

Computer Simulations of Colloidal Solutions using Lu-Marlow or Modified Lennard Jones Potentials

K.ELhasnaoui¹, A.Maarouf¹ and M.Ouarch²

¹LPPPC, Sciences Faculty Ben M'sik, P.O.Box 7955, Casablanca, (Morocco); ²CRMEF, 298 Avenue Al Alaouiyyine, P.O. Box 24000, Eljadida, (Morocco).

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Abstract

The purpose of the present work, to study the structural and thermodynamic properties of three discrete potential fluids: Lennard Jones (L-J), Lu and Marlow (L-M) and modified Lennard Jones (L-J)M types. All quantities of interest were computed using the Ornstein-Zernike (OZ) integral equation and HMSA (hybridized-mean spherical approximation) closure relation. The correlation function, structure we found that the LM contribution corrects structure factors, and pressure of the systems thermodynamic properties of the system by taking into account the effect of particle size.

Keywords: Computer simulation, Colloids, Pair-potential, Structure, Thermodynamics, HMSA.

1. Introduction

The designation 'colloid' is used for particles that can be soft or solid and are of some small dimension, ranging from nanometers to tens of micrometers and are dispersed in a liquid or gas, that have been recently investigated by means of both experimental techniques [1,2] and theoretical [3] and numerical studies [4-10]. The great effort is well justified by the importance that these systems play in industrial, biological, and medical applications (paints, inks, pharmaceutical product, waxes, ferrofluids, etc.) [11]. Colloids immersed in a polar solvent (water for instance) often carry an electric charge. This implies a strong Coulombian interaction between colloidal particles. Actually, this interaction is screened out due to the presence of proper counterions and co-ions coming from a salt or an electrolyte [12]. However, particles also experience a long-range Van der Waals attractive interaction. The former is responsible for dispersion, while the second, for flocculation [13]. Dispersion and flocculation. 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, which is a crucial object for determining most physical properties. But, this equation involves another unknown that is the direct correlation function. 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. In order to study the structure, we used a traditional repulsive potential Verwey and an Overbeek, which come from the mutual interaction of electrical double layers surrounding each particle, and a new form of the attractive Van der Waals potential described by Lu and Marlow (L-M) [19,20]. The main advantage of this attractive potential is that it is proportional to the inverse sixth power of the distance, for large separations, and in addition, it involves the size of the particles which justifies its importance. In Sec III we use the (L-J) pair potential, then we introduce the (L-M) contribution in the repulsive part of the (L-J) pair potential and finally we present the bridge function variation [21] and its dependence on particle sizes or solution density, respectively. 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 how we use the Lennard Jones (L-J) pair potential, then we introduce the Lu and Marlow (L-M) contribution in the repulsive part of the (L-J) pair potential. We draw our conclusions in Sec. IV.

Theory

A. Pair-potential

In this paper, we used a new expression for the potential of van der Waals proposed given by Lu and Marlow (L-M)

[19,20], and that takes into account the effect of finite particle size. This potential has all the characteristics of a semi-empirical potential Van der Waals. Even if it was applied only to an ordinary molecules, it can be used universally in the form:

$$U^{LM}(r) = -\frac{C_6}{r^6} f_6(r) \tag{1}$$

where C_6 is a frequency integration of the polarization density function and the so-called nonretarded distance damping function $f_6(r)$ is:

$$f_6(r, \sigma_j) = \frac{1}{3} \prod_{j=1}^2 \left[1 - \left(1 - \frac{r}{\sigma_j} + \frac{1}{2} \left(\frac{r}{\sigma_j} \right)^2 \right) e^{-r/\sigma_j} \right] + \frac{2}{3} \prod_{j=1}^2 \left[1 - \left(1 - \frac{r}{\sigma_j} + \frac{1}{2} \left(\frac{r}{\sigma_j} \right)^2 + \frac{1}{4} \left(\frac{r}{\sigma_j} \right)^3 \right) e^{-r/\sigma_j} \right]. \tag{2}$$

Here σ_1 and σ_2 are two parameters that characterize the atomic or molecular size in the case of atoms or small molecules. In this article, σ_1 and σ_2 are set equal since the considered condensed bodies are always composed of the same kind of molecules.

$$f_6(r) = \frac{1}{3} \left\{ 1 - \left(1 + \frac{r}{\sigma} + \frac{1}{2} \left(\frac{r}{\sigma} \right)^2 \right) e^{\frac{r}{\sigma}} \right\}^2 + \frac{2}{3} \left\{ 1 - \left(1 + \frac{r}{\sigma} + \frac{1}{2} \left(\frac{r}{\sigma} \right)^2 + \frac{1}{4} \left(\frac{r}{\sigma} \right)^3 \right) e^{\frac{r}{\sigma}} \right\}^2, \tag{3}$$

