

CHAPTER 4

STRUCTURAL ASPECTS OF COLLOIDAL DISPERSIONS

The structure of micells has attracted renewed attention during the recent years due to the widespread use of microemulsions in technology^{224,225} and life science²²⁴⁻²²⁶. The structural information obtained by light, X-ray or neutron-scattering experiments may be interpreted using the technique of liquid state theories.

Light and neutron scattering measurements of the static structure factor, $S(q)$, for aqueous dispersions of charged and uncharged colloidal particles bear a strong resemblance to similar studies of simple liquids^{95,105,108,112,120,140,145,227,228}. Furthermore as the concentration of the charged macroparticles in solution is increased, the suspension undergoes a first order solid to liquid like phase transition in which the

long range order is built up and a colloidal crystal formed²²⁹ . This resemblance to atomic and molecular systems allows the physics of colloidal dispersions to be understood through the techniques of statistical mechanics which probe the fundamental forces acting between the colloidal particles in solution.

Aqueous dispersions of highly charged and uncharged colloidal particles exhibit a considerable amount of shortrange order, evident in light - and neutron-scattering measurements of their static structure factor $S(q)$ ^{95,105,120,140,145,227,228} . Monte Carlo Simulations¹²¹ and approximate theories^{99,120,216,230,231} common in liquid studies, have been successfully applied to an analysis of the structure of these macro ion solutions and uncharged colloidal dispersions^{95,105,111,112,228,231} . Such

studies probe the fundamental forces responsible for colloid stability and statistical mechanical methods have already been used to examine the conditions for which a disorder to order phase transition occurs in colloids^{130,132}. However, whereas the structure of simple fluids is dominated by short-range repulsive forces macro ion solutions are dominated by a strong, long-range coulombs interaction. Few studies have been made of the structure and phase stability of dispersions whose particles carry little or no charge and the Van der waals attractive forces are of a greater range than the repulsive forces between the particles. Light scattering^{95,105,111,112} studies of water-in-oil microemulsions have been analysed only on an empirical basis and it is with monodisperse systems of this type that this thesis is principally concerned.

It is now well established that main features of the structure factor are determined by the short range repulsive forces in simple liquids and liquid metals, and this fact has been exploited in the successful perturbation theories of the liquid state²³³. The longer-range part of the potential is treated as perturbation.

The theory involves a perturbation treatment based on a hard sphere reference system with the long-range interactions treated in the random phase approximation (RPA) and mean spherical model approximation (MSMA).

Modern theories of fluids have been used by several authors^{95,105,111,112} to explain microemulsion experimental results. One of the main conclusions of these theories is that in dense liquids the spatial structure, which can be represented either by the function

of pair distribution $g(r)$, or by the thermodynamic properties, is to a large extent determined by steric repulsions between close particles. The attractive or repulsive effects are treated as perturbation of hard spheres. Vrij et al consider that the intermolecular interaction potential can be expressed as the sum of two terms u_{HS} and u_A ¹¹². The hard sphere contribution to the osmotic pressure P_{HS} is described by the equation of state proposed by Carnahan and Starling²³³. Only binary interactions are considered in the term of perturbation P_A . The total osmotic pressure is $P = P_{HS} + P_A$.

The osmotic pressure due to hard sphere repulsion can be very accurately represented by Carnahan Starling²³³

$$P_{HS} = \rho k_B T / (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3 \dots (4.1)$$

where

$$\eta = \rho (4\pi/3) r_{HS}^3 \dots (4.2)$$

To allow for deviations from the hard sphere interactions Van der Waals perturbation potential is used²⁰². It can semiempirically modeled as

$$P_A = - a e^2 \quad \dots (4.3)$$

and considered ' P_{HS} ' and ' a ' as adjustable parameters.

