PHYSICAL REVIEW E VOLUME 48, NUMBER 6 DECEMBER 1993

Phase transitions in solutions of variably ionizable particles

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(Received 16 July 1993)

The problem of an average charge of variably ionizable particles in solutions is investigated. Contrary to the ordinary counterion-condensation theories where only the interaction of the macroion with its own counterion cloud is considered, all types of interactions, i.e., macroion-counterion, macroion-macroion, and counterion-counterion, are taken into account. We develop a mean-field theory for the case of site-bound counterions, so that the one-site partition function of bound counterions is explicitly incorporated in the theory. We find that a first-order phase transition with abrupt change of the average macroion charge occurs in salt-free solutions when the concentration of the macroions is changed. We also observe that a similar first-order phase transition occurs when the concentration of extra salt ions is changed at a fixed concentration of macroions. Contrary to the ordinary counterion-condensation phenomena, the first-order phase transition implies that two phases with different average charges of macroions may coexist in the system.

PACS number(s): 64.70.−p, 64.60.−i, 61.25.Hq, 82.30.Nr

I. INTRODUCTION

In a great variety of phenomena one deals with solutions of variably ionizable particles. Examples of such systems are numerous and include macromolecular solutions, e.g., protein or DNA solutions, micellar solutions, suspensions of charge-stabilized colloids, etc. These particles whose radii range from approximately 10 to 10^4 Å have approximately $10-10^4$ ionizable groups located on the surface and exposed into the surrounding solvent. Electric interactions between the charged particles play an important role both in the equilibrium structure of the solutions (see, e.g., [1–6]) as well as in translational [2,7–11] and rotational motion [12–16] of the solute particles. Therefore the average charge of the solute particles (or, more generally, their charge distribution) is one of the most important characteristics for such systems.

The problem of the average charge of ionizable particles in solutions has nearly a 40-year history and was studied mainly in a context of counterions localization phenomena. Generally there are two main approaches to this problem. One emerges from the early work of Lifson and Katchalsky [17], which deals with the Poisson-Boltzmann equation (see, e.g., [18–23]). The other one is based on the counterion-condensation theory built up by Oosawa [24] and Manning and co-workers [25–29]. This theory predicts that counterions surrounding the polyion should partially condense on its surface when the counterion concentration exceeds some critical value. The polyions are assumed to be rigid, uniformly charged rods and a double limit is considered: The first limit excludes the end effects of the chain whereas the second limit makes the concentration of all ionic species infinitely small with the Debye length tending to infinity [29]. In this double limit the counterion condensation occurs due to electrical instability of the counterion cloud in the potential of the infinitely long charged rod that models strongly elongated DNA macromolecules [29]. More rigorous considerations performed with use of a nonlinear Poisson-Boltzmann equation for infinitely diluted polyion solution show that counterion condensation can also occur for a spherical polyion if its radius becomes larger than a critical length when the surface charge density is kept constant [20].

A somewhat different approach was developed in a recent study by Reed and Reed [30] where the problem of the average charge of a polyion was treated in terms of the so-called *pK* constants [31]. For extremely dilute solutions the authors calculated these constants both theoretically and by Monte Carlo simulations.

All the above theories of the counterion localization are one-body theories (with respect to the polyion subsystem) since only interactions of the macroion with its own counterion cloud are taken into account. Such an approach is valid only if the average distance between macroions, which is of the order $n^{-1/3}$, is much larger than the extension of the counterion cloud, which may be estimated as the Debye screening length associated with counterions, i.e., as $(4\pi l_B n_c)^{-1/2}$, where n and $n_c = Zn$ are the number densities of macroions and counterions (for the salt-free case) respectively, Ze is the average charge of the macroion, and $l_B = (e^2/kT\epsilon)$ is the Bjerrum length. Here ϵ is the dielectric constant of the solvent, e is the electron charge, k is the Boltzmann constant, and T is an absolute temperature. This one-body consideration obviously is not valid when the counterion clouds of different macroions overlap, i.e., when $n < (4\pi l_B Z)^{-3}$. To generalize the counterion-condensation theory for this range of densities one should consider also the macroion-macroion interactions.

Many-body theories for the polyelectrolyte solutions were developed in a number of papers (see, e.g., [32–38]). Here we mention a recent paper by Vilgis and Borsali [39], where elaborated mean-field theory of concentrated polyelectrolyte solutions is evaluated. In these many-body studies, however, the charge density of the polyelec-

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trolyte chains was assumed to be fixed and the problem of its equilibrium value was not studied.

It should also be noted that the microscopic details of the counterion-polyion binding are not considered in the counterion condensation theories. Although two different types of bound counterions, i.e., territorially bound and site bound, were introduced [27–29], no microscopical parameters specifying the type of binding enter these theories. However, a contribution to the total free energy of the system from the bound counterions strongly depends on the type of binding and, as will be shown below, influence dramatically the average charge of variably ionizable particles.

In the present study the restrictive condition $n \gg (4\pi l_B Z n_M)^{-3}$ is not used and macroion-counterion as well as macroion-macroion interactions are taken into account. The microscopic details of bound counterion-macroion interactions are explicitly considered here. We concentrate mainly on the case of the site-bound counterions [27] when the counterions are tightly bound to some particular surface sites. We find that at certain conditions a first-order phase transition occurs: The average charge of the macroion changes abruptly from low to high values, so one can call this phenomenon a "weakly charged–strongly charged macroion" phase transition. In contrast to the ordinary counterion-condensation theories that deal with the single macroion, the first-order phase transition implies that at certain conditions two phases with different average charges of macroions may coexist in the system.

