Scaled Particle Theory:
Theoretical Background and Computational Aspects for Calculation of Ultrasonic Velocities in Liquids

3.1 Introduction:
The ideal way to predict properties of a liquid is to solve many-body Schrodinger equation describing the nuclei and electrons. Many simplifications have been suggested, such as method of classical statistical mechanics.

3.2 Radial Distribution Function
One can use the Grand-canonical ensemble, method to find the probability of N molecules with coordinates within da_1 .... da_n at a_1 .... a_n and momenta within dp_1 .... dp_n at p_1 .... p_n, which can be described as,

\[ p = \left( \frac{1}{h^{2n}} \cdot z \right) \exp \left[ \beta \left( \mu_0 - H_N \right) \right] \quad \ldots \ldots 3.1 \]

where \( \beta = \frac{1}{kT} \), \( \mu_0 \) is chemical potential, T is the temperature, k is Boltzmann's constant, h is Planck's constant and f is the number of degrees of freedom per molecule. dq_i means an f-dimensional volume element in the generalised coordinate space of molecule i, p_i are the momenta conjugate to the q_i, Z is the grand partition function Hamiltonian of the N-body system and \( H_N \) is given by,

\[ H_N = T_N + U_N \quad \ldots \ldots 3.2 \]

\( T_N \) and \( U_N \) being kinetic and potential energies respectively.

\[ Z = \sum_{N=0}^{\infty} \left( \frac{\beta \mu_0}{N!} \right)^N \int \ldots \int \exp \left( -\beta H_N \right) dq_1 \ldots dq_N dp_1 \ldots dp_N \]

and \( pV = kT \log Z \quad \ldots \ldots 3.3 \)

Differentiating \( \log Z \) with respect to \( V \) and solving for spherical potentials, a relation is obtained as,

\[ \frac{p}{kT} = \rho - \left( \frac{\rho^2}{2\alpha kT} \right) \int r \cdot u'(r) g(r) \, dr \quad \ldots \ldots 3.4 \]
where \( g(r) \) is a radical distribution function which is a function of distance alone and \( u'(r) \) is the potential. For hard-sphere potential which is \(+\infty\) for \( r < d \) and \( 0 \) otherwise, this equation in three dimensions becomes,

\[
\frac{p}{kT} = \rho + \frac{\rho^2}{6} 4\pi \int_0^\infty \frac{d}{dr} \left[ \exp \left\{ -\beta u(r) \right\} \right] r^3 V(r) \, dr
\]

\[
= \rho + \frac{2\pi}{3} d^3 \rho^2 V(d)
\]

where \( V(r) = g(r) \exp \left\{ \beta u(r) \right\} \) is a continuous function.

Substituting \( \frac{N}{V} = \rho_N \), where \( \rho_N \) is the number density and \( \frac{\pi d^3}{6} \) is the volume of the molecule,

\[
\left( \frac{\pi \rho d^3}{6} \right) = \cap \text{ and } V(d) = g(d).
\]

We get the equation of state for hard-sphere of diameter \( d \) as,

\[
\frac{p}{kT} = \frac{N}{V} \left[ 1 + 4\cap g(d) \right]
\]

i.e.,

\[
\frac{pV}{NkT} = 1 + 4\cap g(d)
\]

\[\text{......3.6}\]

### 3.3 Scaled Particle Theory

Hence for hard-spheres, it is only necessary to determine \( g(d) \). Reiss\textsuperscript{12} has developed a simple but accurate method, called Scaled Particle Theory (SPT) for obtaining \( g(d) \) and thus \( \rho \).

Let \( P_0(r) \) be the probability that there is no molecule, whose centre lies within a sphere of radius \( r \), centered about some specified point. Thus \( \frac{dp_0}{d\rho} \) is the probability of finding an empty sphere, whose radius lies between \( r \) and \( r+dr \). This will be equal to the product of the probability of having no molecule within the radius \( r \) and the conditional probability \( 4\pi \rho G(r) \, r^2 \, dr \), of there being a centre of at least one molecule within the shell of thickness \( dr \) of \( r \) when no molecule is inside the sphere of radius \( r \), the function \( g(r) \) gives the \( r \) dependence of the probability.
Let us now assume that, from the centre of any given molecule, no other molecule can have its centre in a sphere of radius \( d \). i.e. the sphere is empty of all other molecules, for the given molecule. Thus an empty sphere of radius "\( d \)" affects the remainder of the fluid exactly like another molecule would do. Hence it is called Scaled Particle Theory. i.e. \( G(d) = g(d) \).

