IJETCR Open Access

ISSN: 2348 - 2117

International Journal of Engineering Technology and Computer Research (IJETCR)
Available Online at www.ijetcr.org
Volume 3; Issue 2; March-April; 2015, Page No. 215-224

Computational Modeling and Simulation of Thermodynamical and Structural Properties Using Different Reference Systems

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ABSTRACT

Keeping in This work deals with a quantitative study of the structural and thermodynamic properties of colloidal solutions, using the variational method Gibbs-Bogoliubov inequality. This method is based on the minimization of free energy, using a reference system and its interaction potential.

In this work, we have used two reference systems, i.e., the system of hard spheres and the charged hard spheres (CHS). We applied this method to the variational polystyrene colloids, using a potential real system purely repellent DLVO type. We have shown that the use of the reference system of hard spheres loaded in the minimization of the free energy is more stable than the use of the reference system of hard spheres (HS). From the minimum free energy were evaluated thermodynamic quantities that are in good agreement with the results obtained from molecular dynamics.

INTRODUCTION

Chinese had observed since ancient times [1], a thin aqueous suspension of carbon black not decanted, separating the solution, when it added gum Arabic, a natural polymer extracted Acacia, the system called the ink is then stable, it is a colloidal system.

Generally called colloidal state, a system formed by a material dispersed in a solvent and whose molecules are grouped into micelles carrying an electric charge of the same sign. A micelle is itself a globular aggregate whose diameter is typically 3 to 5 nm.

The stability of the colloidal system is conditioned by the existence of an electric charge and a shell of solvation in the particles that are dispersed. Colloidal particles absorb a certain species of ions, the system is generally neutral as fillers particles are compensated by those of opposite sign ions present in the solution. It is clear that the fact that the particles of a colloidal system are loaded play a key role in its stability: their loads oppose the coagulation system. The application of an electric field to the colloidal system causes a displacement of all the suspended particles in the direction of one of the electrodes. In colloidal systems consisting of iron hydroxide particles, aluminum or chromium, they carry a positive charge, while the colloidal particles of gold, silver, silica, starch and gum.

Arabian is negatively charged. Found numerous colloidal systems with a particle size between 1 and 200 nm. Some are natural, such as milk and blood (the solvent is a liquid medium), agate and opal correspond to a sound system. Others are from industry and are found in fluid suspensions used in the chemical and oil industry, or metallurgy. One also meets colloidal systems in aerosols, mists or foams, systems where the dispersion medium is a gas. A colloidal system is subject to a large number of particles, whose study is the statistical physics [2]. These measurable physical quantities are the average values of observables associated, and the weights Boltzmann naturally involve interactions between particles. The knowledge of the form of the interaction potential is of major importance in the study of a colloidal system.

The stability of such a system is determined by the knowledge of the interaction forces between the particles. In fact, the theory of Derjaguin Landau [3], and Verwey and Overbeek [4] (DLVO) reports that stability taking into account the long-range attractive forces (the forces of Van der Waals) firstly and repulsive electrostatic forces acting origin with short distances on the other hand. In this work, we are interested in calculating the structural and thermodynamic properties of colloids starting interparticle interactions $U(r)$. We calculate the pair correlation function $g(r)$, which is the base object in the evaluation of the thermodynamic properties(energy, pressure, compressibility, phase transitions, ...) and its Fourier transform leads to factor structure $S(q)$, which is directly proportional to the scattered intensity in a light scattering experiment, X-rays or neutrons, where q is the wave

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vector transfer in which the modulus $q = |q|$ is given as a function of the wavelength of the radiation incident and scattering angles θ by the relation classic: $q = (4\pi/\lambda)\sin(\theta/2)$.

When the form of the potential is complicated, we can accurately calculate the average values of physical observables (pair correlation function, internal energy ...), approximate methods are needed, among which we mention first the method integral equations using the exact relationship Ornstein-Zernike [5], and the approximate closure relation between the structures of interactions between particles. Then, the technique of the variational method for optimizing the Gibbs free energy-Bogoliubov [6], particularly well suited to the calculation of the free energy minimized with respect to one or more parameters. In this technique, the expression of the free energy consists of the free energy of the reference system (unperturbed system), at the same density as the real system, most disruptive term. The latter is other than the difference of potential energy between the actual system and the reference system averaged over the pair correlation function of the reference system.

To apply the approach of the variational method Gibbs-Bogoliubov, we need to specify the reference system. Many authors have applied the reference system of hard spheres (HS) single metals [7] and the transition metals [8] and fluid.

The parameter variational minimization of the free energy is the diameter hard spheres. Returning to the colloidal system, a group of molecules (micelles) dispersed in a solvent.

These molecules, in solution, carry an electrical charge of the same sign and which are compensated by those of opposite sign ions present in the solution. The variational method Gibbs-Bogoliubov applied to the colloidal system can calculate the free energy of the real system with even more precision than the reference system is similar to the real system. It is better to use for the colloidal system, the reference system of charged hard spheres (CHS) than hard spheres (HS).

