CHAPTER 3

PERTURBATION THEORIES

The most significant advance in the
statistical thermodynamics of liquids in the
last few years has been the rapid development of
perturbation theories of various types. Any
system that is slightly perturbed from some
'reference' system can be treated by these per-
turbation theories, provided the properties of
the 'reference' system are known. The natural
choice of this 'reference' system has been the
sphere system because of its success as a good
reference fluid for many liquids and the availa-
bility of good amount of data from computer ex-
periments. This implies that the structure of
a simple liquid is determined primarily by this
hard-core part of the potential and the main
effect of the remaining part of the potential is
to provide a uniform background potential in
which the molecules move. Though the classic

work of Van der Waals[196] laid the foundation

for this type of treatment in his famous

equation of state, it is only recently that the

full potential of perturbation theory has been

realised.

The modern developments of the perturbation

theory date from the work of Zwanzig[58] and Pople[197].

It is Zwanzig who introduced the concept of treat-

ing the attractive forces in a fluid as perturba-

tions on a hard core potential. It was further

studied by Smith and Alder[198] and by Frisch

et al[199], Mansoori and Canfield[200], Henderson and

Barker[201], Smith[202], Steel[203,204]. In addition,

Henderson and Leonard[205], McDonald[206], Henderson[207],

and Gubbins[208] have reviewed the application of

perturbation theory to the theory of liquid mixtures.

Mcquarrie and Katz[209], Henderson et al[210]

combined this with the technique of Rowlinson[59,60]

for taking into account the fact that the repulsive

part of the potential, though steep, and in this way derived a satisfactory equation of state for high temperatures. In general, all this work suggested that the expansion in inverse powers of temperature provided by perturbation theory was useful only at high temperatures and probably not useful at the temperatures and densities characteristic of the liquid. Recent studies of Barker and Henderson[46] clearly indicate that the perturbation treatment of attractive forces gives good results at low temperatures so that the failure at low temperatures of previous perturbation theories must be due to details of the treatment of repulsive forces or the choice of separation into 'unperturbed' and 'perturbed' potentials. Thus the convergence of the 'perturbation' expansion was examined directly by comparison with quasi experimental machine calculations[211,212].

In perturbation theories one essentially uses a power (or Taylor) series expansion of the

required structure (or thermodynamic property) about the corresponding property of some suitable reference system for which the properties are known[46,52,78,213,214]. So in addition to the potential energy, one also requires the properties of the reference system. This may be the disadvantage of perturbation theory. The advantages of perturbations theories over integral equation methods are (i) Some a priori indication of the range of validity of the expansion may be obtained from the order of magnitude of the terms in the expansion and the similarity of the actual and reference systems, (ii) Non linear equations do not have to be solved, (iii) some physical insight into the nature of property may be obtained. If a perturbation expansion fails to meet the desired degree of accuracy more terms in the expansion may be included or a different reference system may be used.

The Virial expansion and the Lennard-Jones
and Devonshire cell model, for instance, are
essentially perturbation expansions about the
ideal gas state and the perfect crystal state,
respectively[78]. One can therefore see immedi-
ately that the Virial expansion is applicable to
very dilute dispersions and the cell model to
ordered dispersions, but it is certainly not
obvious that either of these should be applica-
ble to concentrated disordered dispersions. By
analogy with dense molecular fluids a system of
hard spheres is the most suitable reference systems
for concentrated colloidal dispersions. This was
illustrated some years ago, by Van Megen and Snook[215]
by comparison of the osmotic pressure and phase
behaviour calculated by the MC method and hard-sphere
perturbation theory. The choice of the hard-sphere
system as a reference is also very convenient since
its properties are quite well known and extensively
documented[78,214].

In view of the increasing amount of experimental data on well-defined model colloids becoming available[95,127,137-147,216] and the widespread use of hard-sphere perturbation theory, a critical assessment of this theory over a sufficient wide range of conditions, such as particle size, potential parameters, to encompass most reasonable experimental conditions is presented in this chapter. Static interactions are only considered and electrostatic interactions are neglected because non-polar solvent[95,111,112] systems are choosen. In addition to osmotic compressibility, particular attention is paid to the computations of the static structure factor. With the more widespread application of small angle neutron, X-ray, and light scattering to colloids[95,111,112,143-147,216], one can conveniently calculate the scattering ratio by using perturbation theories.

