2.1 **Liquid State**

Matter exists in liquid state in a relatively small portion of the enormous range of temperatures and pressures. However, they are of vital importance in Science and Technology and in various life processes in the universe. Out of the three main states of matter, the liquid state is intermediate in its properties between a solid and a gas. The greatest resemblance between liquid and gas is that they do not offer a permanent resistance to shearing stress and hence neither of them possess a shape of its own but have the shape of the container. On the other hand, solid offers resistance to shearing stress and possesses a definite form. The most prominent resemblance between solid and liquid is that both possess cohesion which enable them to maintain a free surface.

2.2 **Some Peculiarities of Liquid State**

In solid, forces of long range order exist which prevent the molecules to move away from each other. This results in the rigidity of a crystal. Whereas a liquid state is characterised by short range forces which allow the molecules to move freely. **Density** is also an important factor which shows similarity between solid and liquid. In a solid to liquid change, density change is of the order of 10-50%, but when a liquid changes to gaseous state, density decreases by 100-1000. Hence from density considerations,
one can say that molecules in solid are packed close to each other. In liquid, there is little space, about 5% of the molecular diameter, between the molecules and in case of gas, the space is about six times the molecular diameter.

As the molecules of solid are closely packed, it has low compressibility. And there is a resemblance between the compressibilities of solid and liquid. For solid, it is of the order of 10E-6 atm-1 and for liquid of the order of 10E-5 atm-1.

Solids give a characteristic pattern of Laue spots in X-ray diffraction. The diffraction pattern of liquid is a series of bright and dark rings. Using the pattern [75] one can calculate the radial distribution of atoms surrounding a representative atom. The resemblance between liquid radial density curve and the solid structure is striking which predicts that liquid structure must be a rather irregular version of solid structure.

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied, a minimum, a regular crystal-like structure is formed. But if the volume available to spheres is more, regularity of the structure disappears. This has been demonstrated in two dimensions by a number of workers [76] who have studied the distribution of spheres distributed on a flat surface. Three-dimensional problems have been studied by Morvel & Hildbrand [77] by suspending hard gelatin spheres in a solution.
of same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

Most attempts to develop a theory of liquid state are directed towards the simple consideration of molecules behaving like hard spheres having attractive forces. But a large majority of liquids are complex and consist of polyatomic non-spherical molecules in which some additional molecular forces exist. A short account of different forces is taken as follows:

2.3 *Inter Molecular Forces in Liquids*

a) **Ionic Bond**

W. Kossel developed the first successful theory of chemical reactions on the basis of ionic bonds. Ionic bond is the strongest among the polar bonds.

b) **Dipole-Dipole Forces**

Distortion of electron cloud occurs in most molecules consisting dissimilar atoms and electrical effects are strong enough to constitute a dipole. Such molecules are affected by external electric and magnetic fields. Since attraction and repulsion forces are not spherical, there is an overall force of attraction. This attractive effect is found in almost all molecules except those which are symmetrical such as \( \text{H}_2, \text{N}_2, \text{C}_6\text{H}_6 \).
c) **Dipole-Induced Dipole Forces**

Electron clouds around the nuclei are not stationary but are mobile. Applied electric field tends to disturb the average electric arrangement by pulling electron cloud towards a positive molecule such as Benzene, a dipole may be formed of the other molecule which results in an attraction between two unlike molecules of two different species.

d) **London-Dispersive Forces**

In atoms, electrons are in continuous motion relative to nuclei. At a given instant, electrons in one atom may be on the side next to the other atom. So electrons in the second atom get repelled and shift away from first atom. The next moment, opposite arrangement may occur. In this way, electron clouds may oscillate in phase with each other inducing dipoles of a temporary nature to be set up in the pair of atoms. London had shown that it leads to an overall attraction, the force being called as dispersive force. For completely symmetrical molecules, London force is the only reason for attraction.

e) **Hydrogen-Bonding**

An exposed hydrogen atom covalently bonded to a molecule may have a positive character, particularly if it is part of an OH or NH group. An electrostatic attraction may occur between positive
hydrogen and electronegative atom such as fluorine, oxygen or nitrogen. Hydrogen bonds are usually weaker than regular bonds. These weaker attractive forces cause an association of molecules.

f) **Effect Due To Association**

Not only the shape and size of molecules but their mutual interaction decides the structural arrangement of molecules. Electric dipole moment affect compressibility of molecules because the resulting electric forces pull the molecules into more tight packing. This effect called association is a characteristic of liquids showing pronounced structural properties. However thermal agitation of molecules tries to disturb the molecular order formed by association.

2.4 **Theories Of Liquid State**

a) **The Hole Theory Of Liquid.**

In all lattice theories of liquid state, they require a molecule to be more or less bound to one position in space. This is in opposition to the viewpoint of the gas kinetic theories where the molecule has an almost complete freedom of motion. Once a molecule is restricted to a relatively small volume, analysis can be simplified considerably since in the past approximation, only the nearest neighbourhood be considered. However the concept of the 'holes' i.e. vacant sites in the lattice is required to account for the fluidity of liquids and the theory based on this model is
usually referred to as the hole theory \([78,79]\).

The hole theory treats a liquid as an imperfect solid. The older theories of the liquid state, on the other hand, treated the liquid as an imperfect gas. The fact that a liquid can be converted reversibly into a gas without passing at any time, through a region in which two phases are present, by simply heating the liquid under high pressure to a temperature above its critical point and then allowing it to expand, is a cogent reason for believing that the liquid is somehow gas like in structure.

The mathematical techniques of treating imperfect gases in the neighbourhood of a condensation are too complex but the method of attack is essentially that of Mayer \([80a,b,c]\).

The equation,

\[
P V = R T \left[ 1 + A_1/V + A_2/V^2 + A_3/V^3 + \ldots \right]
\]

\[\ldots \ldots \ 2.1\]

has been used as an empirical equation to describe the pressure-volume relationship for the gases at moderate pressures. Unfortunately it is also known that the phenomenon of condensation is not determined primarily by the early terms in this series, but by the later ones. So that there is no justification for trying to express the properties of liquids in terms of an equation of state extrapolated for low pressure. The failure of such equations of state as that of Vander Waals's to give good results for condensation phenomena is well known.
b) **Perturbation Theories**

Here we shall examine some of the perturbation theories which have been developed and have received attention in the past few years. The reason for the success of the perturbation theory of liquids is that the structure of a simple liquid is determined primarily by the hard core part of potential and that the main effect of the non-hard core part of the potential is to provide a uniform background potential in which the molecules move. This concept has been used for some time which is the basis of the equation of state of Vander Waals

\[
(P + N^2a^2/V^2)(V-Nb) = NkT
\]

This equation gives results which are in poor agreement with the experimental data.

On the other hand, application of the Scaled Particle Theory to fluids with attractive forces, indicated that liquid molecules could be regarded as hard-spheres in an uniform background potential.[81]

Also, Longuet-Higgins & Widom [82] and Guggenheim [83] have shown that the main defect in the Vander Waals' theory lies in the use of an equation,

\[
A_0/NkT = 3 \log \lambda^{-1} - \log V_f + \log N
\]

where, \( V_f = V - Nb \)
for the hard sphere free energy. Thus, if eqn(2.1) is replaced by

\[ P = P_0 - \frac{N^2 a}{V^2} \]

and some more reliable expression for \( P_0 \) is used, then a good agreement is obtained with experimental results. For example, the Percus-Yevick [84] or Carnahan and Starling [85] expressions could be used. However, the Longuent-Higgins and Widom (LHW) equation of state is fairly intensive to the precise form of \( P_0 \).

In fact, Guggenheim [86] showed that good results could be obtained by replacing the Vander Walls' expression,

\[ P_0 V / N k T = (1 - 4n)^{-1} \]
\[ P_0 V / N k T = (1 - n)^{-4} \]

where \( n = (\pi / 6) \rho d^3 \)

\((\pi d^3) / 6\) being the volume of a hard sphere.

It is to be borne in mind that in the (LHW) equation of state, 'a' is a parameter chosen arbitrarily. The value of 'a' which results from equation 2.2 given below,

\[ a = - 2\pi \int_0^1 u(r) r^2 dr \] \[ \cdots \cdots \cdots \cdots \text{2.2} \]

where the potential energy \( u(r) \) given by,

\[ u(r) = \infty, \quad r < \sigma \]
\[ = u_1(r), \quad r > \sigma \]

is quite different from that which is required to fit experimental
data. The work of LHW and that of Reiss and others on the Scaled Particle Theory indicated that the hard-sphere fluid was an excellent reference system for the study of the properties of liquids even at the lowest temperatures.

2.5 **Computer Simulations**

The most severe difficulties in the theory of liquids arise because there is no obvious way of reducing the complex many-body problem posed by the motion of the molecules to a one-body or few-body problem. The straightforward way of meeting this problem is a computer solution of the many-body problem. The question of how many in many-body has been explored very fully by a large amount of work in the last two decades and one can obtain very good estimates of the behaviour of macroscopic systems in almost all conditions except in the neighbourhood of a critical point.