For simplicity, let $\sigma_1 = \sigma_2 = \sigma$. When the distance r tends to infinity, the function $f_6(r)$ tends to 1 and $U^{LM}(r)$ tends asymptotically to $-C_6/r^6$ according to plan, but $U^{LM}(r \rightarrow 0) = -C_6/72a^6$, which shows that the potential is finite for any distance. While extremely low long distance, it is larger than the electrostatic repulsion. The grouping together of the two potentials of interaction leads to a minimum adjacent the point $r = 2a$

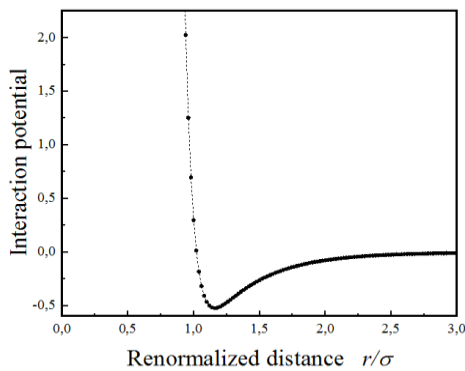


Figure (1) Reduced Lu-Marlow (L-M) potential $U^{LM}(r)/k_B T$ versus the renormalized distance r/σ .

Another pair-potential used here is that derived by Lennard-Jones (L-J).The repulsive part of the potential(L-J)is greater than the attractive part at small distances, and inversely at long distances. After this analysis, the potential has the following expression [21]

$$U^{(L-J)}(r) = \begin{cases} -\varepsilon & r < r_m \\ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r_m < r < r_c \\ 0 & r > r_c \end{cases} \tag{4}$$

where σ and ε are, respectively, the well depth is and distance parameters of the (L-J), r_c is the cutoff distance, r_m is the distance where the intermolecular potential reaches a minimum. In the (L-J) potential, the short-range repulsion is thought to be dominated by the standard r^{-12} law, whereas the long range London attraction varies as r^{-6} law. Thus, the repulsive part is set with a power 12 only for convenience, whereas the attractive part has a good theoretical foundation based on three different effects; the dispersion force, the permanent charge distribution and the induced.

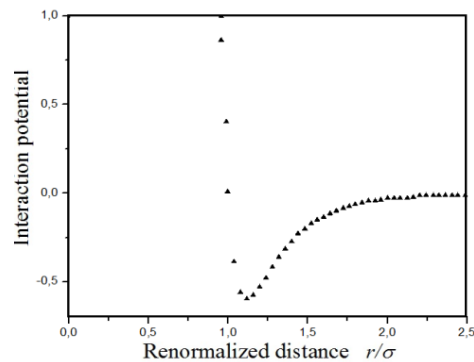


Figure (2) Reduced (L-J) potential $U^{L-J}(r)/k_B T$ versus the renormalized distance r/σ , for three values of temperatures and particles sizes: ($T=308$ K, $\sigma=36nm$)

$$\frac{\partial}{\partial r} U^{(L-J)}(r) = 12\varepsilon \left(\sigma^6 \frac{1}{r^7} - 2\sigma^{12} \frac{1}{r^{13}} \right), \tag{5}$$

The position of the potential minimum r_m is given as

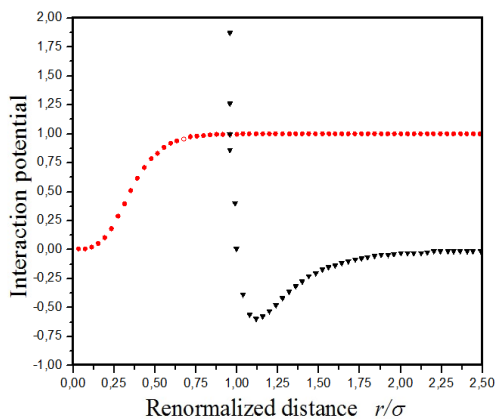
$$r_m = (2\sigma)^{1/6} = 1,122 * \sigma^{1/6}, \tag{6}$$

The expression (3) and (5) in the birth of a new term to the(L-J) potential

$$U^{(L-J)}(r) = \begin{cases} -\varepsilon & r < r_m \\ \varepsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] & r_m < r < r_c \\ 0 & r > r_c \end{cases} \tag{7}$$

The New pair potential, which modifies the (L-J)^Mone [22]:

$$U^{(L-J)^M}(r) = \begin{cases} -\varepsilon & r < r_m \\ 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 f_6(r) \right] & r_m < r < r_c \\ 0 & r > r_c \end{cases} \quad (8)$$



Figure(3) Variation of the pair potential versus the renormalized interparticle distance with (L-J) potential modified by the (L-J)^M contribution

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

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.