Thus,
\[
- \frac{dp_o(r)}{dr} = p_o(r) \, 4\pi \rho r^2 G(d)
\]  \hspace{1cm} \ldots \ldots \text{3.7}

also,
\[
p_o(r) = \exp \left( -\frac{W}{kT} \right)
\]  \hspace{1cm} \ldots \ldots \text{3.8}

where \( W \) is the reversible work necessary to create a cavity of radius \( r \) in the fluid \( p_o \). \( W \) and \( G \) depend upon \( \rho \) as well as \( r \). therefore,
\[
\frac{dp_o(r)}{p_o(r)} = -4\pi \rho r^2 G(r) \, dr
\]

and equation 3.8 gives
\[
\frac{dp_o(r)}{p_o(r)} = -\frac{dW}{kT}
\]

hence \( dW = kT \rho \, G(r) \, 4\pi r^2 dr \)  \hspace{1cm} \ldots \ldots \text{3.9}

but \( dW = pdV + \sigma ds \)  \hspace{1cm} \ldots \ldots \text{3.10}

where \( \sigma \) is the surface tension, \( S \) is the surface area and \( V \) is the volume of the system respectively.

From 3.9 and 3.10, we can have,
\[
G(r) = \frac{1}{\rho kT} \left[ \frac{1}{4\pi \rho r^2} \frac{dV}{dr} + \frac{\sigma}{4\pi r} \frac{ds}{dr} \right]
\]  \hspace{1cm} \ldots \ldots \text{3.11}

now,
\[
dV = 4\pi r^2 dr, \quad ds = 8\pi r dr
\]
\[ G(r) = \frac{1}{\rho kT} \left[ \frac{pdV}{dV} + \frac{\rho dS}{dV} \right] \]

\[ = \frac{1}{\rho kT} \left[ p + \frac{\sigma}{r} \right] \]

\[ \text{.....3.12} \]

which gives, \( G(\infty) = \frac{p}{\rho kT} \)

\[ = \frac{pV}{NkT} \]

\( N/V \) is the number density

As \( \frac{p}{\rho kT} = 1 + 4G(d) \)

\[ G(\infty) = 1 + 4G(d) = \frac{pV}{NkT} \]

Barker and Henderson\(^{120}\) assumed that for 'r' not too small.

Surface tension,

\[ \sigma(r) = \sigma_0 \left[ 1 + 2\delta \left( \frac{d}{T} \right) \right] \]

where \( \sigma_0 \) and \( \delta \) are constants to be determined. Substitution in equation 3.12 gives.

\[ G(r) = \left( \frac{1}{\rho kT} \right) \left[ p + \frac{2\sigma_0}{r} \left( 1 + 2\delta \left( \frac{d}{r} \right) \right) \right] \]

\[ \text{.....3.13} \]

For \( r < \frac{d}{2} \), no more than one molecular center can lie within a sphere of radius \( r \) and therefore \( p_0(r) \) is equal to unity minus the probability of there being a molecular centre within the sphere. Thus,

\[ p_0(r) = \left[ 1 - \left( \frac{4\pi}{3} \right) r^3 \right], \quad r < \frac{d}{2} \]

Therefore,

\[ \frac{dp_0}{dr} = -4\pi r^2 \rho \]
combining with eqn. 3.7
\[ p_o(r) \, 4\pi r^2 \rho \, G(r) = 4\pi r^2 \rho \]
\[ p_o(r) \, G(r) = 1 \]
\[ G(r) = \frac{1}{p_o(r)} = \left[ 1 - \left( \frac{4\pi}{3} \right) r^3 \rho \right]^{-1}, \text{ For } r < \frac{d}{2} \quad \ldots\ldots3.14 \]

Hence equation 3.14 is valid for \( r \) not too small. For \( \frac{d}{2} < r < \frac{d}{\sqrt{3}} \), two molecular centres can lie within the sphere and \( p_o(r) \) and \( G(r) \) cannot be determined without first knowing \( G(r) \). It may be assumed that equation 3.13 is valid for all \( r > \frac{d}{2} \). This is the central approximation of SPT.