The objective of this work lies in the application of the variational method Gibbs-Bogoliubov in direct and reciprocal space, using the reference system of hard spheres then the charged hard spheres (CHS) for the system colloidal we compare the two free energies obtained. The potential of the actual system used here is (DLVO). We determine thereafter the structural and thermodynamic properties of colloids, using a purely repulsive potential type (DLVO).

The latter is needed in the stabilization of the colloidal particles in suspension. Incidentally, the addition of a salt which shields an electrolyte of the repulsive forces, while the attractive forces dominate and induce aggregation (flocculation). When the load is absent after being screened, another method often used to stabilize the particles is to surround them with a polymeric layer (by adsorption or grafting). The particles repel formed and stabilized through excluded volume forces (steric hindrance).

II- Theoretical Formulations

A. PAIR-POTENTIAL

In this contribution, we consider a monodisperse colloidal system made of polystyrene balls (polyballs) of spherical form. For that, we choose a Yukawa potential [18] .We denote by the charge carried by one colloid [18], where σ is the electron elementary charge. Because of the presence of counterions, and eventually, electrolyte or salt ions, Coulomb interactions are screened out and colloids interact through a Yukawa pair-potential defined by

$$U_Y(r) = \begin{cases} \infty, & r < \sigma, \\ \dfrac{\sigma}{\pi\varepsilon\varepsilon_0}\left(\dfrac{Ze}{2+\kappa\sigma}\right)^2 \dfrac{\exp\left[-\kappa\sigma\left(r/\sigma - 1\right)\right]}{r/\sigma} & r \geq \sigma . \end{cases} \quad (1)$$

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

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

The potential (1) takes the form

$$\frac{U_Y(r)}{k_B T} = \begin{cases} \infty, & x < 1, \\ \Gamma\dfrac{\exp(-kx)}{x}, & x \geq 1. \end{cases} \quad (3)$$

We have used the notations $x = r/\sigma$ and $k = \kappa\sigma$ where $\kappa\sigma << 1$, to mean respectively the renormalized interparticle distance and the renormalized electric screening parameter. There,

$$\Gamma = \frac{\sigma}{\pi\varepsilon\varepsilon_0}\left(\frac{Ze}{2+\kappa\sigma}\right)^2 e^k / k_B T \quad (4)$$

Is the coupling constant

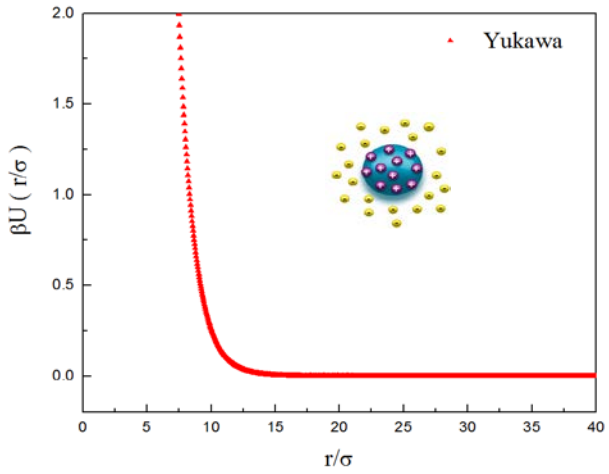

Figure 1: Reduced Yukawa potential $\beta U_Y(r/\sigma)$ versus the renormalized interparticle distance r/σ .

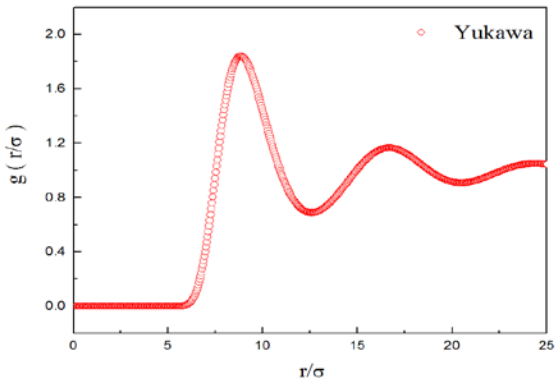

Figure 2: Pair correlation functions $g(r/\sigma)$ versus the renormalized interparticle distance r/σ [30].

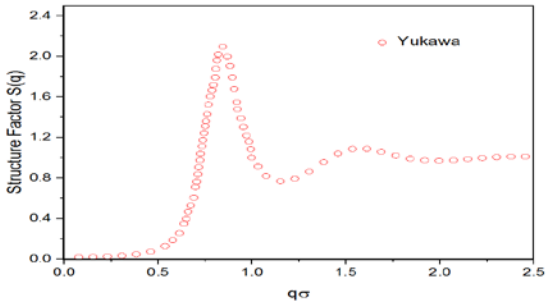

Figure 3: Structure factor $S(q)$ versus the renormalized interparticle

B- THE GIBBS –BOGOLIUBOV INEQUALITY FOR SIMPLE LIQUID

The thermodynamic properties of fluids are frequently studied by thermodynamic perturbation theory. However, among the methods available, the variational methods [30] for optimizing the Gibbs free energy Bogoliubov (GB), which is particularly well suited to the study of fluids. The evaluation of the free energy F of the system requires knowledge of the partition function $g(r)$, which is a sum over all possible configurations of the system and the form of the interaction potential $U(r)$ in the fluid frame, the variational method was developed initially by Firey and Ashcroft [9], in about 1977.

