Equilibrium Structure and Properties of Model Colloidal Suspensions

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Abstract

We report the numerical results on the structure and properties of model colloidal suspensions using the hypernetted-chain (HNC) integral equation due to Allnatt, which has been successfully, applied to asymmetrical electrolyte solutions. We use the primitive model and view our system as highly asymmetrical electrolyte; the colloidal spheres are much larger and more highly charged than the simple ions. The variation of static correlation functions, structure factors and properties, (e.g. excess energies, osmotic coefficients etc.), is reported as a function of size, charge and concentration of colloidal particle. The peak position and the peak height of correlation functions show systematic trends as the asymmetry (in size, charge) increases. The effective one-component potential of the colloid (V_{eff}), calculated by mapping the multicomponent system to an effective one-component colloidal system, is purely repulsive in line with the DLVO potential (with substantial deviations) in most of the cases. However, in some cases (with high asymmetry in charge and size, and at high colloidal concentration), V_{eff} becomes negative.

Keywords: Integral equation theory, ionic solution, Allnatt equation, hypernetted chain, effective potential.

Introduction

Colloidal suspensions are abundant in everyday experience and are used in countless industrial applications in the chemical, pharmaceutical and food industries. The presence of solute components makes it possible to modify at will and on a large scale the static and dynamic macroscopic properties of the whole solution[1]. Different types of colloidal interactions, such as long-range repulsive, short-range attractive, hard-sphere-like and dipolar, can be realized simply by changing the system parameters (e.g. quality of solvent, salt concentration etc.) making them excellent model systems to study a variety of phenomena (such as melting, freezing and glass transitions, etc.) in soft-condensed matter physics[2]. Colloidal suspensions of charged macroparticles dissolved in an electrolyte solution received a long time scientific interests. Experimental techniques [3-6], e.g. light, x-ray or neutron scattering view the colloidal suspensions at length scales where only the colloids (macroparticles) are visible and the rest plays the role of a background. The experimental profiles have to be then interpreted by means of an effective interaction between the colloids, which indirectly includes all the effects of the remaining constituents[7]. This situation has also been reflected in the corresponding theoretical research. Due to the large asymmetry in size, mass, and charge between the mesoscopic polyions (or macroions) and the microscopic coions and counterions, the colloidal suspension is viewed not as a mixture but as a monodisperse system formally equivalent to a simple liquid, the colloid playing the role of atoms[8]. The key ingredient in this effective one-component picture is the determination of the effective interaction potential or force between colloids which implicitly accounts for the effects of the remaining constituents. One such example is the famous Derjaguin-Landau-Verwey-

Overbeek (DLVO) potential[9]. Several attempts have also been made to treat macroions and microscopic ions in the primitive model on an equal footing, using the multicomponent versions of the integral equations[10-18] for the pair structure familiar from the theory of liquids, or resorting to computer simulations[19]. The integral equation theories have a special place in the study of macroionic fluids, because the techniques of computer simulation suffers from technical difficulties associated with very different size (and/or charge) of the solution components. Although the necessary numerical calculations are easy for simple ionic systems, they become much more difficult as the size of the hard cores and the charge asymmetry are increased[14-18]. Allnatt integral equation[20] is known to be very successful for dealing with ionic solutions and has been successfully used to study asymmetric macroionic solutions[21, 22]. In this report, we will present the numerical calculation of correlation functions of macroionic solutions in presence of counterion using Allnatt equation. The variation of these correlations as well as some thermodynamic properties with macroion size, charge and concentration will also be discussed.

Material and Methods

We use the primitive model[7] to study a two component system consisting of negatively charged spherical colloid (m) and equivalent amount of small univalent positive ion (+) in a continuum solvent, interacting by the pair potential

$$\beta u_{ij}(r) = \beta u_{ij}^s(r) + Z_i Z_j L_B / r \quad \text{with} \quad \beta u_{ij}^s(r) = \begin{cases} \infty, \text{ if } r < \sigma_{ij} \\ 0, \text{ otherwise} \end{cases}$$

$$\beta = 1/kT, \ L_B = \beta e^2 / 4\pi\varepsilon_0\varepsilon_r, \ \sigma_{ij} = (\sigma_i + \sigma_j)/2,$$

