PHYSICAL REVIEW E **67**, 031402 (2003)

Stability of charge inversion, Thomson problem, and application to electrophoresis

Michael Patra, Marco Patriarca, and Mikko Karttunen
Biophysics and Statistical Mechanics Group, Laboratory for Computational Engineering, Helsinki University of Technology, P.O. Box 9203, FIN-02015 HUT, Finland

(Received 5 November 2002; published 20 March 2003)

We analyze charge inversion in colloidal systems at zero temperature using stability concepts, and connect this to the classical Thomson problem of arranging electrons on sphere. We show that for a finite microion charge, the globally stable, lowest-energy state of the complex formed by the colloid and the oppositely charged microions is always overcharged. This effect disappears in the continuous limit. Additionally, a layer of at least twice as many microions as required for charge neutrality is always locally stable. In an applied external electric field the stability of the microion cloud is reduced. Finally, this approach is applied to a system of two colloids at low but finite temperature.

DOI: 10.1103/PhysRevE.67.031402 PACS number(s): 82.70.Dd, 41.20.−q

I. INTRODUCTION

We study analytically and numerically charged colloidal particles in the presence of electrolyte solutions in the low-temperature limit. This is equivalent to strong electrostatic coupling at finite temperature [1]. Already at room temperature a colloidal system thus is in the low-temperature regime, provided the electrolyte consists of multivalent ions. In this limit, a certain number of ions condenses onto the surface of the colloid. For consistency, we will call the charged colloids macroions, and the ions of the electrolyte microions. For the general macroion problems, this behavior has recently attracted a lot of attention especially due to its importance in biological systems [2–9].

Macroion complexes exhibit numerous counterintuitive phenomena. The most pronounced one is referred to as overcharging or charge inversion. A certain number of microions is needed to condense for the entire complex (macroion and condensed microions) to become charge neutral. Sometimes an excessive number of microions condenses [5,6,8,10–22] and the complex, the "dressed" macroion, acquires an effective charge that is opposite in sign to that of the bare macroion. This phenomenon is beyond the standard Debye-Hückel [23–25] and Derjaguin-Landau-Verwey-Overbeek (DLVO) theories [26].

Another phenomenon is autoionization [17,18,20]. This means that one macroion transfers some of its microions to another macroion, so that the first one becomes undercharged while at the same time the second one becomes overcharged. Also analyzed in the literature is the important question of transport in an external electric field. A bare macroion will move in the direction determined by its own charge. The binding of microions to it can under certain conditions reverse the direction.

These results have mostly been arrived at by molecular dynamics and Monte Carlo simulations. Simulations offer the advantage that finite temperature can be taken into account in a natural way. Purely analytical approaches have to resort to relatively complicated starting points since mean-field theories are insufficient [23–25]. A successful and often used approach is the model of a two-dimensional Wigner crystal which becomes exact at zero temperature and very large number of microions per macroion [27].

At zero temperature—without any restrictions on the number of microions—the problem is, however, directly related to the classical "Thomson problem" of finding stable configurations of N mutually repelling electrons on the surface of a sphere [28,29]. While the original problem was about the plum pudding model for the atom, where N particles are confined inside a homogeneously charged sphere, both problems actually are identical since the repelling interaction will push all particles inside the sphere toward its surface. This was recently shown by energy minimization arguments by Brito and Fiolhais [30]. This similarity between overcharging and the Thomson problem seems to have been largely unnoticed in the macroion literature.

In this paper we will make use of the Thomson problem to derive rigorous bounds for the phenomena discussed above. At zero temperature, our results are exact, and hence an improvement on previously known results from the Wigner crystal theory. Compared to the results of simulations, our derivation suffers from our inability to include finite temperature in an exact way. However, our method outperforms previous ones in both the ease of the method (both conceptually and numerically) and in allowing to treat many phenomena in a single consistent way.

This paper is organized as follows. In Sec. II we summarize the so-called primitive model. This model is used in basically all studies of macroion complexes. In Secs. III–V we analyze the stability of overcharged macroion complexes. We use concepts from dynamical-systems theory to show that two different stability properties exist, global stability (Sec. III) and local stability (Sec. IV). In Sec. VI we move on to the question of a macroion in an applied external field, i.e., electrophoresis. We will discuss the autoionization of macroions in Sec. VII. We conclude in Sec. VIII.