The rest of the paper is organized as follows. In Sec. II we calculate the free energy of the solution taking into account microscopic details of the counterion-macroion interactions as well as electrostatic interactions between various species. Minimizing then the free energy with respect to the concentration of the free counterions we find an equation for the equilibrium charge of the macroion. To clarify the main ideas of our approach we use in this section "physical" arguments, whereas the more rigorous consideration is given in Appendix. In Sec. III we analyze the results obtained and show that the first-order phase transition occurs at a certain interval of the system's parameters. In Sec. IV we summarize our findings.

II. MEAN-FIELD THEORY FOR THE AVERAGE CHARGE OF VARIABLY IONIZABLE SOLUTE PARTICLES

In this section we give simple mean-field considerations of the problem. The basic ideas of our approach are the following: First we introduce the chemical potential for the bound counterions subsystem μ and calculate the grand thermodynamic potential $\Omega(\mu)$ for this subsystem. The average charge $\overline{Q}(\mu)$, the average square charge $\overline{Q^2}(\mu)$ of the macroions, and the average number of bound counterions $N_b(\mu)$ may then be calculated easily. At the second step we calculate the conditional free energy of the solution $F(N_f)$ with the condition imposed that the number of free counterions in solution is equal to N_f. This conditional free energy depends also on μ. Taking into account that $N_f + N_b(\mu) = N_c$, where N_c is the total number of counterions in the solution that remains fixed, one can consider the chemical potential as a function of N_f, i.e., $\mu = \mu(N_f)$. The last step is to minimize the conditional free energy with respect to N_f in order to obtain an equation for the equilibrium number of free counterions in the solution and thus the average charge of the macroion. As shown in Appendix, these physically reasonable considerations give the same results as the more rigorous ones. Let us now calculate the conditional free energy $F(N_f)$.

Assume for simplicity that our variably ionizable solute particles have a compact globular structure with ionizable groups located on their surface. Also assume that the charge of the solutes does not influence their equilibrium shape. Let the system of interest be composed of N macroions with ℓ ionizable groups per each particle that immersed in dielectric solvent with dielectric constant ϵ (the so-called "primitive model" of the solvent) and V be the volume of the system. First we consider the salt-free case with the site-bound model for counterions binding. The latter means that the counterions are tightly bound to the macroion and are in direct contact with active groups on its surface. The ionizable group may be in two states: a neutral state with a tightly bound counterion and a charged (dissociated) state.

Since the total number of counterions is $N_c = \ell N$, one can write for the partition function of the salt-free solution

$$Z = Z_{\text{int}} (N! N_c!)^{-1} \int d\Gamma\, d\Gamma_c \exp(-\beta H) , \quad (1)$$

$$H = H_M + H_C + H_{MC} + H_0 . \quad (2)$$

Here Z_{int} is the partition functions of the internal degrees of freedom of the solute particles, $\beta = (kT)^{-1}$, H denotes the Hamiltonian of the system with H_0 being the part of the Hamiltonian responsible for the kinetic energy of the macroions and counterions, H_M, H_C, and H_{MC} denote the macroion-macroion, counterion-counterion, and macroion-counterion interactions, respectively. These terms include all the interactions between different species: Coulomb interactions, hard-core, van der Waals, and additional repulsive interactions (see, e.g., [40–42]) that arise when charged solutes are immersed in a dielectric continuum. $d\Gamma = (h^{-3N}) dR_1 \cdots dR_N dP_1 \cdots dP_N$ denotes integration over the coordinates and impulses of N macroions, respectively, whereas $d\Gamma_c$ denotes the same for N_c counterions. Note that writing Eqs. (1) and (2) we assume implicitly that internal degrees of freedom of the macroions are not coupled to the other degrees of freedom. The more general case is considered at the end of the section.

To calculate the conditional free energy one can notice that the imposed condition of N_f free counterions implies that the number of bound counterions N_b is equal to $\ell N - N_f$. Thus it is convenient to extract the subsystem of N_b bound counterions and treat them separately. For definiteness we assume that electrostatic interaction energy of the bound counterions with macroion is more than kT, whereas for the free counterions it is less than kT.

One can neglect interactions of the bound counterions with the free ones since they are negligibly small compared to strong interactions of the tightly bound counterions with the active sites on the macroion. Therefore one can write for the free energy

$$F=F_{\text{int}}+F_b+F_f\ , \tag{3}$$

where F_{int} is the free energy of the internal degrees of freedom of the macroions, F_f is the free energy of macroions (as structureless particles) and free counterions, and F_b is the free energy of bound counterions. The latter may be written as follows:

$$F_b(N_b)=\Omega_b+\mu N_b\ , \tag{4}$$

where Ω_b is the grand thermodynamic potential for the bound counterions and μ is the corresponding chemical potential. Denote $a_1,a_2,\dots,a_N$ as numbers of counterions tightly bound to the 1st,2nd, . . . ,Nth macroion. Let, for simplicity, all the active surface sites of the macroion be identical. Then one has for Ω_b

$$\begin{aligned}\Omega_b&=-kT\ln\Biggl\{\sum_{N_b=0}^{lN}(N_b!)^{-1}\exp(\beta\mu N_b)\sum_{a_1,a_2,\dots,a_N}\Delta(a_1+a_2+\cdots+a_N-N_b)\frac{N_b!}{a_1!a_2!\cdots a_N!}\\&\qquad\times\begin{bmatrix}\ell\\a_1\end{bmatrix}a_1!Z_b^{a_1}\begin{bmatrix}\ell\\a_2\end{bmatrix}a_2!Z_b^{a_2}\cdots\begin{bmatrix}\ell\\a_N\end{bmatrix}a_N!Z_b^{a_N}\Biggr\}\\&=-kT\ln\Biggl\{\sum_{a_1=0}^{\ell}\cdots\sum_{a_N=0}^{\ell}\begin{bmatrix}\ell\\a_1\end{bmatrix}a_1!\zeta^{a_1}\cdots\begin{bmatrix}\ell\\a_N\end{bmatrix}a_N!\zeta^{a_N}\Biggr\}\ .\end{aligned}\tag{5}$$