where σ is particle diameter; ε_0 and ε_r are relative and vacuum dielectric constants, respectively. We solve the Allnatt equation[20] as given by Rasaiah and Friedman[21]

$$\hat{\tau} = \hat{X}\rho\hat{h} + \hat{q}\rho\hat{X} + \hat{q}\rho\hat{X}\rho\hat{h},$$

along with the hypernetted chain (HNC) closure,

$$h_{ij}(r) = \exp\{-\beta u_{ij}^s(r) + \tau_{ij}(r) + q_{ij}(r)\} - 1$$

The *hat* in Allnatt equation indicates the Fourier sine transformation, ρ is the number density, $h_{ij}(r)$ [$= g_{ij}(r) - 1$] and $c_{ij}(r)$ are respectively the total and the direct correlation functions, $q_{ij}(r) = Z_i Z_j L_B \ exp \ \{-\kappa r\}/r$, where κ is the Debye screening length.

The two component system described above can be mapped to an effective one-component macroion system (consisting of only the colloid) described by[16]

$$\hat{h}_{mm}(k) = \hat{c}_{mm}^{eff}(k) + \rho_m \hat{c}_{mm}^{eff}(k)\hat{h}_{mm}(k)$$

with the pair potential of the effective one-component $V_{eff}(r)$ given by

$$h_{mm}(r) = \exp\{-\beta V_{eff}(r) + h_{mm}(r) + c_{mm}^{eff}(r)\} - 1, \ where \ \ c_{mm}^{eff}(r)$$

is the so called effective direct correlation function which takes care of the effects of the small ions. Thus $V_{eff}(r)$ is that pair potential which when used in the HNC calculation in a one-component model gives the $g_{mm}(r)$ calculated in the multicomponent model at a given macroion radius, charge and concentration. The $V_{eff}(r)$ obtained in this report mostly obeys the form of DLVO equation,

$$\beta V_{DLVO}(r) = Ae^{-\kappa r}, \ A = Z^2 L_B e^{\kappa\sigma} \ /(1 + \kappa\sigma/2)^2$$

(noticeable differences at high charge, concentration and particle radius) but the DLVO parameters (A^* and κ^*) differ from that of the classical theory (A and κ). However, at high concentration, charge and size, the form of purely repulsive DLVO potential no longer holds: we obtained an attractive region in the function $V_{eff}(r)$. The colloidal structure factor $S_{mm}(k)$ is calculated from the Fourier transform of $h_{mm}(r)$ by $S_{mm}(k) = 1 + \rho_m \hat{h}_{mm}(k)$. The thermodynamic properties, e.g. excess internal energies, osmotic coefficients and isothermal compressibilities are obtained from the total correlation functions $h_{ij}(r)$ using standard formula[21].

Following earlier authors[21, 22], we use the iterative method for solving the Allnatt equation, where all the functions are evaluated within a range (0, r_{max}). All the functions are assumed to be zero beyond this range. The range is then divided into N [$= r_{max} /\Delta r$] intervals of equal size Δr, and all the functions evaluated at each grid point. The periodic nature of sine and cosine functions is utilized by imposing the condition $\Delta r. \Delta k = \pi/N$, where Δk is the grid size in the Fourier space. We use $N = 2048$, $\Delta r = \sigma_{mm}/40$. The iteration was assumed to be conversed, if the difference in the sum of squares of $\tau_{ij}(r)$ between two successive iterations becomes smaller than 1.0×10^{-8}.

Results and Discussion

The following abbreviations are used: R_m, Z_m, and C_m for macroionic (colloid) radius, charge and concentration, respectively. Similarly, $g_{mm}(r)$ (mm for macroion-macroion), $g_{m+}(r)$ (m+ for macroion-counterion). We take R_m (in nm) = 16, 20, 25, 35, 45 and 50, Z_m (in e) = 25, 50, 75, 80, 90 and 100, C_m (in μM) = 0.1, 0.5, 1.0, 5.0. We use the following common parameters for all the systems: radius of monovalent ion = 0.15 nm, temperature = 298.15 K so that the Bjerrum length L_B = 0.715 nm. We now describe the variation of correlation functions and properties with macroionic charge, size and concentration.

