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## Liquid-state theory of charged colloids

Y. LEVIN, M. C. BARBOSA and M. N. TAMASHIRO

*Instituto de Física, Universidade Federal do Rio Grande do Sul  
Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil*

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**Abstract.** – A simple theory of the fluid state of a charged colloidal suspension is proposed. The full free energy of a polyelectrolyte solution is calculated. It is found that the counterions condense onto the polyions forming clusters composed of one polyion and  $n$  counterions. The distribution of cluster sizes is determined explicitly. In agreement with the current experimental and Monte Carlo results, *no* liquid-gas phase separation was encountered.

The thermodynamic properties of systems in which the predominant interactions are due to the long-ranged Coulomb potential still remain largely not understood in spite of the tremendous effort that has been invested over the span of this century. Nevertheless, it would be unfair to say that no great progress has been done. The pioneering work of Debye and Hückel [1] has led to our understanding of dilute electrolyte solutions. The subsequent improvements by Bjerrum extended the validity of the limiting laws to larger densities [2]. These developments were followed by the introduction of powerful integral equations and by the computational methods such as Monte Carlo (MC) simulations [3]. Surprisingly, the theoretically obtained coexistence curve [4], that is in closest agreement with MC, is based on the fundamental ideas advanced by Debye, Hückel and Bjerrum more than 70 years ago [1]. The simplicity and the transparency of the ideas forming the basis of the Debye-Hückel-Bjerrum (DHBj) theory makes it easy to apply to other Coulombic systems [5].

The charged colloidal suspensions present a severe challenge to any statistical-mechanics theory. The asymmetry between the charge on a polyion and a counterion, which can be as high as 10000:1, makes the usual integral equations of the liquid-state theory impossible to solve. For low charge asymmetry, less than 20:1, it was found that there exists a region in the temperature density plane where the Hypernetted Chain equation (HNC) ceases to have solutions [6]. This could be interpreted as a region of instability, in which the sample phase separates into the coexisting liquid and gas. It is, however, still unknown to what extent the break down in HNC equation can be attributed to the underlying phase separation, since the region of instability of HNC does not coincide with the true spinodal line [7]. Furthermore, the

extensive experimental and simulation search for this gas-liquid transition for polyelectrolytes has, so far, proven to be futile [3] [8].

At high volume fractions the strongly charged polyions form a lattice (bcc or fcc). This “solid state” provides us with a major simplification in that each polyion can be studied individually inclosed in its own Wigner-Seitz cell and surrounded by its own counterions [9]. Unfortunately, once the lattice melts the cell picture is no longer valid [10]. As is usual, the liquid state is significantly more complex than the solid state.

In this letter we shall attempt to construct a theory for the fluid state of a polyelectrolyte solution. We shall work in the context of the Primitive Model of Polyelectrolyte (PMP) [5]. Our system will consist of  $N_p$  polyions inside a volume  $V$ . The polyions will be idealized as hard spheres of radius  $a$ , each carrying  $Z$  ionized groups of charge  $-q$  uniformly spaced along the surface. A total of  $ZN_p$  counterions will be present to preserve the overall charge neutrality of the system. For simplicity, we shall take the counterions to be point-like and to carry charge  $+q$ . The solvent will be represented as a uniform medium of a dielectric constant  $D$ . As was pointed out by Onsager [11], the full non-linear Poisson-Boltzmann (PB) equation is electrostatically inconsistent for the asymmetric systems, linearization then, besides simplifying the calculations, is an important step in restoring the self-consistency of the theory. The fundamental assumption behind the DHBj theory is that the non-linearities omitted in the process of linearization of the PB equation can be reintroduced into the theory through the allowance for ion association. In general, we expect that the fluid state of the asymmetric electrolyte will be composed of free unassociated polyions of density  $\rho_0$ , free counterions of density  $\rho_f$ , and of clusters consisting of *one* polyion and  $0 < n \leq Z$  associated counterions. The density of clusters with  $n$  counterions is  $\rho_n$ . In the discussion that will follow we shall suppose that the condensed counterion neutralizes one of the polyion charges, in such a way that the effective surface charge of a  $n$ -cluster is  $\sigma_n = -q(Z - n)/(4\pi a^2)$ . It is evident that  $\rho_p = \sum_{n=0}^Z \rho_n$  and  $Z\rho_p = \rho_f + \sum_{n=0}^Z n\rho_n$ , where  $\rho_p = N_p/V$  is the total density of polyions (associated or not). All the thermodynamic properties of the polyelectrolyte solution can be determined once the free energy is known. In particular, the osmotic pressure is a Legendre transform of the Helmholtz free-energy density,  $f = -F/V$ ,  $p = f(T, \{\rho_s\}) + \sum_s \mu_s \rho_s$ , where the chemical potential of a specie  $s \in \{f, n\}$  is  $\mu_s = -\partial f / \partial \rho_s$ . The free energy can be expressed as a sum of electrostatic and entropic contributions. The electrostatic free energy is due to the *polyion-counterion*, the *polyion-polyion*, and the *counterion-counterion* interactions. The *polyion-counterion contribution* can be obtained in the framework of the usual DH theory.