In the "Monte-Carlo" method, 'Ensemble Averages' have been evaluated using statistical mechanics. And in the method of 'Molecular Dynamics', the dynamical equations of motion of molecules are solved in which 'Time Averaging' is used.

Most Monte-Carlo calculations have been performed using the canonical ensemble of Gibbs in which number of molecules $N$, volume $V$ and temp $T$ are fixed. The general term "Monte Carlo Method" refers to the use of random sampling techniques to estimate
averages. In the context of statistical mechanics, it refers to a particular and very efficient "Importance Sampling" method introduced by Metropolis et al [87] in which one generates a chain of configurations of a many-body system in such a way that the probability of a particular configuration of energy \( U \) appearing in the chain is proportional to \( e^{-\beta U} \). Then the unweighted average of any function over the configurations of the chain gives an estimate of the canonical average of that function.

2.5.1 Monte-Carlo Method.

The thermodynamic parameters such as pressure, energy, and other quantities like Radial Distribution Function (RDF) can be evaluated by the Monte Carlo method. However, it is not possible to determine directly the free energy or entropy by this method. On the other hand, one can evaluate derivatives of the free energy either with respect to thermodynamic variables such as \( V \) and \( T \) or with respect to parameters which appear in the potential energy function \( U \) describing the system. Thus if the potential energy function \( U(r, \lambda) \) depends on the parameter \( \lambda \) as well as on the configuration of the system (represented by \( r \), describing positions and orientations of all molecules) then,

\[
\frac{\delta A}{\delta \lambda} = -kT \int \left[ \ln \left( \sum \frac{\exp(-\beta U)dr}{\exp(-\beta U)dr} \right) \right] dr
\]

\[
= \left[ \sum \frac{\exp(-\beta U)dr}{\exp(-\beta U)dr} \right] - \int \left[ \sum \frac{\exp(-\beta U)dr}{\exp(-\beta U)dr} \right] dr
\]
\[ \langle \frac{SU(\vec{r}, \lambda)}{\delta \lambda} \rangle \lambda \]

\( < \lambda \) means canonical averaging for the system with potential energy \( U(r, \lambda) \). Hence, by performing Monte Carlo calculations for a number of values of \( \lambda \), one can evaluate \( \delta A/\delta \lambda \) for a range of values of \( \lambda \); by integrating the results, free energy differences can be evaluated, according to the equation

\[ A(\lambda) - A(\lambda_0) = \int_{\lambda_0}^{\lambda} \langle \frac{SU(\vec{r}, \lambda)}{\delta \lambda} \rangle \, d\lambda \]  

..... 2.3

where \( A \) is free energy.

If parameter \( \lambda \) is taken as volume \( V \), then

\[ A(V_1) - A(V_0) = \int_{V_0}^{V_1} p \, dV \]

with the pressure given by the virial expression

\[ \frac{pV}{Nk_BT} = 1 - \frac{<\sum_i^N (SU/S_NT)\rangle}{\nu Nk_BT} \]

where \( \nu \) is the dimensionality of the system. These results have been used to calculate the free energy of dense fluid systems by integrating from low densities to high densities. Results have been obtained in this way for hard discs and spheres [88]. If \( \lambda \) is taken as temperature (T), then

\[ A(T_1)/T_1 - A(T_0)/T_0 = -\int_{T_0}^{T} <U> T(dT/T^2) \]

..... 2.4
which is similar to an integrated form of the Gibbs-Helmholtz equation,

$$A = E - TS = E + T(SA/ST)$$

using eqn. 2.4 by performing Monte Carlo Simulations at a series of temperatures, one can calculate the temperature variation of the free energy.

Similarly, by introducing a parameter $\lambda$ (or several parameters) into $U(r, \lambda)$ instead of confining only the values like $V$ or $T$ to $\lambda$, which changes a system ($\lambda = \lambda_0$) into a more complicated system, one gets,

$$U(r, \lambda) = \sum_{i,j} u(i,j, \lambda)$$

where, $u(i,j, \lambda_0)$ can be the hard-sphere potential and $U(r, i,j, \lambda_1)$ is the 6-12 potential or some other realistic potential.

Replacing the integral in eqn. 2.3 by a truncated Taylor series,

$$\Delta(\lambda_1) - \Delta(\lambda_0) = \sum_{\lambda} \left( \frac{\partial^2}{\partial \lambda^2} \right) \frac{\Delta(\lambda)}{\Delta(\lambda_0)} + \frac{1}{2} \sum_{\lambda} \frac{\partial^4}{\partial \lambda^4} \frac{\Delta(\lambda)}{\Delta(\lambda_0)} (\lambda - \lambda_0)^2 + \ldots$$

we lead to the perturbation theories.

Another method for calculating the free energy of a fluid was explored for the case of hard sphere fluid by Adams (1974). This was based on a result for the chemical potential derived by Widom (1974) that $\mu$ is given by
\[ \mu = -k_B T \left[ \frac{3}{2} \ln(V/N) - \ln(2\pi m g T/h^2) + \ln(\langle \exp(-\beta V) \rangle) \right] \]

Here \( V \) is the potential energy change due to adding of one more molecule to a system of \( N \) molecules. This method which gave reasonable results for densities which were not high, is closely related to the grand canonical method. It is also related to the ideas of the SCALED PARTICLE THEORY and Adams used his results to test this theory.

2.5.1a The Constant-pressure ensemble

The constant pressure or \((T,N,p)\) ensemble is most conveniently described by introducing dimensionless variables scaled by the edge \( L \) of the fundamental cube \( \vec{r}'_i = \vec{r}_i / L \).

The un-normalised weighting function \( p(\vec{r}'_L) \) in the canonical case is \( \exp(-\beta U) \) which becomes in this case as

\[ \exp\left[ -\beta \left( U(\vec{r}'_L) + pL - \beta N \ln L \right) \right] \]

where \( d \) is the dimensionality of the system.

A Monte Carlo Chain for this ensemble can be generated exactly as in the case of canonical ensemble. This method has obvious advantages if we are interested in results at a particular pressure, usually zero pressure. It was used by McDonald [90] to calculate excess enthalpies and volumes of mixtures at zero pressure.
The average of a function $F(\vec{r})$ of configuration in the constant pressure ensemble is given by,

$$
F = \frac{1}{Z} \int d\vec{r} \int_0^\infty \int d\vec{r}' P(\vec{r}'; L) F(\vec{r}'; L) P(\vec{r}', L)
$$

For hard sphere particles in any number of dimensions, Wood [91,92] showed that an alternative and convenient realization of the fixed pressure ensemble could be obtained by explicitly performing the integrations over $L$ in 2.6. This method has the advantage that the pressure is obtained directly rather than by extrapolating the Radial Distribution Function $g(r)$ to the hard sphere diameter $d$.

2.5.1b The Grand Canonical Ensemble

The grand-canonical ensemble $(T, V, \mu)$ in which, neither the number of molecules $N$, nor the pressure $p$ is constant, but the chemical potential $\mu$ is fixed. This had not been used for Monte Carlo calculations on realistic potentials until fairly recently. But the great advantage is that it leads directly to estimates of the free energy (since the chemical potential is fixed).

Using the same scaled coordinates as for the constant pressure ensemble, the un-normalized weighting function $P(\vec{r}', N)$ is given by

$$
P(\vec{r}', N) = \exp \left[ -k_B T \ln N! + N k_B T \ln V + U(\vec{r}', N) - N \mu \right] k_B T
$$
The grand-canonical methods work best at higher temperatures and low densities.

2.5.1c The Micro-canonical Ensemble

In micro-canonical ensemble the system has got fixed values of energy, volume and number of constituent particles \((E,V,N)\). The most simple relation,

\[ TdS = dE - pdV \]

is used here in which both \(T\) and \(p\) are statistical quantities, the temperature \(T\) being derived from the mean kinetic energy,

\[ \langle KE \rangle = \left( \frac{N}{2} \right) k_B T \]

for a monatomic fluid and \(p\) from the average of the virial.

2.5.1d Quantum Statistical Mechanics

The methods discussed above are of classical statistical mechanics which are valid for all substances at sufficiently high temperatures. At low temperatures, there are quantum mechanical deviations from classical behaviour of two kinds such as,

(i) Effects of statistics (and spin),
(ii) Diffraction effects.

For most liquids these effects on equilibrium properties are described by an expansion in powers of \(\hbar^2\) \((93,94)\) (for analytic potentials) or \(\hbar\) \((95a,b)\) (for non-analytic potentials) of which the
first two or three terms are readily evaluated by the Monte Carlo procedures.

The canonical partition function $Z_N$ is given by,

$$Z_N = \frac{\chi^{3N}}{N!} \exp \left[ -\beta (U + \frac{\hbar^2}{96\pi^2mk_BT} \sum \nabla_i^2 U) \right] \, dr_1 \cdots \, dr_N$$

(31)

where $\chi = \hbar/\sqrt{2\pi mk_BT}$

from which thermodynamic energy and pressure can be calculated by differentiating this with respect to temperature and volume which are valid to order $\hbar^2$. These are given explicitly by Barker et al [96].