Variation with the macroion size: The radius of the colloidal particle is varied from 20 to 50 nm at fixed colloid charge of $100e$ and concentration $1\mu M$. The macroion-macroion pair correlations ($g_{mm}(r)$) are plotted as a function of particle radii in figure 1. It is clear from this figure that as the macroionic radius increases, the height of the first peak of $g_{mm}(r)$ steadily increases (1.54 for R_m = 20 nm to 2.36 for R_m = 50 nm)) and the peak positions steadily decreases in r (r/σ = 2.93 to 1.21 for R_m = 20 to 50 nm). The peaks are moving closure to the macroionic surface as we increase the size. Thus, the macroions with bigger size have lesser effective repulsion than the smaller size macroion, and thus the probability of two macroions coming closure (the peak height) increases. The increasing peaks height in the macroion-macroion structure factor (figure 2) with increasing size of colloidal particle is also in consistent with this feature. The contact values of macroion-counterion correlation functions (figure 1, insert) decreases as the size of macroion increases, indicating that the accumulation of counterions near the surface decreases. The accumulation of counterion at the surface of macroion depends on the surface area of the macroion and the probability of finding a counterion at the surface of macroion. It appears that with increasing radius, the second factor decreases in a greater magnitude than the increase of surface area. The effective macroion-macroion potential ($V_{eff}(r)$), shown in figure 3 support this fact. As the size of the macroion increases, the magnitude of $V_{eff}(r)$ decreases and finally becomes negative for R_m = 45 and 50 nm. Thus, the effective interaction between the macroions becomes less and less repulsive as the size increases and finally it becomes attractive. This type of observation in infinitely dilute macroionic solution was obtained recently[23].

Variation of macroion charge: We study the effect of increasing macroion charge at a fixed R_m = 16 nm and C_m = 1.0 μM. The plots showing variations of correlation functions and structure factors are displayed in figures 4-6. The correlation functions obtained for Z_m=25e reproduces as reasonably well, the preliminary results of our molecular dynamic simulation[24]. The variation of $g_{mm}(r)$ and $S_{mm}(k)$ [figure 4 and 5]are very much similar to that of size variation, i.e. The peak heights increases and the peak positions slightly decrease as Z_m increases. However, with the increase of Z_m, the magnitude of

$g_{m+}(r)$ decreases [figure 4, insert] and the magnitude of $V_{eff}(r)$ [Figure 6] first increases (from $Z_m = 25e$ to $75e$) and then decreases and become negative for $Z_m = 90e$ in some portion. Thus, the effective macroion-macroion interactions increases with charge, reaches a maximum and then become less repulsive and eventually becomes attractive (for certain inter-nuclear distances). This may be due to the fact that as Z_m increases, the repulsion between macroion pair increases (which tends to increases $V_{eff}(r)$) and at the same time the condensation of counterions also increases (which tends to decrease $V_{eff}(r)$), and the later dominates at high Z_m.

Variation of macroion concentration: The effect of variation of macroion concentration on correlation function are studied at $Z_m=100e$ and $R_m=20$nm.

The macro ion-macro ion correlation function shown in figure 7 displays an increase in peak height and the peak height is shifted towards smaller distances as the concentration of macro ions in solution increases. This is clearly a consequence of increase in the repulsive interaction between the equally charged macro ions, and has been observed in several previous studies[25-27].

The macroion–counterion correlation function in figure 7, insert display a pronounced decrease of $g_{m+}(r)$ with increasing concentration. In Figure 8 the structure factor is displayed. It shows that with increasing concentration of colloidal particle the peak height increases and the peak position shifts towards

higher inter-particle distance. It also shows secondary peaks. The effective potential V_{eff} is shown in figure 9. It explains that as the concentration of colloidal suspension is increased the potential decreases. The effective potential is negative for colloidal suspensions with the concentrations of 0.5µM, 1µM, 5µM. This shows a shift towards lower inter-particle distance as the concentration increases.

