CHAPTER 1

INTRODUCTION

Langmuir[1] believed that equilibrium colloidal structures could be accounted for by repulsive forces (short range interaction) alone, together with a correct statistical mechanical treatment of the problem. Later Debye and Huckel, Deryaguin, Langmuir, Onsagar and others[1-4] working on bulk and surface properties of electrolytes, derived expressions for the long-range electrostatic interactions between large bodies. A little later Hamaker[5] summed the dispersion forces between the atoms of condensed bodies and obtained expressions for the long-range dispersion interactions between large bodies.

Langmuir and Onsagar[1,4] were acutely aware of the vital role of statistical mechanics in all colloidal systems where two phases coexist in equilibrium. The importance of statistical mechanics is well illustrated in systems where a two-phase equilibrium exists. Such equilibrium are fairly common in colloidal systems. A thorough statistical mechanical treatment is essential for an understanding of miceller stability and structure.

All problems of colloid stability and structure require correct statistical mechanical treatment, but we have yet to establish the relative importance of short range forces and long-range forces in various colloidal systems.

Statistical mechanical theories of classical fluids are based on the evaluation of the partition functions for a system of **N** molecules in a volume V and at a temperature T

$$Z_N = \left[\lambda^{-3N} \quad (1/N!) \right] \times \int e^{-\beta\phi} \; \tilde{dr}_i \dots \tilde{dr}_N \qquad \dots (1.1)$$

where $\lambda = h/(2\pi m \, k_B T)^{\frac{1}{2}}$, h is Planck's constant, m is the molecular mass, k_B is the Boltzmann's constant and $\beta = 1/K_B T$. The potential energy $\phi \, (r_i \dots r_N)$ is given by

$$\phi \, (r_i \dots r_N) = \sum_{i<j} u(ij) + \sum_{i<j<k} u(ijk) + \dots \qquad \dots (1.2)$$

With $u(ij) = u(|\tilde{r}_i - \tilde{r}_j|)$ etc. The first

term in Eq. (1.2) gives the contribution of pair interactions, the second gives the contribution of triplet interactions etc.

The evaluation of integral in Eq. (1.1) is difficult and in general, can only be performed approximately. However this can be evaluated exactly for a one dimensional fluid case.[6] For higher dimensional fluids, a number of approximate theories have been evolved which involve calculating the distribution functions. These functions measure the probability of finding a number of particles in some particular configuration, and once they are known, certain thermodynamic properties can be deduced immediately.

The L-particle distribution function, $n^{(L)} (\widetilde{r}_i ....\widetilde{r}_L)$ is defined so that $n^{(L)} (\widetilde{r}_i ....\widetilde{r}_L) \times \widetilde{dr}_i .....\widetilde{dr}_L$ is the probability of finding a particle in each of the volume elements $\widetilde{dr}_i .....\widetilde{dr}_L$ centered on $\widetilde{r}_i .....\widetilde{r}_L$ (where $L = 1,2,3$ etc.). Thus it is defined by the following equation

$$n^{(L)} (\widetilde{r}_i \ldots \widetilde{r}_L) = (N!/(N-L)!) \int e^{-\beta\phi} \; \widetilde{dr}_{L+1} \ldots \widetilde{dr}_N /$$

$$\left[\int e^{-\beta\phi} \; \widetilde{dr}_i \ldots \widetilde{dr}_N \right] \qquad \ldots\ldots(1.3)$$

where ϕ is the potential energy defined by Eq.(1.2).

Of the heirarchy of distribution functions, the pair distribution function, $n^{(2)} (\widetilde{r}_1, \widetilde{r}_2)$ is the most significant one, since the thermodynamic properties of the fluid are determined by $n^{(2)} (\widetilde{r}_1, \widetilde{r}_2)$[7]. If only pair interactions are considered, then Eq. (1.2) becomes

$$\phi (\widetilde{r}_i \ldots \widetilde{r}_N) = \sum_{i < j} u(ij) \qquad \ldots(1.4)$$

Further, for a homogeneous fluid of particles interacting via central forces $n^{(2)} (\widetilde{r}_1, \widetilde{r}_2)$ depends only on the distances r_{12} between the particles and not on the position of the particle pair or its orientation. Thus one can define a function $g(r)$, known as the radial distribution function (RDF) by

$$n^{(2)} (\widetilde{r}_1, \widetilde{r}_2) = \rho^2 g(r_{12}) \qquad \ldots\ldots (1.5)$$

ρ being the average number density.

