STABILITY OF CHARGED COLLOIDAL SYSTEMS WITH BOTH A SHORT-RANGE YUKAWA ATTRACTION AND LONG-RANGE LIKOS REPULSION

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Abstract- In this overview, The principles that govern colloid stability are of manifold importance to many different technologies, there are at least two general mechanisms whereby colloid stability is imparted : electrostatic stabilization and steric stabilization. The standard method for describing the interaction between two charged particles and in general two charged surfaces in a solvent is the non-linear Poisson Boltzmann equation. The effective colloid-colloid interaction potential is given by the electrostatic part of the classical Derjaguin-Landau-Vervey-Overbeek (DLVO) theory with Combining this elec trostatic repulsion Likos (LR) with Yukawa (YA) attraction forms the basis of theory of colloid stability due to Deyaguin-Landau-Verwey-Overbeek (DLVO theory), this theory can explain the conditions of stability/instability of colloidal particles.

Keywords - Colloids; Charge interaction; Short-range attraction; Long-range repulsion; DLVO Theory; HMSA; Structure; Thermodynamics.

I. INTRODUCTION

The stability of colloidal systems [1-2] is an important subject from both academic and industrial points of view. These systems include various types such as solid–liquid dispersions (suspensions), liquid–liquid dispersions (emulsions) and gas–liquid dispersions (foams). The colloid stability of such systems is governed by the balance of various interaction forces such as van der Waals attraction, double-layer repulsion and steric interaction [3]. These interaction forces have been described at a fundamental level such as in the well-known theory due to Deryaguin and Landau [4] and Verwey and Overbeek [5] (DLVO theory), has been the starting point to understand the stability of charged colloids and their solution properties even though more and more systems have been found that the DLVO potential is not sufficient to describe the observed properties[6-7]

A *DLVO* potential basically consists of two terms: a charge repulsion and a van der Waals attraction. The range of the repulsive interaction can be either longer or shorter than that of the attraction depending on many factors, such as ionic strength and colloidal particle size. In this theory, the van der Waals attraction is combined with the double-layer repulsion and an energy–distance curve can be established to describe the conditions of stability/instability. The origin of stability resulting from the presence of adsorbed or grafted polymer layers was established [8] With an appropriate combination of the potential parameters of both a short-range attraction (*Yukawa*) (*YA*) and a long-range repulsion (*Likos*) (*LR*), computer simulations [9-12] theoretical works [13-16] and experimental results [17-24] have conclusively demonstrated that rich phase behavior can be observed in a system with both a YA and LR (*YALR*) interaction. By controlling the potential parameters, a system can have different phases such as cluster crystals, lamellar phase, and Wigner glass. Therefore, systems with a *YALR* interaction provide scientists great freedom to control the structure of systems by tuning the interaction potential so that the desired

macroscopic properties can be obtained. In particular, controlling cluster formation is very important for many protein systems since protein clusters are important for the understanding of protein crystallization, protein solution phase diagrams, and the formulation stability of monoclonal antibody drugs in the pharmaceutical industry. Especially, the mechanisms of cluster formation in monoclonal antibody solutions are very important for the delivery of therapeutic drugs to patients through the subcutaneous injection [25,26]. According to this theory [4-5] the stability of a colloidal suspension is determined by forces of Van der Waals attractive causing aggregation and repulsive forces which result in the dispersion of the particles. When the electrostatic repulsions dominate the particles remain dispersed in the state that is to say the suspension is stable.

On the other hand, increasing the ionic strength of the medium by addition of a salt, for example, strongly attenuates this repulsion, and the suspension and then becomes unstable and tends to flocculation. Although DLVO [4-5] theory is understanding and justification of several properties of colloidal suspensions [27-30]. The colloidal particles are stabilized when the surface charge of the particle is not zero and when the thickness of the double layer is large (in the presence of low ionic strength, thus a low electrolyte concentration).

The stabilization of colloids with a grafted polymeric layer is the subject of many studies. The fundamental problem to solve is the knowledge of the nature of the effective force between particles. As we said above, such a force results from the excluded volume effect .The first theoretical work was due to Witten and Pincus (*WP*), [31]. In this paper, which is our original contribution, the system studied is that of a colloidal particle charge on its surface grafted polymer chain f polymerization degree N. We seek the appropriate potential, which takes into account the effect of electric loads and of the interaction between colloidal particles, to describe these structural and thermodynamic properties. For this we will use the method of integral equations *HMSA* [32-35]. 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 .The paper is closed with concluding remarks in Sec. IV.