Here $\Delta(j)=\delta_{0j}$, $[{\ell \atop a}]=\ell!/a!(\ell-a)!$, Z_b is a one-site partition function for a bound counterion, and $\zeta=Z_b\exp(\beta\mu)$. Deriving Eq. (5) we assume that (i) only one counterion can be bound to an active site and (ii) counterions bound on different sites do not interact with each other (the latter approximation will be discussed below). The one-site partition function Z_b may be calculated with the use of various models. Here we emphasize that its particular value is determined by local properties of the active-site–counterion interactions. Calculating Ω_b we obtain

$$\Omega_b=-\ell NkT\ln[1+Z_b\exp(\beta\mu)]\ . \tag{6}$$

Therefore one has for the average number of bound counterions per macroion $\bar{a}$

$$\begin{aligned}\bar{a}&=(a_1+a_2+\cdots+a_N)/N\\&=\sum_{a_1,a_2,\dots,a_N}(a_1+a_2+\cdots+a_N)\\&\qquad\times\begin{bmatrix}\ell\\a_1\end{bmatrix}\zeta^{a_1}\cdots\begin{bmatrix}\ell\\a_N\end{bmatrix}\zeta^{a_N}\exp(\beta\Omega_b)/N\\&=-N^{-1}\frac{\partial\Omega_b}{\partial\mu}=\ell Z_b\exp(\beta\mu)[1+Z_b\exp(\beta\mu)]^{-1}\ .\end{aligned}\tag{7}$$

In the same manner it is easy to obtain the following result for the average square of this value $\overline{a^2}$:

$$\begin{aligned}\overline{a^2}&=(a_1^2+a_2^2+\cdots+a_N^2)/N\\&=\sum_{a_1,a_2,\dots,a_N}N^{-1}(a_1^2+a_2^2+\cdots+a_N^2)\\&\qquad\times\begin{bmatrix}\ell\\a_1\end{bmatrix}\zeta^{a_1}\cdots\begin{bmatrix}\ell\\a_N\end{bmatrix}\zeta^{a_N}\exp(\beta\Omega_b)\\&=(1-\ell^{-1})(\bar{a})^2+\bar{a}\ .\end{aligned}\tag{8}$$

Thus we have for the average charge of the macroion

$$\begin{aligned}\bar{Q}&=eN^{-1}[(\ell-a_1)+(l-a_2)+\cdots+(\ell-a_N)]\\&=e(\ell-\bar{a})=\bar{Q}(\mu)\end{aligned}\tag{9}$$

and for the average square charge

$$\begin{aligned}\overline{Q^2}&=e^2N^{-1}[(\ell-a_1)^2+(\ell-a_2)^2+\cdots+(\ell-a_N)^2]\\&=e^2[(\ell-\bar{a})^2+\bar{a}-\bar{a}^{\,2}/l]=\overline{Q^2}(\mu)\ .\end{aligned}\tag{10}$$

Here $\bar{a}=\bar{a}(\mu)$ is given by Eq. (7). Turn now to the calculation of the free energy of the macroions and free counterions F_f. For this function one can write

$$F_f=-kT\ln\left[(N!N_f!)^{-1}\left\langle\int d\Gamma\, d\Gamma_f\exp(-\beta H_f)\right\rangle\right]\ , \tag{11}$$

where $N_f=N_c-N_b=\ell N-N_b$ is the number of free counterions in the solution, $d\Gamma$ and $d\Gamma_f$ denote integration over $6N$ coordinates and impulses of macroions and over $6N_f$ coordinates and impulses of free counterions, respectively. The interaction part of Hamiltonian H_f in Eq. (11) includes only interactions between free counterions, between free counterions and charged sites of macroions, and between charged sites of different macroions. Actually, the particular form of the Hamiltonian H_f depends on the particular distribution of the bound counterions over macroions. Therefore the symbol $\langle\ \rangle$ denotes averaging over all possible distributions of N_b bound counterions over various active sites of N macroions in solution (for details see the Appendix).

Integration over impulses gives the ideal-gas contribution:

$$\begin{aligned}\beta F_{\text{id}}&=N[\ln(N/V)+\ln(\Lambda_M^3)-1]\\&\quad+N_f[\ln(N_f/V)+\ln(\Lambda_c^3)-1]\ ,\end{aligned}\tag{12}$$

where $\Lambda_M = h(2\pi MkT)^{-1/2}$, $\Lambda_c = h(2\pi mkT)^{-1/2}$, and M and m are masses of macroion and counterion, respectively. (Note that since $M \gg m$ the value of F_{id} depends only on N_f and not on the particular bound counterions distribution.)