Thermodynamic properties such as internal energy, U; Pressure P; and isothermal compressibility, β_T can all be expressed in terms of g(r) expressed by S.P.McAlister et al[8].

$$\bar{U}/N = 3k_BT/2 + (\varrho/2) \int \widetilde{dr}\ u(r)\ g\ (r) \quad \ldots \ (1.6)$$

$$P/k_BT = \varrho - (\varrho^2/6) \int \widetilde{dr}\ r\ u'(r)\ g\ (r) \quad \ldots \ (1.7)$$

$$\varrho k_BT\beta_T = 1 + \varrho \int \widetilde{dr}\ h(r) \quad \ldots \ (1.8)$$

where u'(r) is the derivative of u(r) and the indirect or total correlation, h(r), is equal to $\left[g(r) - 1\right]$. Eq. (1.7) can be derived either from the theorem of Claussius[9,10] or alternatively by defferentiating Eq. (1.1) with respect to V. Eq. (1.8) has been obtained by Ornstein and Zernike[11] from the theory of fluctuations.

Other thermodynamic properties such as free energy, F, can be obtained from the relation

$$\partial (\bar{F}/N)\ /\ \partial\varrho\ \bigg|\ _{V,T} = \varrho^{-2}p \quad \ldots \ (1.9)$$

if g(r) is known for all densities in the range (o,ϱ) at a given temperature.

For a given thermodynamic state, the RDF

determined uniquely by the function, $u(r)$, (see Eq.1.3)

so that it is likely that there exists an integral

equation in closed form, perhaps a very complicated

one, relating these two functions. Searches for

such an equation have been going on since 1935, when

Kirkwood[12]and Yvon[13] first proposed a very simplified

varient of an integral relation between $g(r)$ and $u(r)$.

By now several such approximate equations are known,

with different degrees of accuracy. The method of

integral equations in the theory of liquids is attrac-

tive because of two circumstances. (1) The possibi-

lity of obtaining analytically representable results

concerning the structure and thermodynamic properties

of liquids and (2) the possibility of solving the

inverse problem, that of reconstructing the form of

the intermolecular potential, $u(r)$ if $g(r)$ is known.

The first serious progress in the method of

integral equations was made when Kirkwood and Boggs[14],

Bogolybov[15] and Born and Green[16] proposed two varients

of a non-linear integral equation for g(r) using Kirkwood's well known super position approximation which assets that the probability of any triplet configuration is equal to that of the three constituent pairs occuring separately.

Of the many existing theories of predicting molecular distribution functions for liquids, two that have gained recent prominance are the Percus-Yevick (PY) approximation[17,18] and the hypernetted chain (HNC) approximation[19-24]. The acceptance which these two approximate theories have achieved is based on the moderately good agreement between the predicted thermodynamic properties and experimental values.[6]

An important feature of the radial distribution description of fluids is that its central element, g(r), is experimentally accessible by the techniques of X-ray[25-29] and neutron[25,30,31] diffraction. Next important pair correlation function is the direct correlation function (DCF), C(r), first introduced

and defined by Ornstein and Zernike[11] as

$$h(r) = C(r) + \rho \int d\tilde{s} \; C(s) \; h \; (|\tilde{r} - \tilde{s}|) \quad \ldots (1.10)$$

with $\tilde{r} = \tilde{r}_1 - \tilde{r}_2$ and $\tilde{s} = \tilde{r}_1 - \tilde{r}_3$.

As the same "direct correlation function" indicates, it was expected originally by its authors that $C(r)$ depended only on the interaction between a pair of molecules and was independent of the interfering effects of the surrounding molecules. Although this interpretation of $C(r)$ turned out to be incorrect, it was found that simple approximations to $C(r)$ combined with its defining equation led to accurate expressions for the equilibrium properties of classical fluids. The usefulness of the DCF in formulating efficient approximations in the classical treatment of molecular fluids[32,33]. There the properties due to the long range interactions between molecules are formulated in terms of correlation between the charge densities instead of the correlations between

the molecular densities in the classical theory of fluids, but the structure of suitable perturbation (diagram) expansions of these correlation functions have many features in common to those of perturbation expansions of classical correlation functions.