II. MODEL

We consider a spherical macroion of charge Q and radius R_{mac}, surrounded by N spherical microions of charge q and radius R_{mic}. Q and q are of opposite signs, and in the following we assume $Q<0$. The macroion is fixed at the origin and the N microions are distributed at positions $\vec{r}_i$, i

$=1,\dots,N$. The total electrostatic energy V for a particular configuration is then given by

$$V(\{\vec{r}_i\}) = \frac{q^2}{4\pi\epsilon}\sum_{i<j}^{1\dots N}\frac{1}{|\vec{r}_i-\vec{r}_j|}+\frac{qQ}{4\pi\epsilon}\sum_{i=1}^{N}\frac{1}{|\vec{r}_i|}, \tag{1}$$

where the first sum accounts for the mutual repulsion of the microions, and the second for the attraction between the macroion and each microion. The effect of solvent is included through an effective dielectric constant ϵ. Short-range pairwise repulsion is taken into account by hard-core interaction

$$V_{\mathrm{hc}} = \sum_{i=1}^{N} v(|\vec{r}_i| - R_{\mathrm{mac}} - R_{\mathrm{mic}}) + \sum_{i<j}^{1\dots N} v(|\vec{r}_i-\vec{r}_j| - 2R_{\mathrm{mic}}), \tag{2}$$

where $v(r)\to\infty$ for $r<0$ and zero otherwise. Equations (1) and (2) comprise the so-called primitive model [8].

III. GLOBAL STABILITY

We approach the problem by using the well-known Earnshaw's theorem [31] which states that there can be no stable state in a system with only electrostatic interactions present. For stable configurations to exist, short-range repulsive forces must be present in addition to the long-range Coulomb ones. For our system, the short-range forces are due to hard-core interaction [Eq. (2)]. Earnshaw's theorem thus restricts stable configurations to have all microions at a distance $R \equiv R_{\mathrm{mac}} + R_{\mathrm{mic}}$ away from the center of the macroion.

The condition $|\vec{r}_i| = R$ allows us to simplify Eq. (1) to

$$V(\{\vec{r}_i\}) = \frac{q^2}{4\pi\epsilon R}\sum_{i<j}\frac{1}{|\vec{r}^{\circ}_i-\vec{r}^{\circ}_j|}+\frac{qQN}{4\pi\epsilon R}, \tag{3}$$

with the normalized coordinates $\vec{r}^{\circ}_i \equiv (1/R) r_i$. Equation (3) no longer describes the energy of an arbitrary arrangement $\{\vec{r}_i\}$ of particles but the energy of *any stable* arrangement instead. Next, we introduce the function $f(N)$,

$$f(N) = \sum_{i<j}^{1\dots N}\frac{1}{|\vec{r}^{\circ}_i-\vec{r}^{\circ}_j|} \quad \text{with} \quad |\vec{r}^{\circ}_i| = 1, \tag{4}$$

where we demand that the coordinates $\{\vec{r}^{\circ}_i\}$ are those for the lowest-energy state with N microions around the macroion. Thus, the coordinates are completely defined by N.

At the ground state, Eq. (4) becomes minimized. The complete solution can be computed numerically very efficiently [32]. Furthermore, the functional form of $f(N)$ is known to excellent precision [29] to be

$$f(N) = \frac{N^2}{2} - cN^{3/2} \quad \text{with} \quad c = 0.5510. \tag{5}$$

This formula is easy to understand when one notices that the first term is the energy of a continuous layer of charge on a sphere of unit radius while the second term is the self-energy correction due to discrete microions which can be shown to be proportional to $N^{3/2}$. A comparison of Eq. (5) and a numerical solution of the exact formula [Eq. (4)] is shown in Fig. 1.

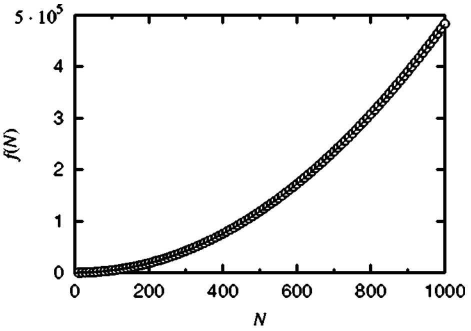

FIG. 1. Comparison of Eq. (5) (solid line) with the result of a numerical computation of Eq. (4) (open circles).