The Gibbs–Bogoliubov inequality is (hereafter all terms are written per atom)

$$F \le F_0 + < U_1 >_0 \quad , \tag{5}$$

Where F is the true Helmholtz free energy of the system; F_0 is the Helmholtz free energy of the reference system [10]; U_1 is the perturbation:

$$U_1 = U - U_0 \ , \tag{6}$$

Where U is the potential energy of the whole system; U_0, the potential energy of the reference system.

The Helmholtz free energy of the reference system is

$$F_0 = \frac{3}{2} k_B \mathrm{T} + U_0 - TS_0 \ , \tag{7}$$

Where S_0 is the entropy of the reference system.

In this work, we present the processing of calculating the free energy of the fluid, by the GB minimization method. We apply the system of hard spheres (hard spheres) *(HS)* [1, 30] as reference system in the direct space, then we express the free energy in reciprocal space.

For this, we need to express the analytical expression of the structural factor of hard spheres as part of the approximation of *Percus- Yevick*. Finally, the variational parameter, which corresponds to the minimum free energy, will recalculate thermodynamic quantities more accurately.

C. HS REFERENCE SYSTEM

HS reference system is characterized by the diameter of the spheres σ, the potential interaction is given by:

$$U_{HS}(r) = \begin{cases} \infty \ ; & r < \sigma \ , \\ 0 \ ; & r \ge \sigma \ , \end{cases} \tag{8}$$

The variational parameter which depends on the free energy will be σ

C.1 The free energy minimization in the direct space and reciprocal space

The second term of the previous inequality (5) which is the difference of potential energy is averaged sue the pair correlation function of the reference system, we then

$$< U - U_{HS} >_{HS} = \frac{\rho N}{2} \int g_{HS}(r) \left[U(r) - U_{HS}(r) \right] 4\pi r^2 dr \quad , \tag{9}$$

Here, $g_{HS}(r)$ is the correlation function of the *HS* fluid [1]. Using the fact that $g_{HS}(r)$ is zero for values of $r < \sigma$, and $U_{HS}(r)$ is zero for $r > \sigma$, the inequality (1) applied to the reference system of hard spheres written as

$$F \le F_{HS}(\eta) + \frac{\rho}{2}\int d^3r\, g_{HS}(r)\left[U(r) - U_{HS}(r)\right] \quad , \qquad (10)$$

Introducing the full correlation function, (10) equation becomes:

$$F \le F_{HS}(\eta) + 2\pi\rho\int_{\sigma}^{\infty}\left[g_{HS}(r) - 1\right]U(r)r^2dr + 2\pi\rho\int_{\sigma}^{\infty} r^2U(r)dr \qquad (11)$$

Or the last member in the inequality is independent of η therefore the relation takes the for The estimate of the free energy F of the real system is easy to do, since it has the free energy of the *HS* system [10], proposed by *Carnahan* and *Starling* (1969)

$$F_{HS}(\eta) = K_BT\left[-\ln(1-\eta) + \frac{3}{2}\frac{\eta(2-\eta)}{2(1-\eta)^2}\right] \quad , \qquad (13)$$

Where η is the packing fraction, also called compactness will be defined later.

$$\eta = \frac{\text{volume of an atom}}{\text{available volume per atom}} = \frac{\pi}{6}\rho\sigma^3 \qquad (14)$$

Equation (12) is written in order to use the structure factor $S(q)$, which is related to the radial distribution function $g(r)$ and which is available in analytical form.

In order to express the calculations in reciprocal space, write the interaction potential in q space by taking its Fourier transform

$$U(r) = \frac{1}{(2\pi)^3}\int d^3q\bar{U}(q)\,\exp(i\vec{q}.\vec{r}) \qquad (15)$$

The Fourier transform of the total correlation function gives the structure factor, is written as:

$$S^{HS}(q) - 1 = \rho\int d^3r\left[g^{HS}(r,\eta) - 1\right]\exp(i\vec{q}.\vec{r}) \qquad (16)$$

Using these last two relations, the free energy in the Fourier space is written in terms of the structure factor $S(q,\eta)$ as

$$F \le F^{HS}(\eta) + \frac{1}{16\pi^3}\int_{\sigma}^{\infty} d^3q\left[S^{HS}(q,\eta) - 1\right]\tilde{U}(q) \quad , \qquad (17)$$

Here, $\tilde{U}(q)$ is the Fourier transform of the potential for interaction in the direct space $U(r)$. The relations (12) and (16) express the minimization of the free energy in the direct and reciprocal space, we will apply these relationships to colloidal systems, and compare parameter values that minimizes the free energy in both spaces. For this, we first need the analytical expression of the structural factor of hard spheres.