Variation in properties: The variation of properties excess free energy (-Uex), osmotic coefficient (oc), isothermal compressibility (compc) and the ratios showing deviations from DLVO potential (A*/A and κ/κ*) as a function of colloid size, charge and concentration is plotted in figure 10. The excess free energy (-Uex) decreases when size is increased while it increases when charge as well as concentration of macroion is increased. The trends in variation of osmotic coefficients (oc) are just opposite to that of –Uex. The compressibility (compc) monotonically increases as the charge of macroion increases. However, the variation is not monotonic with size and concentration. It first decreases with size and then starts increasing, while with increase in concentration of macroion it first increases and then decreases. The ratio (κ/κ*) is almost one for all the cases indicating that the exponent of our V_{eff} (r) is same as that of DLVO potential. However, we obtained substantial deviation in prefactors (A*/A deviating from one). We get maximum deviation (of A*/A) in case of size variation and least variation in case of charge.
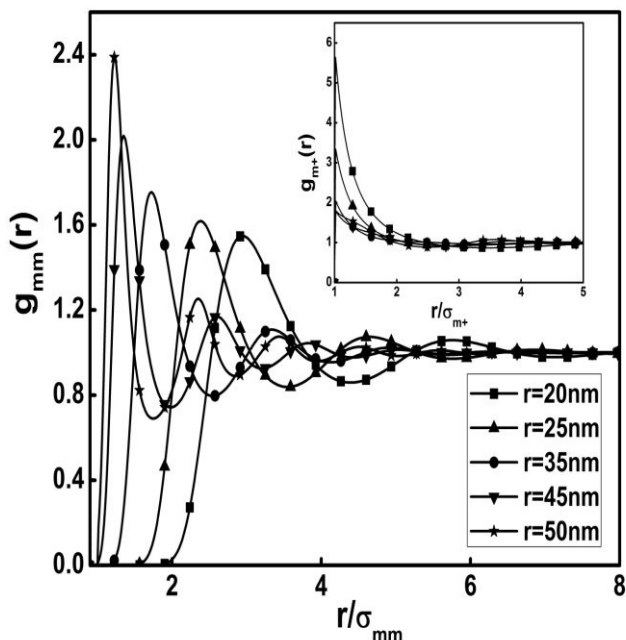

Figure-1
Variation of $g_{mm}(r)$ and $g_{m+}(r)$ with the size of macroion at fixed charge ($Z_m=100e$) and fixed concentration ($C_m=1.0$µM)
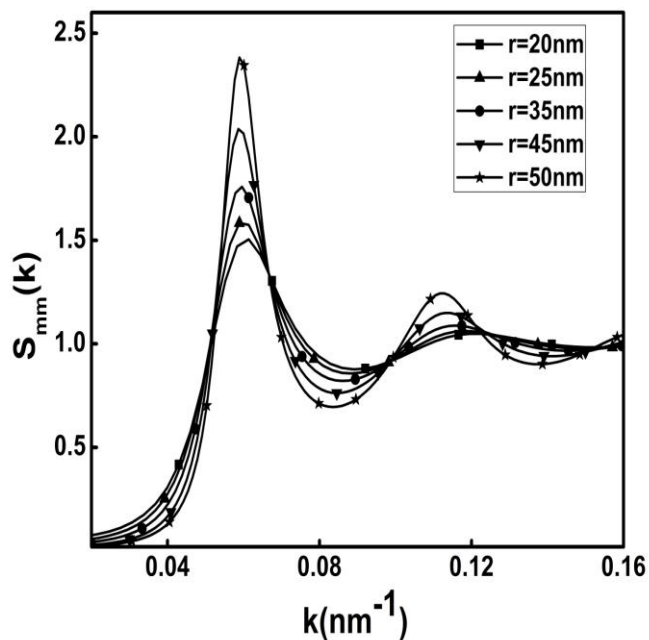

Figure-2
Variation of $S_{mm}(k)$ with the size of macroion having fixed parameters as figure 1