By using the condition $|\vec{r}_i| = R$ for all i we have completely accounted for the hard-core interaction between the macroion and the microions. We can neglect the hard-core interaction between microions since they repel each other as their charges have the same sign. Collecting results, the potential energy of the lowest-energy state for a macroion surrounded by N microions is given by

$$V(N) = \frac{q^2}{4\pi\epsilon R}\left[\frac{N^2}{2} - cN^{3/2}\right] + \frac{qQN}{4\pi\epsilon R}. \tag{6}$$

Earnshaw's theorem gives a necessary but not sufficient criterion for the stability of a system. Furthermore, it states that an unstable microion is immediately pushed to infinity. Let us consider a macroion and N microions where we place the microions at arbitrary positions—not necessarily on the macroion. Due to Earnshaw's theorem, M of them will attach to the macroion while $k = N - M$ will escape to infinity. All N will go to the macroion if it is the state lowest in energy, i.e., if

$$V(N) < V(M) \quad \forall \quad 0 \leq M < N. \tag{7}$$

This condition is much stronger than the simple condition $V(N) < 0$, since the latter only prevents *all* microions from escaping simultaneously while Eq. (7) also prevents *some* from escaping.

Due to Earnshaw's theorem, all stable solutions are enumerated by the number of microions, and we simply have to find the number yielding the lowest energy. Since Eq. (6) possesses only a single extremum for given parameters q, Q, and R, we can simply use $dV(N)/dN = 0$. That yields

$$N_{\mathrm{glob}} = \frac{|Q|}{q} + \frac{9}{8}c^2 + \frac{9c^2}{8}\sqrt{1 + \frac{16}{9c^2}\frac{|Q|}{q}}, \tag{8}$$

where we have used the assumption $Q < 0$ introduced above.

The first term $|Q|/q$ gives the naive result that a complex consisting of macroion and layer of microions should be charge neutral. The other two terms give the excess bound

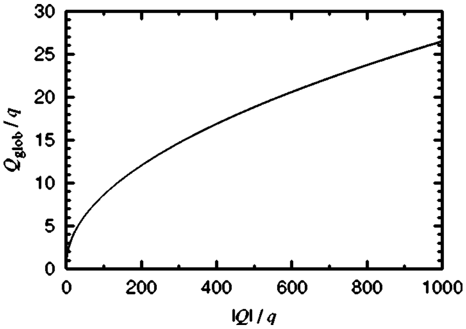

FIG. 2. Globally stable overcharging Q_{glob} as a function of the ratio of the charges of macroion and microion, computed from Eq. (8).

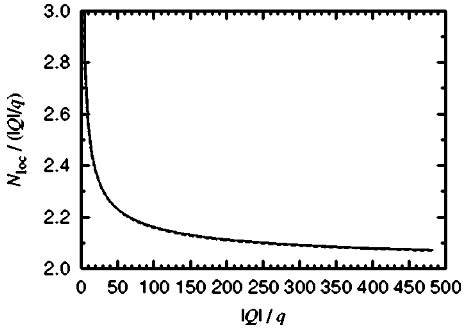

FIG. 3. Number of locally stable microions as a function of the ratio of the charges. The solid line is the analytic upper bound of Eq. (12), while the dashed line is a numerical solution of the exact formula, Eq. (10).

microions. The maximum stable overcharging in terms of charge is $Q_{\mathrm{glob}}=qN_{\mathrm{glob}}-|Q|$, see Fig. 2.

The stability criterion that we derived applies to an arbitrary initial placement of microions. For this reason, this kind of stability is referred to as *global* stability, see any textbook on nonlinear dynamics, e.g., Ref. [33].

IV. LOCAL STABILITY

In addition to global stability, there exists the concept of *local* stability. While global stability states that the microions will move to the macroion independent of their initial positions, local stability means that they will stay at the macroion if they have initially been placed there. The system is locally stable (but not globally) if the system could lower its energy by transferring one (or more) microions from the macroion to infinity but in doing so would need to cross an energy barrier. Since we are restricting ourselves to classical physics at zero temperature, it is impossible to cross such a barrier and the microions would stay touching the macroion forever—if prepared with this initial condition.