C.2 Structure Factors for Particulate Systems

C.2.1 Percus–Yevick approximation (PYa)

The purpose is to remind how we calculate the structure factor of a system of hard spheres. For more details, the reader is referred to reference [10]. The starting point is the Ornstein-Zernike equation [11] (OZ), which is an exact relationship that expresse the total correlation function $h(r)$ as the sum of the direct influence $c(r)$ and a sum of indirect influence of all particles by

$$h(r_{12}) = c(r_{12}) + \rho\int c(r_{13})h(r_{13})\, dr_3 \qquad (18)$$

It is convenient to work in reciprocal space. For this, we express the Fourier transforms of the direct correlation function $c(r)$ and total $h(r)$

$$\tilde{c}(q) = \int c(r)\exp(-iqr)dr \qquad (19)$$

$$\tilde{h}(q) = \int h(r)\exp(-iqr)dr \qquad (20)$$

Note that the second term of equation (18) is a convolution, which turns in the reciprocal space by a simple product of $\tilde{c}(q).\tilde{h}(q)$The Fourier transform of the OZ relation is then given by:

$$\tilde{h}(q) = \tilde{c}(q) + \rho\tilde{c}(q)\tilde{h}(q) \qquad (21)$$

where still

$$\tilde{h}(q) = \frac{\tilde{c}(q)}{1 - \rho\tilde{c}(q)} \qquad (22)$$

Consider now the definition of the structure factor and is given by :

$$S(q) = 1 + \rho\int h(r)\exp(-iqr)dr \qquad (23)$$

With $h(r) = g(r) - 1$. Expression (23) may be rewritten as,

$$S(q) = 1 + \rho\tilde{h}(q) \qquad (24)$$

From these facts and from the relation (22), we obtain:

$$S(q) = \frac{1}{1 - \rho\tilde{c}(q)} \qquad (25)$$

Le facteur de structure est fonction simplement de la transformée de Fourier de la fonction de corrélation directe. As the exact integral equation OZ (18) contains two unknown, ie, $h(r)$ and $c(r)$, it is necessary to use a second indisponsable independent relationship if we wants to determine both $c(r)$ and $g(r)$. This relationship is always approximate nature include that of Percus-Yevick (PY) [12]

$$c^{PY}(r) = g(r)\left[1-\exp\left(-\beta U(r)\right)\right] \quad (26)$$

This comprehensive relationship solving the OZ equation where the unknown is now one is $g(r)$.

C.2.1 Application to hard spheres

The importance of the approximation of PY in the study of dense fluids lies in the fact that this particular equation (26) is solved analytically in the case of hard spheres by expression of the interaction potential given by the relation (8).

We inserting by the expressions of $g(r)$ and $c(r)$ in the OZ equation, gives the analytic form of pair correlation function as:

$$c_{HS}^{PY}(r) = \alpha + \beta\left(\frac{r}{\sigma}\right) + \gamma\left(\frac{r}{\sigma}\right)^2, \quad (27)$$

where,

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4} \; ; \; \beta = 6\eta\frac{\left(1+\frac{\eta}{2}\right)^2}{(1-\eta)^4} \; ; \; \gamma = -\frac{\eta}{2}\alpha$$

Using the expression of $c^{PY}(r)$, is readily obtained an analytical form for the structure factor $S(q)$. Either,

$$S_{HS}^{PY}(q) = \frac{1}{1-\rho c_{HS}^{PY}(q)} \quad (29)$$

With

$$\rho c_{HS}^{PY}(q) = \frac{24\eta}{q\sigma}\left[\alpha J_1(q) + \beta J_2(q) + \gamma J_4(q)\right] \quad (30)$$

here,

$$J_n(q) = -\frac{\cos(q\sigma)}{q\sigma} + \frac{1}{(q\sigma)^2}\left[n\sin(q\sigma) - n(n-1)J_{n-2}(q)\right]; \quad (31)$$

For all values of the integer n. was

$$J_0(q) = \frac{1}{q\sigma}\left[1-\cos(q\sigma)\right] \quad (32)$$

The relations (29) - (32) allow to have an analytical expression of the structure factor in the model of hard spheres in the approximation Percus-Yevick. with the analytical expression of the structure factor, one can determine the analytical expressions of the other thermodynamic quantities.