Goldstein[34] pointed out that $C(r)$ could be vigorously computed from the Fourier transformation of a function experimentally obtained from diffraction studies and reported brief computation for liquid helium[35]. Johnson et al.[36] carried out these calculations for liquid metal systems and for selected states of liquid argon. Mikolaj and Pings[37] exploited this and studied the large angle scattering in the case of argon at 13 different states in the general vicinity of the critical region. $C(r)$, has been computed for some molecular fluids like methane[38], carbon tetrachloride[39,40].

The simplest approximation to $C(r)$ coincides with its asymptotic form for large r, namely

$$C(r) \quad = \quad - u(r)\beta \qquad \qquad \dots(1.11)$$

Evidently Eq.(1.11) fails for short range distances where u(r) becomes strongly repulsive. However for this case of a steep repulsive potential, a good approximation was obtained for C(r) in the form of PY equation 41-44 which assumes the relation

$$C(r) = \left[1 - \exp\{\beta u(r)\} \right] \; g(r) \qquad \dots (1.12)$$

to be valid at all densities. Moreover, for the extreme case of a hard sphere repulsion, improvements to the Py equation have become available[45]. Consequently it has been found useful to devide the range of r values into two separate regions by a characteristic intermolecular distance, d(i) the range r>d where u(r) can be considered as weak and where Eq.(1.11) is assumed to hold and (ii) the range r<d where u(r) can be considered as a strongly repulsive potential and where the PY equation or modifications there of can be applied. This method treats the long (r>d) part of the potential as a perturbation to a reference system where only the short range repulsive part (r<d) of the potential is effective.

It has led to a successful description of
the properties of fluids as demonstrated by
the thermodynamic perturbation theory[46,47], by
the mean spherical model (MSM)[48] and various
recent variations there of[49,50]. In the
latter treatments use is made of the fact that
$C(r)$ has the same range as the potential
(strictly so in the PY approximation) and there-
fore it has been split into two parts, namely
$C_0(r)$ which is the value of $C(r)$ for the reference
system vanishing for r and $C_p(r)$ that can be
treated in turn as a perturbation to $C_0(r)$ of
the reference system.

Although the hard sphere model is an
idealisation, it has been shown[51-54] that the
$g(r)$ for a dense Lennard-Jones (LJ) liquid
agrees closely with that for the fluid in which
the interactions are just the LJ repulsions
without the attractive forces.

A qualitative explanation of this structure
phenomenon follows from a simple description of

the environment of a particle in a dense fluid.
For a LJ fluid, high density corresponds to
thermodynamic states at which $\rho^{-1/3} \leq r_o$, r_o
being the location of the minimum in the LJ
potential. Because $\rho^{-1/3} \leq r_o$, nearest
neighbours in a dense liquid are crushed extremely
close to one another and any displacement of a
particle will cause a large change in the energy
associated with the interparticle repulsive
forces. However, the change in energy associated
with the attractive forces will be relatively
small, because these interactions are not quickly
varying functions of the inter-particle separation.
As a result, the repulsions dominate the high
density structure.

At low and moderate densities, particles
are not so close together and the longer ranged
attractive forces can play a significant role
in forming the structure. Thus the relative
importance of the attractive forces on the
interparticle correlations in a fluid becomes
smaller as the density is increased.

There is some evidence[55-57] that the structure of real fluids can very closely be approximated by that of hard sphere fluids, so that a hard sphere RDF should serve as a reasonable approximation when applied to real systems. Zwanzig[58] first provided the formalism in the form of a perturbation theory of fluids, that is required to correct hard sphere reference fluid to one that obeys a more realistic potential. Several authors have developed theories to relate hard sphere data to the properties of fluids with other repulsive potentials[46,47,51,52,59,60].

S(q) defined by equation given below is called the structure factor and is of utmost importance in the distribution function theory of liquids and concentrated particle dispersions[61]

$$\left[S(q) - 1 \right] = \rho \int_o^\infty 4\pi r^2 \left[g(r) - 1 \right] j_o(qr)\,dr$$

$$\qquad \ldots(1.13)$$

where $j_o(qr)$ is the spherical Bessel function.

$$j_o(qr) = \sin(qr)/qr \qquad \ldots(1.14)$$

Eq.(1.13) is the fundamental relation between observed X-ray scattering intensity and the density of atoms and the RDF, $g(r)$.