To calculate the condition for the existence of such a barrier we move particle k slightly away from the macroion by a distance Δ, keeping all other microions on the surface of the macroion. If this move increases the potential energy, resulting in a restoring force, the system is locally stable.

We label all quantities in the perturbed state by a prime, hence $r_k'=R+\Delta$ and $r_l'=r_l=R\,\forall l\neq k$, and we introduce the abbreviation $d_{kl}=|\vec{r}_k-\vec{r}_l|$. Since we need to consider only small Δ, we can use a series expansion, with the result

$$\frac{1}{d_{kl}'}=\frac{1}{d_{kl}}-\frac{1}{2Rd_{kl}}\Delta \quad \text{and} \quad \frac{1}{|\vec{r}_k'|}=\frac{1}{R}-\frac{1}{R^2}\Delta. \tag{9}$$

Inserting this into Eq. (1) gives

$$V'=V-\frac{q}{4\pi\epsilon R}\left[q\sum_{i\neq k}^{1\ldots N}\frac{1}{2d_{ki}}+\frac{Q}{R}\right]\Delta\equiv V-\frac{h_k}{R}\Delta. \tag{10}$$

The system is locally stable if and only if the expression in brackets is negative for all k since then an increase in Δ will increase the potential energy. Thus, the condition for local stability is $h_k<0\,\forall k$. Since the lowest-energy arrangement of the particles rarely is completely symmetric, this yields the necessary but not sufficient condition $\langle h_k\rangle_k<0$, where this average is over all possible particles k. Noting that $\Sigma_k h_k=V(N)$, this gives the necessary condition for local stability

$$V(N)<0. \tag{11}$$

It should be noted that this simple form for the condition is a coincidence, and for other systems $V(N)<0$ has not necessarily a relation to local stability. With the help of Eq. (6) this condition can be converted into an upper bound for the number of microions that can be bound locally stable,

$$N_{\mathrm{loc}}=2\frac{|Q|}{q}+2c^2\left[1+\sqrt{1+\frac{2|Q|}{c^2q}}\right]. \tag{12}$$

In terms of charge this is $Q_{\mathrm{loc}}=qN_{\mathrm{loc}}-|Q|$.

To check the difference between Eq. (12) and the exact solution, we have numerically computed the lowest-energy state as a function of N, and from that determined the largest h_k for each N. The result in Fig. 3 shows that hardly any difference between the two values can be seen. This does not come as a surprise since the differences between h_k for different k are small as the repelling forces among the microions try to make all mutual distances as equal as possible.

V. SUMMARY OF STABILITY CONCEPTS

For finite q, the number of microions that are bound globally stable is always larger than the value $N=|Q|/q$, i.e., the macroion is overcharged. In the continuous limit $q\rightarrow 0$ this effect disappears. In contrast, the number of locally stable bound microions is at least twice the amount needed for charge neutrality, and this effect persists even in the continuous limit. Figure 4 shows the different regimes as a function of the charges of macroion and microions.

We now want to put our results into perspective of previous results on overcharging [5,6,8,10–22]. At finite T, there are only few simulations done in the geometry employed in this paper, e.g., Ref. [22]. Most analytical work focuses on $T=0$, both due to simplicity and allowing one to focus on the influence of correlations. We employ the same approach.

The main advantage of our approach is the adoption of the

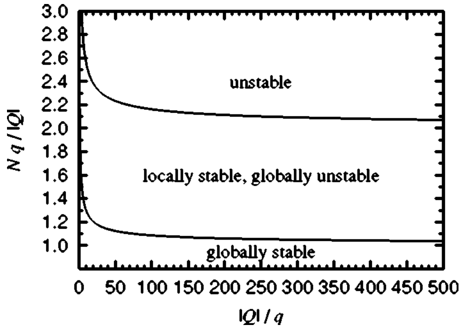

FIG. 4. Number of microions that can be bound globally stable or locally stable to a macroion. $Nq/|Q|=1$ is the number of microions expected from charge neutrality.

exact Thomson model as source for the potential energy $V(N)$, whereas previous papers used an energy estimate for $V(N)$ derived from strongly correlated liquid and the Wigner crystal theory [5,17]. The Wigner crystal theory contains a parameter α whose value can either be determined from simulations as a function of N—which trivially leads to a self-consistent result—or needs to be fixed with the analytical value for α known for a two-dimensional Wigner crystal. In the latter case, this results in an error of up to order 10% for the computed energies [17]. In contrast the error of Eq. (5) is negligible (less than 10^{-4}).