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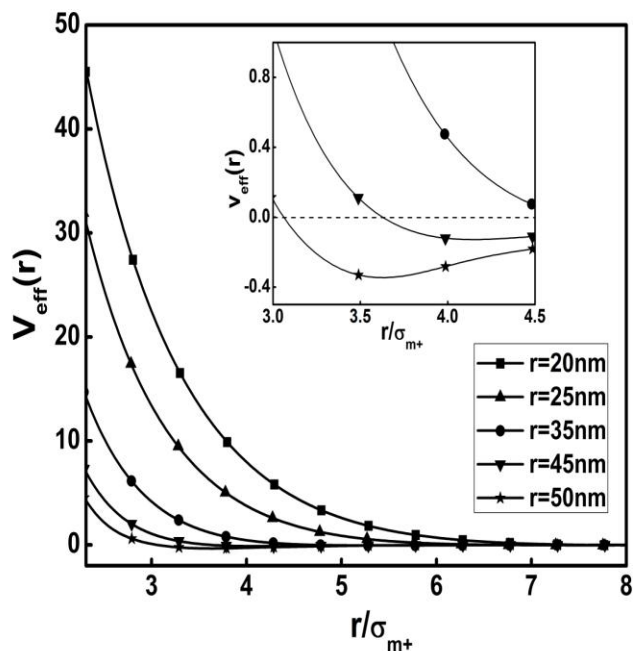Vol. **2(ISC-2012),** 61-66 **(2013)** *Res. J. Recent. Sci.*

Figure-3
Variation of $V_{eff}(r)$ with the size of macroion having fixed parameters as figure 1
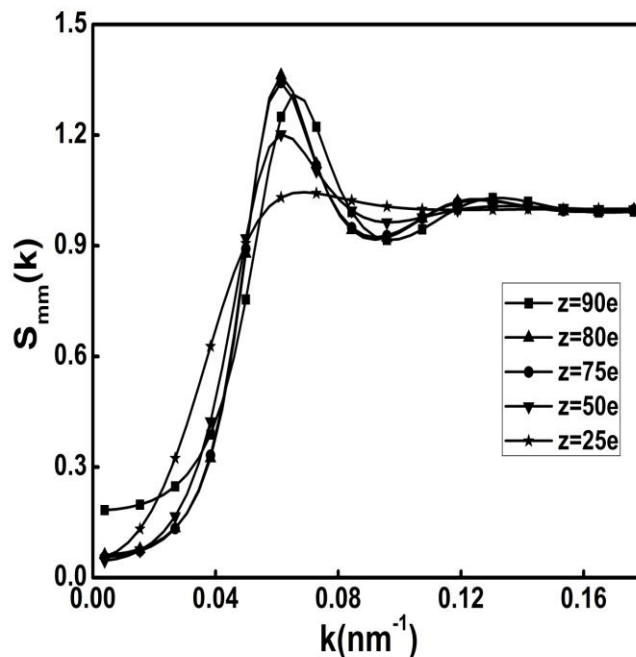

Figure-5
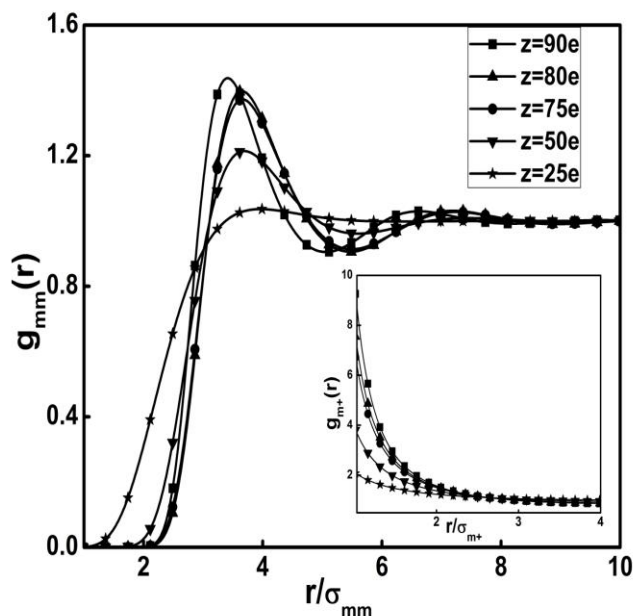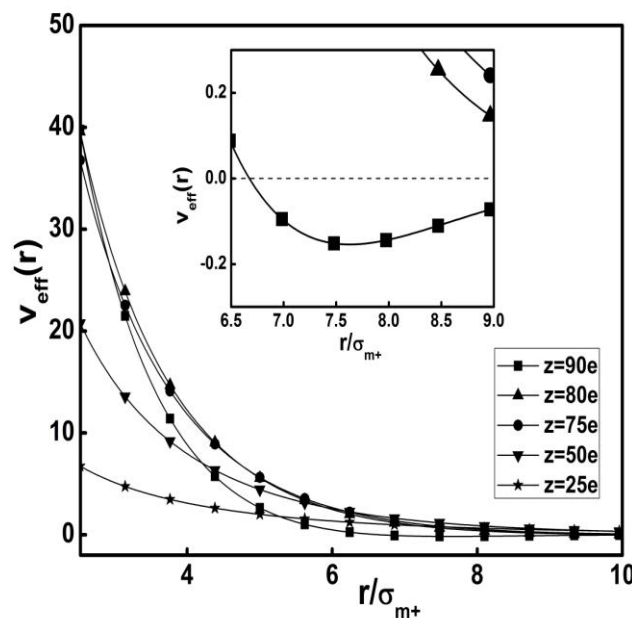**Variation of $S_{mm}(k)$ with the charge of macroion having fixed parameters as figure 4**

