Relationships Between Structure-Thermodynamics And Functional Properties Of Charge-Stabilized Colloidal Systems

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Abstract— in this paper, we present results of computer simulations for determination of the structure and thermodynamics of charge-stabilized colloidal suspensions. We assume that the interaction potential between colloids is of Sogami type. The former is purely repulsive, while the second, it involves, in addition to a repulsive part, a Van der Waals attractive tail. We compute the structure factor and thermodynamics properties, using, the integral equation one with the hybridized mean spherical approximation. We first compare the results relative to this theory, with this obtained within Monte Carlo simulation and with this obtained Jellium modified. We show that results from integral equation method with a Sogami potential and those of simulation are in good quantitative agreement.

Key words— Charged colloids, Pair-potential, Structure, Thermodynamics, Monte Carlo simulation, integral equation.

INTRODUCION

A Charge-stabilized colloidal suspensions (CSCS) consist of (spherical or anisotropic) mesoscopic colloidal particles suspended in a polar solvent with co- and counterions. The radius of the co- and counterions is comparable to that of the solvent molecules, i.e. of the order of 0.1- 0.3 nm. A statistical mechanics description of these highly asymmetric multicomponent fluids represent a major challenge as very different length and time scales are involved for the various species [1]. (CSCS) have been the subject of intense theoretical [2,3] , experimental study[4,5] and computer simulations [6-12]. The great effort is well justified by the importance that these systems play in industrial, biological, and medical applications [13]. A practical problem that arises is how to stabilize suspensions against flocculation and precipitation, resulting. Charged colloidal particles suspended in water interact through hard core repulsions, van der Waals attractions, Coulomb interactions, and hydrodynamic coupling. The particles influence on the surrounding medium modifies these interactions, for instance leading to screening of Coulomb interactions by atomic-scale simple ions.

From a theoretical point of view, colloids constitute special statistical systems. Thus, to study their physical properties such as structure, thermodynamics and phase diagram, use is made of statistical mechanics methods. Among these, we can quote variational and integral equation approaches.

The more reliable approach is the Ornstein-Zernike (OZ) [14] integral equation method [15]. The quantity solving this equation is the pair-correlation function $g(r)$ which is a crucial object for determining most physical properties. But, this equation involves another unknown that is the direct correlation function $c(r)$. Thus, this necessitates a certain closure, that is, a supplementary relationship between these two correlation functions. Integral equation has been intensively used in the modern liquid theory. It has been solved using some techniques, which are based on the analytical or numerical computation. One has used different closures, namely, the Percus-Yevick approximation [16], the hypernetted chain [17], the mean spherical approximation and its modification that is the hybridized-mean spherical approximation [18] (HMSA) we apply in this work.

We assume that particles interact through Sogami (SI) [19,20] potential. To investigate the structure and thermodynamics of the system, we have used the integral equation with HMSA. Finally, we have compared results obtained with Monte Carlo (MC) simulation results [21-23,32] and with Jellium modified (m-J) [22-25] . We have shown that results from integral equation method and those of MC and (m-J) are in good quantitative agreement.

This paper is organized according to the following presentation. In Sec. II, we describe the theory of integral equation with HMSA enabling us to compute the physical properties of interest. We present in Sec. III the results and make discussion. Comparison between

results from integral equation method and those of MC and (m-J) is the aim of Sec. IV. A brief summary with conclusions are given in section V.

I.   THEORY

A. PAIR-POTENTIAL

In this paper, the pair-potential used is that derived by Sogami (SI)[19,20], which describes the effective electrostatic interactions between macrions of charge Ze, This potential involves a short-range Coulomb repulsion, whose origin is self-evident, in addition to a long-range exponential attractive tail. This latter was derived using a self-consistent method [19, 20]. The Sogami potential has been used to describe the vapor-liquid transition and crystallization of charged colloids observed in experiments [33]. Its expression is then [19,20]

$$U^{SI}(r) = \frac{(Ze)^2}{\varepsilon\varepsilon_0\sigma}\left(\frac{\sinh^2(\kappa\sigma/2)}{\kappa\sigma}\right)^2\left[\frac{2+k\coth(k/2)}{r}-\kappa\right]\exp(-\kappa x), \qquad r \succ \sigma, \qquad (1)$$

$$k = \kappa\sigma$$

We have used the notations $x = r/\sigma$ and   , to mean respectively the renormalized interparticle distance and the renormalized electric screening parameter. With $A = 2 + k\coth(k/2)$, we have the following expression

$$U^{SI}(r) = \frac{(Ze)^2}{\varepsilon\varepsilon_0\sigma}\left(\frac{\sinh(k/2)}{k}\right)^2\left[\frac{A}{x}-k\right]\exp(-kx), \qquad x \succ 1,$$

$$(2)$$

There, r is the interparticle center-to-center distance, σ the hard-sphere diameter, ε the relative permittivity of solvent (water), ε_0 the permittivity of free space, and κ the Debye-Hiickel inverse screening length. Parameter, is defined as usual by