The quantum corrections in 2.8 and 2.9 include corrections both to potential energy and kinetic energy; expressions for the kinetic energy corrections are given by Gibson [97,95]. The correct configuration-space probability density $w$ is given for analytic potentials to order $\hbar^2$ by Landau and Lifschitz [98] as,

$$w = \text{const.} \times \exp \left[ -\beta \left( U + \frac{\hbar^2}{96\pi^2(k_BT)^2m} \sum \nabla_i^2 U \right) + \frac{\hbar^2}{48\pi^2(k_BT)^2m} \sum \nabla_i^2 U \right]$$

This result was used by Barker[99] to calculate quantum corrections to the radial distribution function of liquid argon. Landau and Lifschitz [98] also give results for the momentum-space probability density. In quantum mechanics (even to order $\hbar^2$) the configuration-space and momentum-space probabilities are
correlated, not independent as in classical statistical mechanics.

All these results are valid for spherical molecules. The
basic theory for calculation of quantum effects for nonspherical
molecules was given by Kirkwood [100]. Detail results for axially
symmetrical molecules of order $h^2$, with dipolar and quadrupolar
interactions are given by Singh and Dutta [101], McCarty and
Babu [102] and Pompe and Spurling [103].

Quantum mechanical study of dynamical properties poses an
even more difficult problem which has not been attacked by
computer simulation. Heller [104] describes a wavepacket path
integral formulation of semiclassical dynamics which indicates one
possible line of attack.

2.5.2 The Method of Molecular Dynamics

The computational procedure in molecular dynamics involves
numerical solutions of the Newtonian equations of motion (for
spherical molecules) or the coupled Newton-Euler equations of
motion for translations and rotations (for rigid nonspherical
molecules). There are sets of several hundred to several thousand
ordinary differential equations which can be handled readily by
modern computers. Difficulties arise when there are very fast and
very slow motions present, since a time-step small enough to
describe the fast motions will require unreasonably long
computations to describe the slow motions. This has so far
prevented detailed study of polymer motions but for other liquid molecules, this is not a serious problem except to some extent in the case of water. Many important computations were made for hard sphere and square-well potentials, for which a particularly convenient algorithm is available.

2.5.2a **Hard-Sphere and Square-well Potentials**

The first molecular dynamics calculations were made using hard-sphere and square-well potentials [105a,b,106]. These potentials have the property that the forces between the particles are zero except for impulsive forces when the particles reach particular distances (the hard-sphere diameter $\sigma$ and the distance $\lambda\sigma$, corresponding to the outer wall of the square-well). Thus, the dynamics breaks down into a series of binary collisions between which the molecules move in straight lines. The basic time-step for the computation is effectively equal to the mean time between collisions, whereas for continuous potentials the time-step must be small compared to the duration of a collision. This leads to fast computations, so that the dynamics can be followed over relatively long times. A full account of the method for these potentials is given by Alder and Wainwright [105].

The static equilibrium properties are evaluated by means of time averages

$$\langle A \rangle = \frac{1}{\theta} \int_{0}^{\theta} A(t) dt = \frac{1}{M} \sum_{m=1}^{M} A(m \Delta t)$$
in which $A$ can be the kinetic energy from which temperature, the virial or the RDF can be evaluated. In above equation, it is assumed that the system has reached equilibrium at $t = 0$ and $\theta$ is a sufficiently long time, normally the whole duration of the computer "experiment", apart from the preliminary "equilibrium" stage.

2.6 **Results of Computer Simulations**

2.6.1 **Hard Spheres in $\nu$ Dimensions**

Hard-sphere systems, with potential given by

$$u(r) = \begin{cases} \infty, & r < d \\ 0, & r \geq d \end{cases}$$

are of great interest because they throw light on the question of melting transition and because of their use as reference systems for perturbation theories. The partition function for one-dimensional hard sphere system can be evaluated exactly[107]. The pressure is given by

$$\frac{pL}{Nk_B T} = 1/1-(L/Nd)$$

According to Van Hove, there can be no phase transition for a one-dimensional system with interactions of finite range.

There have been very extensive and careful studies both by Monte-Carlo and Molecular Dynamics methods of the equilibrium properties of two-dimensional and three-dimensional hard-sphere systems. The work upto 1967 is summarized by Wood, later references
are by Hoover and Ree (108a,108b), Alder et al (88), Alder and Hecht (109), Chae et al (110), Barker and Henderson (111,96), Young and Alder (112). Another excellent discussion is given by Ree in 1971 [113]. Conclusion of the study is both two and three dimensional hard sphere systems show first - order transitions from fluid at low densities to solid at high densities.

The most extensive tabulation of the Radial Distribution Function (RDF) for three-dimensional hard-spheres is that of Barkar and Henderson [114,111], calculations being made by Monte Carlo method. Chae [110] et al present radial distribution functions for two-dimensional hard spheres at several densities.

Alder et al [115] made a molecular dynamics study of the transport properties (diffusion coefficient, shear and bulk viscosity, thermal conductivity) of three-dimensional hard-spheres over the whole fluid range of densities by evaluating equilibrium time-correlation functions.

2.6.2 The Lennard-Jones 6-12 Potential

Pressures, energies and RDF for the 6-12 fluid were calculated by Monte Carlo and Molecular dynamics method. The first MC calculations were those of Wood and Parker [116]; more recent work includes that of Verlet and Levesque [117], McDonald and Singer [118a,118b]. Molecular dynamics results are given by Verlet [119] for thermodynamic parameters and the RDF [120].
Hansen and Verlet [121] evaluated free energies and constructed the phase diagram which is compared with the experimental results of Argon. This diagram undoubtedly represents a major achievement of statistical mechanics in explaining the phase relationships of solid, liquid and gas. The Lennard-Jones parameters used for Argon are $\epsilon/k = 119.8k$ and $\sigma = 3.405A$.

The quantitative differences between the calculated and experimental liquid-gas coexistence curve in the neighbourhood of critical temp. are found and reasoning was given as they may be partly due to the long range fluctuations not taken into account by the computation. Streett et al [122] and Raveche et al [123] made very detailed MC calculations for the 6-12 substance in the neighbourhood of the solid-fluid transition at many temperatures with particular emphasis on structural properties. Fehder [124a, b] has made a molecular dynamic study of two-dimensional 6-12 fluid. Similarly the MC investigation of the same system showing both liquid-gas and solid-fluid transitions is given by Tsien and Valleau [125].

2.7 Free Length Theory

Jacobson [126] introduced the concept of free length which is nothing but the intermolecular distance. By the knowledge of free length, certain properties of liquid which mainly depend upon
the forces between the molecules such as surface tension, compressibility, viscosity etc can be obtained. This free length is taken as the distance between the surfaces of two molecules instead of the distance between the centers of attraction of molecules.

At absolute zero, a liquid has molar volume $V_0 = M/\rho$ where $\rho$ is the density at 0°K. At this temperature, molecules have their closest possible packing. The total surface of all the molecules is designated by "$Y$" which is called internal surface of the liquid. If "$L$" denotes the free length between the molecules, then it is given as

$$L_f = 2V_a/Y$$

where $V_a$ is an available volume defined by

$$V_a = V_T - V_0$$

$V_T$ being the molar volume at temperature $T$.

If the molecule is spherical, area of molecule = $4\pi r^2$ and volume = $4\pi r^3/3$,

Total Internal Surface for $N$ molecules can be obtained as

$$Y = N*(36\pi V_0^2)^{1/3}$$

and for non-spherical molecules,

$$Y = f*(36\pi V_0^2)^{1/3}$$

where $f$ is a form factor given by the ratio of surface of molecule
and the imagined spherical surface which encloses the same volume as that of the molecule. 

\( V_0 \) can be evaluated using the expression,

\[
V_0 = V_T (1 - T/T_C)^{1/3}
\]

where \( T_C \) is the critical temp of the liquid.

Jacobson observed that the adiabatic compressibility and intermolecular free length are related to each other. For many pure liquids he obtained the relation \( \beta_a = A \cdot L^p \) where \( p = 2.08 = 2 \) where

\[
\log A = 7.097 \text{ at } 20^\circ \text{C}.
\]

As we have, \( \beta_a = 1/(u^2/\rho) \)

\[
1/u^2/\rho = A \cdot L^2
\]

from which we get

\[
L = K/u^4/\rho^{(1/2)} \quad \text{ ...... 2.10}
\]

where \( K \) is temp dependent constant. Jacobson obtained the value of \( K \) at various temps by examining very large number of liquids. Thus by measuring sound velocity and density and by knowing the values of \( K \) at different temps, \( L \) for pure liquids can be calculated.

For binary liquid mixtures, Jacobson extended the formula as

\[
L_{mix} = K/u_{mix}^4/\rho_{mix}^{(1/2)}
\]

\[
L_{mix} = 2 \times \frac{V_m - (x_A V_O^A + x_B V_O^B)}{x_A Y_A + x_B Y_B}
\]

\( V_m \) being molar volume of the mixture.
He calculated free length in 16 binary mixtures using these two equations and reported the deviation of about 0.8% only. But when L was calculated in pure liquids, % deviation was about 3.3%. Thus sound velocity can be computed from these equations. Kaulgud [127a,b] by comparing L_{mix}^{(exp)} and L_{mix}^{(ideal)}, has drawn the conclusions that if L_{mix}^{(exp)} > L_{mix}^{(ideal)}, then sound velocity against composition should be concave upwards and if L_{mix}^{(exp)} < L_{mix}^{(ideal)}, it should be convex upwards, from which it can be inferred that ultrasonic velocity depends upon the free length.