Equation 3.13 can be written as
\[ G(r) = \frac{p}{\rho kT} + \frac{2\sigma_o d}{\rho kT \cdot dr} + \frac{4\sigma_o \delta d^2}{\rho kT \cdot r^2} \]

\[ = \left[ \frac{p}{\rho kT} \right] + A \left[ \frac{d}{r} \right] + B \left[ \frac{d}{r^2} \right], \quad r > \frac{d}{2} \]

where \( A = \frac{2\sigma_o}{\rho kTd} \) and \( B = \frac{4\sigma_o \delta}{\rho kTd} = 2A\delta \)

\[ \frac{p}{\rho kT} = 1 + 4\cap G(d) = 1 + 4\cap \left[ \frac{p}{\rho kT} + A + B \right] \quad \text{(Since } k = k_n) \]

\[ \frac{p}{\rho kT} \left[ 1 - 4\cap \right] = 4\cap (A+B) + 1 \]

\[ \frac{p}{\rho kT} = \left[ 1 + 4\cap (A+B) \right] \quad \frac{1}{(1 - 4\cap)} \quad \ldots\ldots3.15 \]

For \( r < \frac{d}{2} \). from 3.14,
\[ G(r) = \left[ 1 - \left( \frac{4\pi}{3} r^3 \rho \right) \right]^{-1} \] \hspace{1cm} \ldots \ldots 3.16

\[ G(r) = \left[ 1 - 8\eta \left( \frac{r}{d} \right)^3 \right]^{-1} \] \hspace{1cm} \ldots \ldots 3.17

\[ G(r) = \frac{(1 + 4\eta (A + B))}{(1 - 4\eta)} + A \frac{d}{r} + B \frac{d^2}{r^2} \] \hspace{1cm} \ldots \ldots 3.18

Thus expression 3.17 and 3.18 give the value of \( G(r) \) for \( r < \frac{d}{2} \) and \( r > \frac{d}{2} \) respectively. Expressions for \( A \), \( B \) and \( \sigma_0 \) and \( \delta \) can be obtained by requiring that \( G(r) \) and \( \frac{d}{dr} G(r) \) be continuous at \( r = \frac{d}{2} \). Thus \( A \) and \( B \) are found as,

\[ A = -\frac{3\eta (1 + \eta)}{2 (1 - \eta)^3} \quad \text{and} \quad B = \frac{3\eta^2}{4(1 - \eta)^3} \]

Therefore,

\[ \frac{P}{\rho kT} = \frac{1 + 4\eta \left[ -\frac{3\eta (1 + \eta)}{2 (1 - \eta)^3} + \frac{3\eta^2}{4(1 - \eta)^3} \right]}{(1 - 4\eta)} \]

\[ \frac{P}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)} \] \hspace{1cm} \ldots \ldots 3.19

\[ G(d) = \left[ 1 - \frac{P}{\rho kT} \right] \frac{1}{4\eta} \]

\[ G(d) = \left[ \frac{1 + \eta + \eta^2}{(1 - \eta)^3} - 1 \right] \frac{1}{4\eta} \]; thus in SPT we have,

\[ G(d) = \frac{4 - 2\eta + \eta^2}{4(1 - \eta)^3} \] \hspace{1cm} \ldots \ldots 3.20

Eqn. 3.20 gives an exact second and third virial
coefficients. $\cap$ is less than unity and for $p$ to be finite, equation 3.20 must fail at high densities [i.e. for the densities greater than close packing]. However, for the densities at which the hard spheres are fluid, equation 3.19 is in good agreement with the machine simulation results.

now \[ A = \frac{2\sigma_e}{\rho K T d} = -\frac{3}{2} \frac{\cap (1 + \cap)}{(1 - \cap)^3} \]

\[ \sigma_e = -\frac{9}{2} \frac{K T \cap^2 (1 + \cap)}{d^2 (1 - \cap)^3} \]

The negative surface tension need not be taken surprisingly. It is an immediate consequence of the fact that the hard-sphere fluid has no attractive forces and so can be maintained at finite volume only by means of an external pressure. The SPT also gives expression for the equation of state of two-dimensional hard discs and one-dimensional hard rods. The expressions are given as follows.

\[ \frac{pA}{N k T} = \frac{1}{(1 - Y)^2} \quad \text{where} \quad Y = \frac{\pi \rho d^2}{4} \]

and \[ \frac{pA L}{N k T} = \frac{1}{(1 - \rho d)} \quad \ldots \ldots \quad 3.21 \]

respectively for hard discs and hard rods.