We apply methods from nonlinear dynamics, using the concepts of local and global stability. The existence of these two different stability properties seems to be unnoticed in macroion literature. For example, the criterion by Messina *et al.* agrees with our global stability criterion up to the differences caused by their choice for $V(N)$. The concept of local stability, however, is also an important one as can be seen, for example, in the electrophoresis setup treated in the following section.

Finally, for numerical calculations we employ a minimization scheme. Only a few different initial conditions are necessary to make sure that the algorithm does not become stuck in a local minimum. This is in contrast to MD simulations which suffer from the slowing down of the dynamics at low temperature.

VI. MACROION IN AN EXTERNAL ELECTRIC FIELD

Let us consider a macroion with N microions in an external field $\vec{\mathcal{E}}$. We will restrict ourselves to the case of homogeneous external field so that the dipole and higher moments of the macroion complex are irrelevant. Typical electrophoresis experiments are done in the presence of a homogeneous field.

The total force acting on the complex becomes simply

$$\vec{F} = (qN+Q)\vec{\mathcal{E}}. \tag{13}$$

The complex will thus move in the same direction as the bare macroion if the macroion is undercharged, it will move in the opposite direction if it is overcharged, and it will remain at rest if it is charge neutral.

Having a macroion complex with given N, q, and Q, the interesting question is not in which direction the effective force acts [since that question is trivially answered by Eq. (13)] but rather whether the forces become so large that the system disintegrates. (For a system with only gravity, this problem is referred to as stability under tidal forces.) This was noted earlier when the dependence of the mobility of the macroion complex on an applied field was analyzed [14,34]. While it was shown for a few examples that some microions are "ripped off" the macroion, no systematic study of the stability criterion under an applied external field has been done (to the author's knowledge). Here, we aim to fill this gap.

With an applied external field $\vec{\mathcal{E}}$, Eq. (1) has to be extended to

$$V = \frac{q}{4\pi\epsilon R}\left[q \sum_{i<j}^{1\ldots N} \frac{1}{|\vec{r}_i^{\,\circ} - \vec{r}_j^{\,\circ}|} - q\vec{E}\cdot\sum_{i=1}^{N}\vec{r}_i^{\,\circ} + QN \right], \tag{14}$$

with the reduced electric field

$$\vec{E} = \frac{4\pi\epsilon R^2}{q}\vec{\mathcal{E}}. \tag{15}$$

The concept of *globally stability* introduced in Sec. III cannot be applied in the presence of an external field since the potential energy is not bounded from below [35], and *local* stability of the complex is the relevant concept. Again, we move particle k by a distance $\Delta \ll R$ away from the macroion. To first order, the potential energy V' of the new state then becomes

$$V' = V - \frac{q}{4\pi\epsilon R^2}\left[q \sum_{i\neq k}^{1\ldots N} \frac{1}{2|\vec{r}_i^{\,\circ} - \vec{r}_k^{\,\circ}|} + Q + q\vec{E}\cdot\vec{r}_k^{\,\circ} \right]\Delta \tag{16a}$$

$$\equiv V - \frac{1}{R}h_k\Delta. \tag{16b}$$

The third term in the brackets of Eq. (16a) is the difference to Eq. (10). It describes the interaction with the external field and depends on the angle between the position of the particle and the external field.

As in Sec. IV the macroion complex is locally stable if and only if $h_k<0$ for all k. A closer inspection of Eq. (16a) and comparison to Eq. (14) shows that the big bracket no longer is directly related to the energy of the kth particle (as it was in Sec. IV) as the sign in front of $\vec{E}\cdot\vec{r}_k^{\,\circ}$ is inverted [36].