II.2.2 Thermodynamics Properties (HS)

Having determined the structural properties of the colloidal solution, the next step is to study the thermodynamic properties, namely the determination of energy, pressure and isothermal compressibility. The numerical solution of the state equation (33) is difficult to obtain because of the absence of a closed form of the pair correlation function $g(r)$. However, the integral can be solved analytically exact manner, in the case of a potential of hard spheres, by means of the approximation of PY and the analytical expression of $c(r)$.

$$\chi_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T \quad (33)$$

The equation of state takes the following simple form:

$$P = \rho K_B T + \left(\frac{2}{3}\right)\pi\rho^2 K_B T\sigma^3 g(r)\exp\left(\frac{U(\sigma)}{K_B T}\right) \quad (34)$$

Substituting now the pair correlation function $g(r)$ by $c(r)$, using means of the approximation of PY, the pressure state equation becomes simply a function of the charging parameter η

$$\left[\frac{P}{\rho K_B T}\right]^{(P)} = \frac{\left(1+2\eta+3\eta^2\right)}{(1-\eta)^2} \quad (35)$$

(28)

One can also calculate the compressibility equation of state by integrating the relation (34) which, beforehand, is to be transformed as follows, using the relationship

$$\left[1+\rho\tilde{h}(q)\right]\left[1-\rho\tilde{c}(q)\right] = 1 \quad (36)$$

(29)

In which we asked $q = 0$

$$\beta\left(\frac{\partial P}{\partial\rho}\right) = 1 - \rho\int c(r)\,d\,\vec{r} \quad (37)$$

First we see that the knowledge of the direct correlation function is sufficient to calculate the compressibility of a fluid. Using $c(r)$ hard spheres (26), we arrive at a second state equation:

$$\left[\beta\frac{P}{\rho}\right]^{(C)} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \quad (38)$$

The two expressions of the equation of state are different, but this is not surprising since the PY equation is not an exact relationship but an approximation.

The thermodynamic properties of hard spheres system were calculated by both Monte Carlo simulation methods [13-16]. The results of these methods, which are perfectly coincide, constitute a real experience to which one can compare the analytical theories.

By making a virial expansion of the equation of state and adjusting the coefficients on the results of Molecular Dynamics, Carnahan and Starling (CS) [17] have got a third equation of state, which is a combination of first two and which is substantially more accurate

$$\left[\frac{P}{\rho K_B T}\right]^{(CS)} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \qquad (39)$$

The derivation of equation (39) with respect to volume, provides the isothermal compressibility

$$\chi_T^{(CS)} = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho K_B T}\frac{(1-\eta)^4}{(1+2\eta)^2+\eta^3(\eta-4)} \qquad (40)$$

and the internal energy E can be determined using the following regular expression:

$$\frac{E-E_0}{NK_BT} = \frac{\eta(2-\eta)}{(1-\eta)^2} + 2\pi\rho\int_\sigma^\infty g_{HS}(r)U(r)r^2dr \qquad (41)$$

$E_0 = \frac{2}{3}Nk_BT$ is the internal energy of an ideal gas. The pair correlation function $g(r)$ is simply replaced by the reference system HS, $g_{HS}(r)$.

Case the system of charged hard spheres (CHS)

In the case of electrolytes, the particles are charged, the reference system of charged hard spheres (CHS) seems to be best suited for the free energy minimization calculation in the context of the variational method CB

The free energy thus obtained will be compared to that of the free energy of the reference system of hard spheres. The most appropriate reference system for the study of structural and thermodynamic properties of colloids, which is the free energy is minimal.

For this, we rewrite inequality GB this time with the reference system of hard spheres loaded

$$F \le F^{CHS} + < U - U^{CHS} >_{CHS} \qquad (42)$$

where F^{CHS} denotes the free energy of the reference system, and $< U - U^{CHS} >_{CHS}$ denotes the CHS statistical average with respect to the reference system *CHS*.

The minimization of the free energy with the *CHS* reference system is calculated using the expression of the free energy of the reference system F^{CHS} and its potential energy U^{CHS} given by Palmer and Weeks [25]

$$\beta U^{CHS}(\eta) = \beta U_1^{CHS}(\eta) + \beta U_2^{CHS}(\eta) \qquad (43)$$

Where

$$\beta U_1^{CHS}(\eta) = -\left(\frac{1}{24\eta}\right)\left(1+\eta-\frac{\eta^2}{5}\right)k^2 \qquad (43-a)$$

And

$$\beta U_2^{CHS}(\eta) = -\left(\frac{1}{24\eta}\right)(1+2\eta)k\left[1-\left(1+\frac{2(1-\eta)^3k}{(1+2\eta)^2}\right)^{\frac{1}{2}}\right] \qquad (43-b)$$

$$J_1 = Q^3(1-Q)\sin Q,\ J_6 = \frac{\cos Q}{Q^2},\ J_2^* = J_2 + 2Q^2,\ J_5^* = J_5 + \frac{720}{Q^2}$$

At a given temperature T and a number density ρ, k is the constant of screening. Its inverse is the screening length of *Debye-Huckel*:

(40)

$$k = \left(24\eta\beta Z_p^2 e^2/\sigma\right)^{\frac{1}{2}} \qquad (44)$$

Where $\beta = 1/k_BT$ and Z_p is the ionic charge, F^{CHS} is given by

(41)

$$\frac{F^{CHS}}{k_BT} = \frac{\eta(4-3\eta)}{(1-\eta)^2} - \frac{k^2}{24\eta}\left(1+\eta-\frac{\eta^2}{5}\right) - \frac{(1+2\eta)^3}{36\eta(1-\eta)^3}\left[1-\left(1+\frac{2(1-\eta)^3}{(1+2\eta)^2}k\right)^{\frac{3}{2}}\right] - \frac{(1+2\eta)}{12\eta}k \qquad (45)$$