Eq.(1.13) can also be rewritten as

$$\left[g(r) - 1 \right] = (1/2\ \pi^2 \rho) \int_0^\infty \left[S(q) - 1 \right] q^2\ j_0(qr) dr \qquad \ldots (1.15)$$

Thus $g(r)$ can be calculated from the measured $S(q)$ defining the Fourier transform, $H(q)$ of any function $H(r)$ as

$$H(q) = \int \widetilde{dr}\ \exp\ (iq.r)\ H(r) \qquad \ldots (1.16)$$

the Ornstein-Zernike equation in q-space can be written in the form

$$h(q) = C(q) + \rho\ C(q)\ h(q)$$

or

$$C(q) = h(q) / \left[1 + \rho h(q) \right] \qquad \ldots (1.17)$$

where $h(q)$ and $C(q)$ are the Fourier transforms of $h(r)$ and $C(r)$ respectively. From Eqs.(1.16 and (1.13), it is clear that

$$\rho h(q) = \left[S(q) - 1 \right] \qquad \ldots (1.18)$$

and hence

$$\rho C(q) = \left[S(q) - 1 \right] / S(q) \qquad \ldots (1.19)$$

or alternatively

$$C(r) = (1/2\pi^2 \rho\ r) \int_0^\infty \left[\{ S(q) - 1 \} / S(q) \right] q \sin qr\ dr \qquad \ldots (1.20)$$

Thus from the measured structure factor, S(q), one can compute both g(r) and C(r).

Structure factor can be evaluated for certain models and can be compared with experimental data. Previously Furukawa[62], Ashcroft and Leckner[56] and Enderby and North[63] reported that the structure of liquids including the metallic liquids and alloys could be represented by the hard sphere model. Recent studies[64-69] have also shown the applicability of square well potential in representing the structure of liquid metals and alloys. Besides liquid metals and alloys, the same potential has been found to represent the structure of non-metallic liquids like argon, krypton, helium and methane[70-72] satisfactory.

The interrelationship for h(r) and C(r) may also be viewed in terms of modification functions of Waser and Schomaker[37,73]. The Ornstein-Zernike equation has the consequence that the compressibility equation of Zernike and Prins[74]

$$k_B T \quad (\partial \rho / \partial p) = 1 + \rho \int h(r) \; \widetilde{dr} = S(o) \quad \cdots \quad (1.21)$$

can be written in alternative form

$$(1/k_B T) \quad (\partial p / \partial \rho) = 1 - \rho \int C(r) \; \widetilde{dr} = S(o)$$

$$\cdots \cdots \quad (1.22)$$

Here $S(o)$ is the structure factor for limitingly small scattering angles and is a second route to thermodynamic behaviour.

For a highly compressible fluid, near its critical point $(\partial p / \partial \rho) \to 0$, and thus the integral on the right of Eq. (1.21) becomes very large indicating that $h(r)$ approaches zero less rapidly than r^{-3}. In the same limit, the integral on the right of Eq. (1.22), tends to a finite value. Thus in the vicinity of the critical state, $h(r)$ becomes long range in the sense that its volume integral (or zeroth moment), diverses, while $C(r)$ remains bounded and finite.

Recent advances in the statistical mechanics of simple fluids employing perturbation theory

methods[46,51,64-72] suggests that a similar approach may be useful for concentrated particle dispersion[75-77]. The fundamental strategy of such methods is the relation of the structure of the fluid in someway to that of an underlying hard sphere (HS) fluid, about which much is known, both from approximate theories[36,37] and from computer simulations.[78]

For many years the solution of the Ornstein-Zernike integral equation for the radial distribution function has been an important problem in the theory of fluids.

The well known Percus-Yevick and Hypernetted chain approximations are examples of approximate closure rules for the Ornstein-Zernike equation[79]. The non-linearity of these two rules severely inhibits any analytical treatment except in the simplest case of a hard sphere fluid although when solved numerically for other potentials they

give reasonable agreement with computer experiments[80].