Figure-4
Variation of $g_{mm}(r)$ and $g_{m+}(r)$ with the charge of macroion at fixed size (R_m=16nm) and fixed concentration at (C_m=1.0μM)

Figure-6
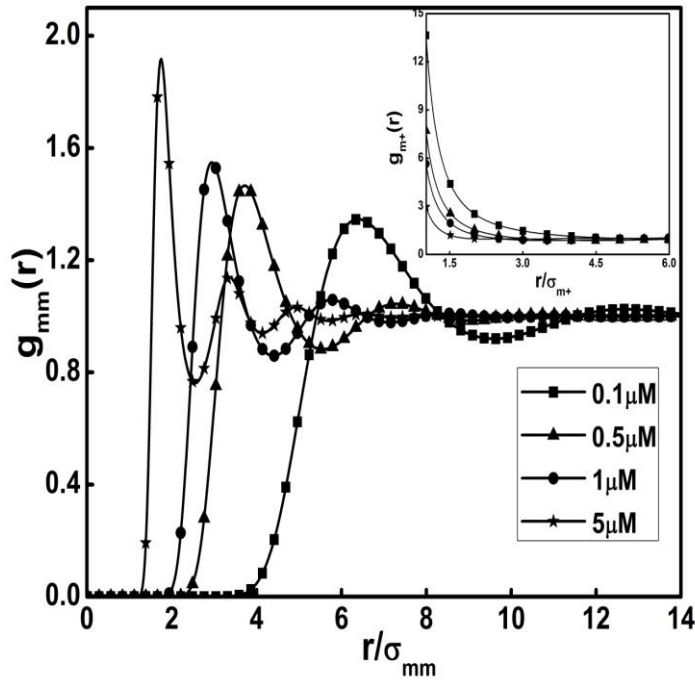**Variation of $V_{eff}(r)$ with the charge of macroion having fixed parameters as figure 4**

Figure-7
Variation of $g_{mm}(r)$ and $g_{m+}(r)$ with the concentration of macroion at fixed size (R_m=16nm) and fixed charge (Z_m=100e)