The structure factor $S^{CHS}(q,\eta)$ is similar to that of hard spheres (Eq.19) that expressed in reciprocal space in terms of the direct correlation function $\tilde{C}^{CHS}(q,\eta)$ as:

$$S^{CHS}(q,\eta) = \left[1-\rho\tilde{C}^{CHS}(q,\eta)\right]^{-1} \qquad (46)$$

Where

$$\rho\tilde{C}^{CHS}(Q,\eta) = \frac{24\eta}{Q^6}\sum_{i=1}^{6}A_iJ_i(Q) \qquad (47)$$

With, $Q = q\sigma$ is the reduced variable in rninimisation free energy. The explicit expressions for the coefficients A_i CHS system, are given in [26] as follows:

$$A_i = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{R^2}{4(1-\eta)^2} - \frac{(1+\eta)Rk}{\left[12\eta-\left(5+\eta^2\right)k^2\right]60\eta} \qquad (48)$$

$$R = \left[\frac{(1+2\eta)}{(1-\eta)}\right]\left[1-\left(1+\frac{2(1-\eta)^3k}{(1+2\eta)^2}\right)^{\frac{1}{2}}\right] \qquad (49)$$

$$U = -\left(\frac{1}{12\eta}\right)\left(1+\eta-\frac{\eta^2}{5}\right)-\left(\frac{R}{12\eta k}\right)(1-\eta) \quad (50)$$

$$\begin{pmatrix} J_2^* \\ J_3 \\ J_4 \\ J_5^* \end{pmatrix} = \begin{pmatrix} \frac{2}{(1-Q)} & -(Q^2-2)Q^4 \\ 6\frac{(Q^2-2)}{Q^2(1-Q)} & -(Q^2-6)Q^4 \\ 8\frac{(Q-8)}{Q^2(1-Q)} & -(Q^4-12Q^2+24)Q^2 \\ 12\frac{(Q^4-20Q+120)}{Q^4(1-Q)} & -4(Q^6-30Q^4+360Q^2-720) \end{pmatrix} \begin{pmatrix} J_1 \\ J_6 \end{pmatrix} \quad (51)$$

In this section, we first describe the variational method Gibbs Bogolyubov in the direct space and reciproque. To determine the minimization of the free energy in direct and reciprocal space, we used the exact equation of OZ and the approximate relationship of PY to determine the analytical expression of the structural factor. It was explained last, the corresponding thermodynamic quantities.

III- CHARGED COLLOIDAL SOLUTION SYSTEM (*CHS*)

The theory describing the colloidal solutions stabilization principle was proposed to 40 years in two pioneers articles, one of Derjaguin and Landau [18] and the other Verwey, and Overbeck [19] We talk about the *DLVO* theory. In these two articles, our interest has been focused on the potential of colloidal particle pair interactions including the Van der Waals attractions and electrostatic repulsion. If electrostatic repulsion is sufficient, the suspension is stable.

On the other hand, increasing the ionic strength of the medium by addition of salt, for example, strongly attenuates this repulsion, and the suspension is then made unstable and tends to fluctuations.

In this section we describe the structure and thermodynamics of fluid colloidal particles, which interact via a potential type *DLVO*, which additionally contains a repelling portion attractive part of short-range and generally negligible in permanent suspensions .

In the limit of large dilutions, small colloidal charge, and monovalent electrolyte, a linearized Debye–Hückel theory can be applied and the pair potential takes a simple Yukawa-like form, known as the Derjaguin–Landau–Overbeek–Verwey (DLVO) potential. For a system of colloidal particles of radius *a*, charge of polyion $(-Z_p q)$, density, and microions of valence z_i the DLVO potential is given by

In this section, we first describe the variational method Gibbs Bogolyubov in the direct space and reciproque. To determine the minimization of the free energy in direct and reciprocal space, we used the exact equation of OZ and the approximate relationship of PY to determine the analytical expression of the structural factor. It was explained last, the corresponding thermodynamic quantities.

Where $l_b = \beta q^2/\varepsilon$ is the Bjerrum length, $\beta = 1/k_B T$, q is the elementary charge, ε is the dielectric constant, and $\kappa = \sqrt{4\pi l_B \sum_{i\neq 0}\rho_i z_i^2}$ defines the inverse Debye screening length. If we choose as a unit of length, the potential *DLVO* takes the following form

$$\beta U_{DLVO}(r) = \begin{cases} \infty & , \quad x<1 \\ J\dfrac{e^{\kappa r}}{1+\kappa r} & , \quad x\geq 1 \end{cases} \quad (52)$$

with $$J = Z_p^2 l_B \sigma \left(\frac{\exp(\kappa a)}{1+\kappa a}\right)^2 l_B$$

We use the notation $x = r/\sigma$ and $\lambda = \kappa\sigma$, respectively denote the reduced distance and the screening renormalized constant. J is the coupling constant, which is given by [21].