4.1 THEORY

✓ Most of the reasonably successful theoretical attempts to calculate $g(r)$ for hard spheres are based on approximations for the direct correlation function $C(r)$, which is defined Eq.(1.1). This equation, for one component fluids of spherically symmetric particles, takes the form

$$h(r) = C(r) + e \int dr C(|r - r'|) h(r') \quad \dots (4.4)$$

where $h(r) = g(r) - 1$ and e the number density of the fluid. For the hard sphere fluid

$$h(r) = -1 \quad r < d \quad \dots \quad (4.5)$$

Perhaps the most famous closure relation for Eq. (4.4) is that due to Percus & Yevick¹⁷, and can be stated in two ways. One is the approximation that

$$C_{PY}(r) = 0 \quad r > d \quad \dots \quad (4.6)$$

Combined with Eq. (4.1) and (4.2). The other more general statement is that

$$C_{PY}(r) = g(r) \left[1 - \exp\{\beta u(r)\} \right] \quad r < d \quad \dots \quad (4.7)$$

This equation has been called analytically by Wertheim⁴¹ and Thiele⁴². The analogous equation for multicomponent hard sphere fluids with additive diameters was solved by Lebowitz¹⁷² and for a particular example of a binary mixture of hard spheres with non additive diameters by Ahn and Lebowitz²³⁴. It gives a qualitatively correct description of the hard sphere fluid

and it has been used to describe fluids with short ranged attractive tails, such as square well, triangular well fluid.

For a Square well, Triangular well fluid, the potential can be separated into attractive and repulsive parts. The pair correlation function is derived for the purely repulsive potential and then for the entire potential and observing how the structure changes as the attractive well is added. From comparison of computer calculations and reliable theoretical results, one knows that adding the attractions at high density lowers the height of the first major peak and shifts the height of the first-peak to slightly larger distances. This is found for both the Lennard-Jones potential^{49,54} and the square well fluid²³⁵. Thus attractions tend to pull nearest neighbours into the middle of

the attractive well. In the Percus-Yevick approximations, the effect of attractions is exactly the opposite at high densities namely the first peak tends to get higher²³⁵. Thus, for high density and low temperature the Percus-Yevick equation in general predicts too high a first peak. This has been observed for the square well fluid²³⁵ the Lennard-Jones fluid⁸⁰, and a model of a liquid metal²³⁶.

Percus-Yevick equation is extensively used for colloidal dispersions.

The mean spherical model approximation (MSM) was originally constructed by Lebowitz and Percus⁴⁸ as a generalization to continuous fluids of the spherical model for Ising spin systems, is based on simple approximations for the two-particle distribution

function. It is most straight forwardly applied to fluids. The mean spherical approximation provides a linear closure rule which allows the Ornstein-Zernike equation to be solved analytically for a number of cases in which the intermolecular potential is a purely repulsive hard-core part plus an attractive tail. The closure statements of the MSM are

(1) $h(r) = -1$ for $r < d$ where d is the diameter of hard core and

(2) $C(r) = -\beta u(r)$ for $r > d$. Here $u(r)$ is the attractive part of the potential and

$$\beta = 1/k_B T$$

Mean spherical approximation is extended to macro ion²¹⁶ and to colloidal dispersions^{75,77,113-116}.

Random phase approximation (PRA) is of limited usefulness but it can be easily used for the direct correlation function, $C(r)$ of a monodisperse colloidal dispersion.

In the present investigations, it is proposed to apply square well, triangular well and square-plus-triangular well potential tails on perturbation over PY hard sphere model.

4.1.a HARD SPHERE POTENTIAL

The hard sphere model is widely used to interpret the light scattering^{108,110,146,237} and neutron scattering data for microemulsions¹⁴⁵ micells²¹⁶, latexes^{105,228}, diblock copolymer²³⁸ and gels²³⁹.

Barker-Henderson (BH)^{46,47} division of the potential is given by Eqs.(3.1). In order

to avoid the necessity of introduction a perturbation scheme associated with the softening of the hard core of the interparticle potential has a hard core of diameter, d . This immediately gives a reference potential $u_0(r)$ of the form^{47, 240, 241}

$$\begin{aligned} u_0(r) &= \infty & r \leq d \\ &= 0 & r > d \end{aligned} \quad \dots (4.8)$$

For a fluid of particles interacting through a hard sphere potential plus a perturbation, the MSM approximation

$$\begin{aligned} C(r) &= g(r) [1 - \exp\{u(r)\beta\}] & r < d \\ &= -u(r)\beta & \lambda d \geq r \geq d \dots (4.9) \end{aligned}$$

Here λ is the width of either SW or TW .