2.8 Collision Factor Theory (CFT)

W. Schaaffs was the first person to propose a relationship between sound velocity and structural properties. He assumed that Vander Waal's equation of state is valid for liquids in which parameters 'a' and 'b' are not constant but are the functions of temp. T and density $\rho$. Thus,

$$\left[ (P + a(T, \rho) \cdot (\rho^2/M^2)) \cdot ((M/\rho) - b(T, \rho)) \right] = RT$$

and sound velocity is given by

$$u^2 = (dP/d\gamma), \text{ where } \gamma = C_p/C_v$$

from these two eqns and making some approximations, Schaaffs deduced the equation as

$$u^2 = (RT/M) \cdot \left[ \frac{1}{3} (1-b/V)^2 - \frac{2}{1-b/V} \right]$$
where $V = M/\rho = \text{Molar volume}$. Effective volume $B$ occupied by molecules per mole is related to $b$, as $b = 4B$, also $B = 4\pi r^3/3$, $r$ being the radius of molecule. Using these equations he obtained the relation for molecular radius as

$$r = \left[ \frac{3M}{16\pi N\phi} \left( 1 - \frac{RT\sqrt[3]{\frac{M}{\mu^2} + 1}}{\mu^2} \right) \right]^{1/3}$$

The ratio $B/V = \gamma$ is called the space filling factor. Schaaffs found the empirical relation between u.s. velocity and this $\gamma$ which is given by

$$u = W \cdot \gamma = W \cdot B/V$$

where the constant $W$ has an approximate value of 5000 m/s.

Calculated values of velocities have been satisfactorily found to agree with experimental values of compounds formed by C, H, O and N atoms. Schaaffs assumed that collisions among the molecules are elastic and modified the relation as, $b = r_f \cdot B$ where $r_f$ is the collision factor characterising the collision. Observing many cases, he established a general formula for sound velocity at constant temperature as,

$$u = u_\infty \cdot r_f \cdot \gamma$$

where $u_\infty = 1600 \text{ m/s}$.

This equation suggests that ultrasonic velocity is proportional to the factor which describes the elasticity of collisions and to the
space-filling factor. Nutsch-Kuhnekies[128] have extended the CFT to binary mixtures of liquids by giving the relation

\[ u_{\text{mix}} = u_\infty \left\{ \left( x_A S_A + x_B S_B \right) \left( x_A B_A + x_B B_B \right) / V \right\}^{3} \]

where \( x_A, x_B \) are mole fractions of components A and B, \( B_A, B_B \) are effective volumes per mole of the components, \( S_A, S_B \) are collision factors and \( V \) is the molar volume of the mixture given by

\[ V = (M_A x_A + M_B x_B) / \rho_{\text{mix}} \]

2.9 Nomoto's Theory

According to Rao [1,2]

\[ M.u^{1/3} / \rho = R \]

called the Molar Sound Velocity.

Wada has also introduced a quantity known as Wada Constant or Molecular Adiabatic Compressibility given by

\[ B_w = M B_a^{-1/7} / \rho \]

from which we get

\[ B_w = (M / \rho) (u^2 / \rho )^{1/7} = M^{1/7} R^{6/7} \]

Nomoto [129] developed the theory of molecular sound velocity in mixtures of two liquids. Nomoto has classified binary liquid mixtures in 6 groups, according to the velocity vs. molar fraction curves as:
(1) Mixtures exhibiting maxima of sound velocity.
(2) Mixtures in which vel. curve is convex upwards,
(3) Mixtures showing points of inflation both for vel. and comp.,
(4) Mixtures in which vel. curve is linear,
(5) Mixtures for which vel. curve is concave upwards,
(6) Mixtures showing minimum of sound velocity.

For studying variation of sound vel. in binary liquid mixtures, Nomoto derived an empirical formula by assuming the ideal mixture as

$$u = \left(\frac{R}{V}\right)^3 = \left[\frac{X_AR_A + X_BR_B}{X_AV_A + X_BV_B}\right]^3 \quad \ldots \ldots \ 2.11$$

where $R_A, R_B$ are molar sound velocities, $V_A, V_B$ are molar volumes for two components and $X_A, X_B$ are their molar fractions.

Nomoto had used this eqn. for 31 binary liquid mixtures and concluded that the formula 2.11 holds good for such mixtures for which linearity of molecular sound velocity and additivity of molar volume is comparatively good.

2.10 Scaled Particle Theory

2.10.1 Introduction

The aim of Physics of liquids is to understand why particular phases are stable in particular ranges of density and temperature and to relate the stability, structure and dynamical properties of fluid phases to the size and shape of molecules,
atoms or ions and the nature of forces between them.

One way, to attempt, to predict the properties of a liquid (or solid or gas) would be to solve, subject to appropriate antisymmetry conditions, the many-body Schrödinger equation describing the nuclei and electrons given by

\[
\left( -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{ij} \frac{q_i q_j}{r_{ij}} \right) \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial t} \quad \cdots \quad (2.12)
\]

the sums are taken over all nuclei and electrons with appropriate masses \( m_i \) and charges \( q_i \). There are many simplifications suggested in which one is classical statistical mechanics method, supplemented where necessary by quantum corrections. This procedure is inadequate for helium and hydrogen at very low temperatures, but may be adequate for most other liquids.

Using grand-canonical ensemble, the probability of finding \( N \) molecules with coordinates in elements \( dq_i \) \( \ldots \) \( dq_N \) at \( q_1 \) \( \ldots \) \( q_N \) and momenta in \( dp_i \) \( \ldots \) \( dp_N \) at \( p_1 \) \( \ldots \) \( p_N \) is

\[
P = \frac{1}{(h f N^* Z)^N} \exp \left[ \beta (N \mu_0 - H_N) \right]
\]

where \( \beta = 1/k_B T \), \( \mu_0 \) is chemical potential, \( T \) is the temperature, \( k_B \) 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 is \( H_N \) given by

\[
H_N = T_N + U_N
\]

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

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

and \( PV = k_B T \log Z \)

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

\[
p/k_B T = \rho - \left( \rho^2/2k_B T \right) \int r u'(r) g(r) \, dr
\]

where \( g(r) \) is a radial 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 becomes in three dimensions as,

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

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

where \( y(r) = g(r) \exp(\beta u(r)) \) is a continuous function. Substituting \( N/V = \rho \) where \( \rho \) is the number density, \( \pi d^3/6 \) is the volume of the molecule, \( (\pi \rho d^3/6) = \eta \) and \( y(d) = g(d) \).
We get the equation of state for hard-spheres of diameter \( d \) as

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

ie \( pV/N\kappa B T = 1 + 4 \cap g(d) \) \hspace{1cm} \text{2.13}

Hence for hard-spheres, it is only necessary to determine \( g(d) \) and Reiss et al [84] have developed a simple but accurate method called the \textit{Scaled Particle Theory (SPT)} for obtaining \( g(d) \) and thus \( p \).

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 \(-dP_0/dr\) 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 \( 4\pi r^2 G(r) r^2 dr \), 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.

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,

\[-dP_0(r)/dr = P_0(r)4\pi \rho r^2 G(r) \quad \cdots \quad 2.14\]

also

\[P_0(r) = \exp(-W/k_B) \quad \cdots \quad 2.15\]

where \( W(r) \) is the reversible work necessary to create a cavity of radius \( r \) in the fluid. \( P_0 \), \( W \) and \( G \) depend upon \( \rho \) as well as \( r \).

Therefore

\[dP_0(r)/P_0(r) = -4\pi \rho r^2 G(r) dr\]

and 2.15 gives

\[dP_0(r)/P_0(r) = -dW/k_B\]

hence

\[dW = k_B T \rho G(r)4\pi r^2 dr \quad \cdots \quad 2.16\]

But

\[dW = pdV + \sigma dS \quad \cdots \quad 2.17\]

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

From 2.16 and 2.17,

\[G(r) = \frac{1}{\rho k_B T} \left[ \frac{1}{4\pi r^2 dr} \right] \left( pdV + \sigma dS \right)\]

now \( dV = 4\pi r^2 dr \), \( dS = 8\pi r dr \)
\[
G(r) = \frac{1}{\rho k_b T} \left[ \frac{pdV}{dV} + \frac{\sigma dS}{dV} \right] = \frac{1}{\rho k_b T} \left[ p + \frac{\sigma}{r} \right]
\]

This gives, \( G(\infty) = \frac{1}{\rho k_b T} p \)

\[
\frac{p}{\rho k_b T} = 1 + 4\pi G(d)
\]

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

Barker and Henderson [130] assumed that for "r" not too small, Surface tension,

\[
\sigma(r) = \sigma_0 \left[ 1 + 2\delta(d/r) \right]
\]

where \( \sigma_0 \) and \( \delta \) are constants to be determined. Substituting in 2.18 gives,

\[
G(r) = \frac{1}{\rho k_b T} \left[ p + \frac{2\sigma_0}{r} \left\{ 1 + 2\delta(d/r) \right\} \right]
\]
For \( r < d/2 \), no more than one molecular centre 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,

\[
P_0(r) = 1 - \frac{4\pi}{3}r^3 \rho \quad r < d/2
\]

Therefore, \( dP_0(r)/dr = -4\pi r^2 \rho \)

Combining with 2.14,

\[
P_0(r) 4\pi r^2 \rho G(r) = 4\pi r^2 \rho
\]

\[
\therefore \quad P_0(r)G(r) = 1
\]

\[
G(r) = \frac{1}{P_0(r)} = \left[ 1 - \frac{4\pi}{3}r^3 \rho \right]^{-1}, \quad \text{for } r < d/2 \ldots \ldots 2.20
\]

Hence equation 2.20 is valid for \( r \) not too small. For \( d/2 < r < d/\sqrt{3} \), two molecular centres can lie within the sphere and \( P_0(r) \) and \( G(r) \) cannot be determined without first knowing \( G(r) \).