### 3.4 Scaled Particle Theory As Applied to Mixtures:

Many attempts have been made\textsuperscript{80,88,91} to use Scaled Particle Theory to obtain an equation of state of hard sphere mixtures. The equation of state is described as

\[ \frac{p}{\rho k T} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3} \cdot \frac{\pi}{2} \frac{\rho}{(1 - \rho)^3} \sum_{i < j = 1}^{m} x_i x_j (d_{ij} d_{jj})^2 \left[ 2d_{ij} + d_{ai} d_{ij} x \right] \]

\[ \ldots \ldots \quad 3.22 \]

where $d_{ij}$ are the diameters of the $m$-components, and

\[ \xi = \frac{\pi}{6} \rho \sum_{k = 1}^{m} x_k d_{kk}^3 \]
\[ \chi = \frac{\pi}{6} \rho \sum_{k=1}^{m} x_k d_{kk}^2, \quad d_{ij} = \frac{d_i + d_{jj}}{2}, \quad x_i = \frac{N_i}{N} \]

where \( N_i \) is the number of hard spheres of species \( i \) and \( N \) is the total number of molecules in the mixtures.

3.5 Hard Convex Molecules:

Gibbons\(^{121}\) and Boublick\(^{122}\) applied SPT to mixtures of hard convex molecules (not necessarily spheres) and obtained an equation of state as

\[ \frac{P}{\rho kT} = \frac{1}{1 - Y\rho} + \frac{A B \rho}{(1 - Y\rho)^2} + \frac{1}{3} \frac{B^2 C \rho^2}{(1 - Y\rho)^3} \quad \ldots \ldots 3.23 \]

Where \( A = \sum_{i=1}^{m} x_i \tilde{R}_i \), \( B = \sum_{i=1}^{m} x_i S_i \), \( C = \sum_{i=1}^{m} x_i \tilde{R}_i^2 \), \( Y = \sum_{i=1}^{m} x_i V_i \)

and \( \tilde{R}_i \), \( S_i \) and \( V_i \) are the mean radius of curvature, surface area and volume respectively of a molecule of species \( i \). For a particular case of pure fluid, eqn. 3.23 becomes,

\[ \frac{P}{\rho kT} = \frac{1}{1 - V_i \rho} + \frac{R_i S_i \rho}{(1 - V_i \rho)^2} + \frac{1}{3} \frac{R_i^2 S_i^2 \rho^2}{(1 - V_i \rho)^3} \quad \ldots \ldots 3.24 \]

for hard spheres \( R_i = \frac{d_i}{2}, S_i = \pi d_i^2 \) and \( V_i = \left( \frac{\pi}{6} \right) d_i^3 \)

Eqn. 3.24 gives equation 3.19 and equation 3.24 and 3.23 gives the correct second virial coefficient and for hard spheres, gives the correct third virial coefficient. For prolate spherocylinders, equation 3.24 gives an accurate third virial coefficient. It has been proved that SPT works well for hard spherocylinders as well as for hard spheres. SPT is reliable for any isotropic fluid of hard convex molecules.
Reiss used SPT to obtain the radial distribution of hard spheres and their thermodynamic properties.

3.6 Ultrasonic Velocity and Equation of State:
We know that,
\[ \gamma \left( \frac{dp}{d\rho} \right)_T = u^2 \]

\[ \ldots \ldots 3.25 \]

where "u" is the u.s. velocity in liquid, \( \rho \) is molecular density and \( \gamma = \frac{C_p}{C_v} \).

On solving equation 3.23 and 3.25, we get an equation of state.

\[ \frac{M u^2}{\gamma RT} = \frac{1}{(1 - \gamma \rho)^2} \left[ 1 + 2AB \left\{ \frac{\rho}{(1 - Y \rho)} \right\} + B^2C \left\{ \frac{\rho}{(1 - Y \rho)} \right\}^2 \right] \]

\[ \ldots \ldots 3.26 \]

which is used to evaluate u.s. velocity in pure liquids as well as their mixtures.