For hard spheres, $u(r)$, is zero for $r > d$ and the hard sphere Percus-Yevick is

defined by the following equation

$$C(r) = 0 \quad r > d \dots (4.10)$$

Thus the hard sphere PY approximation can be regarded as the MSM approximation applied to hard spheres. Wertheim equation for hard sphere potential and their result can conveniently be written as

$$C(r) = -\left[a + b\left(\frac{r}{d}\right) + c\left(\frac{r}{d}\right)^3 \right] \dots (4.11)$$

with

$$\begin{aligned} \eta &= \pi \rho d^3/6 \\ a &= (1 + 2\eta)^2 / (1 - \eta)^4 \\ b &= -6\eta(1 + 0.5\eta)^2 / (1 - \eta)^4 \\ c &= 0.5(1 + 2\eta)^2 / (1 - \eta)^4 \dots (4.12) \end{aligned}$$

The Fourier transforms of direct correlation function for both hard sphere plus perturbation potential can be written as

$$C(q) = \int_0^\infty \vec{d}\vec{r} \exp(i\vec{k} \cdot \vec{r}) C(r) \dots (4.13)$$

It is conveniently written as

$$C(q) = \int_0^d \vec{dr} \exp(i\vec{k} \cdot \vec{j}) C_{hs}(r) + \int_d^\infty \vec{dr} \exp(i\vec{k} \cdot \vec{j}) C_p(r) \quad \dots (4.14)$$

By using perturbation potential conditions, the 2nd term of RHS of Eq.(4.14) can be further truncated.

$C_{hs}(r)$ and $C_p(r)$ are hard sphere potential and perturbation potential correlation functions respectively. The 1st term of RHS of Eq. (4.14) is represented for $C_{hs}(q)$.

Eqs. (4.11) can be inserted in first term of Eq. (4.14) and the expression is

$$C_{hs}(q) = - \left(\frac{4\pi}{q} \right) \int_0^d r \sin qr \times \left[a + b \left(\frac{r}{d} \right) + c \left(\frac{r}{d} \right)^3 \right] dr \quad \dots (4.15)$$

After a little algebra it can be shown that

$$\rho C_{hs}(q) = \left[-24\pi / (qd)^6 \right] \left[a(qd)^3 \times (\sin qd - qd \cos qd) + b(qd)^3 \times \right]$$

$$\begin{aligned} & \{ 2 qd \sin qd - (q^2 d^2 - 2) \cos qd - 2 \} \\ + c & \{ (4q^3 d^3 - 24qd) \sin qd - \\ & (q^4 d^4 - 12q^2 d^2 + 24) \cos qd + 24 \} \dots (4.16) \end{aligned}$$

For binary mixtures of hard spheres,¹⁷¹ the direct correlation function, $C_{ij}(r)$ is given in MSM approximation by

$$\begin{aligned} C_{ij}(r) &= C_{ij}(r) & 0 < r < d_{ij} \\ &= -u(r) & d_{ij} < r \leq \lambda_{ij} d_{ij} \\ &= 0 & r > \lambda_{ij} d_{ij} \dots (4.17) \end{aligned}$$

Here $C_{ij}(r)$ stands for the hard sphere solution of Percus-Yevick equation for binary liquid mixtures proposed by Lebowitz¹⁷² and later by Baxter¹⁷⁵. The mixed parameters or unlike parameters may be defined using the well known Lorentz-Berthelot rules²⁴² as follows

$$\begin{aligned} d_{ij} &= (d_{ii} + d_{jj})/2 \\ \epsilon_{ij} &= (\epsilon_i \epsilon_j)^{1/2} \\ \lambda_{ij} &= (\lambda_i d_i + \lambda_j d_j)/(d_i + d_j) \dots (4.18) \end{aligned}$$

Here $d_i, \epsilon_i, \lambda_i$ stand for hard sphere diameter, depth and breadth respectively of either square well or triangular well used for species i .