II. THEORETICAL FORMULATION

A. SHORT-RANGE YUKAWA TYPE ATTRACTIONS

The system studied in this paper is that colloidal particles in presence of electric charges. On a particle graft polymer chains of degree of polymerization N. When the size of the colloids is very small compared to the radius of gyration of the polymer chains, the assembly is then similar to the polymer system star, whose theory is well established by Cotton Daoud like [32]. In fact, the charged systems are generally more complex than neutral polymers such systems. The interactions between the charged colloids, which determine the phase and structural behavior of the suspension, is mediated by the presence of micro-ions clouds. The complete description of the system is thus a formidable task in general. However in view of the large asymmetry of size and charge between macro-and micro- ions, one expects to be able to integrate out the micro-ions degrees of freedom, and obtain an effective description involving macro-ions only. In the pioneering work of Derjaguin, Landau, Verwey, and Overbeek [5] micro-ions clouds are treated at the mean-field Poisson-Boltzmann level, yielding the foundations of the prominent DLVO theory for the stability of lyophobic colloids. An important prediction of the theory is the effective interaction pair potential between two spherical colloids of radii a in a solvent which, within a linearization approximation, takes the Yukawa or Debye–Huckel [36] form,

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

There, r is the interparticle center-to-center distance,σ the hard-sphere diameter, ε_d the relative permittivity of solvent (water), ε the permittivity of free space, and κ the Debye- Hückel, 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

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

We have used the notations $x = r/\sigma$ and $k = \kappa\sigma$ where $\kappa\sigma \ll 1$, 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.

B. LONG-RANGE LIKOS TYPE REPULSION

Let us now turn to star polymer solutions. A star polymer consists of f linear polymer chains that are attached to a common microscopic core [37]. The typical extension of such a star in a good solvent is governed by the so-called corona diameter σ, which measures the spatial extension of the monomer density around a single star. In a concentrated solution with a finite star number density ρ, the stars are interacting. The interaction is repulsive due to the restriction of allowed configurations for the polymer chains from different centers. In a first approximation, the interaction is pairwise. An explicit form for the pair potential V(r) (where r denotes the interparticle distance) was proposed recently: it consists of an ultra-soft part inside the coronae and falls off exponentially with core–core distance r outside the coronae of two stars. In detail,

$$\beta U_{LR}(r) = \frac{5}{18}f^{3/2}\begin{cases} -\ln\left(\dfrac{r}{\sigma}\right)+\left(1+\dfrac{\sqrt{f}}{2}\right)^{-1} & r \leq \sigma, \\ \left(1+\dfrac{\sqrt{f}}{2}\right)^{-1}\left(\dfrac{\sigma}{r}\right)\exp\left[-\dfrac{\sqrt{f}}{2}\left(\dfrac{r}{\sigma}-1\right)\right] & r > \sigma. \end{cases} \quad (5)$$

Here $k_B T$ is the thermal energy and f is the arm number of a single star. As the effective interaction is purely entropic, it simply scales with the thermal energy. There are many facts confirming that this pair potential (4) provides for a reasonable description of the effective interaction between the stars:

(i) The behavior for very small $r(r \ll \sigma)$ is consistent with scaling theory [38,39].

(ii) Microscopic molecular dynamics computer simulations have been performed for several values of f and different numbers of monomers per chains [40].

They reproduce perfectly the overall shape of the effective interaction.

(iii) The scattering intensity for small-angle neutron scattering data could be well described by this pair potential without any fitting parameter for an 18-arm star [39, 41].

We are going to be considering the case of stars with long chains in semi-dilute solvent of start-polymer, we propose the following change of variables in the expression of potential, we set

$$\frac{r}{\sigma} = \frac{r}{R_g} \times \frac{R_g}{\sigma} \quad (6)$$

$$x = \frac{r}{R_g} , \ \xi = \frac{R_g}{\sigma} \quad (7)$$

Potential can be written

$$\beta V(r) = \frac{5}{18}f^{3/2}\begin{cases} -\ln\left(x.\xi\right)+\left(1+\dfrac{\sqrt{f}}{2}\right)^{-1} & x \leq 1, \\ \dfrac{1}{x\xi}\left(1+\dfrac{\sqrt{f}}{2}\right)^{-1}.\exp\left[-\dfrac{\sqrt{f}}{2}\left(x.\xi-1\right)\right] & x > 1. \end{cases} \quad (8)$$