After defining the shape of the potential *DLVO* interaction, it is time to present our original results that will be devoted to the application of the variational method *GB* using two reference systems, namely hard spheres then charged hard spheres.

Results by the variational method

In the variational method, to perform the calculation for minimizing the free energy, one needs a certain number of physical parameters. The selected system is that of polystyrene polyion [22,23]

Table 1: The details of the simulated colloidal systems.

σ (Å)	T(K)	ε	Z	κσ	$\rho.10^{18}\,(m^{-3})$
1060	300	78	600	0.558	2

First, draw the shape of the potential DLVO

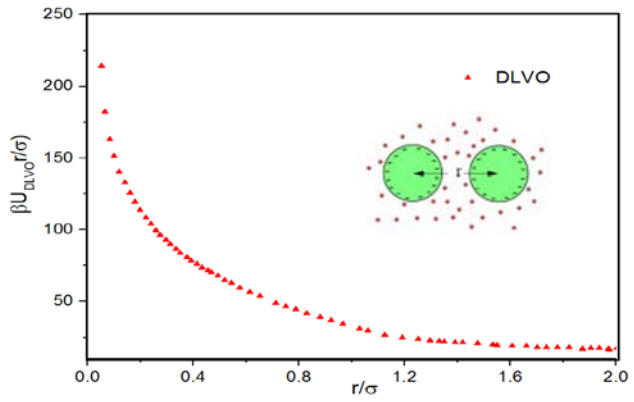

Figure 2: Reduced DLVO potential $\beta U_{DLVO}(r/\sigma)$ versus the renormalized interparticle distance r/σ .

As we reported earlier, the purpose of this section is to make a quantitative study of the structure and thermodynamic properties of dilute colloidal solution of polyballs (in water), using the variational method, with models *HS*, and *CHS*. We will focus on the minimization of the free energy both in the direct space in reciprocal space.

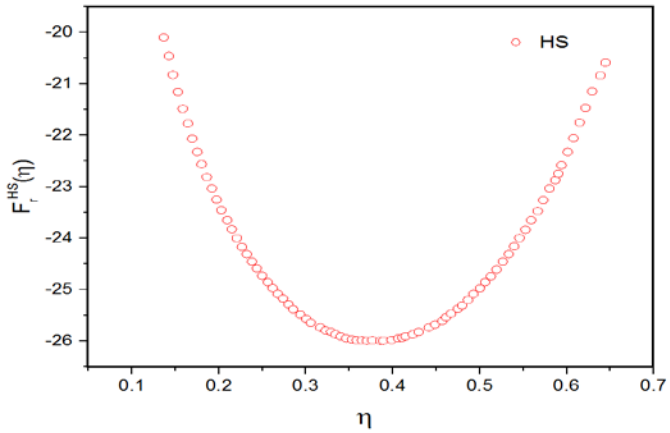

Figure 3: Free energy $F_r^{HS}(\eta)$ in real space as function η , with the HS model.

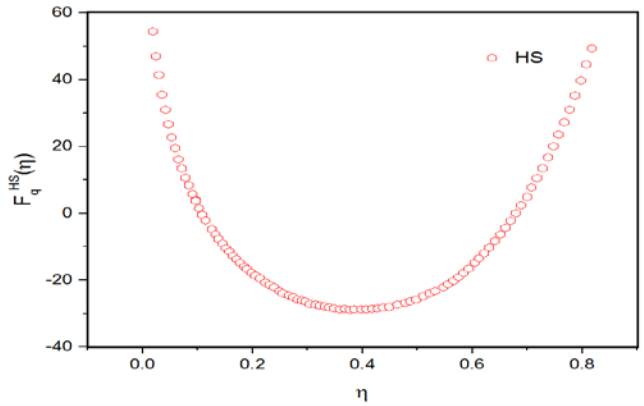

Figure 4: Free energy $F_q^{HS}(\eta)$ in reciprocal space as function η , with the HS model

The first point to be drawn from the curves (3) and (4) is that the value of η corresponding to the minimization of the free energy in the direct and reciprocal space is the same. We can conclude that the value of $\eta_{\min}$ is independent of the space used.

Now let the reference system of charged hard spheres (CHS) used in the minimization of energy by the variational method of GB is the purpose of the following section.

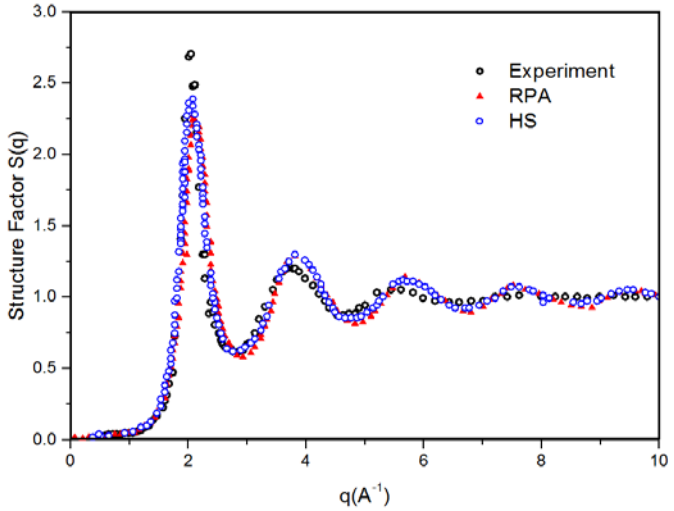

Figure 5: The structure factor $S(q)$ obtained with the RPA reference system in comparison with one obtained with HS reference system and experimental data [30].