The correlation function $C_{12}(r)$, is given by Lebowitz¹⁷² and Baxter¹⁷⁵ as

$$\begin{aligned}
 C_{12}(r) &= -A_1 & r < s = (d_2 - d_1)/2 \\
 &= -[A_1 + \{B(r - s)^2 + 4SD(r - \lambda)^3 + \\
 &\quad + D(r - s)^4\}/r] & s < r < d_{12} \\
 &= 0 & r > d_{12} \quad \dots \quad (4.19)
 \end{aligned}$$

with

$$s = (d_2 - d_1)/2 \quad \dots \quad (4.20)$$

$$\eta_i = \pi \rho_i d_i^3/6 \quad \dots \quad (4.21)$$

$$\eta = \eta_1 + \eta_2 \quad \dots \quad (4.22)$$

$$\alpha = d_1/d_2 \quad \dots \quad (4.23)$$

$$\begin{aligned}
A_1 = & [(\eta_1 + \alpha^3 \eta_2) (4 + 4\eta + \eta^2) \\
& - 3\eta_2 (1 - \alpha)^2 \{1 + \eta_1 + \alpha(1 + \eta_2)\} \times \\
& (1 + 2\eta_1 - \eta_2) + (1 - \eta^3) - \\
& - 3\eta_1 \eta_2 (1 - \eta) (1 - \alpha)^2] (1 - \eta)^{-4} \dots (4.24)
\end{aligned}$$

$$\begin{aligned}
\alpha^3 A_2 = & [(\eta_1 + \alpha^3 \eta_2) (4 + 4\eta + \eta^2) - 3\eta_1 \\
& (1 - \alpha)^2 (1 - \eta_1 + 2\eta_2) \{1 + \eta_1 + \alpha(1 + \eta_2) \\
& + (1 - \eta^3) \alpha^3 - 3\eta_1 \eta_2 (1 - \alpha)^2 \alpha (1 - \eta)\} \times \\
& (1 - \eta)^{-4} \dots (4.25)
\end{aligned}$$

$$D = [\eta_1 A_1 + \alpha^3 A_2 \eta_2] / 2 d_1^3 \dots (4.26)$$

$$\begin{aligned}
B = & -[3(1 + \alpha)/d_2] [\eta_1 g_{11}/\alpha^2 + \\
& + \eta_2 g_{22}] g_{12} \dots (4.27)
\end{aligned}$$

$$\begin{aligned}
g_{11} = & [(1 + \eta/2) + 3\eta_2(\alpha - 1)/2] \times \\
& (1 - \eta)^{-2} \dots (4.28)
\end{aligned}$$

$$\begin{aligned}
g_{22} = & [(1 + \eta/2) + \{3\eta_1(1 - \alpha)/2\alpha\}] \times \\
& (1 - \eta)^{-2} \dots (4.29)
\end{aligned}$$

$$g_{12} = \left[(1 + \alpha/2) + \left\{ \frac{3(1 - \alpha)(\eta_1 - \eta_2)}{(1 + \alpha)} \right\} (1 - \alpha)^{-2} \right] \dots (4.30)$$

The above constants are defined by Lebowitz¹⁷² and Ashcroft and Langreth²⁴³. For the sake of convenience and to reduce the confusion, the original notations, of the constants are changed.