When comparing the part of the potential by Yukawa described [42] with the Boltzmann factor $\exp\left[-V(r)/k_B T\right]$ found that the number of branch f plays the role of the inverse temperature.
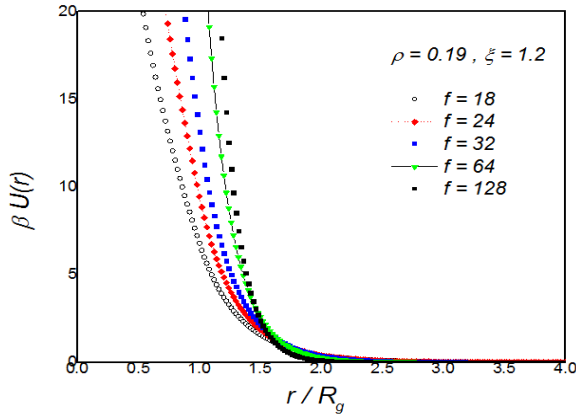
Fg.1 Potential interaction of Likos (LR) as function of distance for various f -values [43].

The potential is shown in figure 1 for various values of functionality f .It can be seen that it becomes harder with increasing f ,tending eventually to a hard-spheres (HS) interaction which formally obtains in the limit $f \rightarrow \infty$ [40].

Table.1. Typical values of isotherm compressibility, virial pressure and energy , for 4 values of f , with fixed parameters (T(K)=298, σ (Å)=1090 and ρ =0.19.

α_i	f	$\alpha_f /10$	$\rho k_B T\chi 10^{-2}$	$\Delta E / E_0$	P_{virial}
0.6	18	7.5	5.24253	4.98171	8.68308
0.7	32	7	3.85131	4.88312	10.57060
0.7	64	6.099	3.13501	4.22339	11.61335
0.5	128	5.4	3.04212	2.73978	12.38417

The table. **1** shows that the pressure increases with the number of chains f , but both energy and the compressibility decreases. This is in agreement with the physical prediction which are essentially due to the increase of the material in the solution, and the system becomes less compressible.
The combination of the two potential equation leads to the following relationship mixtures Yukawa-Likos potential (YALR).

$$\beta U_{YALR}(r): \begin{cases} \beta\dfrac{(Ze)^2}{4\pi\varepsilon\varepsilon_0}\left(\dfrac{e^{\kappa a}}{1+\kappa a}\right)^2\dfrac{e^{-\kappa r}}{r}-\dfrac{5}{18}f^{3/2}\left[\ln\left(\dfrac{r}{\sigma}\right)-\left(1+\dfrac{\sqrt{f}}{2}\right)^{-1}\right] & r\le\sigma, \\[3mm] \beta\dfrac{(Ze)^2}{4\pi\varepsilon\varepsilon_0}\left(\dfrac{e^{\kappa a}}{1+\kappa a}\right)^2\dfrac{e^{-\kappa r}}{r}+\dfrac{5}{18}f^{3/2}\left[\left(1+\dfrac{\sqrt{f}}{2}\right)^{-1}\left(\dfrac{\sigma}{r}\right)\exp\left[\dfrac{\sqrt{f}}{2}\left(\dfrac{r}{\sigma}-1\right)\right]\right] & r>\sigma, \end{cases} \quad (9)$$

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 pair potential $u(r)$ which mobilize the interactions between the particles. The calculation of the structure, represented by the function of radial distribution $g(r)$, is an 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

$$S(q) = 1 + \rho\int\left(g(r)-1\right)\exp(iqr)dr \qquad (10)$$

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

$$E / \langle N \rangle = (3/2)k_B T + 2\pi\int u(r) g(r) r^2 dr, \qquad (11)$$

k_B is the constant of Boltzmann, the virial pressure

$$P = \rho k_B T - 2\frac{\pi\rho^2}{3}\int\frac{rdu(r)}{dr}g(r)r^2 dr \qquad (12)$$

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

$$\chi_T^{-1} = \rho k_B T - \left(\frac{4\pi\rho^2}{3}\right)\int r\left\{\frac{d u(r)}{d r}\right\}\left\{g(r)+\left(\frac{\rho}{2}\right)\left(\frac{\partial g(r)}{\partial\rho}\right)\right\}r^2 d r, \qquad (13)$$

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

$$S(q{=}0) = \rho k_B T.\chi_T = 1 + 4\pi\rho\int\left(g(r)-1\right)r^2 dr \qquad (14)$$

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

$$h(r) = g(r)-1 \qquad (15)$$

The OZ integral equation that involves the so-called direct correlation function [44, 45], $c(r)$ is given by

$$h(r) = c(r) + n\int c\left(|r-r'|\right) h(r')dr' , \qquad (16)$$

where n is the number density of macro ions. 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

$$g(r) = \exp\left[-\beta U_1(r)\right]\times\left\{1+\frac{\exp\left[f(r)\{\gamma(r)-\beta U_2(r)\}-1\right]}{f(r)}\right\}, \qquad (17)$$