Using three different values of the load , $Z = 200 - 400 \; and \; 600$ the curves representing the calculation of minimization of the free energy by the method of GB admit the same value of $\eta = \eta_{\min}$

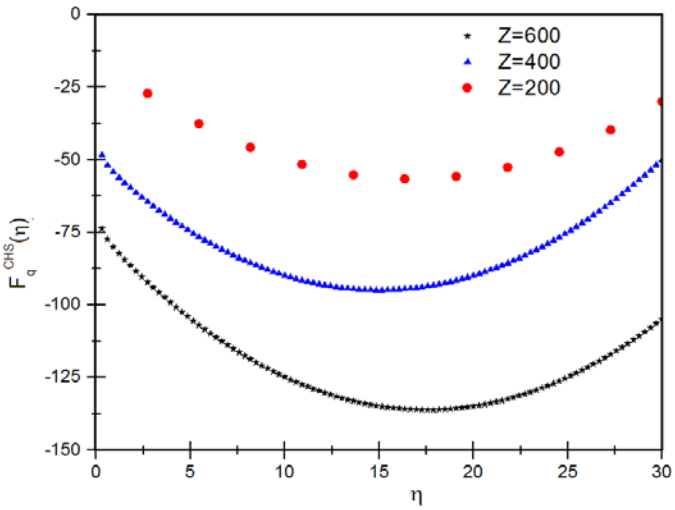

Figure 6: Free energy $F_q^{CHS}(\eta)$ in reciprocal space as function η , with the CHS model.

There is now minimization of the free energy curves with both systems CHS and HS references. In Figure 7, the free energy of CHS system is more stable than that of the HS reference system, with a slight shift of the free energy minimum to the low value of η,

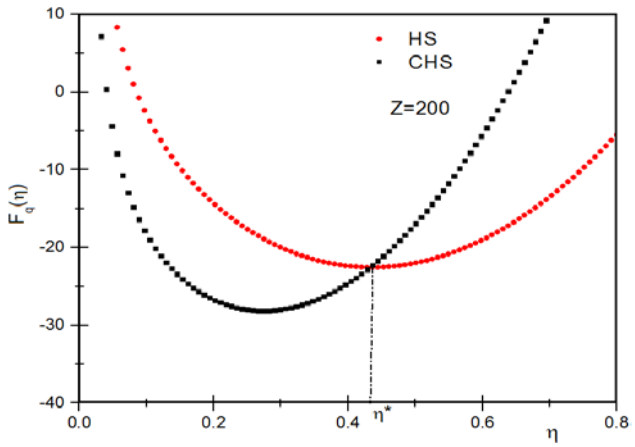

Figure 7: Free energy $F_q(\eta)$ in reciprocal space as function η, with HS and CHS models.

The following table relates the values of the pressure, compressibility and minimal free energy at $\eta = \eta_{\min}$ respectively for *HS* and *CHS* systems, with the load *Z = 600*.

Table 2: Thermodynamic quantities determined by HS and CHS

Z = 600	$\eta_{\min}$	$P/\rho k_B \chi$	$\rho k_B T \chi$
HS	0.53125	16.152	0.129
CHS	0.36875	5.7827	0.056
Potential Yukawa	0.37726	6.0699	0.052

In this table, we used the $\eta_{\min}$ value obtained from the minimization of the free energy in reciprocal space with the model of hard spheres (*HS)* and the model of hard spheres loaded (*CHS)*. As a first approach, we carried the $\eta_{\min}$ in the expression (Eq.72) and (Eq.73), we have compared with the *Yukawa* potential [28]. It turns out that the reference system of hard spheres loaded is in good agreement with the use of the *Yukawa* potential.

Conclusion

In this work, we performed a description of the structural and thermodynamic properties of colloidal solutions. In particular, we have focused on writing the thermodynamic and structural properties based on the variational method for minimizing the Gibbs free energy Bogolyubov (GB), is studied with reference system of hard spheres (HS). The value of η minimizing the free energy, we can calculate the thermodynamic properties of colloidal solutions. The third section is devoted to recall the shape of the potential interaction interionic DLVO necessary in the minimization of the free energy with the reference system of hard spheres loaded (CHS).

Our original contribution concerns the comparison of the two free energy given by the two reference systems. It is the model of CHS and more suited to colloidal systems charged as the HS model. Based on η that minimize the free energy, we calculated the pressure and compressibility that we compared to those obtained by the DM. We conclude that the CHS reference system is more accurate than the HS reference system for the study of colloidal solutions.

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