Figure-9
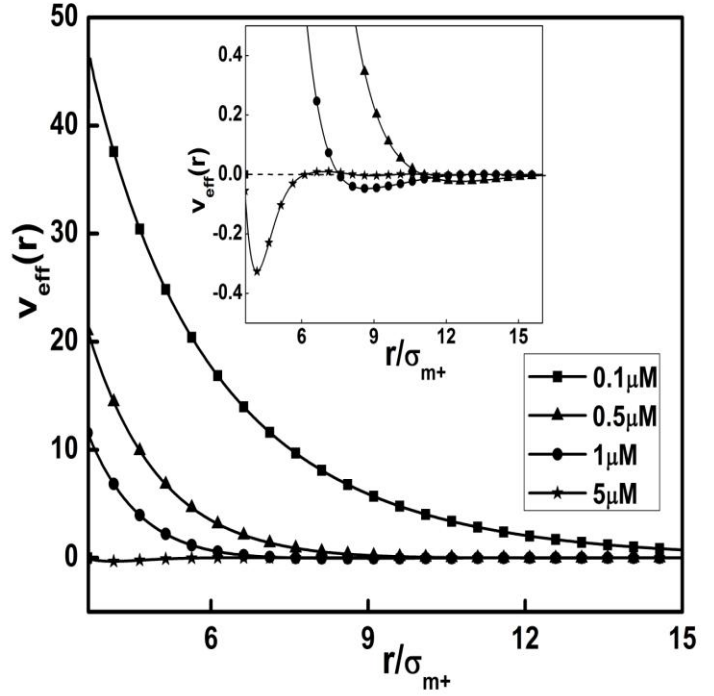**Variation of $V_{eff}(r)$ with the concentration of macroion having fixed parameters as figure 7**
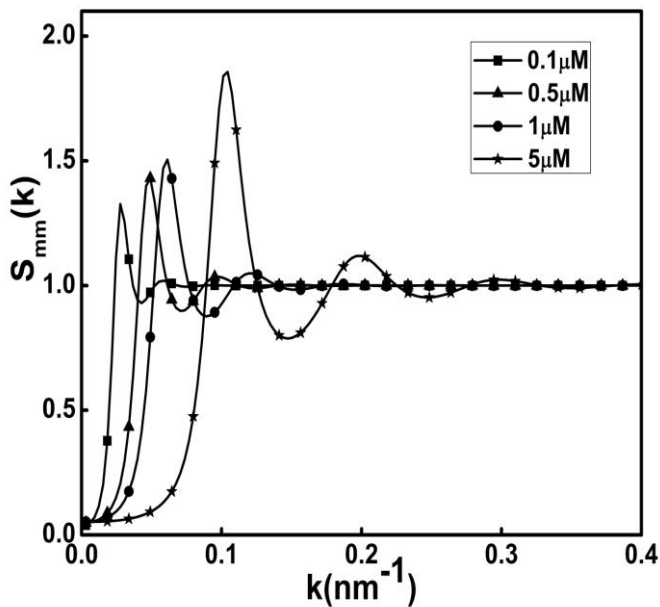

Figure-8
Variation of $S_{mm}(k)$ with the concentration of macroion having fixed parameters as figure 7

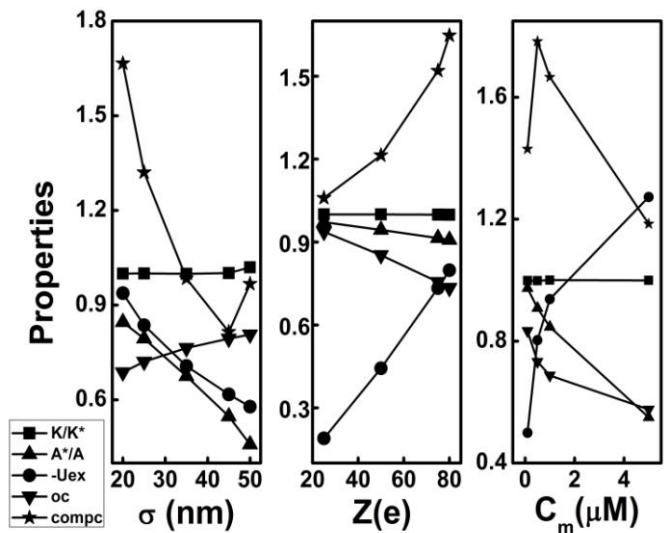**Figure-10**
Plots of different thermodynamic properties (K/K* and A*/A (DLVO parameters), -Uex: Excess internal energy, oc: osmotic coefficient, compc: isothermal compressibility) with varying the size, charge and concentration of colloidal suspension

Conclusion

The structure of a solution of model charged colloid is studied using Allnatt equation. We find systematic variation in pair correlation functions and structure factors as the size, charge and concentration of colloid is varied. The colloid-colloid interactions, calculated from effective one-component model are mostly repulsive like DLVO potential (with substantial deviation) but it turns to attractive one at high charge, size and concentration of colloid.