As an approximation, it is assumed that 2.19 is valid for all \( r > d/2 \). This is the central approximation of SPT.

Eqn 2.19 can be written as

\[
G(r) = \frac{\rho}{\rho kT} + \frac{2 \sigma_0 d}{\rho kT dr} + \frac{4 \sigma_0 \delta d^2}{\rho kTr^2 d}
\]

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

where \( A = \frac{2 \sigma_0}{\rho kT d} \) and \( B = \frac{4 \sigma_0 \delta}{\rho kT d} = 2A \delta \)
hence,

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

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

\[ \frac{P}{\rho kT} = \frac{1 + 4\eta (A + B)}{1 - 4\eta} \] \hspace{1cm} \ldots \ldots \hspace{1cm} 2.21

For \( r < d/2 \), from 2.20

\[ G(r) = \left[ 1 - \frac{4\pi}{3} r^3 \rho \right]^{-1} \]

\[ = \left[ 1 - \frac{8\eta}{d} \left( \frac{r}{d} \right)^3 \right]^{-1} \] \hspace{1cm} \ldots \ldots \hspace{1cm} 2.22

for \( r > d/2 \), \[ G(r) = \frac{1 + 4\eta(A + B)}{1 - 4\eta} + A \frac{d}{r} + B \frac{d^2}{r^2} \] \hspace{1cm} \ldots \ldots \hspace{1cm} 2.23

Thus expressions 2.22 and 2.23 give the value of \( G(r) \) for \( r < d/2 \) and \( r > d/2 \) respectively.

Expressions for \( A, B \) and \( \sigma_0, \varepsilon \) can be obtained by requiring that \( G(r) \) and \( \frac{d}{dr} G(r) \) be continuous at \( r = d/2 \).

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 - \frac{3\eta(1+\eta)}{2(1-\eta)^3} + \frac{3\eta^2}{4(1-\eta)^3}}{1 - 4\eta}

\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad \ldots \ldots \quad 2.24

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

thus in SPT,

G(d) = \frac{4 - 2\eta + \eta^2}{4(1 - \eta)^3} \quad \ldots \ldots \quad 2.25

Equation 2.25 gives an exact second and third virial coefficient, \( \eta \) is less than unity and for \( p \) to be finite, 2.25 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, eqn. 2.24 is in good agreement with the machine simulation results.
now, \[ A = \frac{2\sigma_0}{\rho kTd} = \frac{-3N(1+N)}{2(1-N)^3} \]
gives, \[ \sigma_0 = \frac{9kT}{2\pi d^2} \frac{1+N}{N^2} \frac{1}{(1-N)^3} \]

The negative surface tension need not be taken surprising. 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:

\[ \frac{pA}{Nk_BT} = \frac{1}{(1-y)^2} \quad \text{where} \quad y = \pi \rho d^2 / 4 \]

and

\[ \frac{pL}{Nk_BT} = \frac{1}{(1-\rho d)} \]

respectively for hard discs and hard rods.

2.10.2 Scaled Particle Theory applied to mixtures.

The SPT have been used to obtain an equation of state of hard-sphere mixtures by Lebowitz, Helfand and Praestgaard in 1965 [131]. Their result is

\[ \frac{\rho}{\rho kT} = \frac{1+\xi+\xi^2}{(1-\xi)^3} - \frac{n}{2} \frac{\rho}{(1-\rho)^3} \sum_{i<j=1}^m \chi_i \chi_j (d_{ii} - d_{jj})^2 [2d_{ij} + d_{ii} d_{jj} \chi] \]

\[ \ldots \ldots \quad 2.26 \]
where \( d_{ij} \) are the diameters of the \( m \)-components.

and

\[
\xi_j = \frac{\pi}{6} \rho \sum_{k=1}^{m} \chi_k d_{kk}^3
\]

\[
X = \frac{\pi}{6} \rho \sum_{k=1}^{m} \chi_k d_{kk}^2
\]

\[
d_{ij} = \frac{d_{ii} + d_{jj}}{2}, \quad \chi_i = \frac{N_i}{N}
\]

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

2.10.3 Hard Convex Molecules

Considering the molecules as hard convex molecules (not necessarily spheres), Gibbons [132a,b] & Boublik [133] have applied the SPT to mixtures of hard convex molecules. The result is

\[
\frac{P}{\rho k_B T} = \frac{1}{1-Y\rho} + \frac{AB\rho}{(1-Y\rho)^2} + \frac{1}{3\rho} \frac{B^2 C\rho^2}{(1-Y\rho)^3}
\]

where \( A = \sum_{i=1}^{m} R_i^2 \), \( B = \sum_{i=1}^{m} S_i \), \( C = \sum_{i=1}^{m} \rho R_i^2 \), \( Y = \sum_{i=1}^{m} V_i \), and \( R_i, S_i \) 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, Eq. 2.27 becomes

\[
\frac{P}{\rho k_B T} = \frac{1}{1-V_1\rho} + \frac{\bar{R}_1 S_1 \rho}{(1-V_1\rho)^2} + \frac{1}{3\rho} \frac{\bar{R}_1^2 S_1 \rho^2}{(1-V_1\rho)^3}
\]

For hard spheres \( \bar{R}_i = d_{ii}/2 \), \( S_i = \pi d_{ii}^2 \), \( V_i = (\pi/6) d_{ii}^3 \)
Eqn (2.18) gives (2.24) and eqns (2.28) and (2.27) give the correct second virial coefficient and for hard spheres, give the correct third virial coefficient. For prolate spherocylinders, (2.28) gives an accurate third virial coefficient [134]. 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.

Helfand and Stillinger (1962) [135], Harris and Tully-Smith et al. (1970) [136] and Reiss and Casberg (1974) [137] have attempted to use SPT to obtain the radial distribution of hard spheres as well as their thermodynamic properties.

2.10.4 Ultrasonic Velocity and Equation of State

As we know that, \[ \frac{d\rho}{dT} = u^2 \] ....... 2.29

where \( u \) is the velocity of sound in liquid, \( \rho \) is molecular density and \( \gamma = C_p/C_v \n\)

On solving eqns. (2.27) and (2.29), we get

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

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

For pure liquid, \( A = R, B = S, C = R^2 \) and \( Y = \bar{V} \)
Putting \( \frac{\overline{RS}}{\overline{V}} = X \) defined as shape factor and \( V\rho = \eta \), then

\[
\frac{\mu^2}{\sqrt[3]{RT}} = \frac{1}{(1-\overline{V}\rho)^2} \left[ 1 + 2\overline{RS} \left( \frac{\rho}{1-\overline{V}\rho} \right) + \overline{R}^2 S^2 \left( \frac{\rho}{1-\overline{V}\rho} \right)^2 \right]^{2}
\]

\[
\frac{\mu^2}{\sqrt[3]{RT}} = \frac{1}{(1-\overline{V}\rho)^2} \left[ 1 + \overline{RS} \left( \frac{\rho}{1-\overline{V}\rho} \right) \right]^{2}
\]

\[
= \frac{1}{(1-\overline{V}\rho)^2} \left[ \frac{[1 + (\overline{RS} - \overline{V})\rho]^2}{(1-\overline{V}\rho)^2} \right]
\]

Cotter and Martire have used the SPT to obtain an equation of state for perfectly aligned as well as isotropic, hard spherocylinders. Different workers [138] have attempted to find the phase change by using Monte-Carlo method with the above equations of state for spherical or other type of molecules.

2.11 Flory's Theory

2.11.1 Introduction

Flory, Orwoll and Vrij[139] have stated that there is a need for a basis on which the properties of macromolecular liquids and
their solutions could be interpreted and correlated. According to them, in the Lattice model, there are discrepancies between theory and experiment on macromolecular solutions. By its disregard of changes in volume and local disorder with composition, lattice model fails to reflect changes in liquid structure. Prigogine and his coworkers have adopted the cell model to chain molecule liquids, but an equation of state thus derived proved to be of no value. The difficulty is related to the unsatisfactory representation of intermolecular energy and its dependence on volume in cell model. In later papers Prigogine et al. [140,141] formulated a law of corresponding states to chain molecules and this has met with tremendous success. The law of corresponding states applied to entire range of n-paraffin hydrocarbons encouraged the search for partition function for chain liquids to rationalize the experimental results.