Let us concentrate our attention on one cluster of size  $n$  fixed at  $r = 0$ . Due to the excluded volume, no counterions will be found inside  $r < a$ . Therefore the electrostatic potential  $\Psi_n$  in this region satisfies the Laplace equation  $\nabla^2 \Psi_n = 0$ . Outside  $r > a - \epsilon$ , the mean charge distribution will be specified by the cluster-counterion correlation function. Within the DH theory this is approximated by a Boltzmann factor leading to the charge density  $\rho_q(r) = -\sum_{n=0}^Z q(Z - n)\rho_n + q\rho_f e^{-\beta q \Psi_n(r)} + \sigma_n \delta(|\mathbf{r}| - a)$ . Notice that only free unassociated counterions get polarized; the free unassociated polyions and clusters are too massive to be affected by the electrostatic fluctuations and only contribute to the neutralizing background. Substituting this expression into the Poisson equation,  $\nabla^2 \Psi_n = -4\pi \rho_q / D$ , one obtains the non-linear Poisson-Boltzmann equation. After the linearization of the exponential factor, we are led to the Helmholtz equation,  $\nabla^2 \Psi_n = \kappa^2 \Psi_n$ , where  $\kappa a = \sqrt{4\pi \rho_f^* / T^*}$  and the reduced temperature and density are, respectively,  $T^* \equiv a D k_B T / q^2$  and  $\rho^* = \rho a^3$ . In principle the linearization is valid only in the limit  $\beta q \psi_n < 1$ , however, when the formation of clusters is properly taken into account the validity of the theory extends far into the non-linear regime [4].

Both the Laplace and the Helmholtz equations can now be solved, supplemented by the boundary condition of continuity of the electrostatic potential, and discontinuity in the normal

component of the electric field related to the presence of surface charge at  $r = a$  [12]. Under these conditions, it is easily found that the electrostatic potential of a  $n$ -cluster is  $\Psi_n^{\text{in}}(qn, qZ) = -(Z - n)q/(Da(1 + \kappa a))$  for  $r < a$ , and  $\Psi_n^{\text{out}}(qn, qZ) = -(Z - n)qe^{\kappa(a-r)}/(Dr(1 + \kappa a))$  for  $r \geq a$ . The electrostatic energy of a  $n$ -cluster is

$$\beta U_n(qn, qZ) = 2\pi\beta \int_a^\infty \rho_q(r)\Psi_n(qn, qZ)r^2 dr, \quad (1)$$

where  $\beta = 1/(k_B T)$ . The electrostatic *free-energy density* for the polyion-counterion interaction is obtained through the Debye charging process, where all the particles are charged from 0 to their final charge [1], [13],

$$\beta f_{\text{DH}} = - \sum_{n=0}^Z \rho_n \int_0^1 \frac{2\beta U_n(\lambda qn, \lambda qZ)}{\lambda} d\lambda = - \sum_{n=0}^Z \frac{(Z - n)^2}{2T^*(1 + \kappa a)} \rho_n. \quad (2)$$

