

PREFACE

This thesis is concerned with the application of hard sphere perturbation theories to concentrated colloidal dispersions interacting with additive pair-wise potentials.

The thesis is divided into five chapters.

Chapter I deals with critical survey of the literature. The main aim of the thesis is explained in this chapter.

The recent theoretical developments in colloidal dispersions and application of liquid state theories to interpret the light scattering data to arrive at the structural information for concentrated dispersions are discussed in Chapter II. Chapter II also includes light scattering equations in terms

of direct correlation functions and Baxter functions for monodisperse and polydisperse systems and the scattering ratio (or Rayleigh ratio) which is related to the structure and shape of the colloidal particles.

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. Modern theories of fluids established that in dense liquids, the spatial structure, represented by the radial distribution function $g(r)$, is mainly determined by hard sphere repulsions between the particles in close proximity and the effect of the weaker, less steep attractive or repulsive tails may be treated as perturbations over a hard sphere reference fluid. It was found that the light

scattering intensity variation with the angle of observation showed characteristic maxima which point to strong interparticle interferences caused by a short-range ordering of the scattering particles. This phenomenon is analogous to the behaviour of simple atoms in the liquid state. This similarity takes it convenient to treat the structure and interaction in concentrated colloidal dispersions the same was as in simple liquids. Chapter III relates to the discussions on the use of modern theories of fluids, especially perturbation theories to concentrated colloidal dispersions.

Chapter IV deals with structural aspects of colloidal dispersions and describes the application of the Percus-Yevick (PY), Mean Spherical Model Approximation (MSMA) and

Random Phase Approximation (RPA) for the Square Well (SW), Triangular Well (TW) and Square-Plus-Triangular well (STW) colloidal dispersions. SW, TW and STW potentials are used as perturbation potentials over the hard sphere potential. In particular, the structure factors $S(q)$ are derived by using first order Barker-Henderson (BH) perturbation theories and the same are extended to derive partial structure factors for a binary mixture. Scattering ratios (or Rayleigh ratio) are calculated at the thermodynamic limit for monodisperse systems and they are compared with the experimental data. Good agreement is obtained between theory and experiment. In the same thermodynamic limit, Rayleigh ratio and partial structure factors for polydisperse systems are also calculated. Structure factors of monodisperse systems are computed.

The results lead to the conclusion that the Rayleigh ratios for microemulsions which have been calculated using the square well, triangular well and Square-plus-triangular well as perturbations over the Percus-Yevick hard sphere model within the mean approximation (MSMA) and Random phase approximation (RPA), are in better agreement with experiment than are those from the semi-empirical Van der Waals type attractive tail. The relation between SW, TW, STW and Van der Waals potential parameters for microemulsions is also discussed.

The same potential parameters are used to compute the structure factors $S(q)$ at various wavevectors. The good agreement between the present theoretical results and

the experimental data conclusively proves that the static and dynamic structural properties of concentrated dispersions can be inferred by using modern liquid state theories. The conclusions are presented in the final chapter.