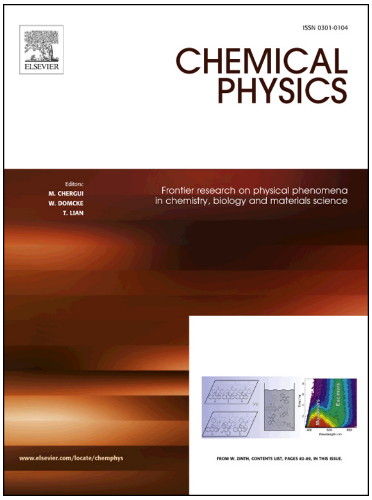

Theoretical investigation of a polarizable colloid in the salt medium

Amin Bakhshandeh

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Theoretical investigation of a polarizable colloid in the salt medium

Amin Bakhshandeh[1, a)]
Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil

In the present work, we have extended a weak coupling theory [A. Bakhshandeh, A. P. dos Santos and Y. Levin Phys. Rev. Lett 107, 107801 (2011)] for systems with added 1:1 electrolyte. To study the accuracy of the developed theory, we compare its numerical predictions with Monte Carlo simulation data and a recent theory which accounts for the surface polarization. A very good agreement is found for the case of monovalent electrolytes, up to very high salt concentrations and different colloidal charges.

I. INTRODUCTION

Ionic systems always have been a central subject of Chemistry and Physics as well as Biology. There are very interesting and counterintuitive observations in ionic systems, such as attraction of like-charged macromolecules in solutions where multivalent counterions exist[1–5]. This observation has been detected in bacteriophage heads and some viruses too[3,6–9].

Recently, Huang and Lapitsky have shown that monovalent salt increases colloidal stability when Chitosan-Tripolyphosphate Microgels are forming, and they related this phenomenon with weakening chitosan-Tripolyphosphate binding [10]. It is also well known that in biological systems maintenance of concentration of monovalent salt ions such as K and Na is very important for the cell stability, as the increase or decrease of the concentration of salt can lead to death of a cell [11].

Because of long-range interaction nature of these systems,the theoretical modeling of ionic systems is a rather challenging task. One of the most successful approaches to investigate these systems was proposed by Debye and Hückel back in 1923[12]. This theory allows us to calculate the chemical potential of positive and negative ions in the limit of very weak electrostatic couplings.

However, in the case of colloidal particles, the situation becomes more complicated. Since colloids have acidic or basic charged groups on their surfaces, in a polar medium, these groups become ionized and the particles become charged[13] and the DH theory looses its validity for such highly asymmetric systems. Repulsion between like-charged colloidal particles keep them separated, however, it is well known that by addition of electrolyte to colloidal suspension, at a critical concentration, the repulsive energy becomes weak enough, and coagulation takes place[3,14,15].

One successful theory which explains this phenomenon belongs to Derjaguin, Landau, Verwey, and Overbeek (DLVO) which accounts for the interaction between weakly charged homogeneous surface. It simply assumes that the net interaction between two colloidal surfaces is a combination of electrostatic double layer forces and van der Waals force[3,16–19].

The van der Waals force dominates when the separation distance between the surfaces is small, while the electrostatic force becomes relevant on larger distances. The mentioned theory works reasonably well for weakly charged homogeneously surfaces and gives us a clear insight into coagulation phenomenon [3,14,20,21].

Due to the strong variation of electric potential near a surface, electrical double layer (EDL) can be formed. EDL has a significant effect on the behavior of colloids in contact with solutions. Guerrero-García *et al.*[22–24] have shown the importance of coions in the electric double layer so that they are able to induce correlations which modify the EDLs potential and this, for instance, causes an increase of the charge reversal phenomenon for 1: α salts (*viz.*, univalent counterions and multivalent coions).

In general, in the presence of monovalent ions, charge renormalization stabilizes colloidal suspensions and phase separation does not happen in water[3,25]. As we mentioned earlier, there are many chemical and biochemical systems which monovalent salt ions play important roles to stabilize them. Therefore, by studying the monovalent salt behavior around charged colloidal particles, we are able to evaluate the stability of colloidal suspensions in the mentioned systems that can be great of interest.

In aqueous colloidal systems with monovalent counterions, the Poisson-Boltzmann (PB) equation is in very good agreement with the experiments and simulation data, but the PB equation does not account for the correlations between the counterions and breaks down for low dielectric solvents, when such correlations become strong[3,26,27].

Besides, in many colloidal suspensions the dielectric constant of colloidal particles is smaller than that dielectric constant of the surrounding medium and, as a result, ions near colloidal surface feel a strong ion-image repulsion[21]. The interaction between ions and image charges creates an extra force which can affect the effective charge of the colloidal particles. This extra interaction leads to the modification of colloid-colloid and colloid-counterion interaction potentials[3,14,21,28] and for this reason, for describing real systems, one should consider this issue.

However, since it is difficult to include the dielectric discontinuities in spherical or other complicated geometries, most of the theoretical and numerical works on colloidal suspensions ignore the effects of the dielectric discontinuity at the interface.

[a)] Electronic mail: amin.bakhshandeh@ufrgs.br