Integration over coordinates in Eq. (11) (with the subsequent averaging) actually means the calculation of the configurational integral for a multisort system where the "sort" of the macroion particle corresponds to some particular distribution of the bound counterions over its active sites. The configurational integral should then be averaged over various bound counterion distributions. One can also use a more direct way of calculating this function if the thermodynamic limit $N \to \infty, V \to \infty$, $n = N/V = \text{const}$ is implied. In this limit all the possible distributions of the counterions over the macroion active sites (all the possible sorts) are represented in the system. The number of macroions corresponding to some particular distribution of counterions (i.e., the number of particles of some particular sort) is proportional to the probability of this particular distribution. Therefore in the latter approach one deals only with the multisort system and does not need the subsequent averaging. Calculation of the configurational integral actually may be performed only in a framework of some approximation scheme. It may be done in a number of ways, e.g., with the use of integral equations, or a diagrammatic or collective-coordinate method. In our case of the multisort system with a great number of different sorts, the diagrammatic [43] or collective-coordinate method [40] seems to be the most convenient.

Calculations are significantly simplified for dilute systems. In the latter case one can treat the Coulomb interactions as basic interactions and interactions of the other types as a perturbation. In a random-phase approximation (RPA) that is widely used for Coulomb systems one can write for the free energy

$$F_f = F_{\text{id}} + F_{\text{RPA}} + \beta^{-1}(B_2 + B_3 + \cdots) , \tag{13}$$

where F_{RPA} is the leading term in the RPA expansion for the multisort system. It may be obtained in the usual manner [43] of summing up all the ring diagrams in the expansion of the function $\exp(-\beta H_f)$ in Eq. (11). It is not difficult to show that the free energy in the random-phase approximation is the following:

$$-\beta F_{\text{RPA}} = (V/8\pi^3)2\pi \times \int_0^\infty k^2 dk \left\{ \frac{\overline{\chi^2(\mathbf{k})}}{\mathbf{k}^2} - \ln\left[1 + \frac{\overline{\chi^2(\mathbf{k})}}{\mathbf{k}^2}\right]\right\} \tag{14}$$

where

$$\overline{\chi^2(k)} = (4\pi\beta/\epsilon)[n_f q_c^2 + n e^2 \overline{S(\mathbf{k}) S^*(\mathbf{k})}] \tag{15}$$

is k-dependent inverse Debye screening length (note that ϵ also may be considered as a $\mathbf{k}$-dependent value), $n = N/V$, $n_f = N_f/V$, and q_c is counterion charge. The value $\overline{S(\mathbf{k}) S^*(\mathbf{k})}$ can be called a charge structure factor for a single macroion:

$$\begin{aligned} e^2\overline{(\mathbf{k}) S^*(\mathbf{k})} &= \int d\omega \left\langle \sum_{\alpha,\gamma} q_\alpha q_\gamma \exp[i\mathbf{k}\cdot(\mathbf{r}_\alpha - \mathbf{r}_\gamma)] \right\rangle \\ &= N^{-1} \sum_{i=1}^{N} \int d\omega_i \sum_{\alpha_i,\gamma_i} q_{\alpha_i} q_{\gamma_i} \exp[i\mathbf{k}\cdot(\mathbf{r}_{\alpha_i} - \mathbf{r}_{\gamma_i})] \\ &= \left\langle \sum_{\alpha,\gamma} q_\alpha q_\gamma \frac{\sin(kl_{\alpha\gamma})}{kl_{\alpha\gamma}} \right\rangle . \end{aligned} \tag{16}$$

Here $\int d\omega_i$ denotes integration over the orientational coordinates of the ith macroion, q_{α_i} is the charge on the αth active site of the ith macroion, and $\mathbf{r}_{\alpha_i}$ is its radius vector with respect to macroion axes. $l_{\alpha\gamma} = |\mathbf{r}_\alpha - \mathbf{r}_\gamma|$ is the distance between the αth and γth active sites on the macroion surface. The summation in Eq. (16) is carried out over all the active surface sites of the macroion (indexes α and γ). Note that the thermodynamic limit in Eq. (16) is implied, so that the averaging over all possible counterions distributions and averaging (i.e., summation) over all macroions in the system give the same result. The values $B_2, B_3, \ldots$ in expansion (13) are, respectively, the second, third, etc. ionic virial coefficients that may be expressed in terms of equilibrium structure functions of pure Coulomb systems and short-range non-Coulomb interaction potentials [40,43]. Since the characteristic length of these short-range interactions is of the order of R, where R is some characteristic size of the macroion, one concludes that these coefficients may be roughly estimated to be of the order (nR^3) for B_2, $(nR^3)^2$ for B_3, etc. [40,43].

Details of the derivation of Eqs. (14)–(16) can be found in the Appendix, where the method of collective coordinates is used. It should be noted that the RPA, which has the same range of applications as the linear Debye-Huckel theory, is a rather relevant approximation in our case since we assume that the electrostatic interaction energy for the free counterions is less than the average thermal energy kT.

Since we assume that counterions bound on different active sites of a macroion do not interact with each other and thus the binding occurs independently, one obtains for the structure factor (for details see the Appendix)

$$e^2\overline{S(\mathbf{k})\, S^*(\mathbf{k})} = [(1-\ell^{-1})^{-1} f(k) + (1-\ell)^{-1}](\bar{Q}^2 - \bar{Q}e) + \bar{Q}e , \tag{17}$$