We have been unable to find analytical expressions for the critical external field at which the macroion complex becomes unstable and had to resort to a numerical solution of Eq. (16). The numerical procedure, however, is basically identical to the one without an applied external field, hence numerically very inexpensive. The result is depicted in Fig. 5. The roughness of the curves is not a sign of a numerical problem but rather due to the physics of the problem. De-

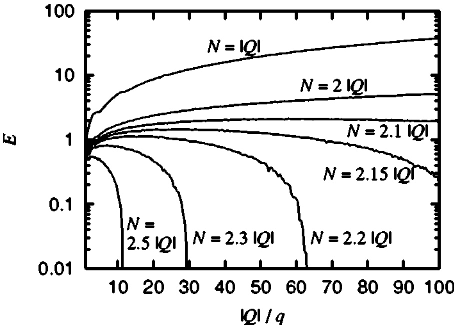

FIG. 5. (Reduced) electric field E above which a state with N microions bound to the macroion is destroyed. (All labels "$|Q|$" inside the figure are to be understood as $|Q|/q$.)

pending on the precise value for N, the geometrical arrangement is more or less symmetrical, resulting in large changes in the dipole moment when N is changed by only 1. Without an external field, this dipole moment is not relevant, and all quantities are smooth functions of N. This is no longer the case now.

In Sec. IV we have shown that it is always possible to bind at least $2|Q|/q$ microions in a locally stable manner. Thus, for $N \leqslant 2|Q|/q$ a finite electric field is necessary to break up the complex. For larger N, however, the critical field may vanish, explaining the division of the diagram into two separate regions by the line $N=2|Q|/q$.

VII. CHARGE DISTRIBUTION BETWEEN TWO MACROIONS

Next, we apply our approach to the case of two well-separated macroions, with charges Q_1 and Q_2, and radii R_1 and R_2, respectively, together with $M \equiv |Q_1+Q_2|/q$ microions so as to achieve charge neutrality. According to Fig. 3 and Eq. (12), there are many different possibilities for distributing those M particles among the two macroions in a locally stable way. The naive result is the one where each dressed macroion becomes charge neutral. However, it is possible that δ microions will be transferred from the first macroion to the second (if $\delta<0$, $|\delta|$ ions are transferred in the opposite direction). Such a state is called "ionized" [17,18,20]. Neglecting interactions among the two macroions, since they are well separated, and applying Eq. (6) gives the potential energy $V(\delta)$,

$$V(\delta)=\frac{q^2}{4\pi\epsilon}\left[\frac{1}{R_1}f(|Q_1|/q+\delta)+\frac{1}{R_2}f(|Q_2|/q-\delta)\right] + \frac{q}{4\pi\epsilon}\left[(|Q_1|/q+\delta)\frac{Q_1}{R_1}+(|Q_2|/q-\delta)\frac{Q_2}{R_2}\right]. \tag{17}$$

We assume that the ions are at very low but finite temperature such that the system can break out of a locally stable state, and to find its lowest-energy state [37]. This state is easily computed from Eq. (17) and provides a relation between Q_1, Q_2, and δ for the ground state. This result is most easily displayed when Q_2 is expressed in terms of the other parameters,

$$|Q_2|=\delta+(\delta+|Q_1|)\frac{R_2^2}{R_1^2}+\frac{4\delta^2}{9c^2}\left(1+\frac{R_2}{R_1}\right)^2 - 4\frac{\delta\sqrt{|Q_1|+\delta}}{c}R_2\frac{R_1+R_2}{R_1^2}. \tag{18}$$

This curve is depicted in Fig. 6 for different ratios of R_1 and R_2. For two identical macroions we find that the lowest-energy state is the nonionized one, whereas for $Q_1 \neq Q_2$ but $R_1=R_2$ the macroion with higher charge attracts more microions than naively expected. This is in agreement with earlier results for $R_1=R_2$ where the correlation effects in a three-dimensional layer were approximated by the effects in a two-dimensional Wigner crystal and confirmed by numerical simulations [17,18,20]. For $R_1 \neq R_2$ the macroions are uncharged only if

$$\frac{Q_1}{R_1^2}=\frac{Q_2}{R_2^2}. \tag{19}$$

Other configurations than the lowest-energy state can be excited thermally, and, due to local stability, can persist for relatively long times.