Flory et al. [139] thought to have an analytical expression for the partition function and an equation of state from it which will be preferred over the graphical empirical methods of application of law of corresponding states. It is patterned in a same way as introduced by Eyring and Hirschfelder [142a,b,143] for simple liquids.

2.11.2 Partition Function

The development of Flory's theory started from chain molecules. The partition function has been derived for macr-
molecules as described below. Consider a linear chain molecule e.g. H(CH$_2$)$_n$-H, consisting of a succession of $n$ repeating units and bounded by terminal groups. Imagine the chain to be subdivided into $x$ segments, segment is not explicitly defined. In general the segment does not correspond to the repeating unit i.e. $x \neq n$. However $x$ is taken as linear with $n$ for homologous members of the series. More particularly, $x$ will be taken proportional to the "hard core" molecular volume $V^*$ or net volume, thus $V^* = xv^*$, where $v^*$ is the net volume of a segment.

The segment is defined so as to have a length equal to the diameter of the chain if commitment to a lattice model is essential. In the treatment of solutions of chain polymers in monomeric solvents, e.g., it is expedient to so define the segment as to render its volume, or its net volume, equal to that of the solvent, in which case $x$ becomes the ratio of the molecular volumes.

Let $S$ represents the mean number of external contact sites per segment of the molecule. If $S_m$ denotes the number of contacts for internal segment and $S_e$, the added number for chain ends, then

$$xS = xS_m + S_e$$

This $xS$ may be regarded as the measure of molecular surface.

Following Prigogine, Trappeniers and Mathot [140,144a,b] they assume that the normal oscillatory modes of the isolated
chain molecule can be separated unambiguously into two categories, internal (intramolecular) and external (intermolecular). The former comprising modes of higher frequency are considered to be inappreciably affected by neighbors in the liquid. The later comprising of lower frequency modes of the isolated molecule, are subject to much weaker intramolecular restraining potentials and therefore experience greater perturbation by interactions with neighbors. It is assumed that the intramolecular potentials associated with these later modes can be disregarded altogether and hence that they may be treated as translational (external) motions. Add to them the three degrees of freedom of the molecular center of gravity and the total number of intermolecular degrees of freedom is

$$3xC = 3(xC_m + C_e)$$

per molecule i.e. the number of degrees of freedom is taken to be linear in $x$, and therefore in $n$ also. $C$ is assumed to be independent of volume and temperature.

Assuming hard sphere repulsion between segments, if we have,

- $V =$ Volume of the system
- $N =$ Number of $x$-meric molecules in the system
- $v =$ Volume per segment $= V/N$

and $v^*$ = Net volume per segment,

then free length associated with each molecular degrees of freedom can be taken of the form

$$.$$
\[ Z = \frac{1}{V^{1/3} \left( v^{1/3} - v^{*1/3} \right)} \]

where \( \gamma \) is the geometric constant [free space = 1/3rd volume - 1/3rd net volume]. This expression is usually identified with cell model. It is also given by treatment of hard-sphere liquid in one dimension according to the method of Tonks. On the basis of these concepts, the configuration partition function of the liquid may be written as

\[ Z = Z^* \left( \frac{1}{V^{1/3} \left( v^{1/3} - v^{*1/3} \right)} \right)^{xNC} \exp \left( -E_0/kT \right) \]

where \( E_0 \) is the intermolecular energy, \( Z^* \) is the combinatorial factor having to do with the gross disposition of segments among one another in space. In terms of a lattice model, expresses the number of ways of arranging the segments of \( N \) molecules over a spacial array of \( xN \) sites (it is taken independent of volume and temperature). (2.31) is identical in form with partition function introduced by Prigogine, Trappeniers and Mathot [140, 144]. But treatment of \( E_0 \) is different than them.

The factor \( C<1 \) is supposed to take into account the restrictions on the precise location of a given segment by its neighbors in the same chain.

The cell model is rejected on the basis of expressing the intermolecular energy \( E_0 \). The energy of interaction between a pair of molecules is a sensitive function of intermolecular distance and relegation of all members of the first shell to the same
distance introduces a considerable error in the energy and its
dependence on the mean distance (i.e., on volume). Irrespective of the
density of packing & of the displacement of a given molecule from
its mean position, one or more of its neighbors is likely to be in
proximity to the distance of closest approach. The contribution of
these molecules to the energy is most important.

Such considerations serve to emphasize the intimate
connection between the radial distribution function and the
energy. If energy is pairwise additive in intermolecular segment
pairs then in the approximation that the familiar correlation
function \( g^{(1)}(r) \) is independent of the volume, the intermolecular
energy must be proportional to the density \( \rho \), as Hildebrand and
Scott have stressed [145]. On this approximation, the mean
intermolecular energy per contact pair is expressed as

\[
\epsilon = -\frac{\Omega}{v}
\]

where \( \Omega \) characterizes the mean interaction between a segment pair
in the liquid of \( x \)-meric chains. Whereas \( \Omega \) will be treated as a
constant for a given chain homolog, allowance will be made for its
dependence on \( x \) to the extent that interactions of end segments
differ from those within the chain. Hence it follows that

\[
E_0 = -\frac{xNSN}{2v}
\]  \[\ldots\ldots\ldots\text{2.32}\]

Expression of the intermolecular energy in a form resembling
eqn(2.32), namely
\[ E_0 = - \text{Constant}/V^m \]

where \( m \) is a power near unity, has been advocated by Hildebrand et al. [145] and Frank [146]. Hildebrand has successfully correlated energies of vapourization and \((\Sigma E/\Sigma V)_T\) for non-polar simple liquids on this basis. A relation of this form is thus implied to hold for the entire range of densities from liquid to vapour. Since \( x_C > 1 \), vapour is obviously excluded from consideration.

Terminal segments offer different forces of attraction to neighbors than the mid-chain segments. The intermolecular energy can be written as

\[ E_0 = -(1/v) \left( N_m \alpha_m^2 + N_{em} \alpha_{em}^2 + N_e \alpha_e^2 \right) \]

where \( \alpha_m, \alpha_{em}, \alpha_e \) characterize interactions between sites on two neighboring mid-chain segments, between a mid-chain and a terminal segment site and between two terminal sites respectively. The \( N \)'s denote the numbers of neighbor pairs in the respective categories. These numbers are assumed to equal those for random mixing of sites.

\[ E_0 = \frac{xN}{2vS} \left[ S_m^2 \alpha_m^2 + 2(S_m S_e/x) \alpha_{em}^2 + (S_e^2/x^2) \alpha_e^2 \right] \]

which by comparison with (2.32) defines \( \alpha \) as

\[ \alpha = (S_m^2/S^2) \alpha_m^2 + 2(S_m S_e/S^2 x) \alpha_{em}^2 + (S_e^2/S^2 x^2) \alpha_e^2 \]
In the familiar approximation

\[ \eta_{em} = (\eta_e \eta_m)^{1/2} \] ........ 2.33

appropriate for dispersion interactions

\[ \eta = (S_m/S)^2 \eta_m [1 + (\eta_e \eta_g^{1/2}/S_m \eta_m^{1/2})/x]^2 \] ........ 2.34

The artificial designation of terminal sites introduced above invalidates literal adoption of this approximation in the form of eqn (2.33) and (2.34).

Substituting eqn (2.32) in (2.31), we get

\[
Z = Z^* \left[ \frac{\sqrt{v^*}}{(v/v^*)^{1/3}} \right]^{3xNC} \exp{-xNSN/2vK}\] ........ 2.35

Reduced variables are introduced as

\[ \bar{v} = \frac{v}{v^*} \]

\[ \bar{T} = \frac{T}{T^*} \]

\[ \bar{T} = \left( \frac{2v^* CkT/SN}{(2vCkT/VSN)} \right) \]

putting \( v^* = v/\bar{v} \)

\[ SN/2v = (CkT/\bar{v}^{*}) \]

substituting for \( SN/2v \), we get,

\[
Z = Z^* (\sqrt{v^*})^{xNC} \left( \frac{1}{\sqrt{3} - 1} \right)^{3xNC} \exp(xNCkT/\bar{T}\bar{v}kT) \]

\[ = Z^* (\sqrt{v^*})^{xNC} \left( \frac{1}{\sqrt{3} - 1} \right)^{3xNC} \exp(xNC/\bar{v}T) \] ........ 2.36
2.11.3 The Equation of State

An attempt has been made to derive reduced equation of state stated by Flory as follows-

Reduced variables are defined as

\[ \bar{v} = \frac{v}{v^*}, \quad \bar{T} = \frac{2v^* CkT}{SN}, \quad \bar{p} = \frac{p}{p^*} = \frac{2pv^*/S}{SN} \]

A thermodynamic relation between pressure and partition function is given by

\[ p = kT \frac{S}{SV} \left[ \log Z \right] \]

where \( Z \) is the partition function for the system of \( N \) molecules of volume \( V \). From (2.36), we have,

\[ p = kT \frac{S}{SV} \left[ \log Z + xNC \log(v^*) + 3xNC \log(v^{-1/3} - 1) + xNC/\bar{v} \right] \]

\[ = kT \left[ 3xNC \frac{S}{SV} \log(v^{-1/3} - 1) + (xNC/\bar{T}) \frac{S}{SV} (1/\bar{v}) \right] \]

now,

\[ \bar{v} = \frac{v}{v^*} \quad \text{and} \quad v = \frac{V}{xN} \]