where $\bar{Q}$ is the average charge and $\overline{Q^2}$ is the average square charge of the macroions, which are given by Eqs. (7), (9), and (10), whereas the function $f(k) = \ell^{-2}\sum_{\alpha,\gamma} \sin(kl_{\alpha\gamma})/kl_{\alpha\gamma}$ characterizes the distribution of the active sites on the macroion surface. If the surface groups are distributed uniformly and randomly over the macroion's surface, one has $f(k) = [\sin(kR)/kR]^2$ for a spherical particle of radius R and $f(k) = (kL)^{-1}\int_0^{kL} (\sin x/x)^2 dx$ for an infinitely thin needle of length L. Note that if $k \ll R^{-1}$, or $k \ll L^{-1}$, then $f(k) \simeq 1$ and thus $e^2\overline{S(\mathbf{k}) S^*(\mathbf{k})} = \overline{Q^2}$. Therefore one concludes that if $\chi(0)R \ll 1$, where R is some characteristic size of the macroion, one can use the latter result for $e^2S(\mathbf{k})S^*(\mathbf{k})$ and obtain from Eq. (14) the usual RPA expression for the free energy [40,43]:

$$-\beta F_{\rm RPA}=(V/12\pi)(\bar{\chi}_D)^3\ , \tag{18}$$

$$(\bar{\chi}_D)^2=(4\pi\beta/\epsilon)(n\overline{Q^2}+n_f q_c^2)\ . \tag{19}$$

Using Eq. (10) and taking into account that $\bar{a}=N_b/N=(\ell N-N)/N=\ell-n/n_f$, one finally obtains for monovalent counterions

$$-\beta F_{\rm RPA}=(V/12\pi)(4\pi e^2\beta/\epsilon)^{3/2}(2n_f+n_f^2/n)^{3/2}\ . \tag{20}$$

Since $N_b=\ell N-N_f$ one can write

$$F(N_f)=\Omega_b(\mu)+\mu(\ell N-N_f)+F_f(N_f)\ . \tag{21}$$

Equation (21), together with Eqs (6), (12), (13), and (20) for $F_f(N_f)$, gives the desired result for the conditional free energy of the solution. Assume that the system is dilute enough so that one can neglect the virial coefficient $B_2, B_3, \ldots$. In this case Eqs. (6), (12), (13), (20), and (21) form a complete set of equations. The condition for the minimum of the free energy $(\partial F/\partial N_b=-\partial F/\partial N_f=0)$ yields the relation for the chemical potentials:

$$\mu=\mu_f=\frac{\partial F_f}{\partial N_f}\ , \tag{22}$$

where μ_f is a chemical potential for the free counterions in the solution. Equation (22), together with the relation $N_b=\ell N-N_f=-\partial\Omega_b/\partial\mu$, gives the system of equations:

$$\mu=\beta^{-1}\ln(\alpha n\Lambda_c^3)-(\chi_D e^2/\epsilon)(2\alpha+\alpha^2)^{1/2}(1+\alpha)\ , \tag{23}$$

$$\alpha=\ell[1+Z_b\exp(\beta\mu)]^{-1}\ . \tag{24}$$

Here we introduce the dissociation rate $\alpha=N_f/N$ that is actually the dimensionless average charge of the macroion, i.e., $\bar{Q}=e\alpha$ and the parameter χ_D corresponds to the inverse Debye screening length associated with the macroions, i.e., $\chi_D^2=(4\pi\beta e^2 n/\epsilon)$. Equations (23) and (24) may be rewritten as follows.

$$\frac{\ell-\alpha}{\alpha^2}=n(Z_b\Lambda_c^3)\exp\left[-\frac{\beta e^2\chi_D}{\epsilon}(2\alpha+\alpha^2)^{1/2}(1+\alpha)\right]\ . \tag{25}$$

Equation (25), corresponding to the salt-free case, may be easily generalized to take into account the added salt ions:

$$\frac{\ell-\alpha}{\alpha^2}=n(Z_b\Lambda_c^3)\times\exp\left[-\frac{\beta e^2\chi_D}{\epsilon}(2\alpha+\alpha^2+i_s)^{1/2}(1+\alpha)\right]\ , \tag{26}$$

with $i_s=2I_s/ne^2$, where $I_s=\frac{1}{2}\sum_a q_a^2 n_a$ is the partial ionic strength of the solution associated with the added salt, and q_a and n_a are, respectively, the charge and number density for ions of a sort a. Using Eqs. (23) and (24) one can also write down the conditional free energy as a function of α (up to a temperature dependent constant):

$$\beta F(\alpha)/N=\ell\ln\left[\frac{\ell-\alpha}{\ell Z_b}\right]+\alpha\ln\left[\frac{\alpha Z_b}{\ell-\alpha}\right]+\alpha\ln(n\alpha\Lambda_c^3)+\frac{\chi_D^{3/2}}{12\pi n}(\alpha^2+2\alpha)^{3/2}-\alpha+\ln(n\Lambda_M^3)\ . \tag{27}$$

Equation (27), written for the salt-free case, is simply generalized for the added-salt case, substituting the factor $(\alpha^2+2\alpha)$ by the factor $(\alpha^2+2\alpha+i_s)$. Equations (25)–(27) are the main result of our study.

