere theory for gases was developed by assuming molecules are spherical and inelastic, and collide much like billiard balls, with only bimolecular collisions occuring. Although the theory matches data well for diffusion in low pressure gases, the theory breaks down for dense gases and liquids since some of the basic assumptions are no longer valid.

The hard sphere theory equation has been scaled using the radial distribution function $g(\sigma_{12})$, which accounts for the increased frequency of collisions in a dense gas or liquid. The rough hard sphere theory was then developed by applying two additional correctional terms, C and A, which account for correlated molecular velocities and the exchange of rotational energy which occurs when 'rough' molecules collide. Since the behavior of $g(\sigma_{12})$, A, and C is not well understood, recent research has attempted to represent these groups in terms of well-known fluid properties.

It has been found (Dymond, 1974) that the molecular dynamics calculations of the group $C/g(\sigma_2)$ for self diffusion can be fit to a straight line as follows:

$$\frac{V}{V_0} \cdot C(\sigma_2, m_2, V/V_0) \cdot \frac{1}{g(\sigma_{22})} = a\left[\frac{V}{V_0} - b\right] \qquad (3.13)$$

where V is the molar volume of the liquid mixture at the temperature and pressure of the system, V_0 is defined by equation (3.11), and a is a different constant for each solvent. Using least squares regression, Dymond (1974) found the constant b to be 1.384. This constant was found to be independent of the solvent properties. Dymond (1974) developed the following expression, which, when written for rough hard spheres, takes the form:

$$10^9 D_{RHS} = A \cdot 2.527(RT/M)^{1/2} V_o^{-2/3}[V - 1.384V_o] \quad meters^2/sec \qquad (3.14)$$

where D_{RHS} is the diffusion coefficient for rough hard spheres and M is the molecular weight of the liquid.

Chen et al. (1982) tested the hypothesis that the following general form of Equation 3.14 would also apply to mutual diffusion at infinite dilution;

$$D_{12}^o/\sqrt{T} = \beta(V - V_D) \qquad (3.15)$$

In this equation β is the slope of $D_{12}^o/\sqrt{T}$ versus V and V_D is the intercept where diffusion goes to zero. Chen plotted data for several solutes in the solvents C_8, C_{10}, and C_{12} at temperatures up to 160°C and found that $D_{12}^o/\sqrt{T}$ versus the solvent molar volume, V, was highly linear in every case. Expressions for β and V_D were not given. For infinite dilution coefficients, the constant β is expected to depend on both the solute and the solvent, and V_D is expected to depend on only the solvent.

Equation (3.15) will provide the starting point for analysis of the experimental data. Rough hard sphere theory predicts that $D/\sqrt{T}$ should form a straight line when plotted versus molar volume. It is worth noting that a similar linear behavior was observed and discussed by Batchinski (1913) and later by Hildebrand (1971). Both reasoned that viscosity (and diffusivity) should be a function of the free volume within the fluid, where the free volume is the difference between the molar volume V at the prevailing conditions and a limiting hard core volume V_o, which is analgous to V_D in equation (3.15). Batchinski (1913) plotted viscosity η versus molar volume for 87 liquids and observed straight lines for non–associated liquids. Hildebrand (1971) did the same for other liquids with the same result, and noted that the value V_o was very close to 0.31 V_c for most liquids, where V_c is the liquid critical volume. Hildebrand then extended the reasoning to diffusion, and for a limited number of data was able to show a linear relation between diffusivity and molar volume. Although Hildebrand's explanation of the linear relationship was based on intuitive arguments, it is seen that the Rough Hard Sphere (RHS) theory provides a more theoretical explanation.