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon\varepsilon_0 k_B T}\sum_i n_i Z_i^2,$$

$$(3)$$

$$Z_i$$

where n_i stands for the number density of ions of type i and   , in the limit of weak screening , $\kappa\sigma << 1$ [26]. The shape of such a potential is depicted in Fig. 1.
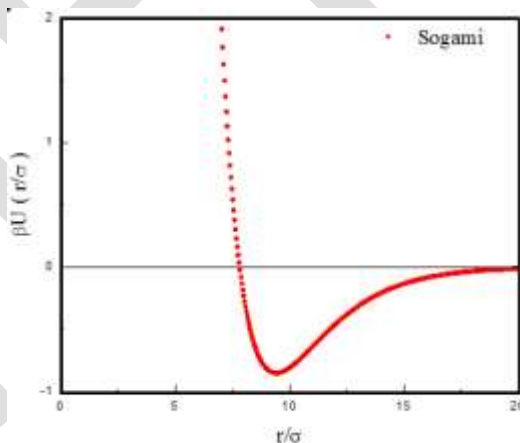

Figure 1:Reduced Sogami potential $U(r)/k_B T$ versus the renormalized interparticle distance r/σ,

Sogami potential is canceled in both cases, either $r = 2(2 + k\coth(k/2))/\kappa$, or when $r \to \infty$

The first derivative of the expression of the potential of Sogami he presented as follows

$$\frac{\partial}{\partial r}U^S(r) = -\frac{(Ze)^2}{\varepsilon\varepsilon_0\sigma}\frac{\sinh^2(k/2)}{k^2}\frac{\exp(-kx)}{x^2}\left[-k^2 x^2 + Akx + A\right], \qquad (4)$$

The position of the potential minimum R_m is given as

$$R_m = \left\{ A + \left[A(A+4) \right]^{1/2} \right\} \Big/ 2\kappa = \left\{ 2 + \text{k}\coth(k/2) + \left[\left(2 + \text{k}\coth(k/2) \right)\left(6 + \text{k}\coth(k/2) \right) \right]^{1/2} \right\} \Big/ 2\kappa. \qquad (5)$$

R_m decreases monotonically, with increasing $k = \kappa\sigma$, to the limiting value 2σ. The depth of the pair potential grows rapidly in the interval $0 \prec \kappa\sigma \prec 1$, reaches its maximum around $\kappa\sigma \approx 1.19$, and then decreases gradually to

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zero. Since R_m behaves as $R_m \approx 2\left(1+\sqrt{2}\right)\big/\kappa$ for small $\kappa\sigma$, the interparticle distance can take a very large value in the suspension with small latex particle concentration so far as the potential minimum keeps up a sufficient depth. [19,33]

Table 1. Comparison of the calculated distance R_m and the observed interparticle distance R_{exp} in dilute colloidal suspensions of charged (charge number $Z = 4 \times 10^3$) and spherical polymer particles for different particle concentrations [19]

Concentration vol (%)	$\kappa\sigma$	$U^S(R_m)$	$R_m\left(10^3\,\mathring{A}\right)$	$R_{\text{exp}}\left(10^3\,\mathring{A}\right)$
0.4	0.48	-0.49	18.0	18.0
0.55	0.56	-0.55	15.0	15.0
1.5	0.92	-0.73	11.0	10.0
4	1.50	-0.33	7.2	8.0

The following step consists in recalling the essential of the integral equation method used in this work.

B. METHOD OF EQUATIONS INTEGRALS (MEI)

Several approaches exist to study the structural property and thermodynamic a fluid from its interactions. The method of integral equations is one of these techniques which allows to determine the structure of a fluid in a thermodynamic state given, characterized by its density ρ and its temperature T, for a potential pair of $u(r)$ which mobilize the interactions between the particles. The calculation of the structure, represented by the function of radial distribution $g(r)$, is a own approach to the theory. In fact, the fact that in a liquid the particles are partially disordered implies his ignorance apriority. The function $g(r)$, which describes the arrangement medium of particles as a function of distance from an origin theory on the one hand, the Fourier transform of $g(r)$ is the factor of structure

$$S(q) = 1 + \rho \int \left(g(r) - 1 \right) \exp\left(iqr \right) dr \qquad (6)$$