The partition function for the bound counterion Z_b may be calculated if some particular model is chosen. Here we consider the case of site-bound counterions. Let the counterions be tightly bound to the active sites, being in a direct contact with the macroion surface. One can write for the one-site counterion partition function Z_b

$$Z_b=h^{-3}\int\exp(-\beta\mathbf{p}^2/2\mu_0)d\mathbf{p}\times\int\exp[-\beta u(\mathbf{r})-\beta\phi(\mathbf{r})]d\mathbf{r}\ , \tag{28}$$

where $\mathbf{r}=\mathbf{R}_M-\mathbf{r}_c$ is the relative coordinate of the counterion with respect to macroion, $\mu_0=mM(m+M)^{-1}\simeq m$ is the reduced mass, and $\mathbf{p}$ is the relative impulse. $u(\mathbf{r})$ and $\phi(\mathbf{r})$ respectively denote the Coulomb and short-range non-Coulomb interactions (e.g., van der Waals, hard-core, etc.) of the counterion with the active surface site. For the tightly bound counterion we use here the harmonic approximation. The latter means that the total interaction potential is expanded at the equilibrium point, say $\mathbf{r}_0$, up to the second-order terms, i.e.,

$$u(\mathbf{r})+\phi(\mathbf{r})=-E_0+(m\omega_\perp^2\delta r_\perp^2)/2+2(m\omega_\parallel^2\delta r_\parallel^2)/2\ . \tag{29}$$

Here $-E_0=u(\mathbf{r}_0)+\phi(\mathbf{r}_0)$ is an energy of the bound counterion at its equilibrium position ("binding energy"). Note that $E_0>0$ by its definition. $\delta r_\parallel$ and $\delta r_\perp$ denote, respectively, tangential and normal (with respect to the macroion surface) deviations of the counterion from its equilibrium position $\mathbf{r}_0$. $m\omega_\parallel^2$ and $m\omega_\perp^2$ are, respectively, the tangential and normal second-order derivatives of the total counterion-macroion potential, calculated at point $\mathbf{r}_0$. Actually, $\omega_\parallel$ and $\omega_\perp$ are frequencies of tangential and normal vibrations that the counterion performs when it is bound at some active site. In the harmonic approximation the value of Z_b may be easily evaluated:

$$Z_b=\Lambda_c^{-3}(2\pi/m\omega_0^2\beta)^{3/2}\exp(\beta E_0)\ , \tag{30}$$

where $\omega_0^3=\omega_\perp\omega_\parallel^2$. Strictly speaking, the expansion in Eq. (29) is not complete. Actually, the interaction potential of the bound counterion with the macroion depends on the positions of the macroion atoms, say $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_k$, i.e., $u(\mathbf{r})+\phi(\mathbf{r})=\mathcal{V}(\mathbf{r},\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_k)$. These macroion atoms also perform permanent vibrations, but this is not taken into account in Eq. (31). Therefore one should expand the total potential with respect to small deviations from the equilibrium positions not only for the counterion but also for the macroion atoms, i.e.,

$$u(\mathbf{r})+\phi(\mathbf{r})=-E_0+(m\omega_\perp^2\delta r_\perp^2)/2+2(m\omega_\parallel^2\delta r_\parallel^2)/2 -U_0+\sum_\alpha \mathcal{K}_\alpha^2\xi_\alpha^2/2 +\sum_\alpha (g_{\alpha\perp}\xi_\alpha\delta r_\perp+2g_{\alpha\parallel}\xi_\alpha\delta r_\parallel) , \tag{31}$$

where $-U_0$ is the energy of macroions atoms at equilibrium positions without bound counterions and ξ_α and $\mathcal{K}_\alpha$ are, respectively, amplitudes and frequencies (multiplied on a square root of effective masses) of the αth normal mode for the macroion atoms, such that the deviation of jth atom from its equilibrium position δx_j is given by the linear combination of normal modes, i.e., $\delta x_j=\sum_\alpha b_{j\alpha}\xi_\alpha$. The last sum in Eq. (31) describes the coupling of the counterion vibration modes with the normal vibration modes of the macroion atoms. The coupling constants $g_{\alpha\perp}$ and $g_{\alpha\parallel}$ are given by the relations $g_{\alpha\perp,\parallel}=\sum_j b_{j\alpha}\partial^2\mathcal{V}(\mathbf{r},\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_k)/\partial x_j\partial(\delta r_{\perp,\parallel})$, where the derivatives are taken at the equilibrium positions.

One can see that the internal degrees of freedom of the macroions are coupled now with degrees of freedom of bound counterions. Therefore Eqs. (1)–(3) should be generalized. This may be simply done rewriting Eq. (3) in the following way:

$$F=F_{\text{int}}+\langle F_b\rangle_{\text{int}}+F_f , \tag{32}$$

where F_{int} is, as previously, the part of the free energy associated with the internal degrees of freedom of the macroions:

$$\exp(-\beta F_{\text{int}})=\int d\Gamma_{\text{int}}\exp(-\beta H_{\text{int}}^0) . \tag{33}$$

Here H_{int}^0 is Hamiltonian for the internal degrees of freedom of the macroions (with no coupling terms to the other degrees of freedom of the system) and $d\Gamma_{\text{int}}$ denotes integration over the internal degrees of freedom. $\langle F_b\rangle_{\text{int}}$ is defined as follows:

$$\exp(-\beta\langle F_b\rangle_{\text{int}})=\int d\Gamma_{\text{int}}\exp\{\beta F_{\text{int}}-\beta H_{\text{int}}^0\} \times\left[\int d\Gamma_b\exp\{-\beta H_b-\beta H_{\text{int},b}\}\right] . \tag{34}$$

