Ground state of two unlike charged colloids: An analogy with ionic bonding

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Abstract. – In this letter, we study the ground state of two spherical macroions of identical radius, but asymmetric bare charge (Q_A > Q_B). Electroneutrality of the system is insured by the presence of the surrounding divalent counterions. Using Molecular Dynamics simulations within the framework of the primitive model, we show that the ground state of such a system consists of an overcharged and an undercharged colloid. For a given macroion separation the stability of these ionized-like states is a function of the difference (\sqrt{N_A} - \sqrt{N_B}) of neutralizing counterions N_A and N_B. Furthermore the degree of ionization, or equivalently, the degree of overcharging, is also governed by the distance separation of the macroions. The natural analogy with ionic bonding is briefly discussed.

Charged colloids are found in a great variety of materials such as latex, clays, paints, and many biological systems, and thus have an important place in the every-day life. To understand the complex interaction between charged colloids and their surrounding neutralizing counterions, a reasonable starting point is to study the elementary case of a pair of spherical macroions. From the theoretical side such a system is described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1,2], which lead to purely repulsive effective forces. More sophisticated modified Poisson-Boltzmann approaches based on density-functional theory [3] or inhomogeneous HNC techniques [4,5] have been developed in order to incorporate the ion-ion correlations which are neglected in DLVO. Surprisingly recent experiments showed effective attractive forces between like-charged colloids [6–8] when they are confined near charged walls, and for which no clear theoretical explanation is available. This triggered reinvestigations of the pair-interactions in the bulk with computer simulations [9–13]. A common feature of all these studies is that they assume the two macroions identically charged. The results of refs. [9–12] show for high Coulomb coupling an attractive force in a range of the order of a few counterion radii. However, Messina et al. [13] have demonstrated that it is possible to get a strong long-range attraction between two like-charged colloids due to metastable ionized states. In particular it has been shown that the energy difference between the compensated

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bare charge case, where each colloid is exactly neutralized by the surrounding counterions, and the ionized state can be very small (less than $2 k_B T$).

In this letter, we use molecular dynamics (MD) simulations to investigate the case where the colloidal radii are identical but the bare colloidal charges are different. It is found that in this asymmetric situation the ground state is no longer the intuitive bare charge compensated case, provided that the charge asymmetry is high enough and/or the colloid separation is not too large. We derive a simple formula valid for large separations which gives a sufficient condition for the bare charge asymmetry, to produce a ground state consisting of an ionic pair leading to a natural long-range attractive force.

The system under consideration is made up of two spheres: (i) macroions $A$ and $B$ of diameter $d$ with bare charges $Q_A = -Z_A e$ (where $e$ is the elementary charge and $Z_A = 180$ is fixed) for the highly charged sphere and $Q_B = -Z_B e$ (variable) for the less charged one and (ii) a sufficiently number of small counterions of diameter $\sigma$ with charge $q = \pmZe$ ($Z_e = 2$) to neutralize the whole system. The macroions center-center separation is given by $R$. The ions are confined in a cubic box of length $L$, and the two macroions are held fixed and disposed symmetrically along the axis passing by the two centers of opposite faces. The colloid volume fraction $f_m$ is defined as $2 \cdot 4\pi(d/2)^3/3L^3$. For describing the charge asymmetry we define the quantity $\alpha = \sqrt{N_A} - \sqrt{N_B}$, where $N_A = -Q_A/q$, and $N_B = -Q_B/q$.

The motion of the counterions is coupled to a heat bath acting through a weak stochastic force $W_i(t)$. The equation of motion of counterion $i$ reads

$$m \frac{d^2 r_i}{dt^2} = -\nabla_i U - m\Gamma \frac{dr_i}{dt} + W_i(t), \quad (1)$$

where $m$ is the counterion mass, $\Gamma$ is the friction coefficient, chosen here between $0.1$ and $1.0$, and $U$ is the potential consisting of the Coulomb interaction and the excluded volume interaction. Friction and stochastic force are linked by the fluctuation-dissipation theorem $(W_i(t) \cdot W_j(t')) = 6m\Gamma k_B T \delta(t - t')$. In the ground state $T = 0$ and thus the stochastic force vanishes.

Excluded volume interactions are taken into account with a pure repulsive Lennard-Jones (LJ) potential given by

$$U_{LJ}(r) = \begin{cases} 4\varepsilon \left[ \left( \frac{\sigma}{r - r_0} \right)^{12} - \left( \frac{\sigma}{r - r_0} \right)^{6} \right] + \varepsilon, & \text{for } r - r_0 < \sigma^{1/6}, \\ 0, & \text{for } r - r_0 \geq \sigma^{1/6}, \end{cases} \quad (2)$$

where $r_0 = 0$ for the counterion-counterion interaction, $r_0 = 7\sigma$ for the macroion-counterion interaction, thus leading to a macroion diameter $d = 2r_0 + \sigma$ and electrostatically more important to a macroion-counterion distance of closest approach $a = 8\sigma$.