The Fourier transform of $C_{12}(q)$ can be written by using the above solutions to represent $C_{ij}(r)$ in the region, $0 < r < d_{ij}$ as

$$C_{12}(q) = \left[-\frac{4\pi}{q^6} \right] \left\{ q^2 \left[A_1 + 2Bd_1 + 4Dd_1^2(d_{12} + 2S) \right] \right. \\ \left. - 24Dd_{12} \right\} q \sin qd_{12} + \left[q^2(2B + 12Dd_1d_2) \right. \\ \left. - q^4 \left[A_1d_{12} + Bd_1^2 + Dd_1^3(d_{12} + 3S) \right] \right. \\ \left. - 24D \right] \cos qd_{12} + (24D - 12Bq^2) \\ \left. \cos Sq + 24DSq \sin Sq \right] \dots (4.31)$$

For $q = 0$, some terms of the RHS of Eqs.(4.16) and (4.31) is zero because 'sin' value is zero. Hence according to L' Hospital's rule, both numerator and denominator are differentiated till q terms are removed or cancelled to avoid getting zero value. Final expressions for single hard sphere and for mixture of hard spheres can be written as

$$\sqrt{e} c_{hs}(0) = -\eta [8a + 6B + 4c] \dots (4.32)$$

and

$$c_{12}(0) = -\frac{4}{3} \pi A_1 d_{12}^3 - 4\pi d_1^3 \times$$

$$\left[\frac{1}{12} B(d_1 + 2d_2) + \frac{1}{10} S D d_1 (3d_1 + 5d_2) + \frac{1}{30} D d_1^2 (2d_1 + 3d_2) \right] \dots (4.33)$$

4.1.b. SQUARE WELL POTENTIAL :

Fairly extensive Monte Carlo and Molecular dynamics^{212,244} results for the square well potential with $\lambda = 1.5$ are available. Square well potential is applied to colloidal dispersions also^{75,76,112,113-115}.

The second term of RHS of Eq.(4.14) is the direct correlation functions, of square well potential. This is represented as $C_{SW}(r)$.

This is equal to " $-u(r) = \epsilon\beta$ " in the case of square well potential in the region of $d \leq r \leq d\lambda$ as shown in Eq.(4.9). Here $\beta = (k_B T)^{-1}$.

After little algebra the Fourier Transform of $C_{SW}(r)$ can be written as

$$e C_{SW}(q) = [24\gamma\beta\epsilon/(qd)^3] [\sin q\lambda d - q\lambda d \cos q\lambda d + qd \cos qd - \sin qd] \dots (4.34)$$

At thermodynamic limit the Eq.(4.34) takes the shape of

$$e C_{SW}(0) = 8\gamma\epsilon(\lambda^3 - 1)\beta \dots (4.35)$$

4.1.c. TRIANGULAR WELL POTENTIAL :

The results in the above section show that the representation of the attractive forces by the square well potential is quite satisfactory for concentrated particles dispersions. There have also been studies of MSM calculations on liquid sodium^{65,245} using a potential derived by Shyu et al²⁴⁶ and on argon with either LJ²⁴⁷ or square well tails⁶⁵. So the validity of triangular well potential has been tested in the framework of MSM approximations.

The triangular well potential is defined as²⁴⁸

$$\begin{aligned}
 u(r) &= \infty & 0 < r \leq d \\
 &= (\lambda \epsilon / \lambda - 1) (r / \lambda d - 1) & d \leq r \leq d \lambda \\
 &= 0 & r > \lambda d \quad \dots (4.36)
 \end{aligned}$$

From Eq. (4.9)

$$\begin{aligned}
c(r) &= -u(r) \beta \\
\text{TW} &= -(\epsilon \beta) (\lambda / \lambda - 1) (r / \lambda d - 1), d \leq r \leq d \lambda \\
&\dots (4.37)
\end{aligned}$$

After substitution of Eq. (4.37) in the second term of RHS of Eq. (4.14), the Fourier transform of $C_{\text{TW}}(r)$ can be written as

$$\begin{aligned}
e^{C_{\text{TW}}(q)} &= \left[-24 \gamma \epsilon \beta / q (qd)^4 (\lambda - 1) \right] \times \\
&\quad \left[q \lambda d \sin q \lambda d + 2 \cos q \lambda d - \right. \\
&\quad \left. - (\lambda q^2 d^2 - q^2 d^2 + 2) \times \right. \\
&\quad \left. \cos qd - (2 - \lambda) dq \sin qd \right] \dots (4.38)
\end{aligned}$$