That is measured by the experiences of diffraction of X-ray or neutron in function of the vector transfer q. On the other hand, the thermodynamic quantities of the fluids are functions of $g(r)$ and the $u(r)$ as the internal energy per particle

$$E / \langle N \rangle = \left(3/2 \right) k_B T + 2\pi \int u(r) g(r) r^2 dr, \qquad (7)$$

k_B is the constant of Boltzmann, the pressure of the viriel

$$P = \rho k_B T - 2\frac{\pi\rho^2}{3} \int \frac{r\, du(r)}{dr} g(r) r^2 dr \qquad (8)$$

Or the isothermal compressibility χ_T. This last can be obtained by two independent see, either by deriving the pressure (6) by report to the density:

$$\chi_T^{-1} = \rho \left| \frac{\partial P}{\partial \rho} \right|_T = \rho k_B T - \left(\frac{4\pi\rho^2}{3} \right) \int r \left(\frac{du(r)}{dr} \right) \left\{ g(r) + \left(\frac{\rho}{2} \right) \left(\frac{\partial g(r)}{\partial \rho} \right) \right\} r^2 dr, \tag{9}$$

Either share the intermediare of a study of fluctuations in the number of particles in the whole grand canonical

$$S(q=0) = \rho k_B T . \chi_T = 1 + 4\pi\rho \int (g(r)-1) r^2 dr \tag{10}$$

We can note that the isothermal compressibility χ_T deducted from the pressure of virial is equal to that calculated from the angle limit the diffusion of the zero factor structure.

C. INTEGRAL EQUATION APPROACH

The starting point of such a method is the Ornstein-Zernike (OZ) integral equation satisfied by the total correlation function $.h(r) = g(r) - 1.$ The OZ integral equation that involves the so-called direct correlation function $c(r)$ [27,28] is given by

$$h(r) = c(r) + n \int c(|r - r'|) h(r') dr', \tag{11}$$

where n is the number density of macroions. This equation, however, contains two unknown quantities $h(r)$ and $c(r)$. To solve it, we need a closure relation between these two quantities. In this paper, we decide to choose the HMSA, and write

$$g^{HMSA}(r) = \exp[-\beta U_1(r)] \times \left\{ 1 + \frac{\exp\left[f(r)\left\{\gamma(r) - \beta U_2(r)\right\} - 1\right]}{f(r)} \right\}, \tag{12}$$

where the interaction potential is divided into short-range part $U_1(r)$ and long-range attractive tail $U_2(r)$ as prescripted by Weeks et al [29]. There, the function $\gamma(r)$ is simply the difference between the total and direct correlation functions, i.e., $\gamma(r) = h(r) - c(r)$, and is illustrated in figure 2. Quantity $f(r)$ is the mixing function [30], whose a new form was proposed by Bretonnet and Jakse [18]. The virtue of such a form is that, it ensures the thermodynamic consistency in calculating the internal compressibility by two different ways. The form proposed by the authors is [30]

$$f(r) = f_0 + (1-f_0)\exp(-1/r), \tag{13}$$

where the f_0 is the interpolation constant. This is an adjustable parameter such as $0 \le f_0 \le 1$. This constant that serves to eliminate the incoherence thermodynamic, can be fixed equating the compressibility deduced from virial pressure to that calculated from the zero-scattering angle limit of the structure factor, i.e.,

$$S(0) = n k_B T \chi_T. \tag{14}$$

Now, it remains the presentation and discussion of our results, and their comparison with those relative of MC simulation [32] and (m-J) [12].
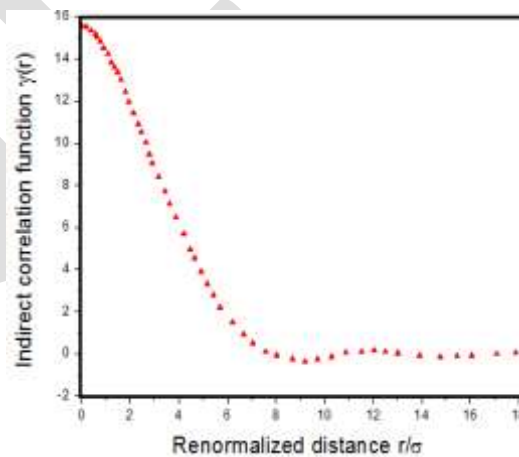
Figure 2: Example plot of $\gamma(r)$, the `indirect' correlation function, for a Fluid colloid system interacting via an exponential decay potential $U(r) \propto exp(-r/\sigma)$ at a reduced density $\rho^* = \rho d^2 = 0,015$. [30].