Therefore \( \bar{v} = \frac{V}{xNv^*} \), \( V = xv^* \bar{v} \)

\[ p = kT \left[ \frac{3xNC}{\bar{v}^{1/3} - 1} \frac{S}{SV} \left\{ \left( \frac{V}{xNv^*} \right)^{1/3} - 1 \right\} - \frac{xNC}{\bar{T}} \frac{1}{\bar{v}^2} \frac{S}{SV} \left( \frac{V}{xNv^*} \right) \right] \]
\[
\frac{CkT}{\nu^{2/3}(\nu^{1/3} - 1)\nu^*} - \frac{CkT}{\frac{TT\nu^*}{v^*}}
\]

multiplying by \(\bar{v}/T\),

\[
\frac{p}{\bar{v}} = \frac{Ck\bar{v}T}{v^*} - \frac{Ck\bar{v}T}{TTv^*}
\]

as \(2v^*CkT\)

\[
= \frac{SN}{T}, \quad \frac{SN}{2v^*}
\]

\(CkT^* = \frac{SN}{2v^*}\) and \(p = \frac{pv^*}{CkT^*}\) also \(\frac{SN}{v^*} = \frac{p}{CkT^*}\)

\[
\frac{p}{\bar{v}} = \frac{CkT^*}{\nu^*}\left[\frac{-1/3}{(\nu^{1/3} - 1)\nu^*} - \frac{1}{T\nu}\right]
\]

\[
\frac{p}{\bar{v}} = \frac{p}{\bar{p}}\left[\frac{-1/3}{(\nu^{1/3} - 1)T\nu}\right]
\]

\[
\frac{\bar{p}}{\bar{v}} = \frac{\nu^{1/3}}{(\nu^{1/3} - 1)T\nu}
\]

\[\ldots \ldots \ldots 2.37\]

is the equation of state expressed in reduced form, where

\[
\frac{p}{p^*} = \frac{2pv^*}{SN} = \frac{pv^*}{CkT^*}
\]

Equation 2.37 corresponds to the reduced equation of state of Hirschfelder and Eyring \([142]\) However the parameters differ through the introduction of C and these differences vanish for C=1.
Most sophisticated treatments of liquid mixtures derive their conceptual basis from (a) the cell model for liquids and (b) or from the postulation of a universal form for the intermolecular potential expressed by

\[ \epsilon_{ij} = \epsilon \phi (r_{ij}/r^*) \]

where \( r_{ij} \) is the distance between centers of the molecules i and j, \( \epsilon \) and \( r^* \) are characteristic parameters for the pair and \( \phi (r/r^*) \) is an universal function of its argument. But experimental results failed to give the account of treatments based on the cell model, and reasons relate to the limitations of the cell model.

The definition of the cell, consisting of neighbor molecules in fixed array about the central "wanderer", ascribes crystal-like characteristics to the liquid. Each molecule is required to perform duel, mutually inconsistent roles, it must function both as a fixed neighbor and as the wanderer within its own cell. Thus, not only does the cell model incorporate the acknowledged deficiencies of Einstein model for a solid, but it also fails to take account of those features which set a liquid apart from a solid. These shortcomings of the cell model have been stressed by Hildebrand and his co-workers [145].

The intermolecular energy is usually discussed on the basis of the familiar Lennard-Jones potential operating between molecular centers. Even in comparatively simple polyatomic molecules, e.g. CH\(_4\) or CCl\(_4\), the accentric distribution of polarizable electrons necessitates fairly drastic modification of
this potential. Kihara[147], Hamann and Lambert[148] and Pitzer[149] have offered modified intermolecular potentials for polyatomic molecules, especially those approximating spherical symmetry in form. Pitzer replaces each molecule with a smooth distribution of interacting elements (electrons), these being distributed uniformly on the surface of a spherical core or throughout the volume of the core. In either case, a Lennard-Jones interaction is ascribed to each pair of elements, one from the distribution for each of two neighboring molecules, and the total interaction is obtained by integrating over the respective cores.

An extension of these considerations which suggests itself as a basis for treating the intermolecular energy in liquids consists in integrating the interactions of elements of the core of one molecule with the elements of all surrounding molecules. The result obtained departs markedly from the form of intermolecular energy according to the theory of Lennard-Jones and Devonshire[150]. For a ratio of core to cavity diameters greater than 1/5, the energy is approximately proportional to the density; it depends also on a simple function of the cavity diameter. In, as much as, the form of potentials depends on parameters peculiar to the molecular species, it does not lend itself to reduction to a parametric expression such as is required to sustain a law of corresponding states.

In the limit of very large particles such that the range
of intermolecular interactions attractive as well as repulsive is small compared to the molecular diameter and to the distance between boundaries of the domains of neighboring molecules, the intermolecular energy can be treated as arising effectively from interactions between the surfaces of adjoining molecules. The calculations [150] described support an account of the intermolecular energy on this basis and they indicate further that this should be satisfactory, even for small polyatomic molecules such as CCl₄. Certainly this approximation is preferable to central force potentials of the Lennard-Jones type for virtually all molecules of interest. It offers the additional advantage of being adoptable to treatment of non-spherical molecules and of mixtures of molecules differing in size.

Flory applied a simple partition function suitable for liquids comprising chain molecules to homologues of the normal paraffin hydrocarbon series H-(CH₂)ₙ-H with n>5. The same partition function has been adopted to mixtures of the straight-chain hydrocarbons. Thermodynamic properties of these mixtures are related to parameters obtained from equation of state characteristics of the pure component hydrocarbons. There is a very good agreement between calculated and observed chemical potentials for a variety of systems at different temperatures.

This formulation was addressed specifically to chain
molecules and to mixtures of chain homologues. Then Flory presented the mixtures of unrelated type. One of the merits of the theory is its adoptability to mixtures of molecules differing in size and shape [150]. He has suggested that it may be broadly applicable to mixtures of homopolar molecules.

2.11.4 Binary Mixtures

A molecule is assumed to be made up of small elements or segments. Let there be $r_1$ and $r_2$ elements in a molecule of two components of the mixture. $v_1^*$ and $v_2^*$ denote the molar core volumes, then $r_1$ and $r_2$ are defined such as to be in the ratio of respective molar core volumes. Similarly, $S_1$ and $S_2$ shall be in the ratio of molecular surface areas of contact per segment.

Let $A_{11}, A_{12}$ and $A_{22}$ represent the numbers of contact pairs between the respective species, and let $\eta_{11}/v$ etc be the energies associated with each.

Then

$$-E_0 = \frac{(A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})}{v} \quad \ldots \ldots \ldots 2.38$$

since $2A_{11} + A_{12} = S_1r_1N_1$, $2A_{22} + A_{12} = S_2r_2N_2$

Therefore

$$-E_0 = \frac{(S_1r_1N_1\eta_{11} + S_2r_2N_2\eta_{22} - A_{12}\Delta\eta)}{2v}$$

where $\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$

Mixing of the two species is assumed to be random. As a further approximation, it is expected that a species of kind $i$ neighbors at any given site, to be equal to its site fraction $\theta_i$, defined for
a binary mixture by

\[ \theta_2 = 1 \theta_1 = \frac{S_2 r_2 N_2}{S r N} \]

On this basis,

\[ A_{12} = S_1 r_1 N_1 \theta_2 = S_2 r_2 N_2 \theta_1 \]

where \( \bar{r} = \frac{(r_1 N_1 + r_2 N_2)}{N} \)

\[ S = \frac{S_1 r_1 N_1 + S_2 r_2 N_2}{\bar{r} N} \]

\[ N = N_1 + N_2 \]

By substituting in (2.38),

\[ -\frac{E_0}{\bar{r} N} = \frac{(S/2v)}{(\theta_1 \bar{n}_{11} + \theta_2 \bar{n}_{22} - 2 \theta_1 \theta_2 \bar{\Delta} \bar{n})} \]

or \[ -\frac{E_0}{\bar{r} N} = \frac{(S/2v)}{(\theta_1^2 \bar{n}_{11} + \theta_2^2 \bar{n}_{22} + 2 \theta_1 \theta_2 \bar{n}_{12})} \]

Defining the segment fractions \( \phi_1 \) and \( \phi_2 \) by

\[ \phi_2 = 1 - \phi_1 = \frac{r_2 N_2}{\bar{r} N} \]

\[ \frac{1}{\bar{r}} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \]

\[ S = \phi_1 S_1 + \phi_2 S_2 \]

\[ \theta_2 = (S_2/S) \phi_2 \]