The polyion-polyion contribution to the free energy can be calculated in the spirit of the usual Van-der-Waals (VdW) theory [4]. In particular, the tremendous difference in mass between the polyion and the counterion,  $m_c/m_p \ll 1$ , leads to the effective separation in characteristic time scales  $\tau_c \ll \tau_p$ . Thus, any change in the configuration of one polyion will be accompanied by an almost instantaneous rearrangement of the counterion cloud. Under these conditions, the degrees of freedom associated with the motion of counterions can be effectively integrated out, resulting in a *short*-ranged effective pair potential of a DLVO form [14],  $V_{n,m}^{\text{eff}} = q^2(Z - n)(Z - m)\theta(\kappa a)^2 e^{-\kappa r}/(Dr)$ , where the enhancement factor  $\theta(\kappa a) = e^{\kappa a}/(1 + \kappa a)$  is the result of the absence of screening inside the volume occupied by two polyions. Within the VdW theory

$$\begin{aligned} \beta f_{\text{PP}} &= - \sum_{n=0, m=0}^{Z, Z} \frac{\beta \rho_n \rho_m}{2} \int V_{n,m}^{\text{eff}}(r) d^3 r \\ &= - \sum_{n=0, m=0}^{Z, Z} \frac{2\pi a^3 (Z - n)(Z - m) \rho_n \rho_m}{T^*} \frac{1 + 2\kappa a}{(\kappa a + (\kappa a)^2)^2}. \end{aligned} \quad (3)$$

Now, the electrostatic free energy due to the interactions between free ions can be estimated as that of a One-Component Plasma (OCP) [15]. In particular, although within our treatment the counterions are taken to be point particles, the electrostatic repulsion between the two equally charged counterions will keep them from approaching each other closer than a distance  $d$ . This can be calculated using the OCP theory to be  $d = [(1 + 3\kappa a/T^*)^{1/3} - 1]/\kappa$  [16a]. As one might have expected, in the limit of small densities this reduces to the Bjerrum length,  $d \approx a/T^* \equiv \lambda_B$ . The electrostatic free energy is found through the Debye charging process and an analytic expression valid over a wide range of coupling strengths is presented in ref. [16b].

Finally, the entropic (mixing) contribution to the free energy is expressed using the Flory theory as  $\beta f_{\text{EN}} = \sum_s [\rho_s - \rho_s \ln(\phi_s/\zeta_s)]$ , where  $\phi_s$  is the volume fraction occupied by each specie  $s$ ;  $\phi_n = 4\pi\rho_n^*/3$ ,  $\phi_f \equiv 4\pi\rho_f d^3/3$ , and  $\zeta_s$  is the internal partition function of  $s$ ,  $\zeta_0 = \zeta_f = 1$ , and  $\zeta_n = [Z!/((Z - n)!n!)]e^{-\beta E_n}$ . Here  $E_n$  is the electrostatic energy of  $n$  counterions condensed onto the surface of a polyion and can be obtained through the charging process

$$\begin{aligned} \beta E_n &= -\beta q^2 n \int_0^1 \frac{Z - n\lambda}{Da} d\lambda \\ &= -\frac{Zn - n^2/2}{T^*}. \end{aligned} \quad (4)$$