Here 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 [46]. There, the function $\gamma(r)$ is simply the difference between the total and direct correlation functions, $\gamma(r)=h(r)-c(r)$ i.e., Quantity $f(r)$ is the mixing function [47], whose a new form was proposed by Bretonnet and Jakse [48]. 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 [48]

$$f(r) = f_0 + (1-f_0)\exp(-1/r), \qquad (18)$$

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

$$S(q{=}0) = \rho k_B T.\chi_T \qquad (19)$$

III. RESULTS AND DISCUSSION

we first start with the study of the Yukawa potential before the introduction in the code.

Table. 2. The details of the simulated colloidal systems.

σ (Å)	1090
T(K)	298
ε	78
Γ	2537
ρ	0.00037
$\kappa\sigma$	0.558

We begin to plot the shape of the Yukawa potential for different values of Z.
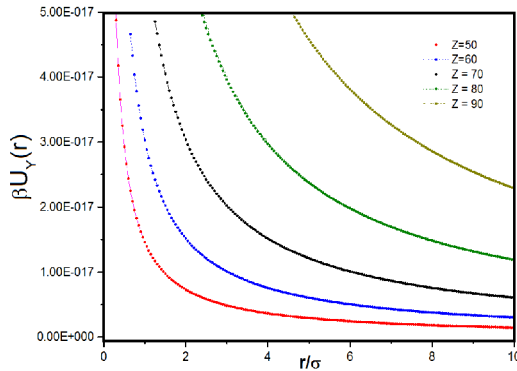
✓ **Small values of Z**

Fg.2 Yukawa potential as function of distance r/σ for different values of Z

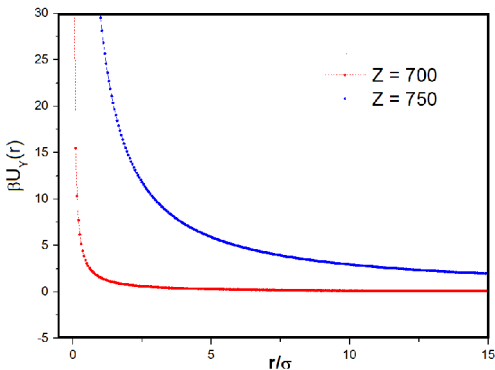✓ **Large values Z**

Fg.3 Yukawa potential as function of distance r/σ for different values of Z

We see that when the charge z increases, the Yukawa potential believes. In fact when electrical charge are increasing in a system, the interactions are growing as it should be

A- Charge variation on electrostatic

As a first result, it is interesting to compare the Yukawa potential electrostatic origin, for different values of Z than likos that governs the interactions of colloids of them

as
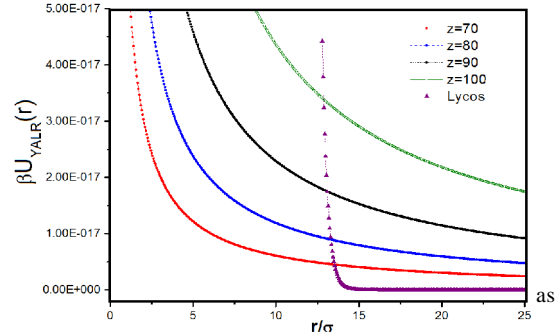
B- Variation of number of Chains

In this part, we present the calculations, we have the same values of parameters as in experiment by Tata et al [49].

Table. 3. The details of the simulated colloidal systems.

σ (Å)	1090
T(K)	298
z	800
ρ	0.19

Table.4. Typical values of isotherm compressibility, virial pressure and energy, for 4 values of f , with fixed parameters (see table **3**).

α_i	f	$\alpha_f/10$	$\rho k_B T\chi 10^{-2}$	$\Delta E/E_o$	P_{virial}
0.79	18	8	4.35694	5.97108	10.43857
0.79	32	7.6	3.11357	6.40256	13.25465
0.79	64	7.1	2.46031	4.78171	14.50069
0.79	128	5.2	2.23954	3.95437	15.30790