In a strict mathematical sense, at finite temperature microions cannot be bound to a three-dimensional structure like a sphere. This is in contrast to a rod or a planar geometry [7]. If the temperature is not too high, or equivalently, if the electrostatic coupling is strong enough (i.e., large $|Q_1|$, $|Q_2|$

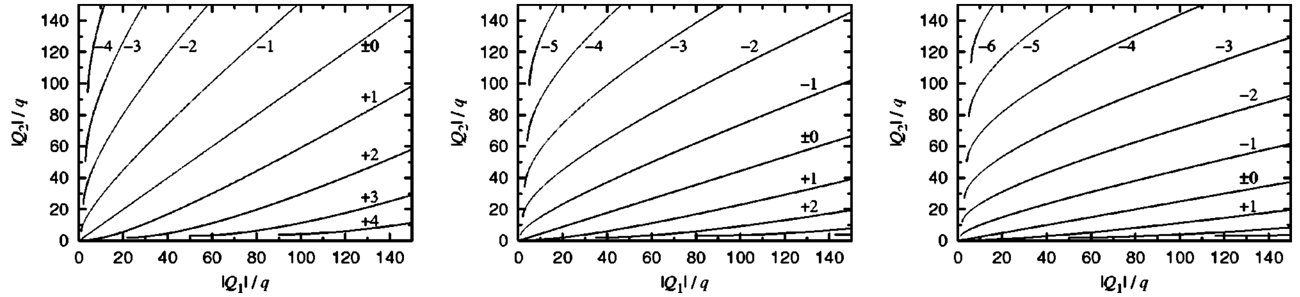

FIG. 6. Overcharging (>0) or undercharging (<0) of the first macroion (in units of q) as a function of the charges Q_1 and Q_2 of the two macroions. The radii of the two macroions are $R_1=R_2$ (left), $R_1=1.5R_2$ (center), and $R_1=2R_2$ (right). The lines are for the lowest-energy configuration.

and q as well as small R), the methods presented in this paper can still be applied in an approximate fashion. Microions stay very close to one macroion for most of the time, before they hop (i.e., move within a time that is short compared to the time that they remain effectively bound) to the other macroion. If we neglect the short hopping phases, the probability for a given ionization level δ is then given by the Boltzmann factor, $P(\Delta)\propto\exp[-\beta V(\delta)]$, and is easily evaluated numerically for arbitrary parameters.

VIII. CONCLUSIONS

To conclude, using general stability concepts we have shown that for a charged macroion a stable overcharged state persists at zero temperature. The number of globally stable microions is given by Eq. (8), the number of locally stable microions is given by Eq. (12). Physically, global stability means that a random arrangement of microions will move to form a layer around the macroion, whereas local stability means that a layer that exists due to initial conditions will persist forever. An applied external field, as used in electrophoresis, decreases the stability of the microion cloud, as demonstrated in Fig. 5. We have also applied this approach to a system of two macroions. In its ground state each of the two macroions acquires a nonvanishing net charge, see Eq. (18), unless Eq. (19) is fulfilled.

At finite temperature, the concept of analyzing the energy as a function of the number of bound microions can still be used to compute the number of globally and locally, respectively, stable microions—provided that the potential energy is replaced by the free energy. The microion free energy is difficult to compute in a precision comparable to that of the potential energy, however, and this is why we refrain from presenting formulas for the finite-temperature case.

In a simple approximation [9], the contribution of each bound microion to the free energy is given by the difference in chemical potential of an ideal gas at the higher density of the bound microions and the lower density of the microions in the bulk solvent. No microions can be bound at finite temperature in the infinite dilution limit. Further complications (e.g., the formation of double layers) can arise if the solvent contains two different species of microions. These effects are outside the scope of this paper.

The value of our approach lies in the fact that it is exact, and by that clarifies the effects caused by finite size, finite charge, correlations, and electrostatic interactions.

ACKNOWLEDGMENTS

This work has been supported by the Academy of Finland Grant No. 54113 (M.K.), the Finnish Academy of Science and Letters (M.K.), and by the Academy of Finland Center for Excellence Program (2000-2005) Project No. 44897 (M. Patriarca).