The Hamiltonian H_b in Eq. (34) includes only degrees of freedom of bound counterions whereas $H_{\text{int},b}$ describes the coupling between bound counterions and the internal degrees of freedom. For a single bound counterion the value of $H_{\text{int},b}$ is given by the last sum in Eq. (31) whereas for the whole system summation over all the bound counterions and macroions should be carried out. Assume for simplicity that the normal vibrations of the macroion atoms may be treated classically [this corresponds to the high-temperature Boltzmann distribution for the normal modes (phonons) of the macroions atoms]. Then simple but tedious calculations show that for the case of weak coupling, i.e., when $\omega_0^2\gg\Omega^2=\sum_\alpha(g_\alpha^2/2\mathcal{K}_\alpha^2)$, an explicit expression for the value of $\langle F_b\rangle_{\text{int}}$ may be evaluated. The latter coincides with F_b, obtained previously for the case when the internal degrees of freedom of macroions are not coupled to the other degrees of freedom but with the one-site partition function Z_b substituted by the averaged one-site partition function $\langle Z_b\rangle_{\text{int}}$:

$$\langle Z_b\rangle_{\text{int}}=\Lambda_c^{-3}(2\pi/m\tilde{\omega}^2\beta)^{3/2}\exp(\beta E_0) , \tag{35}$$

where $\tilde{\omega}$ is renormalized vibrational frequency

$$\tilde{\omega}^2=\omega_0^2-\Omega^2=\omega_0^2-\sum_\alpha(g_\alpha^2/2\mathcal{K}_\alpha^2) . \tag{36}$$

Deriving Eqs. (35) and (36) we assume that $\omega_0=\omega_\parallel=\omega_\perp$ and $g_\alpha=g_{\alpha\parallel}=g_{\alpha\perp}$. As one can see from Eq. (36) the renormalized frequency $\tilde{\omega}$ is less than the frequency ω_0, corresponding to the case when the internal motions of the macroions are "frozen" (the model of the "hard" macroion). That means that the value of $\langle Z_b\rangle_{\text{int}}$ increases when the internal vibrations in macroions are taken into account (the model of the "soft" macroion). Although the simple explicit expression may be obtained only in the case of a weak coupling, analysis shows that this conclusion generally holds true: the value $\langle Z_b\rangle_{\text{int}}$ for the soft-macroion model exceeds the latter one for the hard-macroion model. Moreover, at some particular cases, when a soft mode with a low frequency proportional to $\mathcal{K}_0$ exists, such that the coefficient g_0 is nonzero and the phonon distribution function at these frequencies does not tend to zero, one can expect a significant increase of the average one-site partition function $\langle Z_b\rangle_{\text{int}}$.

If the counterions are not in direct contact with the macroion surface one can use the Bjerrum approach to calculate the partition function Z_b. Following Bjerrum, define the bound ions as ions which electrostatic interaction energy with the macroion exceeds the average thermal energy β^{-1}. Thus a natural length scale, the so-called Bjerrum length $l_B=e^2\beta/\epsilon$, arises. It gives a distance at which the electrostatic energy of two unit charges immersed in a solvent with dielectric constant ϵ is equal to the average thermal energy. In spirit of the Bjerrum approach we obtain the following estimate for the value of Z_b:

$$Z_b=h^{-3}\int\exp(-\beta\mathbf{p}^2/2\mu_0)d\mathbf{p} \times\int\exp[-\beta u(\mathbf{r})-\beta\phi(\mathbf{r})] \times\Theta(|\beta u(\mathbf{r})+\beta\phi(\mathbf{r})|-1)d\mathbf{r} . \tag{37}$$

Here $\Theta(x)=1$ if $x\geq 0$ and $\Theta(x)=0$ otherwise. Note that in the framework of this approach one can consider not only the site-bound but also territorially bound counterions. If the Bjerrum length l_B exceeds an average distance between the active sites on the macroion surface b, then one deals with the territorially bound counterions; in the opposite case $l_B<b$, one has the site-bound counterions. Here we study the latter case. Note that if $l_B\ll b$, one can consider the binding of the counterions on the different sites as independent.

Let the short-range interactions $\phi(\mathbf{r})$ be the hard-core interactions of a hard spheres of radii R (macroion) and r_0 (counterion) (the so-called "restricted primitive model"). Let the active site be located at depth r_0 from the macroion surface; then one obtains for the one-site partition function (note that when the counterion is not tightly bound to macroion there is no need to consider the internal vibrational modes of macroion)

$$Z_b=\Lambda_C^{-3}2\pi l_B^3 \int_1^b dy\, \exp(-y)y^{-4} \times\{1-(1-r_0/R)^{-1} \times[1-(r_0/R)(b/y)^2](y/b)\} \,, \tag{38}$$

where $b=l_B/2r_0$. If $r_0 \ll R$, Eq. (38) is reduced to

$$Z_b=\Lambda_C^{-3}2\pi l_B^3 \int_1^b dy\, \exp(-y)(y^{-4}-b^{-1}y^{-3}) \,. \tag{39}$$

The case of territorially bound ions is not considered in the present study. Here we only mention that the corresponding partition function for counterions, which for this case are delocalized on the macroion surface, may be calculated following the line of counterion-condensation theory (see, e.g., [25]).

III. RESULTS AND DISCUSSION

Let us now analyze the obtained results. First consider the dependence of the free energy of the solution on the dissociation rate $\alpha=N_f/N$ (i.e., on the average macroion charge $\bar{Q}=\alpha e$). This dependence is given by Eq. (27). Calculating $F(\alpha)$ for different values of the macroions concentration we observe the following behavior of this function: When the macroion concentration n is less than n_1 or more than n_2, the $F(\alpha)$ dependence has only one minimum corresponding to the equilibrium value of α. At the same time in the concentration region $n_1<n<n_2$ the function $F(\alpha)$ has two minima. The lower minimum corresponds to the stable state of the system while the upper minimum to the metastable one. At $n=n_0$ these two minima have an equal depth, which means that two stable phases with different values of α (the average charges of macroions) coexist in the system. Thus we conclude that the first-order phase transition occurs when the macroion density n becomes equal to n_0.