In order to describe the structure of polymers in the molten or vitreous state four different kinds of static correlation functions should be studied experimentally (1) pair distribution function of the monomer units, (ii) the distance distribution function of the repeating units of a single chain, (iii) the orientation correlation function of the bond vectors and (iv) the density fluctuation correlation function of the bulk sample. The approximate methods include: X-ray wide angle scattering and electron diffraction, small angle neutron diffraction of deuterium bagged molecules, depolarised light scattering and magnetic birefriengence, small angle X-ray and polarised light scattering.

Dealing with amorphous systems there is
no general theory available which allows evalua-
tion of the partition function and description
of the properties of the amorphous bulk material
in a good approximation. Therefore models have
to be used, and it is well known that in the
theories of the liquid state two different kinds
of models have been developed approaching the
problem either from the crystal side or from the
gas side. That means, attempts have been made
to describe the kind of disorder which distinguish
a liquid from an ideal crystal and, on the other
hand theories on the variation of properties of
a gas with increasing density (i.e. virial
expansions) have been developed.

The situation is very similar to the case
of high polymers. Two kinds of models for the
structure of amorphous polymers in the bulk have

been proposed (i) In the "coil model", it is assumed that the configuration statistics of a single molecule in the melt or glassy state are the same as those of an unperturbed molecule in solution[81,82]. (ii) The various "bundle models" are based on the assumption of domains with nematic liquid-crystal like arrangements of the macromolecules[83-87].

The coil model follows, according to P.J.Flory[82] "from considerations of a theoretical nature which are at once simple and virtually incontrovertible". Newer theoretical considerations[88,89] dealing with the whole range of concentration are consistant with the assumption that the molecular conformations in the bulk of and in a -solvent are identical. The concept of a "granular" structure of amorphous polymers, is mainly based on electron microscopical evidence[84,90-92,

the meander model[85,86] starts from the assumption
of molecular bundles[83] as a thermodynamic stable
form. This point of view is mainly justified
by qualitative packing density considerations.

Much work has been done in the last few
years in order to solve the problem. In some
cases a considerable confusion resulted from
misinterpreting experimental results in terms
of long range order where actually some liquid
type of short range order was detected.

Spontaneous solution and swelling do not
occur when there is no affinity between a polymer
and a low molecular liquid. However, colloidal
dispersions may form in such systems. If a
polymer is amorphous, such dispersions may be re-
garded as emulsions. For example, the milky juice
of rubber-bearing plants, known as latex, is an
emulsion. It is a system with drops of globules

of rubber suspended in water. Polymer emul-

sions produced in emulsion polymerisation

are known as synthetic latexes. They are

also aqueous dispersions of polymers.

Theoretical understandings of model

fluids in particular hard sphere fluids reached

new heights in the last decade. Where as in

practice only a small class of molecules is

spherical it is of interest to observe that

there is in principle no objection to apply

these theories to much larger spherical par-

ticles suspended in a liquid medium. So the

basic behind these investigations is that the

structure and interparticle interactions in

colloidal dispersions may be treated in the

sameway as in the simple liquids[93,94]. It

turns out that the interaction potential between

molecules (in vacuo) has to be replaced by a

potential of mean force[95,96] (with a free energy

character) between all the dispersed particles.

The solvent properties appear as parameters
in the potential of mean force. The charac-
teristics of this potential are determined by
the properties of the particle surfaces and
by certain parameters (chemical potentials)
of the liquid mixture in which the particles
are suspended. By changing the composition
of the fluid mixture the potential can often
be varied continuously. The solvent may
often be treated as a homogeneous medium, if
the particle size is sufficiently large.
Early investigators in the field were Onsager[4],
Riley and Oster[97] and Kirkwood and Mazur[98].
However accurate fluid models were not
available at that time.

Computer simulations[99] have shown that
the spatial structure, represented by the radial
distribution function is mainly determined by the
hard repulsion between the particles in close

contact in particular at higher concentra-
tions. The same is true for some thermo-
dynamic properties like the pressure. The
effect of a weaker longer ranged attractive
or repulsive tail in the pair potential may
then be considered as perturbation. There-
fore it is interesting to get a better under-
standing of colloidal systems from the analogy
with the liquid state perturbation theory.