At thermodynamic limit the equs. (4.38) takes the shape of

$$e^{C_{\text{TW}}(0)} = 2 \gamma \epsilon \beta (\lambda^3 + \lambda^2 + \lambda - 3) \dots (4.39)$$

4.1.d. SQUARE-PLUS-TRIANGULAR WELL POTENTIAL :

Perturbation theories have received a lot of attraction in recent years as a means of calculating liquid state properties^{58,59,198} and to interpret the structural information of colloidal dispersions, obtained by light scattering experiments^{75,77,110-116}. Boghdadi computed the free energy values of fluids by using square-plus-Sutherland²⁴⁹, triangular²⁵⁰ and square-plus-triangular potential²⁵¹ as perturbation over the hard sphere model. In light of all these applications, here the hard sphere perturbation theory has been applied to monodisperse colloidal dispersions whose particles interact through a square plus triangular well potential. Further it is interesting to see how the square-plus-triangular well works within the frame work of Random phase approximation (RPA).

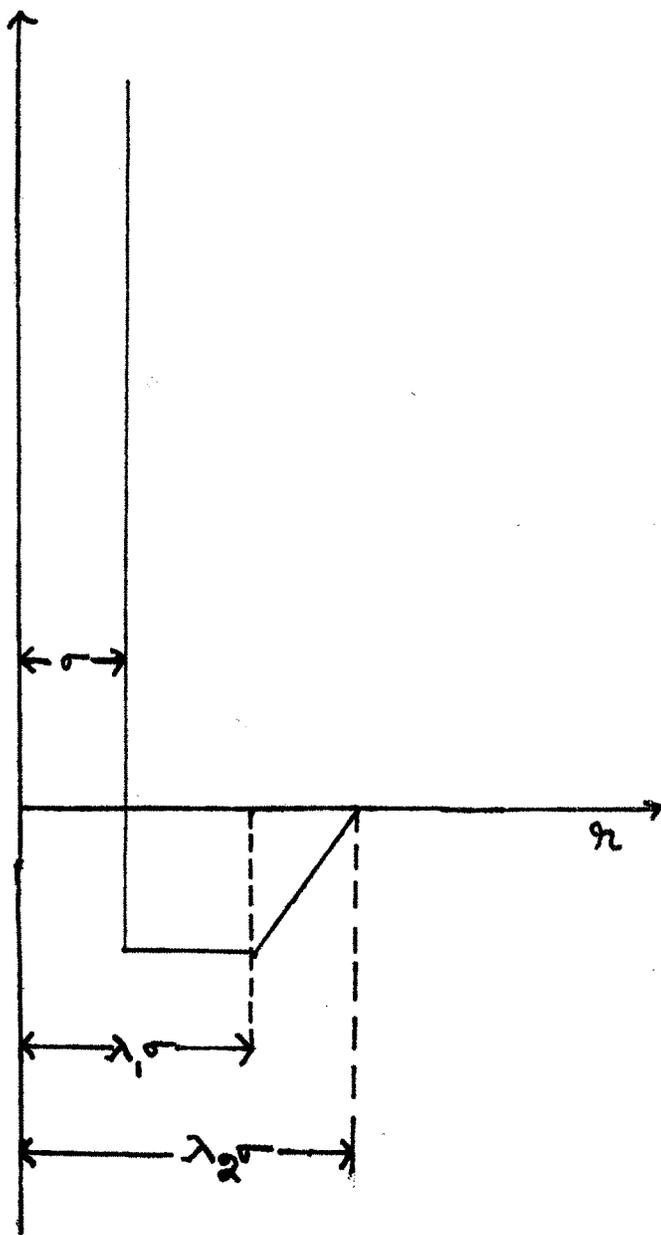
The theory involves a perturbation treatment based on a hard-sphere reference system with the long range interactions treated in the random phase approximation (RPA) for the direct correlation function, $C(r)$ of monodisperse colloidal dispersions. Mean spherical model approximation (MSMA) used in the case of square well, and triangular well potential models.