The perturbation approach was first applied to simple fluids like argon, Krypton etc[100], and then extended to systems like electrolyte solutions[217], fused salts[218], liquid metals[65,219], polymer solutions[220], macromolecules[216], and colloidal dispersions[95,101-116].

There are several competing hard sphere perturbation theories[46,52,78,213-214] such as variational theory, Barker-Henderson perturbation theory (BH), Weeks-Chandler-Anderson (WCA) theory, optimised Cluster theory (OCT), variational solution of OCT and Integral equation perturbation theory. Each of them may be taken to different levels of approximation.

The two perturbation theories that are most successfully and widely used are those proposed by Barker and Henderson (BH)[78] and Weeks, Chandler and Anderson (WCA)[52]. These differ essentially in the manner in which they

divide the pair potential into reference and perturbation components.

3.1 THEORY :

An operational outline and the main physical ideas underlying the theory required for the application to colloidal dispersions of spherical particles are presented in this section. Hard sphere perturbation theory rests on the realization that the structure of a dense fluid, or a concentrated dispersion, is primarily determined by the hard core or steeply repulsive part of the pair potential. The remaining longer ranged attractive component merely provides a background potential which produces only a small correction to the structure due to the hard core.

In all perturbation theories[202] one
divides the total potential energy $u(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$
of a system of N particles to a reference
part $u_0(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$ and a perturbation
part $u_1(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$, i.e.

$$u(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) = u_0(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) + D\, u_p(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$$

$$\ldots (3.1)$$

The parameter D characterizes the strength
of the perturbation and is eventually set equal
to unity. The configurational partition
function Z_N can be written as

$$Z_N = Z_{N,o} \int \cdots \int \frac{\exp(-\beta u_0)}{Z_{N,o}} \exp(-\beta u_p)\, d\vec{r}_1 \ldots d\vec{r}_N$$

$$= Z_{N,o} \int \cdots \int P_{N,o} \exp(-\beta u_p)\, d\vec{r}_1 \ldots d\vec{r}_N \qquad \ldots (3.2)$$

where

$$Z_{N,o} = \int \cdots \int \exp(-\beta u_0)\, d\vec{r}_1 \ldots d\vec{r}_N$$

is the configurational partition function for
the reference system of N particles and

$$P_{N,0} = \exp(-\beta u_0)/Z_{N,0} \qquad \ldots (3.3)$$

is the probability of finding N particle con-
figuration of potential energy u_0 in this
reference system. Thus eq.(3.1) becomes

$$Z_N = Z_{N,0} \langle \exp(-\beta u_p) \rangle_0 \qquad \ldots (3.4)$$

where $\langle \ \rangle_0$ represents ensemble average over the
reference system. Expanding the Helmoltz free
energy in powers of $\beta \{= K_B T)^{-1}\}$ one get

$$\frac{A - A_0}{K_B T} = \sum_{i=1}^{\infty} A_i (\beta \varepsilon)^i =$$

$$= \beta \langle u_p \rangle_0 - \frac{\beta^2}{2} \left[\langle u_p^2 \rangle_0 - \langle u_p \rangle_0^2 \right] + O(\beta)^3$$

$$\ldots (3.5)$$

Here A_o is the free energy of the reference system. This result was originally obtained by Zwanzig[58] for pairwise additive interactions.

$$u = u_o + u_p$$

$$= \sum_{i<j} u_o (r_{ij}) + \sum_{i<j} u_p (r_{ij}) \quad .. \quad (3.6)$$

and

$$\langle u_p \rangle_o = \frac{\rho}{2} \int \vec{dr} \; g_o(r) \; u_1(r) \quad ..(3.7)$$

This result was obtained by Zwanzig by assuming the reference system to be a system of hard spheres

$$u_o(r) = \begin{cases} \infty & r < d \\ 0 & r > d \end{cases} \quad ... \quad (3.8)$$

But no satisfactory criterion was provided for determining the hard sphere diameter, d. The higher order terms in eq. (3.5) involve higher order (three body, four body etc.) correlation

functions and since information about these
is too meagre, the utility of perturbation
theory where higher order terms are needed
is limited. Further the problem is compli-
cated by the need to evaluate these terms in the
grand canonical ensemble to obtain results
valid in the thermodynamic limit

$$(N \rightarrow \infty, \; N/V = \text{Fixed}).$$

3.2 WEEKS-CHANDLER-ANDERSON (WCA) THEORY:

Weeks-Chandler-Anderson (WCA)[52,53,221] and
independently Gubbins et al[222] have proposed
the choice

$$u_o(r) \;\; = \;\; u(r) + \varepsilon \quad r < r_m \qquad \ldots (3.9)$$

$$= 0 \qquad r > r_m$$

$$u_p(r) \;\; = \; -\varepsilon \qquad r < r_m \quad \ldots (3.10)$$

$$= u(r) \qquad r > r_m$$

where r_m is the value of r for which u(r) is
a minimum and $u(r_m) = -\varepsilon$