[1] A.G. Moreira and R.R. Netz, Europhys. Lett. **52**, 705 (2000).
[2] G.S. Manning, J. Chem. Phys. **51**, 924 (1969).
[3] G.S. Manning, J. Chem. Phys. **51**, 934 (1969).
[4] F. Oosawa, *Polyelectrolytes* (Marcel Decker, New York, 1970).
[5] B.I. Shklovskii, Phys. Rev. E **60**, 5802 (1999).
[6] S.Y. Park, R.F. Bruinsma, and W.M. Gelbart, Europhysics. Lett. **46**, 454 (1999).
[7] W.M. Gelbart, R.F. Bruinsma, P.A. Pincus, and V.A. Parsegian, Phys. Today **53**(9), 38 (2000).
[8] A.Y. Grosberg, T.T. Nguyen, and B.I. Shklovskii, Rev. Mod. Phys. **74**, 329 (2002).
[9] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).
[10] E. Allahyarov, I. D'Amici, and H. Löwen, Phys. Rev. Lett. **81**, 1334 (1998).
[11] P. Linse and V. Lobaskin, Phys. Rev. Lett. **83**, 4208 (1999).
[12] M. Mateescu, C. Jeppesen, and P. Pincus, Europhys. Lett. **46**, 493 (1999).
[13] E. Gurovitch and P. Sens, Phys. Rev. Lett. **82**, 339 (1999).
[14] M. Lozada-Cassou, E. González-Tovar, and W. Olivares, Phys. Rev. E **60**, 17 (1999).
[15] T.T. Nguyen, A.Y. Grosberg, and B.I. Shklovskii, J. Chem. Phys. **113**, 1110 (2000).
[16] T.T. Nguyen, A.Y. Grosberg, and B.I. Shklovskii, Phys. Rev. Lett. **85**, 1568 (2000).
[17] R. Messina, C. Holm, and K. Kremer, Phys. Rev. Lett. **85**, 872 (2000).
[18] R. Messina, C. Holm, and K. Kremer, Europhys. Lett. **51**, 461 (2000).
[19] M. Tanaka and A.Y. Grosberg, J. Chem. Phys. **115**, 567 (2001).
[20] R. Messina, C. Holm, and K. Kremer, Phys. Rev. E **64**, 021405 (2001).
[21] R. Messina, C. Holm, and K. Kremer, Comput. Phys. Commun. **147**, 282 (2002).
[22] T. Terao and T. Nakayama, Phys. Rev. E **63**, 041401 (2001).
[23] J.C. Neu, Phys. Rev. Lett. **82**, 1072 (1999).
[24] J.E. Sader and D.Y.C. Chan, J. Colloid Interface Sci. **213**, 268 (1999).
[25] E. Trizac and J.-L. Raimbault, Phys. Rev. E **60**, 6530 (1999).
[26] D. F. Evans and H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet*, 2nd ed. (Wiley, New York, 1999).
[27] At very large number of microions, the curvature of the macroion surface seen by each microion becomes negligible. Then and only then the microion layer becomes two dimensional.
[28] J.J. Thomson, Philos. Mag. **7**, 237 (1904).
[29] T. Erber and G.M. Hockney, J. Phys. A **24**, L1369 (1991).
[30] L. Brito and M. Fiolhais, Eur. J. Phys. **23**, 427 (2002).
[31] S. Earnshaw, Trans. Cambridge Philos. Soc. **7**, 97 (1842).
[32] V. Bulatov, URL http://www.math.niu.edu/ ˜rusin /known-math/96/repulsion
[33] P. G. Drazin, *Nonlinear Systems* (Cambridge University Press, Cambridge, 1992).
[34] M. Tanaka and A.Y. Grosberg, Eur. Phys. J. E. **7**, 371 (2002).
[35] Imagine the bare macroion moving against the direction of the field to infinity, and the microions in the direction of the field.

[36] This sign is easily understood by noting that the energies due to macroion-microion interaction as well as due to microion-microion interaction become smaller in magnitude when the kth microion is moved away but the energy due to the external field becomes larger in magnitude.

[37] Note that this state is not globally stable even though it is the state of lowest energy. In contrast to Sec. III, where no energy barriers existed, they do now.