For pure liquid, \( A = R \), \( B = S \), \( C = R^2 \) and \( Y = V \) so

\[ \frac{M u^2}{\gamma RT} = \frac{1}{(1 - V \rho)^2} \left[ 1 + 2R S \left\{ \frac{\rho}{(1 - V \rho)} \right\} + R^2S^2 \left\{ \frac{\rho}{(1 - V \rho)} \right\}^2 \right] \]

\[ \ldots \ldots 3.27 \]

also,

\[ \frac{M u^2}{\gamma RT} = \frac{1}{(1 - V \rho)^2} \left[ 1 + R S \left\{ \frac{\rho}{(1 - V \rho)} \right\} \right]^2 \]

therefore,

\[ = \frac{1}{(1 - V \rho)^2} \left[ \frac{[1 + (R S - V)\rho]^2}{(1 - V \rho)^2} \right] \]
Putting $\frac{R}{S} = X$ defined as shape factor and $\nabla \rho = \cap$ then above expression reduces to,

$$\frac{\mu^2}{\gamma RT} = \frac{(1 + (X - 1) \cap)^2}{(1 - \cap)^4} \quad \cdots 3.28$$

SPT has been used to obtain an equation of state for perfectly aligned and isotropic hard spherocylinders. Many workers\textsuperscript{123} have used above equation of state for spherical or other type of molecules to study phenomena of phase change by Monte Carlo method\textsuperscript{123}

3.7 Computational Technique For Evaluation of Ultrasonic Velocities And Assigning Molecular Shapes To Interacting Molecules In Mixture.

In binary liquid mixture systems the component molecules may be assigned different molecular shapes, such as Spherical, Cubical, Tetrahedral and Disc of various depths etc.

If $R$, $S$ & $V$ denote the Radius, Surface area and Volume of a molecule as shown in Table - 3 respectively, then shape factor [denoted by $Z(3)$] is given by.

$$Z(3) = \frac{R}{S} = X$$

For pure liquids,

$$\frac{\mu^2}{\gamma RT} = \frac{(1 + (x - 1) \cap)^2}{(1 - \cap)^4} \quad \cdots 3.29$$

where $\cap = V\rho_N \cdot \rho_N$ being the number density, $v = \text{hard core volume}$ and other quantities have their usual meaning.

A solution of above equation is obtained as,

$$\cap = A = B \sqrt{(B^2 + C - 1)} \quad \cdots 3.30$$
where \( B = 1 + \frac{CY}{2} \) \hspace{1cm} \( \ldots 3.31 \)

\[ C = \sqrt{\frac{(G/M)}{u}} \] \hspace{1cm} \( \ldots 3.32 \)

\[ G = \gamma RT \] \hspace{1cm} \( \ldots 3.33 \)

and \( Y = Z(3) - 1 \) \hspace{1cm} \( \ldots 3.34 \)

using experimental ultrasonic velocity \( u \), molecular weight \( M \) and \( \gamma \), obtained from literature. \( \cap \) is calculated for pure liquids and the values of \( \cap \) are given in Table - 4 for various model shapes under consideration.

Now, \( \cap = \nu \rho_N \)

\[ \nu = \frac{\cap}{\rho_N} = \frac{\cap}{H} \] \hspace{1cm} \( \ldots 3.35 \)

\[ = \frac{H \rho}{M} \] \hspace{1cm} \( \ldots 3.36 \)

by knowing \( \cap \), molecular weight \( M \), molecular density \( \rho \) and Avagadro's number \( H \), \( \nu \) can be calculated.

For a spherical molecule, volume \( \nu = \frac{4\pi A^3}{3} \) hence,

\[ A = \left[ \frac{3\nu}{4\pi} \right]^{1/3} \]

or \( A = Z(5)\nu^{1/3} \) \hspace{1cm} \( \ldots 3.37 \)

area of a molecule \( B = 4\pi A^2 \)

\[ = Z(7) A^2 \]

\[ C = A^2 \]

and \( \text{Volume} = \nu \) \hspace{1cm} \( \ldots 3.38 \)
The values of shape constants of SPT for different molecular shapes are given in Table - 5.