ε is the depth of the potential at the
minimum r_m Eqs. (3.9) and (3.10) divide u(r)
into purely repulsive and purely attractive
regions. A_o and $g_o(r)$ of the reference fluid
is obtained by an expansion of exp $[-\beta u_o(r)]$
about that of the hard sphere system[223]. Defining

$$\exp\left[-\beta u(r)\right] = \exp\left[-\beta u_{HS}(r)\right] + \alpha\left\{\exp\left[-\beta u_o(r)\right]\right.$$

$$\left. - \exp\left[-\beta u_{HS}(r)\right]\right\} \qquad \ldots(3.11)$$

where α is an expansion parameter $(0 \leq \alpha \leq 1)$
which takes the hard sphere system into the system
with potential $u_o(r)$ and $u_{HS}(r)$ is the hard sphere
potential of diameter d. Insertion of Eq. (3.11)
into the configurational partition function for
the system and expanding about $\alpha = 0$ gives

$$A_o = A_{HS} - 2\pi N \rho \alpha \int \left\{\exp\left[-\beta u_o(r)\right] - \exp\left[-\beta u_{HS}(r)\right]\right\}$$

$$y_{HS}(r) \ \overrightarrow{dr} \ + \ 0 \ (\alpha^2) \qquad \ldots(3.12)$$

where

$$Y_{HS}(r) = \exp\left[\beta u_{HS}(r)\right] g_{HS}(r)$$

$$\ldots(3.13)$$

The hard sphere diameter d is determined by annulling the first order term, i.e. d is determined by the condition

$$\int_{0}^{r_m} d\vec{r} \left\{\exp\left[-\beta u_o(r)\right] - \exp\left[-\beta u_{HS}(r)\right]\right\} Y_{HS}(r) = 0$$

$$\ldots(3.14)$$

The hard sphere diameter thus obtained is temperature and density dependent

In addition, the other essential feature of this approach is to set.

$$g(r) = g_o(r) = \exp\left[-\beta u_o(r)\right] Y_{HS}(r) \qquad \ldots(3.15)$$

This approximation is called the high temperature approximation (HTA) since at high temperatures the repulsive part of the potential dominates the structure. The Helmholtz free energy is computed from the equation.

$$A = A_{HS} + 2\pi N \rho \int \exp\left\{-\beta u_0(r)\right\} Y_{HS}(r)_{u_1}(r) \; r^2 dr$$

$$\dots (3.16)$$

Computer experiments by Verlet and Weis[45] have shown that the convergence of eq.(3.16) is excellent at liquid densities. Eq.(3.16) is essentially a first order theory whereas the BH expansion must be taken to second order to yield comparable results.

3.3 Barker-Henderson Perturbation Theory:

Barker and Henderson[46,47] (BH) have developed a perturbation theory for potentials with a soft core by dividing the potentials such that

$$u_0(r) = u(r) \qquad r < d$$
$$= 0 \qquad r > d$$

and

$$u_p(r) = 0 \qquad r < d$$
$$= u(r) \qquad r > d \quad \dots (3.17)$$

where d is the value of r for which u(r) is equal to zero. The free energy is given by

$$A = A_{HS} + 2\pi N\rho \int g_{HS}(r) \; u(r) \; r^2 dr + \text{higher}$$

order term $\qquad \qquad \dots \quad (3.18)$

provided the hard sphere diameter is chosen such that

$$d = \int_0^\infty \{1 - \exp\left[-\beta u_o(r)\right]\} \; dr \quad \dots (3.19)$$

In Eq.(3.18) A_{HS} and $g_{HS}(r)$ are the free energy and radial distribution function for a system of hard spheres of diameter, d. The hard sphere diameter obtained using Eq.(3.19) is temperature dependent but independent of density. The radial distribution function can be obtained from BH theory using the expansion

$$g(r) = g_{HS}(r) \; + \sum_i (\beta\epsilon)^i \; g_i(r) \quad \dots (3.20)$$

The computation of the first order term $g_1(r)$ involves the computation of A_2 in Eq.(3.5) for the Helmotz free energy. It is essential to include $g_1(r)$ in order to get good agreement with simulation results.