The RPA consists of writing²⁵²

$$C(r) = C_{hs}(r) - \beta U_p(r) \quad \dots (4.40)$$

A potential function has been proposed as shown in Fig.(4.1) with a hard repulsion and an attractive well which is a combination of the square plus triangular well denoted here after by (STW) is

$u(x)$



SQUARE PLUS TRIANGULAR WELL POTENTIAL

FIG. 41

$$\begin{aligned}
U_p(r) &= \infty & r < d \\
&= -\varepsilon & d < r < \lambda_1 d \\
&= \varepsilon (r - \lambda_2 d) (\lambda_2 d - \lambda_1 d), & \lambda_1 d < r < \lambda_2 d \\
&= 0 & r > \lambda_2 d \quad \dots (4.41)
\end{aligned}$$

ε represented the depth of the STW and the square width is taken as $\lambda_1 d - d$, and the triangular width is as $\lambda_2 d - \lambda_1 d$ where 'd' is the diameter of the particles.

The Fourier transform of the perturbation $U_p(r)$ given by Eq. (4.41) can be performed, and after a little algebra it can be shown that

$$\begin{aligned}
u_{STW}(q) &= \left[\frac{-24 \varepsilon \eta}{(\lambda_2 - \lambda_1) (qd)^4} \right] \left[\lambda_2 qd \sin \lambda_2 qd \right. \\
&\quad + 2 \cos \lambda_2 qd + \left. \left\{ qd (\lambda_1 - \lambda_2) \times \right. \right. \\
&\quad \quad \left. \left. (\lambda_1 qd - 1) - 2 \right\} \times \right. \\
&\quad \left. \cos \lambda_1 qd - q \lambda_1 d \sin \lambda_1 qd - \right. \\
&\quad \left. - qd (\lambda_2 - \lambda_1) (\cos qd + \sin qd) \right] \dots (4.42)
\end{aligned}$$

The Fourier transform of Eq. (4.40) gives

$$C(q) = C_{hs}(q) - \beta \bar{u}_{STW}(q) \quad \dots (4.43)$$

which may be combined with result of Eq. (4.16) and Eqs. (4.42) to produce an explicit result for the direct correlation function for STW.

At thermodynamic limit, the correlation function for the $C_{STW}(q)$ can be written as

$$e^{C_{STW}(0)} = 2\eta\epsilon\beta \left[\lambda_1^3 + \lambda_2^3 + \lambda_1 \lambda_2^x \right. \\ \left. (\lambda_1 + \lambda_2) - 4 \right] \quad \dots (4.44)$$

4.2 Structure and Partial Structure factors

The function, $C(q)$, depends on the volume fraction, η , the hard sphere diameter, d , and the scattering angle q . This is related to the structure factor, $S(q)$, through the usual Ornstein-Zernike relation²⁵³

$$S(q) = 1 / [1 - e C(q)] \quad \dots (4.45)$$

Structure factors of colloidal dispersions are reported in literature^{144,228}. The same has been extended to microemulsions and polymethylmethacrylate (PMMA) latex and results are presented in chapter V.

4.2 a Partial structure Factors:

A binary system is characterised by three partial structure factors, S_{11} , S_{22} and S_{12} .²⁴³ The S_{ij} are related to the pair distribution function $g_{ij}(r)$, which is proportional to the probability that a molecule of species 'i' is at a distance r from one of the species, j as

$$S_{ij}(q) = \delta_{ij} + 4\pi (e_i e_j)^{1/2} \int_0^{\infty} \{g_{ij}(r) - 1\} r^2 j_0(qr) dr \quad \dots (4.46)$$

where $j_0(qr)$ is the spherical Bessel function.

$$j_0(qr) = \sin qr / qr \quad \dots (4.47)$$

The function $g_{ij}(r)$ plays a central role in understanding physical properties of monatomic fluid mixtures. Examples of such properties are configurational thermodynamic functions like internal energy, pressure, isothermal compressibility etc^{68,254}.