For pure liquids, A, B, C and V are denoted by
\[ A_1 = I(1), \quad B_1 = K(1), \quad C = N(1), \quad V_1 = p(1) \] and \[ A_2 = I(2), \quad B_2 = K(2), \quad C = N(2), \quad V_2 = p(2) \] respectively.

Now, molecular weight of the mixture is expressed as
\[ M = R(1) + x [R(2) - R(1)] \] .....3.39

where \( x \) is the volume fraction.

\( R(1) \) and \( R(2) \) are molecular weights of two components. Let \( T(1) \) and \( T(2) \) be the densities of pure liquids. Then from eqn. 3.36
\[ v_1 = \frac{\cap_1}{R(1)} \quad \text{and} \quad v_2 = \frac{\cap_2}{R(2)} \] .....3.40

Volume of mixture is given by,
\[ V_o = \frac{R(1)}{T(1)} + \left[ \frac{R(2)}{T(2)} - \frac{R(1)}{T(2)} \right] x \]

i.e. \[ V_o = \bar{V}_1 + \left[ (V_2 - V_1) x \right] \]

For a binary mixture, different molecular dimensions are
\[ I(3) = I(1) + x [I(2) - I(1)] = A \] .....3.41
\[ K(3) = K(1) + x [K(2) - K(1)] = B \] .....3.42
\[ N(3) = N(1) + x [N(2) - N(1)] = C \] .....3.43
\[ P(3) = P(1) + x [P(2) - P(1)] = v \] .....3.44

By substituting these values in an equation,
\[ \frac{\mu^2}{\gamma RT} = 1 + 2AB \left[ \frac{\rho_N}{(1 - \rho_N v)} \right] + B^2C \left[ \frac{\rho_N}{(1 - \rho_N v)} \right]^2 \]

\[ \left[ 1 - \rho_N v \right]^2 \] .....3.45
where $\rho_N = \frac{N}{V_0}$.

Ultrasound velocity "u" for a mixture can be calculated. This gives the velocity of a mixture at temperature $T$ from the pure liquid parameters, assuming no interaction in the mixture. Chi square ($\chi^2$) test of significance may be applied to calculated velocities in a representative binary liquid mixture of acrylonitrile + p-dioxane, to test the theory. For any mixture, various different shape combinations may be considered and velocities may be predicted. Sum deviation of theoretical velocities and experimental velocities may be calculated. The minimum value of sum deviation would predict the particular molecular shape of component liquid in binary liquid mixture at a given temperature. In a mixture, the deviation in the value of a thermodynamic property from that of an ideal mixture is indicative of an interaction between the molecules of the two species i.e. an AB interaction. The AB interaction may cause the formation of new molecules if the interaction is strong enough. But in the case of weak AB interaction, it may cause a distortion in molecules. The distortion can be either in the shape of a molecule or a change in the volume (size) of both the molecules or both types of distortions may occur. Considering only the changes in shape without the change in size, the mixture can be considered as an assembly of non-interacting distorted molecules.

1] Assuming AB interaction taking place in a mixture, volume of the mixture is modified as,

$$V_0 = V_1 + (V_2 - V_1)X + (X - X^2)(\alpha + \beta X) \quad \ldots \ldots \text{3.46}$$

where $\alpha$ and $\beta$ are taken as adjustable parameters.

If densities, taking volume additive, do not differ from experimental values, then the mixture is supposed to have no interaction but as density values are different, equation 3.46 is used. $\alpha$ and $\beta$ are adjusted to get experimental values of densities for a given set of different composition of two liquids.
In the present investigation the calculations are carried out with the help of computer assigning value to $\alpha$ and $\beta$ in the range from -17 to 17 at an interval of 0.0001. All possible combinations of numbers were tried to get the minimum deviation from experimental values of densities.