The pair electrostatic interaction between any pair $ij$, where $i$ and $j$ denote either a macroion or a counterion, reads

$$U_{\text{coul}}(r) = k_B T_0 l_B \frac{Z_i Z_j}{r}, \quad (3)$$

where $l_B = \varepsilon^2/4\pi\varepsilon_0 \varepsilon_r k_B T_0$ is the Bjerrum length describing the electrostatic strength. To link this to experimental units and room temperature we denote $\varepsilon = k_B T_0$ ($T_0 = 298$ K). Fixing $\sigma = 3.57$ Å would then lead to the Bjerrum length of water at room temperature (7.14 Å).

Being interested in the strong Coulomb coupling regime we choose the relative permittivity $\varepsilon_r = 16$, corresponding to $l_B = 10\sigma$. 

The electrostatic energy of the system is investigated for different uncompensated bare charge cases [14] by simply summing up eq. (3) over all Coulomb pairs. Note that for the zero temperature ground state study entropic effects are nonexistent. We define the degree of ionization (DI) as the number of counterions overcharging colloid A (or, equivalently, undercharging colloid B). The system is prepared in various DI and measure the respective energies. These states are separated by kinetic energy barriers, as was demonstrated in Ref. [13]. We consider three typical macroionic charges $Z_B$ (30, 90 and 150) and separations $R/a$ (2.4, 3.0 and 4.25). The main results are given in Fig. 1. For the largest separation $R/a = 4.25$ and largest charge $Z_B = 150$ (see Fig. 1a), one notices that the ground state corresponds to the classical compensated bare charge situation (referred as the neutral state). Moreover the energy increases stronger than linear with the degree of ionization. If one diminishes the bare charge $Z_B$ to 90 and 30, the ground state is actually the ionized state for a DI of 1 and 3, respectively. The ionized ground state is about 8 and 36 $k_B T_0$, respectively, lower in energy compared to the neutral state. This shows that even for a relative large colloid separation, stable ionized states should exist for sufficient low temperatures and that their stability is

Fig. 1 – Total electrostatic energy as a function of the degree of ionization for zero temperature configurations of two colloids (A and B), for three typical charges $Q_B/e$ ($-30$, $-90$ and $-150$) for macroion B and for three given distance separations: a) $R/a = 4.25$, b) $R/a = 3.0$ and c) $R/a = 2.4$. Dashed lines are obtained using eq. 7.
conditioned by the structural charge asymmetry $\alpha$.

For a shorter separation $R/a = 3.0$, ionized ground states are found (see Fig. 1 b) for the same charges $Z_B$ as previously. Nevertheless, in the ground state the DI is now increased and it corresponds to 2 and 4 for $Z_B = 90$ and 30 respectively. The gain in energy is also significantly enhanced. For the shortest separation under consideration $R/a = 2.4$, the ground state corresponds for all investigated values of $Z_B$ to the ionized state, even for $Z_B = 150$. We conclude that decreasing the macroion separation $R$ enhances the DI and the stability of the ionized state.

To understand this ionization phenomenon, it is sufficient to consider an isolated macroion surrounded by its neutralizing counterions. We have investigated the energies involved in the ionization (taking out counterions) and overcharging (adding counterions) processes. We show in Ref. [13] how they can be separated into two parts: (i) a pure correlational term ($\Delta E^{\text{cor}}$) and (ii) a monopole contribution ($\Delta E^{\text{mon}}$), see also Ref. [15] for the case of added salt. The main assumption is that the correlational energy per ion can be written as a pure surface term $\epsilon(N) = -\gamma \sqrt{N}$ (with $\gamma > 0$), as is predicted for example in a theory where the counterions on the surface of the colloids form a Wigner crystal (WC) [13,16]. The gain in energy when adding the first counterion is simply a pure correlation term of the form

$$\Delta E_{1}^{\text{OC}} = \Delta E_{1}^{\text{cor}} = (N_A + 1)\epsilon(N_A + 1) - (N_A)\epsilon(N_A) = -\gamma \sqrt{N_A} \left[ \frac{3}{2} + \frac{3}{8N_A} + O(N_A^{-2}) \right].$$  \hspace{1cm} (4)