II.   RESULTS AND DISCUSSION

According to Eq. (1), the interaction between colloidal particles is determined by many factors, such as the salt concentration, surface charge density and volume fraction of the colloid, etc. Different values of those factors which influence the interactions will result in different phase behaviors of the system. In this paper, we have used those parameters values reported by [22,23]. These are, T = 293 K (absolute temperature), $\varepsilon = 78$ (Relative permittivity of water), $\lambda_B = e^2/(4\pi\varepsilon k_B T) = 7.198\text{Å}$ is the Bjerrum length,.

System	σ (Å)	$k = \kappa\sigma$	λ_B/σ	$Z\lambda_B/\sigma$	λ_B/σ
A	20	0.419	0.3558	5.877	0.3558
B	40	0.360	0.1779	5.093	0.1779
C	160	0.386	0.0445	4.972	0.0445

Our purpose is a quantitative investigation of thermodynamic and structural properties of a dilute solution of polyballs (in water), using the integral equations method.

INTEGRAL EQUATION METHOD RESULTS

The HMSA integral equation is applied here for accomplishing an alternative computation of structural and thermodynamics properties of the colloidal solution under investigation. Potential used here is of (SI) type, and the choosing mixing function $f(r)$ is pointed out in [29].
First, we have computed the main object that is the pair-correlation function $g(r)$ versus the renormalized interparticle distance r/σ. In Fig. 3, we plot the macroion-macroion correlation functions calculated using the HMSA integral equation above and compare it with the results of the Jellium modified (m-J) and MC simulations.
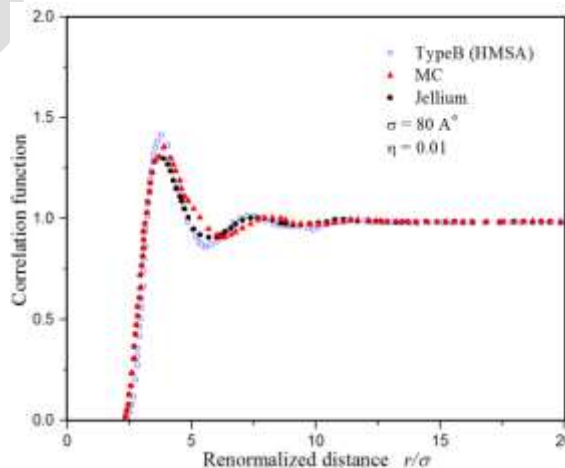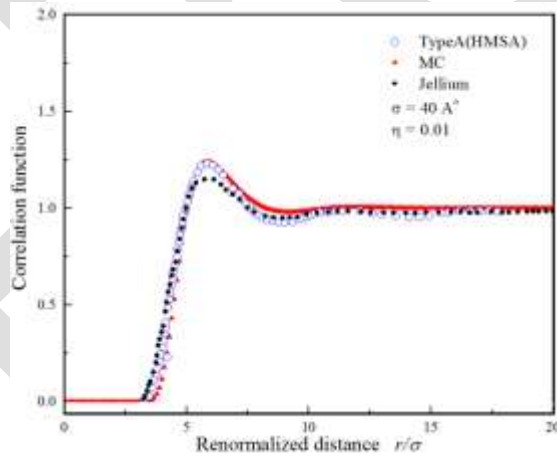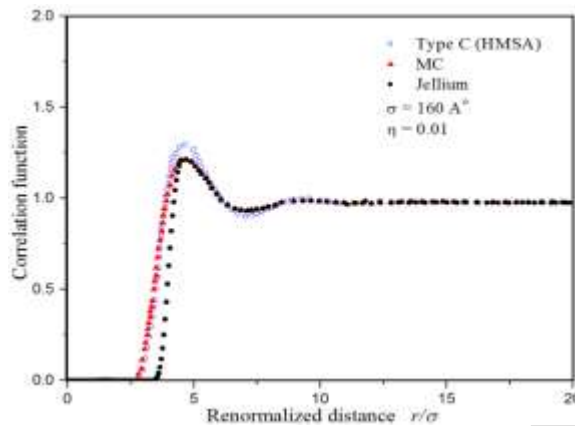
Figure 3:Correlation function with a (SI) potential using HMSA integral equation theory compared with,

(m-J) and MC simulations for three system have the same volume fraction and particle size is respectively $\sigma_A = 40(\mathring{A}), \sigma_B = 80(\mathring{A})$ and $\sigma_C = 160(\mathring{A})$.