The perturbation technique originally
applied to simple fluids[39,40,64,65,67,100]
is now being incorporated more and more into
the field of colloidal dispersions[75-77,95,101-116].
In aqueous dispersions stabilized by extended
electrical double layers, structural properties[117-122],
and osmotic pressure[123,124] have been measured
and interpreted. Recently much interest has
been shown in the order-disorder transitions
found in these systems[125-134]. Fewer studies

have been made of this phenomenon in disper-
sions in non-aqueous Solvents[123,135,136].
In this thesis, some of the ideas taken from
the field of liquids have been applied to
concentrated dispersions in non-aqueous
media[111,112].

In the last decade or so there has been
a considerable upsurge in research on stable
concentrated dispersions[95,111,127,137,147].
This contrasts the most traditional colloid
chemistry which has been largely concerned
with the stability of dispersions and the study
of the transition from a stable dispersion to
a coagulate, as expressed, for example, in the
Schulze-Hardy rule[148]. In recent years there
appears to have been a greater interest in the
measurement of the osmotic pressure[111,137-140],
phase equilibria[127], elastic constants[141,142],
static and dynamic structure factors[95,143-146]

and diffusion constants[146,147] of stable con-
centrated colloidal dispersions. From a
fundamental point of view such measurements
are very interesting, since they are capable
of providing insight into the forces between
colloidal particles and the structure and
dynamics of systems of colloidal particles.
When such measurements are performed on
so-called 'model' colloids, such as almost
monodisperse systems of latex spheres, which
are characterized in terms of the parameters
appearing in some model interaction potential,
it is possible to directly compare experimental
and computed properties for the same dispersion
and thereby determine the accuracy of the model
potential.

The methods used to compute the excess
equilibrium properties of colloidal dispersions
are identical to those used for molecular poten-
tial of meand force[95,96]. The essentially

exact methods of **numerical** statistical mechanics[99]
such as the Monte Carlo (MC) and molecular dynamics(MD)
can be used to compute the measured properties and
thus test model potential energy functions. However
these exact computer simulation methods are often
complicated, always computationally time consuming
and therefore expensive and they may be completely
impractical when a large amount of data needs to
be analyzed in terms of a number of potential
energy functions. Hence there is a considerable
incentive to have available approximate statistical
mechanical theories with which experimental data
can be quickly and precisely analyzed and interpreted.

Statistical mechanical theories circumvent
the laborious explicit computer evaluation of the
required properties by making one or more simpli-
fying approximations or assumptions. Such theories
or approximate methods, may be categorized into
integral equation methods and perturbation methods[99].
The first of these categories, which includes the
Percus-Yevick (PY), Hypernetted chain (HNC), mean

spherical approximation (MSA), and the Born-Green-

Kirkwood (BGK) methods, has the advantage that,

apart from the potential energy function, no

additional information about the system is required,

However, these methods usually involve the numerical

solution of a non linear integral equation and are

accurate only for a small class of potential

functions and a small range of physical conditions[99,149].

Thus in most circumstances these methods are not very

useful for analyzing experimental results.   In

principle, these methods can be made more generally

applicable over a wide range of physical conditions.

However this can only be achieved at the expense of

much greater complexity which may result in these

approximate theories becoming as computationally

demanding as the exact computer simulation methods[149].

Perturbation theories are the most advantageous

over the integral equation (discussion is given in

III Chapter)   So perturbation theories are chosen

to state the validity of liquid state theories to

concentrated colloidal dispersions.

The size, shape and relative positions of colloidally dispersed particles (eg. Microemulsions of micelles) may be determined in principle by either X-ray or light scattering methods. The theory of the angular dependence of the intensity of scattering for these two types of radiation is identical if, in the case of light scattering, the particles have an index of refraction close to that of the medium. A further identity exists between the Kinetic theory of gases and the thermodynamic theory of solutions of compact macromolecules, the equation of state, in the latter case, being given by the osmotic pressure as a function of concentration and temperature.

In this thesis, application of these ideas are used to explain the osmotic compressibility of concentrated dispersions of very small stable droplets in an organic solvent as a function of particle number density. This osmotic compressibility is equivalent to the compressibility of a one component dense gas of spherical molecules.