Adding the summed up monopole contributions, one obtains the energy gained by adding the $n$th counterion to leading order in $1/N_A$:

$$\Delta E_{n}^{\text{OC}} = \Delta E^{\text{cor}} + \Delta E^{\text{mon}} = -n\gamma \sqrt{N_A} \left[ \frac{3}{2} + \frac{3n}{8N_A} \right] + (k_BT_0)l_B Z_c^2 \frac{(n-1)n}{2a},$$  \hspace{1cm} (5)

which has been verified to give a correct description when compared to simulations [13]. A derivation of the formula describing the ionization energy $\Delta E^{\text{ion}}$ proceeds completely analogously and gives for the $n$th degree of ionization

$$\Delta E_{n}^{\text{ion}} = n\gamma \sqrt{N_B} \left[ \frac{3}{2} - \frac{3n}{8N_B} \right] + (k_BT_0)l_B Z_c^2 \frac{(n+1)n}{2a}.$$  \hspace{1cm} (6)

In Fig. 2 we compare the predictions of eqs. (5, 6) to our simulation data, which shows excellent agreement. Our numerical data for $\Delta E_{1}^{\text{ion}}$ for $N_B = 15, 45,$ and $75$, the value of $\Delta E_{1}^{\text{OC}}$ for $N_A = 90$, as well as the corresponding values for $\gamma$, which have been used for Fig. 2 can be found in Table 1. They show that $\gamma$ is almost independent of $N$. The value of $\gamma$ can also be compared to the prediction of WC theory applied to an infinite plane which leads to the value $1.96l_B Z_c^2 \sqrt{\frac{1}{N}} \approx 2.76$ [17], where $F$ denotes the surface area of the colloid. The difference of 10 % to WC theory is presumably related to the fact that we do not deal with purely planar correlations, but have a finite spherical geometry.

With the help of Eqs. (5, 6), one can try to predict the curves of Fig. 1 for finite center-center separation $R$. Using for colloid $A$ and $B$ the measured values $\gamma_A$ and $\gamma_B$, we obtain for the electrostatic energy difference at finite center-center separation $R$

$$\Delta E_{n}(R) = \Delta E_{n}^{\text{ion}} + \Delta E_{n}^{\text{OC}} = \frac{3}{2} n\gamma_B \sqrt{N_B} \left[ 1 - \frac{n}{4N_B} \right] + \frac{3}{2} n\gamma_A \sqrt{N_A} \left[ 1 + \frac{n}{4N_A} \right] + k_BT_0 l_B Z_c^2 \frac{n^2}{a} \left( 1 - \frac{a}{R} \right).$$  \hspace{1cm} (7)

The quality of the theoretical curves can be inspected in Fig. 1. The prediction is is very good for large separations, but the discrepancies become larger for smaller separations, and
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Table I – Measured value, for an isolated colloid, of the first ionization energy $\Delta E_{1}^{\text{ion}}$ for $N_B = 15, 45, 75$, and the energy gain for the first overcharging counter ion $\Delta E_{1}^{\text{OC}}$ for $N_A = 90$. The value of $\gamma$ can be compared to the prediction of WC theory for an infinite plane, which gives 2.76, compare text.

| $Q/e$ | $N$  | $\Delta E_1/k_B T_0$ | $\gamma/k_B T_0$ |
|-------|------|----------------------|------------------|
| -30   | 15   | 17.9                 | 2.26             |
| -90   | 45   | 29.2                 | 2.42             |
| -150  | 75   | 37.4                 | 2.50             |
| -180  | 90   | -35.3                | 2.47             |

one observes that the actual simulated energies are lower. With the help of Eq. (7) we can establish a simple criterion, valid for large macroionic separations, for the necessary charge asymmetry $\alpha$ to produce an ionized ground state of two unlike charged colloids with the same size:

$$\frac{3}{2} \gamma \left( \sqrt{N_A} - \sqrt{N_B} \right) > \frac{(k_B T_0) |B Z^2_c|}{\alpha}.$$  (8)

The physical interpretation of this criterion is straightforward. The left term represents the difference in correlation energy and the right term the monopole penalty due to the ionization process. This means that the correlational energy gained by overcharging the highly charged

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Fig. 2 – Total electrostatic energy as a function of the degree of ionization for zero temperature configurations of an isolated colloid. The three upper curves correspond to the ionization energy for the three typical charges $Q_B/e$ ($-30, -90$ and $-150$). The lower curve corresponds to the energy gained by overcharging ($Q_A/e = -180$). Dashed lines were obtained using eqs. (5, 6) with the measured values for $\gamma$ from Table 1.