Second, we have reported in Fig. 4 the pair-correlation function for a (SI) potential, together with that computed using the MC simulation or (m-J) [22,23]. In fact, the three curves are in good quantitative agreement. The effective charge, the coupling parameter, the radius of the colloids and the value of the contact potential of each system are summarized in Table 3. The renormalized parameters were calculated according to the (m-J) model. The selected values are for the regime saturation dictated by Fig 4.
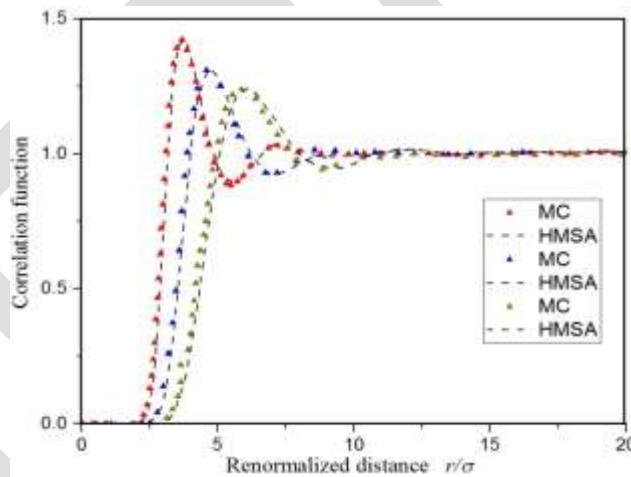

Figure.4: Macroion-macroion correlation functions calculated using the HMSA integral equation theory

(dashed lines), and MC simulations from left to right, the volume fractions are respectively

($\blacktriangle$- $\eta = 0.08$),($\blacktriangle$- $\eta = 0.04$), and($\blacktriangle$- $\eta = 0.02$)

for a deionized colloidal suspension with coupling parameter $\lambda_B / \sigma = 0.3558$.

Table 2. *Thermodynamic proprieties for* (SI) *potential, within HMSA integral equation method*

$T\ (K)$	E_{int}/N	$P/\rho k_B T$	$\rho k_B T \chi$
	-0.207614	0.635371	1.484716
	-0.992903	0.524017	4.864628
	-1.804557	2.286026	11.257641
90	-2.539001	5.544148	15.065502
	-3.034279	7.093886	10.820960
	-2.766866	10.676855	4.1048034
	-0.322489	0.6746724	1.2576419
	-1.032450	0.6026200	2.4192139
	-1.906250	1.6048034	3.4497816
100	-2.380813	3.8973799	1.8340611
	-1.684033	7.5131004	0.3930131
	-0.373335	11.338427	0.1397379
	-0.175600	0.7336244	1.1004366
	-0.815884	0.9956331	1.5807860
	-1.550327	2.4759825	1.6593886
120	-1.804557	5.7117903	1.0043668
	-1.228302	8.2860262	0.4454148
	-0.435480	10.997816	0.1222707
	-0.100272	0.9235807	1.0567685
	-0.633215	1.0152838	1.1790393
	-0.974072	2.0567685	1.0567685
160	-1.120960	4.6899563	0.5240174
	-0.684061	7.1921397	0.1921397
	-0.001419	9.2554585	0.1222707

The table shows that for a fixed temperature, there is a decrease of the compressibility and the internal energy has a certain value, while the pressure increases. It is therefore interesting to study the variation in detail the thermodynamic properties of charge-stabilized colloidal suspensions.

Table 3. *Thermodynamic proprieties for Sogami potential, within HMSA integral equation method*

$T\left(k\right)$	$E_{\text{int}}^{\min}/N$	η^*
90	-3.032396	0.049902
100	-2.363864	0.045300
120	-1.808324	0.043099
140	-1.420387	0.042058
160	-1.132259	0.041698

In the table 3, we shows that as the temperature increases, we notice a peak deviation of minimum energy and takes an oval shape with the Rating Decrease volume fraction and thus the system becomes more stable.

III.   CONCLUSIONS

Dispersions of charge-stabilized colloidal particles are ubiquitous in environmental and food industry, and in life sciences. Examples of such dispersions are viruses or proteins in water, paints, waste water, and model systems of strongly charged spherical latex or silica spheres. This work is devoted to the structural and thermodynamic properties of three system (A,B and C) It has the same volume fraction and particle size   respectively $\sigma_A = 40\left(\mathring{A}\right), \sigma_B = 80\left(\mathring{A}\right)$ and $\sigma_C = 160\left(\mathring{A}\right)$. We have computed the structure and thermodynamics, using, the integral equation one with HMSA. We compared the results relative to this theory to the obtained within MC and (m-J) . We have shown that results from integral equation method and those of MC are in good quantitative

Further developments such as the studies of the phase behavior and density effects are in progress.

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