Let the basic parameters used to modify the equation of bulk volume be ‘a’ and ‘b’. These parameters are used to obtain corrected volume of individual liquids in mixture as,

$$V_1^c = V_1 [1 + a (x-x_1^2)] \quad \text{and} \quad V_2^c = V_2 [1 + b (x-x_2^2)]$$

Volume of the mixture is given by,

$$V = (1 - x) \ V_1^c + xV_2^c$$

$$V = (1 - x) \ V_1 [1 + a (x-x_1^2)] + xV_2 [1 + b(x-x_2^2)]$$

$$V = (1-x) \ V_1 + xV_2 + V_ia \ (x-x_1^2) \ (1-x) + V_2b \ x(x-x_2^2)$$

hence,

$$V^a = (x - x^2) \ [V_1a + x(V_2b - V_1a)]$$

$$V^b = (x - x^2) \ (\alpha + x\beta)$$

where $V_1a = \alpha$ and $[V_2b - V_1a] = \beta$

Hence $\alpha$ and $\beta$ gives nonideal contribution to bulk volume of the mixture. When a & b compared to each other may provide useful information about, as to which liquid component in binary liquid mixture is contributing to the change in volume after mixing. Therefore bulk volume of the mixture is considered as,

$$V = V_1 (1-x) + V_2x + (x - x^2) \ [\alpha + \beta x]$$

where $V_1 = \frac{M_1}{\rho_1}$ and $V_2 = \frac{M_2}{\rho_2}$ for two constituent liquids.

Hence $\alpha$ and $\beta$ parameters can be called as “transfer paramters”, which ultimately are indicative of either first or second liquid which gives non ideal part in the volume equation.

2] Assuming distortion of molecules in case of weak interactions, correction is applied to hard core volume as,
\[ V^C_1 = V_1 \left[ 1 + Y(x - x^2) \right] \]

and

\[ V^C_2 = V_2 \left[ 1 + Z(x - x^2) \right] \]

is obtained as,

\[ V = V^C_1 + \left[ V^C_2 - V^C_1 \right] x \]

.....3.47

and proceeding in the same way for calculation of u.s. velocity by keeping \( \alpha \) and \( \beta \) constant as adjusted earlier and by varying the values of \( Y \) and \( Z \) between -5 and 5 at the interval of 0.0001, all combinations are tried to get the minimum deviation from the experimental velocities.

The same procedure may be repeated by considering different shapes of component molecules in a mixture such as

1. spherical + spherical
2. Spherical + cubical
3. Spherical + tetrahedral
4. Spherical + disc (a),
5. Spherical + disc (b),
6. Spherical + disc (c),
7. Spherical + disc (d),
8. Cubical + spherical,
9. Cubical + cubical,
10. Cubical + tetrahedral,
11. Cubical + disc (a),
12. Cubical + disc (b),
13. Cubical + disc (c),
14. Cubical + disc (d),
15. tetrahedra + spherical,
16. tetrahedral + cubical,
17. tetrahedral + tetrahedral,
18. tetrahedral + disc (a),
19. tetrahedral + disc (b),
20. tetrahedral + disc (c),
21. tetrahedral + disc (d),
43. disc (d) + spherical,  
44. disc (d) + cubical,  
45. disc (d) + tetrahedral.  
46. disc (d) + disc (a),

respectively.

All the above shapes of molecules can be tried using equivalent radius, corresponding area and volume of molecules and a particular shape would be fixed for which u.s. velocity would be in close agreement with the experimental values (for which the total sum of deviation is minimum). Chi-square test of significance can be applied to calculated velocities to test the theory. For a given mixture various combination of shapes may be considered and velocities may be calculated. In the present work only spherical-spherical shape has been considered for evaluating u.s. velocities for compoenent molecules in the binary liquid mixtures, in order to have a comparison of results, with those obtained from Khasare’s theory. The computer programme written in BASIC for evaluation of u.s. velocities has been given in Appendix 1. The \( u_{SPT} \) values for the value of interaction parameter \( Y=Z=0 \) and \( Y \& Z \) = some numerical values have been presented in Table 2.

3.8 Remarks:

The hard sphere model has been employed to understand the structure of bulk properties of liquids. It is relatively easy to obtain this thermodynamic parameter using mathematical approximations at different levels in the development of any liquid state theory. At high temperature or near the critical temperature the behaviour of hard sphere model fluid approximates to that of a real fluid. The equilibrium thermodynamic properties may be predicted accurately for pure fluids by methods of statistical mechanics. The equation of state developed in scaled particle theory has been found to be superior to previous equation of state of its kind. Hence SPT has been applied to the systems under investigation. The results of the theoretical evaluation of u.s. velocities, for pure liquids and their binary liquid mixtures, has been presented along with relevant discussion in Chapter 5.