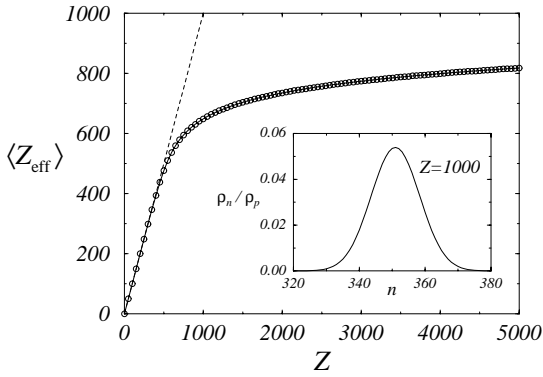


Fig. 1

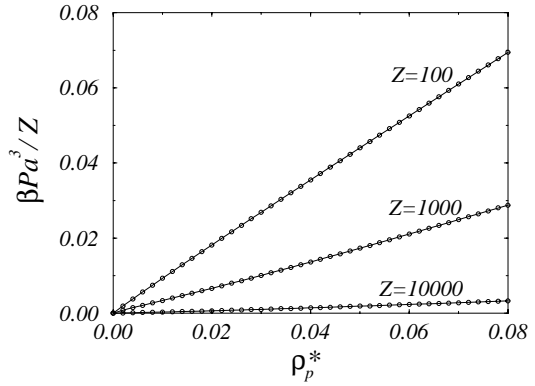


Fig. 2

Fig. 1. – Effective charge,  $\langle Z_{\text{eff}} \rangle$  as a function of the bare charge  $Z$  for a temperature  $T^* = 100$  and density of polyions  $\rho_p^* = 3/(32\pi)$ . The solid line is calculated using the full theory (distribution of cluster sizes), while the circles were obtained within one-size cluster approximation. The inset depicts the distribution of cluster sizes for  $Z = 1000$ . The dashed line is the bare charge.

Fig. 2. – Dependence of the renormalized dimensionless pressure  $\beta p a^3 / Z$  on the density of macroions  $\rho_p^*$  for several values of  $Z$  (100, 1000, 10000). The solid lines were calculated using the full theory (distribution), while the circles were obtained using one-size cluster approximation.

The minimization of the total free energy  $f = f_{\text{EN}} + f_{\text{PC}} + f_{\text{PP}} + f_{\text{CC}}$  leads to the law of mass action  $\mu_0 + n\mu_f = \mu_n$ . This is a set of  $Z$  coupled non-linear algebraic equations. We were able to solve these iteratively, starting with a uniform distribution of clusters. A sample of the distribution obtained is presented in the inset of fig. 1. The average cluster size is  $\langle n \rangle = \sum n \rho_n / \rho_p$ , and the average cluster charge is  $\langle Z_{\text{eff}} \rangle = Z - \langle n \rangle$ . We note that the width of the distribution remains quite narrow and is not very sensitive to the variations in density or temperature. This suggests that the polydispersivity in cluster sizes is not very important and can be replaced by *one* characteristic cluster size,  $n^*$ . In this case the theory becomes extremely simple, since the free energy will be an explicit function of the number of bound counterions  $n_B$ . The thermodynamically stable cluster,  $n^*$ , will be the one for which the free energy,  $f(Z, n_B)$ , attains a minimum,  $f(Z, n^*) = \min_{n_B} f(Z, n_B)$ . Thus, we must solve only *one* algebraic equation, instead of  $Z$  coupled ones. Indeed, as expected, the one-cluster approximation is in excellent agreement with the full theory. In fig. 1 we present the effective charge as a function of the polyion bare charge, while in fig. 2 the osmotic pressure inside the polyelectrolyte solution is computed.

An interesting question that arises is, what happened to the phase transition, so successfully predicted by the DHBj theory in the case of symmetric electrolyte [4]? The answer to this question is far from clear. However, our derivation does shed some light on the mechanism of the disappearance of the phase transition. The fundamental postulate that only the counterions are polarized by the electric-field fluctuations, can be seen to lie behind the disappearance of the transition. Indeed if this postulate is waved aside, so that both polyions and counterions can be polarized [17], it is a simple matter to show that the pure DH theory predicts that the suspension will undergo a phase separation when the temperature is reduced below  $T_C^* = Z/16$ . The fundamental question of what is the maximum charge asymmetry above which the polyelectrolyte solution will remain stable still needs to be answered.

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