Acknowledgement

References

1. Russel W.B., Condensed-matter physics: Tunable Colloidal Crystals, *Nature* **421**, 490-491 **(2003)**

2. Lowen H., Colloidal soft matter under external control, *J. Phys.:Condens. Matter* **13,** R415-R432 **(2001)**

3. *Brown J.C., Pusey P.N, Goodwin J.W., and Ottewill R.H., Light scattering study of dynamic and time-averaged correlations in dispersions of charged particles* J. Phys., A *8, 664 (1975)*

4. *Ottewill R.H. and Richardson R.A., Studies of particle-particle interactions using polystyrene lattices and time average light scattering,* Colloid Polym. Sci.*, 260, 708 (1982)*

5. *Cebula D.H., Goodwin J.W., Jeffery G.C., Ottewill R.H., Parentich A. and Richaardson R.A., Properties of concentrated polystyrene latex dispersions,* Faraday Discuss.Chem. Soc.*, 76, 37 (1983)*

6. Hartl W., Versrnold H., Wittig U. and Marohn V., Liquid like structure of charged colloidal dispersions in the presence of screening ions, *Mol. Phys.* **50**, 815 **(1983)**

7. Belloni L., Colloidal Interactions, *J. Phys.: Condens. Matter,* **12**, R549-R587 **(2000)**

8. Likos C.N., Effective interactions in soft condensed matter in physics, *Phys. Rep.,* **348**, 267-439 **(2001)**

9. Verwey E.J.W. and Overbeek J.T.G., *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, **(1948)**

10. Rasaiah J.C., Computations for higher valence electrolytes in the restricted primitive model, *J. Chem. Phys.*, **56**, 3071(**1972**)

11. Springer J. F., Pokrant M. A., and Stevens F. A., Jr., Integral equation solutions for classical the electron gas, *J. Chem. Phys.* **58,** 4863 (**1973**)

12. Ng K.C., Hypernetted chain solutions for the classical one component plasma upto $\Gamma = 7000$, *J. Chem. Phys.* **61,** 2680 **(1974)**

13. Larsen B., Studies in statistical mechanics of Coloumbic systems. III. Numerical solutions of HNC and RHNC equations for the restricted primitive model, *J. Chem. Phys.,* **68,** 4511 (**1978**)

14. Elkoubi D., Turq P., and Hansen J.P., Application of the HNC approximation to systems of highly charged hard spheres (micelles), *Chem. Phys. Lett.*, **52,** 493 (**1977**)

15. Rogers F.J., A HNC study of asymmetrically charged hard spheres, *J. Chem Phys.* **73,** 6272 (**1980**)

16. Beresford-Smith B. and Chan D. Y. C., Highly asymmetric electrolytes: A model for strongly interacting colloidal systems, *Chem. Phys. Lett.* **92,** 474 (**1982**)

17. Belloni L., A hypernetted chain study of highly asymmetrical polyelectrolytes, *Chem. Phys.*, **99,** 43 (**1985**)

18. Bratko D., Friedman H.L. and Zhong E.C., An integral equation approach to structure and dynamics of ionic colloidal solutions *J. Chem. Phys.,* **85**, 377 (**1986**)

19. Vladimir Lobaskin and Per Linse, Simulation of an asymmetric electrolyte with charge asymmetry 60:1 using hard-sphere and soft-sphere models, *J. Chem. Phys.,* **111,** 4300 (**1999**)

20. Allnatt A. R., Integral equations in ionic solution theory, *Mol. Phys.,* **8**, 533 (**1964**)

21. Rasaiah J.C. and Friedman H.L., Integral Equation Methods in the Computation of Equilibrium Properties of Ionic Solutions, J. Chem. Phys., **48**, 2742 (**1968**)

22. Das B. and Gupta-Bhaya P., Hpernetted chain calculation of static correlation function of macroions in solution using Allnatt equation, *Mol. Phys.* **86**, 1397 (**1995**)

23. Behera R.N. and Gupta-Bhaya P., On attractive interaction of a colloid pair of like charge at infinite dilution, *J. Chem. Phys.* **126**, 044908 (**2007**)

24. Khanna T. and Behera R.N., manuscript under preparation.

25. Kalyuzhnyi Yu. V. and Vlachy V., Integral-equation theory for highly asymmetric electrolyte solutions, *Chem. Phys. Lett.* **215**, 518 (**1993**)

26. Kalyuzhnyi Yu. V., Vlachy V., Holovko M. F., Stell G., Multidensity integral equation theory for highly asymmetric electrolyte solutions *J.Chem.Phys.,* **102,** 5770 (**1995**)

27. Hribar B., Kalyuzhnyi Yu. V. and Vlachy V., Ion-ion correlations in highly asymmetrical electrolytes, *Mol. Phys.,* **87**, 1317 (**1996**)