The table 4 shows that for a electric charges, the pressure increases with the number of chain *f*, while energy and compressibility decreases as in the case of potential Likos (see table 2). If we compare the results in Table 4 to that of Table 2, we see the influence of the presence of electric charges primarily for low values of *f*. So when *f* increases (*f* = 128) the values of energy, pressure and compressibility of the two tables coincide, ie the effect that the load effect is completely shielded by the polymer chains *f*.
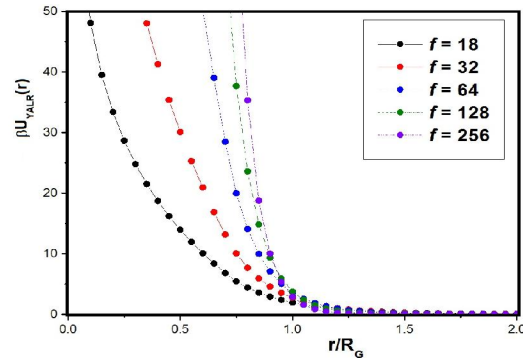

Fg.5 Potential interaction of Yukawa-Likos(YALR) as function of distance for various f -values.

A- Variation of number of Chains

Table.5. Typical values of isotherm compressibility, virial pressure and energy, for 4 values of f , with fixed parameters (see table **3**)

α_i	f	$\alpha_f /10$	$\rho k_B T \chi 10^{-2}$	$\Delta E / E_0$	P_{virial}
0.79	32	7.6	3.11357	6.40256	14.25465
0.79	64	7.1	2.46031	5.78171	13.50000
0.79	128	5.2	2.23954	3.95437	12.30790
0.43	256	4.3	2.1064	2.17231	10.75768

The table 5, shows that the pressure increases and energy decreases with the number of system, while the compressibility decreases, In fact, the system is less compressible with the increase of the number of grafted chains, as well as the energy excess.
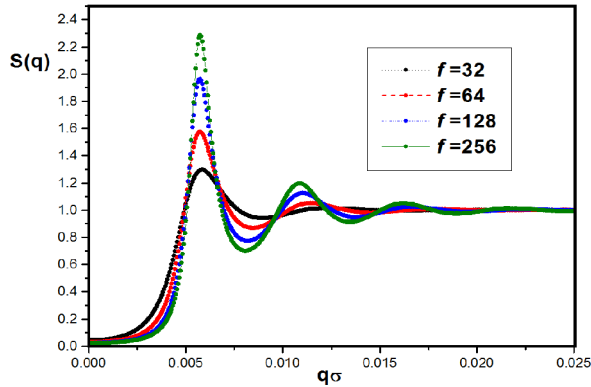

Fg.6 Structure factor $S(q)$ versus the dimensionless wavenumber $q\sigma$ as for 4 values of f, with fixed parameters :
T = 298 K, Z = 800, ρ/ρ^* = 0.8 .

Table.6. Typical values of isotherm compressibility, virial pressure and energy, for 4 values of ρ/ρ^* , with fixed parameters : T = 298 K, Z = 800, f = 32

α_i	ρ/ρ^*	$\alpha_f /10$	$\rho k_B T \chi 10^{-2}$	$\Delta E / E_o$	P_{virial}
0.79	0.6	7.1	3.84829	4.88874	10.57859
0.79	0.7	7.6	3.11415	6.40201	13.25378
0.3	0.8	7.9	2.65216	8.07479	16.13467
0.3	0.9	8.3	2.29104	9.90749	19.21361

The table 6 shows that pressure and energy increases with increasing the density, but the isotherm compressibility decreases.
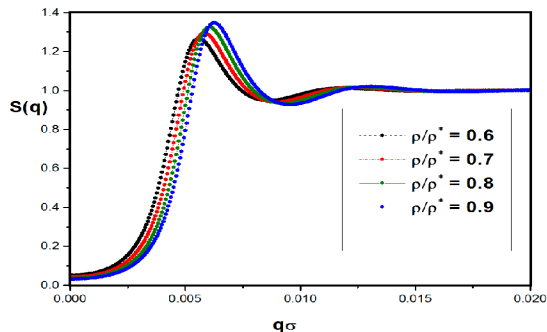

Fg.7 Structure factor $S(q)$ versus the dimensionless wavenumber $q\sigma$ as for 4 values of ρ/ρ^*, with fixed parameters :
T = 298 K, Z = 800, f = 32

III. CONCLUSIONS

In this study, we have introduced various forms of Likos type then the Yukawa potential to reflect the presence of electrical charge. We considered a physical system of a semi-dilute colloids small diameters on which was grafted polymer chains f polymerization degree N, which can be seen as a star polymers in the presence of electric charges. We have combined for it forms of two potential namely to Likos for the interaction of the star polymers then Yukawa to study the influence of the presence of electric charges. It is found that the presence of electric charge affects the structural and thermodynamic properties as the number of grafted polymers f branch is low.

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