Characteristic pressures for pure components are

\[ p_{1}^* = \frac{S_{1} \bar{n}_{11}}{2v_{1}^*} \]

\[ p_{2}^* = \frac{S_{2} \bar{n}_{22}}{2v_{2}^*} \]
By analogy, we define

\[ X_{12} = \frac{S_1 \Delta \eta / 2 \nu^*}{\nu} \]

then,

\[ \frac{-E_0}{r N} = \frac{p^*}{\nu} = \frac{C k T^*}{\nu} \]

where

\[ p^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12} \]  \hspace{1cm} \ldots \ldots \hspace{1cm} 2.39 \]

\[ C = \frac{(C_1 r_1 N_1 + C_2 r_2 N_2)}{r \cdot N} \]

\[ = \phi_1 C_1 + \phi_2 C_2 \]

Hence, \( T^* \) for the mixture is given by

\[ \frac{1}{T^*} = \left( \frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*} \right) \left( \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12} \right)^{-1} \]  \hspace{1cm} \ldots \ldots \hspace{1cm} 2.40 \]

where the characteristic temps \( T_1^* \) and \( T_2^* \) are defined as

\[ T^* = \frac{T}{T^*} = 2 \nu^* CRT^*/\Delta \eta \]

Adopting the Berthelot relationship [158],

\[ \eta_{12} = (\eta_{11} \cdot \eta_{22})^{1/2} \]

for homopolar species whose interactions are dominated by intermolecular dispersion energy leads to

\[ \Delta \eta = (\eta_{11} - \eta_{22})^2 \]

Hence,

\[ X_{12} = p_1^* \left[ \left( 1 - (S_1 / S_2) \right)^{1/2} \left( \frac{p_2^*}{p_1^*} \right)^{1/2} \right]^2 \]  \hspace{1cm} \ldots \ldots \hspace{1cm} 2.41
Flory et al [150] calculated from these, the following parameters.

1) Enthalpy of mixing
2) The Residual Free Energy and Entropy

Adopting the reduced partition function and the equation (2.38) for intermolecular energy on the assumption of random mixing underlies the theory developed above.

The expressions derived for the various residual or excess properties of a binary mixture involve a single parameter, $X_{12}$, beyond those furnished by the properties of the two pure components. The equations given for calculating the above excess parameters [150] $(H,V,S)$ are related explicitly to one another in terms of this parameter charactering the given mixture.

All excess quantities for binary mixtures have been calculated from the sets of characteristic parameters for the respective pure components together with the parameter $X_{12}$ or $(\Theta_{2}X_{12})$ for a particular pair. They calculated, first the value of $X_{12}$ from observed excess enthalpy, then calculated the other excess parameters to test the theory. The quantity $(v_{1}\Theta_{2}X_{12}/2v)$ identified through $(H^{E} = H_{M}/N)$ where
\[ \Delta H_M = N_1 p_1^* v_1^* \left( \frac{1}{v_1} - \frac{1}{v} \right) + N_2 p_2^* v_2^* \left( \frac{1}{v_2} - \frac{1}{v} \right) + \frac{N_1 v_1^* \theta_2}{v} x_{12} \]

Eqn as the "contact interaction" contribution to the enthalpy of mixing. The difference between \( H_{\text{obsd}}^E \) and the contact term represents the "equation of state" contribution to the enthalpy. This contribution depends not only on the reduced volume of the mixture and therefore on the excess volume, but also on the difference between the reduced volumes \( \bar{v}_1 \) and \( \bar{v}_2 \) of the pure components.

The equation of state contribution is positive for all systems considered by them. The contribution tends to be negative for mixtures of components with very different reduced volumes [151].

2.11.5 Flory's Theory For Sound Velocity

Starting with the reduced equation of state,

\[ \frac{\bar{p} \bar{v}}{\bar{T}} = \bar{v}^{1/3} \frac{1}{\bar{v}'^{1/3} - 1} \]

where \( \bar{p}, \bar{v}, \bar{T} \) are reduced parameters given by

\[ \bar{p} = p/p^* , \bar{v} = v/v^* , \bar{T} = T/T^* \]

\( p^*, v^*, T^* \) being the characteristic parameters.

At zero pressure,
\[ \frac{-1/3 - 1}{1 + \alpha T} = \frac{\alpha T/3}{1 + \alpha T} \]

\[ \frac{-1/3 - 1}{1 + \alpha T} \]

\[ T = \frac{-1/3 - 1}{1 + \alpha T} \]

From experimental values of adiabatic compressibility \( \beta_\alpha \) and specific heat at constant pressure \( C_p \), thermal pressure coefficient is obtained for pure components from,

\[ \gamma = \frac{\alpha C_p}{\beta_\alpha C_p + \alpha^2 T v} \]

similarly \[ p^* = \gamma T v^2 \]

and isothermal compressibility as \( k_T = \alpha/\gamma \)

If \( x_1, x_2 \) are mole fractions of two liquids, then reduced volume of the mixture is given by

\[ \frac{V_{\text{exp}}}{v} = \frac{x_1 v_1 + x_2 v_2}{x_1 v_1 + x_2 v_2} \]

where \( V_{\text{exp}} \) is the experimental molar volume of the mixture.

Segment fractions \( \phi_1 \) and \( \phi_2 \) are obtained as

\[ \phi_1 = \frac{x_1 v_1}{x_1 v_1^* + x_2 v_2^*} \quad \text{and} \quad \phi_2 = \frac{x_2 v_2}{x_1 v_1^* + x_2 v_2^*} \]

If \( S_1, S_2 \) denote the mean number of external contact sites per segment,
then
\[ \frac{S_1}{S_2} = \left[ \frac{v_2^*}{v_1^*} \right]^{1/3} \]

Site fraction is given by \( \phi_2 = \frac{\phi_2}{(S_1/S_2)\phi_1 + \phi_2} \)

And interaction parameter
\[
X_{12} = \left( \frac{S_1}{P_1} \right)^2 \left[ 1 - \left( \frac{S_1}{S_2} \right) \left( \frac{P_2}{P_1} \right) \right]^{1/3} \]

Characteristic pressure of the mixture
\[
p^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 X_{12} \]

and
\[
T = (\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 X_{12}) \cdot \left[ \frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*} \right]^{-1} \]

Substituting for \( T \) in (2.43)
\[
\frac{1}{3} \gamma = \frac{\alpha p^* / 3 \gamma}{1 + \alpha p^* / \gamma} - 1
\]

as
\[
\frac{1}{3} \gamma = \frac{\beta_T p^*/3 \gamma^2}{1 + \beta_T p^*/\gamma^2} \]

Substituting
\[
\beta_T p^* \left[ 1 - 3(\frac{1}{3} - 1) \right] = 3(\frac{1}{3} - 1) \gamma^2
\]

Thus,
\[
p^* \beta_T = \frac{3(\frac{1}{3} - 1) \gamma^2}{1 - 3(\frac{1}{3} - 1)} = \frac{3 \gamma^2}{[(\frac{1}{3} - 1) - 1 - 3]}
\]
all quantities being for the mixture.

Excess isothermal compressibility is given by [152]

\[ \beta_T^E = \frac{3\tilde{v}^2}{p^*[\tilde{v}^{1/3} - 1]} - \frac{\phi_1\tilde{v}_1\beta_T^1 + \phi_2\tilde{v}_2\beta_T^2}{\tilde{v}} \]  \[ \ldots \ldots \quad \ldots \ldots \quad 2.47 \]

Isothermal compressibility is given by [153],

\[ \beta_T = \beta_0 + \frac{T\alpha^2}{C_p} \]

Hence, excess adiabatic compressibility [153] is given by,

\[ \beta_a^E = \beta_T^E - \left[ \frac{T\alpha^2}{C_p} \left( \frac{\phi_1\tilde{v}_1\alpha_1^2}{C_p} + \frac{\phi_2\tilde{v}_2\alpha_2^2}{C_p} \right) \right] \]  \[ \ldots \ldots \quad \ldots \ldots \quad 2.48 \]

Adiabatic compressibility-

\[ \beta_a = \phi_1 \beta_{a1} + \phi_2 \beta_{a2} + \beta_a^E \]  \[ \ldots \ldots \quad \ldots \ldots \quad 2.49 \]

And ultrasonic velocity

\[ u = \frac{1}{\sqrt{\beta_a \rho}} \]  \[ \ldots \ldots \quad \ldots \ldots \quad 2.50 \]

where \( \rho \) is the experimental density.

In this way by using the different thermodynamic parameters of
pure components constituting the mixture, ultrasonic velocity for
the mixture is evaluated from the equation 2.50.

Present approach

In Flory's formulations, $-\Theta_1 \Theta_2 X_{12}$ is used as interaction
parameter added to the characteristic pressure equation given by
2.45. In addition to this an attempt has been made by correcting
the characteristic volume equation of the mixture as

$$v^*_{\text{mix}} = x_1 v^*_1 + x_2 v^*_2 + x_1 x_2 (Y + Z x_4)$$

where $Y$ and $Z$ are adjustable parameters. Similarly using the equat­
ions stated in 2.10.4, ultrasonic velocities are calculated for
mixtures for different compositions by applying Scaled Particle
Theory. While calculating u.s.velocities, different shapes of
molecules are considered and an attempt is made to predict the
shape of a particular molecule in liquid form in a given mixture
using both the theories. In SPT, volume correction is applied to
bulk volume as well as hard sphere volume. Details of the computa­
tional technique used is given in chapter III.

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