Fig. 3 – Relaxation, at room temperature $T_0 = 298K$, of an initial neutral state towards ionized state. Plotted is the total electrostatic energy versus time (LJ units), for $Z_B = 30$ and $R/a = 2.4$. Dashed lines lines represent the mean energy for each DI state. Each jump in energy corresponds to a counterion transfer from the macroion $B$ to macroion $A$ leading to an ionized state ($DI = 2$) which is lower in energy than the neutral one. The two energy jumps $\Delta E_1/k_B T_0 = -20$ and $\Delta E_2/k_B T_0 = -17$ are in very good agreement with those of Fig. 1c (-20.1 and -16.3).
Fig. 4 – Snapshot of the ionized state \( (DI = 2) \) obtained in the relaxation process depicted in Fig. 3, with the net charges \(+4e\) and \(-4e\) as indicated.

colloid \( A \) must overcome the loss of correlation energy as well as the monopole contribution (two penalties) involved in the ionization of colloid \( B \). If one uses the parameters of the present study one finds the requirement \( N_B < 66 \) to get a stable ionized state. This is consistent with our findings where we show in Fig. 1 that for \( N_B = 75 \), and \( R/a = 4.25 \), no ionized ground state exists whereas for \( N_B = 60 \) we observed one even for infinite separation. The criterion Eq. (8) is merely a sufficient condition, since we showed in Fig. 1 that when the colloids are close enough this ionized state can appear even for smaller macroion charge asymmetry due to enhanced intercolloidal correlations. If the colloids have the different radii this can be can accounted for by simply replacing \( N_i^{1/2} \) by the concentration of counterions \( (N_i/F_i)^{1/2} \), and redefining \( \gamma \) Eq. (8), in Eq. (8).

At this stage, on looking at the results presented above, it appears natural and straightforward to establish an analogy with the concept of ionic bonding. It is well known in chemistry that the electro-negativity concept provides a simple yet powerful way to predict the nature of the chemical bonding [18]. If one refers to the original definition of the electro-negativity given by Pauling [18], “the power of an atom in a molecule to attract electrons to itself”, the role of the bare charge asymmetry becomes obvious. Indeed, it has an equivalent role at the mesoscopic scale as the electron affinity at the microscopic scale. Another interesting analogy is the influence of the colloidal separation on the stability of the ionized state. Like in diatomic molecules, the ionized state will be (very) stable only for sufficiently short colloid separations. Nevertheless, one should not push too far this analogy. Indeed, in many respects it breaks down, and these are in fact important and interesting points. One concerns the existence of an ionized ground state in colloidal system for large colloid separation, providing that \( \alpha \) is large enough. In an atomistic system this is impossible since even for the most favorable thermodynamical case, namely CsCl, there is a cost in energy to transfer an electron from a cesium atom to a chlorine atom. Indeed, the smallest existing ionization energy (for Cs, 376 kJ mol\(^{-1}\)) is greater in magnitude than the largest existing electron affinity (for Cs, 349 kJ mol\(^{-1}\)). In other terms, for atoms separated by large distances in the gas phase, electron transfer to form ions is always energetically unfavorable.

As a last result, aimed at experimental verification, we show that an ionized state can also exist at \( \text{room temperature} \ T_0 \). Figure 3 shows the time evolution of the electrostatic energy of a
system $Z_A = 180$ with $Z_B = 30$, $R/a = 2.4$ and $f_m = 7 \cdot 10^{-3}$, where the starting configuration is the neutral state ($DI = 0$). One clearly observes two jumps in energy, $\Delta E_1 = -19.5 k_BT_0$ and $\Delta E_2 = -17.4 k_BT_0$, which corresponds each to a counterion transfer from colloid B to colloid A. These values are consistent with the ones obtained for the ground state, which are $-20.1 k_BT_0$ and $-16.3 k_BT_0$ respectively. Note that this ionized state ($DI = 2$) is more stable than the neutral but is expected to be metastable, since it was shown previously that the most stable ground state corresponds to $DI = 5$. The other stable ionized states for higher $DI$ are not accessible with reasonable computer time because of the high energy barrier made up of the correlational term and the monopole term which increases with $DI$ [13]. In Fig. 4 we display a typical snapshot of the ionized state ($DI = 2$) of this system at room temperature.

Obviously, these results are not expected by a DLVO theory even in the asymmetric case (see e. g. [19]). Previous simulations of asymmetric (charge and size) spherical macroions [20] were also far away to predict such a phenomenon since the Coulomb coupling was weak (water, monovalent counterions).

In summary, we have shown that the ground state of two unlike charged spherical macroions is mainly governed by two important parameters, namely the bare charge asymmetry $\alpha$ and the colloids separation $R$. If $\alpha$ is high enough, the ground state corresponds to the so-called ionized state, whatever the macroions separation $R$ is. In return, the degree of ionization depends on $R$. Furthermore, for large $R$, we have established a criterion for $\alpha$, allowing to predict when a stable ionized configuration can be expected. The bare charge difference $\alpha$ plays an analogous role to the electron affinity difference between two atoms forming a molecule with ionic bonding. We demonstrated that the results presented here for the ground state can lead to a stable ionic state even at room temperature providing that the Coulomb coupling and/or the charge asymmetry is sufficiently large. This is a possible mechanism which could lead to long range attractions, even in bulk. Future work will treat the case where salt ions are present. Finally, it would be desirable to theoretically quantify the influence of intercolloidal correlations at short separations in a similar fashion as we have done for large separations.

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