It is easy to see that, on the right hand side of the above equation. By convention, repulsive (short-range) forces are positive while attractive (long-range) forces are negative.

The first derivative of the expression of (L-J) potential he presented as follows

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

$$S(q) = 1 + \rho \int (g(r) - 1) \exp(iqr) dr \quad (9)$$

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

$$E / \langle N \rangle = (3/2) k_B T + 2\pi \int u(r) g(r) r^2 dr, \quad (10)$$

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

$$P = \rho k_B T - 2 \frac{\pi \rho^2}{3} \int \frac{r du(r)}{dr} g(r) r^2 dr \quad (11)$$

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:

$$\chi_T^{-1} = \rho \left[\frac{\partial P}{\partial \rho} \right]_T = \rho k_B T - \left(\frac{4\pi \rho^2}{3} \right) \int r \left(\frac{du(r)}{dr} \right) \left\{ g(r) + \left(\frac{\rho}{2} \right) \left(\frac{\partial g(r)}{\partial \rho} \right) \right\} r^2 dr, \quad (12)$$

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

$$S(q=0) = \rho k_B T \cdot \chi_T = 1 + 4\pi \rho \int (g(r) - 1) r^2 dr \quad (13)$$

We can note that the isothermal compressibility χ_T deduced 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 $c(r)$ [23, 24], is given by

$$h(r) = c(r) + n \int c(|r-r'|) h(r') dr', \quad (14)$$

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

$$g^{HMSA}(r) = \exp[-\beta U_1(r)] \times \left\{ 1 + \frac{\exp [f(r) \{ \gamma(r) - \beta U_2(r) \} - 1]}{f(r)} \right\}, \quad (15)$$

where the interaction potential is divided into short-range part $U_1(r)$ and long-range attractive tail $U_2(r)$ as prescribed by Weeks et al [25]. There, the function $\gamma(r)$ is simply the difference between the total and direct correlation functions, i.e., Quantity $\gamma(r) = h(r) - c(r)$ is the mixing function [6], whose a new form was proposed by Bretonnet and Jakse [26]. 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 [26]

$$f(r) = f_0 + (1 - f_0) \exp(-1/r), \quad (16)$$

where the is f_0 the interpolation constant. This an adjustable parameter such that $0 \leq f_0 \leq 1$. 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.,

$$S(0) = nk_B T \chi_T. \tag{17}$$

3. Results and Discussion

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. Potentials used here are of Lu-Marlow type, and the choosing mixing function is that pointed out in [26].

Firstly, we have computed the main object that is the pair-correlation function $g(r)$ versus the renormalized interparticle distance r/σ Fig2.

Secondly, we have reported in Fig. 3 the structure factors versus the renormalized wave-vector computed using integral equations method. Remark, first, that the results obtained within the integral equations HMSA are in good agreement as in the case of the pair-correlation function discussed above. The important remark is that, the height of the peak of increase proportionately with increasing density with (L-M) potential for $T=308\text{ K}$ and $\sigma=36\text{nm}$.

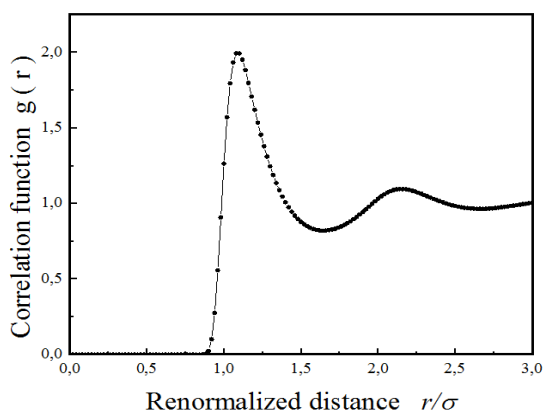


Figure (4) Plot representing the correlation function $g(r)$ with (L-M) potential for ($T=308\text{K}$, $\sigma=36\text{nm}$)

Thirdly, in Fig. 4, we have reported the structure factors computed using the integral equation versus the renormalized wave-vector $q\sigma$. The obtained results present our numerical prediction concerning the variation of the structure factor in the (L-J) pair-potential

case, it is easy to see that , the structure factor presents some oscillations reflecting the interaction between near neighbors and the system's fluctuations. These oscillations design generally a morphologic transition in the Pluronic solution.

Finally, in the same figure, Fig. 6, we plot the structure factor in the (L-J)^M pair-potential. That is to be expected since, from its definition, $f_6(r)$ corrects the London attraction. This correction appears clearly in the (L-J)^M potential and confirms the difference between (L-J)^M and (L-J) pair potentials.