From the above one can immediately see some
of the technical drawbacks and virtues of the two
different approaches. First, for pair potentials
with a minimum, the BH hard-sphere diameter is
obtained from a straight-forward integration and
is independent of e. The WCA hard-sphere diameter
needs to be obtained theoretically from eq. (3.14).

The typical structure factors, $S(q)$ of mono-
atomic liquid and of colloidal dispersion, with a
variation of wave vectors are shown in Fig. No.
(3.1). Peaks are observed in both the figures.
The $S(q)$ values are oscillating around 'unity'.
The curve maxima indicating the existance of local
ordering in the dispersion. This may be due to
particle-particle interactions of consisting of
both repulsion and attraction forces. By observing
this close analogy between the $S(q)$ of liquid and
colloidal dispersions, interest led to apply the
liquid state theories to concentrated particle
dispersion.
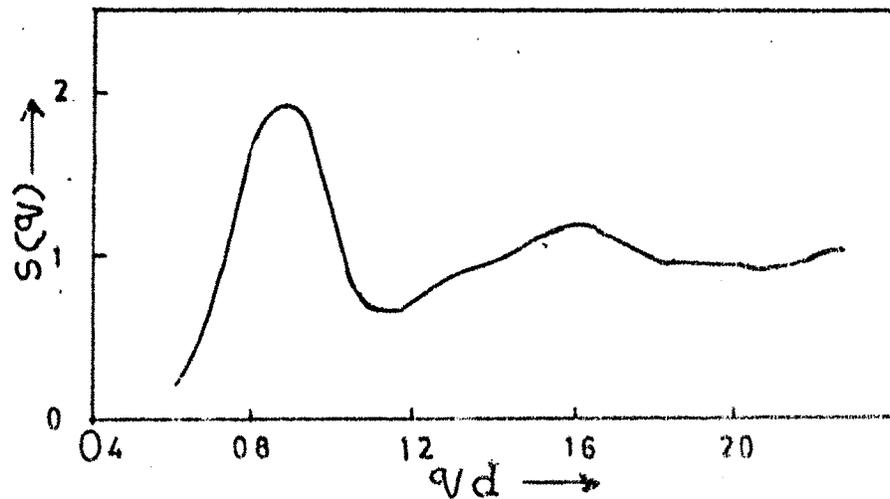
(a) TYPICAL STRUCTUREFACTOR OF COLLOIDAL DISPERSION.
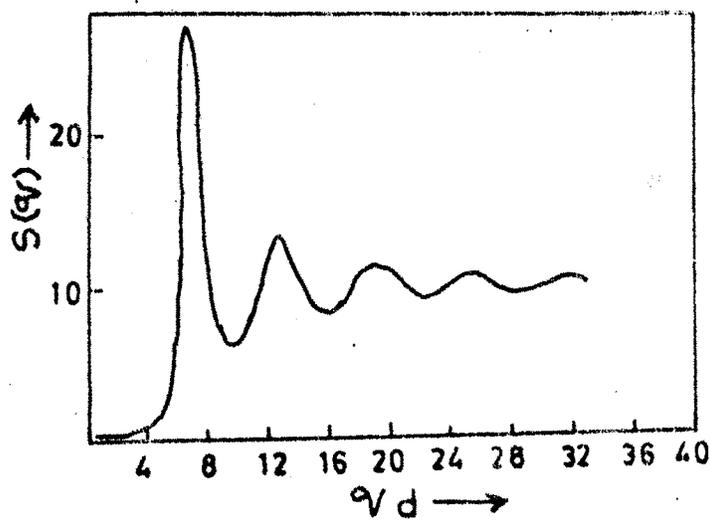
(b) TYPICAL STRUCTURE FACTOR OF SIMPLE LIQUID

FIG. 3.1

In this thesis, Barker-Henderson first order perturbation theory has been used extensively to discuss structure of colloidal dispersions. Square (SW) and triangular (TW) and Square-plus triangular (STW) attractive tails have been taken as perturbations over the Percus-Yevick hard sphere model under the mean-spherical approximation (MSM) and randum phase approximation (PRA) The results are presented in Chapter IV.