In the usual way one can define the radial distribution functions, $g_{ij}(r)$ and the indirect or total correlation functions

$$h_{ij}(r) = g_{ij}(r) - 1 \quad \dots (4.48)$$

and further the direct correlation functions by²⁵⁵,

$$h_{ij}(r) = c_{ij}(r) + \sum_{\lambda=1,2} \rho_{\lambda} \int c_{1\lambda}(|r-r'|) h_{1j}(r') dr \quad \dots (4.49)$$

Eq. (4.49) is the generalised OZ equation and from the well known properties of the Fourier

transform of a convolution, it follows that,

$$h_{ij}(q) = c_{ij}(q) + \sum_{k=1,2} e_k c_{ik}(q) h_{kj}(q) \dots (4.50)$$

For a binary system Eq. (4.50) represents four equations: $i = 1, j = 1,$

$$h_{11}(q) = c_{11}(q) + e_1 c_{11}(q) h_{11}(q) + e_2 c_{12}(q) h_{21}(q) \dots (4.51)$$

$i = 1, j = 2,$

$$h_{12}(q) = c_{12}(q) + e_1 c_{11}(q) h_{12}(q) + e_2 c_{12}(q) h_{22}(q) \dots (4.52)$$

$i = 2, j = 1,$

$$h_{21}(q) = c_{21}(q) + e_1 c_{21}(q) h_{11}(q) + e_2 c_{22}(q) h_{21}(q) \dots (4.53)$$

$i = 2, j = 2,$

$$h_{22}(q) = c_{22}(q) + e_1 c_{21}(q) h_{12}(q) + e_2 c_{22}(q) h_{22}(q) \dots (4.54)$$

Since the PY solution for hard spheres²⁵⁵ requires $C_{12} = C_{21}$ and $h_{12} = h_{21}$, only three of Eqs. 4.51, 4.52 and 4.54 have to be considered. Then Eqs. (4.49) can be solved to give

$$h_{11}(q) = \left\{ c_{11}(q) [1 - e_2 c_{22}(q)] + e_2 c_{12}^2(q) \right\} \times [B(q)]^{-1} \quad \dots (4.55)$$

$$h_{22}(q) = \left\{ c_{22}(q) [1 - e_1 c_{11}(q)] + e_1 c_{12}^2(q) \right\} \times [B(q)]^{-1} \quad \dots (4.56)$$

$$h_{12}(q) = h_{21}(q) = c_{12}(q) [B(q)]^{-1} \quad \dots (4.57)$$

where

$$B(q) = [1 - e_1 c_{11}(q) - e_2 c_{22}(q) + e_1 e_2 c_{11}(q) c_{22}(q) - e_1 e_2 c_{12}^2(q)] \quad \dots (4.58)$$

From Eq. (4.46) it is known that,

$$s_{ij}(k) = \delta_{ij} + (e_i e_j)^{1/2} h_{ij}(q) \quad \dots (4.59)$$

and hence $C_{ij}(q)$ are related to $S_{ij}(q)$ by

$$s_{11}(q) = \left\{ 1 - e_1 c_{11}(q) - e_1 e_2 c_{12}^2(q) / [1 - e_2 c_{22}(q)] \right\}^{-1} \dots (4.60)$$

$$s_{22}(q) = [1 - e_1 c_{11}(q)] s_{11}(q) / [1 - e_2 c_{22}(q)] \dots (4.61)$$

and

$$s_{12}(q) = (e_1 e_2)^{1/2} c_{12}(q) s_{11}(q) / [1 - e_2 c_{22}(q)] \dots (4.62)$$

$C_{11}(q)$, $C_{22}(q)$ and $C_{12}(q)$ can be taken from Eqs. (4.32), (4.33), (4.35) and (4.39) to compute the partial structure factors in the thermodynamic limit.

Recent studies proved the usefulness of square well potential and triangular well

potential^{75,77,113-116} in the theoretical investigations of microemulsions. The same is extended to binary mixture of microemulsion with the same parameters. Further these partials have been used to calculate the reduced scattering for the microemulsions, at thermodynamic limit and results are arranged in Chapter V.