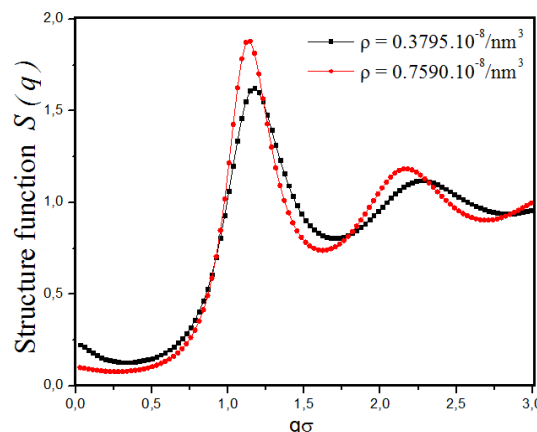


Figure (5) Variation of the structure factor for various densities with (L-J) potential for ($T=308\text{K}$, $\sigma=36\text{nm}$)

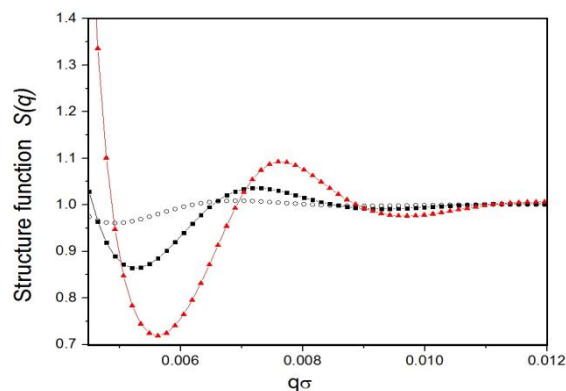


Figure (6) Comparison of the structure functions computed with the modified (L-J)^M potential by the HMSA integral equation for various temperatures and particle sizes

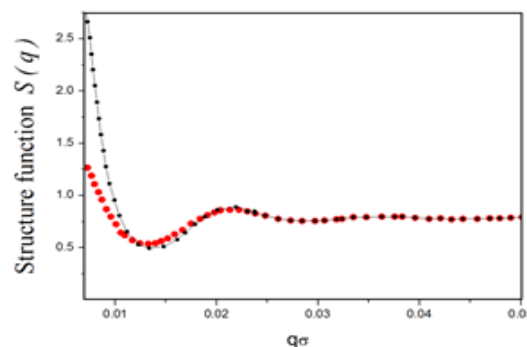


Figure (7) Comparison between the structure factors calculated with the (L-J) potential and with the (L-J)^M potential for

Table (4) Thermodynamic proprieties for (L-J) and (L-J)^M potentials, within HMSA integralequation method, for value of the interpolation constant

(L-J) Potential				(L-J) ^M Potential			
$T(K)$	$\rho k_B T \chi$	$E / nk_B T$	$P / \rho k_B T$	$T(K)$	$\rho k_B T \chi$	$E / nk_B T$	$P / \rho k_B T$
308	2.62	-0.62	0.67	308	1.38	-0.36	0.67
310	2.35	-0.58	0.70	310	1.35	-0.34	0.70
312	2.16	-0.54	0.72	312	1.31	-0.31	0.72
315	1.93	-0.48	0.74	315	1.24	-0.28	0.74
318	1.71	-0.41	0.78	318	1.18	-0.23	0.78
321	1.76	-0.45	0.77	321	1.23	-0.27	0.77
323	1.81	-0.46	0.76	323	1.26	-0.29	0.76
325	1.86	-0.48	0.75	325	1.28	-0.31	0.75
328	1.95	-0.51	0.74	328	1.30	-0.32	0.74

First, it can be observed that the parameter f_0 ensuring thermodynamic coherence, defined in ref. [30], takes the same values for the two considered pair potentials. On the other hand, and in the two cases presented below, $T = 318$ K is a remarkable temperature for all thermodynamic quantities. Indeed, in the range of temperatures between 308 K and 318 K, the compressibility of the system decreases. In parallel, the internal energy .From these considerations, we can confirm that the thermodynamics of the system is related to the particle size if we compare it with the hydrodynamic diameter variation. Consequently, $T = 318$ K is a veritable temperature of transition of the particles' morphology leading to a transition in the thermodynamic properties of the considered system.

Conclusion

We recall that the purpose of this paper is the determination of the structure and thermodynamics of a monodisperse colloidal solution. We assumed that the interaction potential between colloids is of (L-J)^M or (L-M) types . In this work we are interested in studying the stability of a colloidal solution. The stability of such a solution results from the balance between attractive and repulsive interactions exerted on the particles by preventing the aggregation of particles of the dispersed phase. The two main mechanisms of stabilization are steric stabilization and electrostatic stabilization case before us that we have at hand. In this study, we have used a new expression for the potential of Van der Waals described by (L-M) and (L-J)^M, which takes into account the finite size of the particles. To test these potentials, we have calculated the structure factor. As a method, we use the HMSA method.

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