To find the equilibrium charge of the macroion one can also solve Eq. (25), which gives the free-energy extrema. This equation was solved numerically and the results are shown in Figs. 1 and 2 for two different systems. For the first system we take $\ell=100$ and for the second one $\ell=500$ active sites on the macroion surface. The first-order phase transition appears as van der Waals loops at isotherms $\alpha=\alpha(n)=\bar{Q}(n)/e$. The Maxwell construction may be used in a proper way to find the coexistence points and suppress unstable and metastable regions. However, since the expression for the free energy is known explicitly [see Eq. (27)], there is no need to use the Maxwell construction. Actually, using Eq. (27) one can easily find the root of Eq. (25) corresponding to the stable minimum. In Figs. 1 and 2 the parts of the isotherms corresponding to the stable minimum are shown by the thick dots, while the isotherms corresponding to the unstable minimum and maximum of the free energy are shown by medium and thin dots, respectively. The actual isotherms are those that are built up by the thick-dotted lines. If the isotherm has two branches of the thick-dotted line, the upper and lower branches should be connected by a vertical line (the latter are not shown in Figs. 1 and 2). Since the average charge of the macroions $\bar{Q}=\alpha e$ changes from the low values $\bar{Q}/e\simeq 1$ to the high ones $\bar{Q}/e\simeq \ell \gg 1$, one can call this transition a "weakly

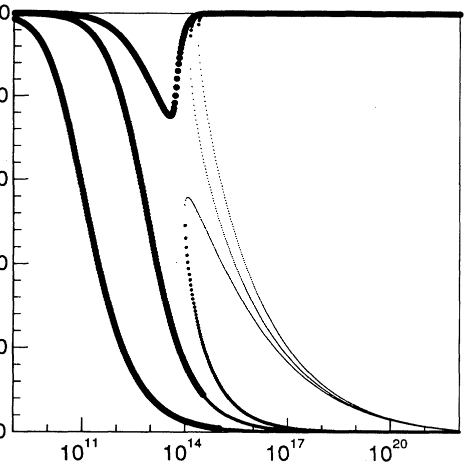

FIG. 1. Concentration dependence of the average macroion charge $\bar{Q}/e$ versus concentration of macroions n for the salt-free case. Here the thick-dotted lines correspond to the lower (stable) minimum of the free energy, the medium-dotted lines to the upper minimum, and the thin-dotted lines to its maximum value. The number of active sites $\ell=100$. $\omega_0=10^{14}$ s^{-1}, $m=1.64\times10^{-24}$ g, and $E_0/kT_0=26$ at $T_0=300$ K. The curves from left to right correspond to $T=0.91T_0$, $1.05T_0$, and $1.12T_0$, respectively.

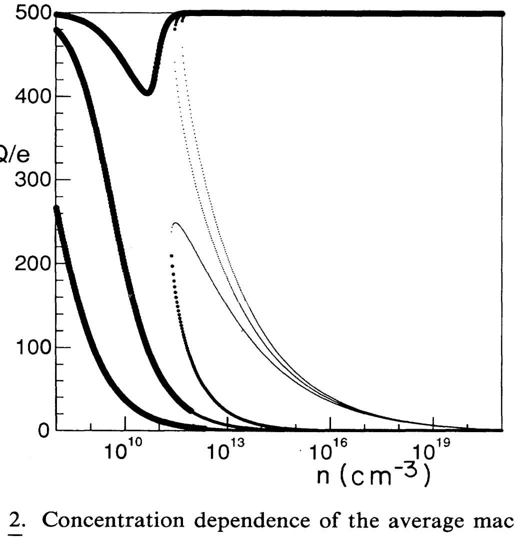

FIG. 2. Concentration dependence of the average macroion charge $\bar{Q}/e$ versus concentration of macroions n for the salt-free case. The number of active sites $\ell=500$. $\omega_0=10^{14}$ s^{-1}, $m=1.64\times10^{-24}$ g, and $E_0/kT_0=31$ at $T_0=300$ K. The curves from left to right correspond to $T=0.91T_0$, $1.02T_0$, and $1.11T_0$, respectively. The designations are the same as in Fig. 1.

charged macroion–strongly charged macroion" phase transition.

From Figs. 1 and 2 one can see that at an extremely dilute limit, when $n \rightarrow 0$, the macroions are practically completely ionized, i.e., $\bar{Q}/e \simeq \ell$. This result is in agreement with the conclusion of Zimm and LeBret [44] and also with a later conclusion by Ramanathan [20] that a sphere of a fixed radius and charge cannot confine a cloud of counterions around itself, if the limit of infinite dilution is considered. When the concentration of macroions increases, the average charge decreases since some of the counterions become bound on the active sites of the macroions. This resembles in some sense the usual absorption of a gas on active sites on a surface when the average coverage rate increase with increasing density of gas. When the concentration further increases the sudden jump of the average charge up to the highest value occurs. However, if the temperature exceeds the critical temperature (one of the most important parameters for the first-order phase transitions) no abrupt changes of the average charge occur and the system is always in a one-phase state (the right-hand curves in Figs. 1 and 2).

In the same manner we study the added-salt case when the extra salt ions are present in the solution. The novel property of these systems is that the first-order phase transition may occur when the concentration of the macroions is fixed while the concentration of the extra salt ions is changed. The corresponding isotherms $\alpha=\alpha(i_s, n$ fixed), where $i_s=4I_s/ne^2$ and I_s is the partial ionic strength of the solution associated with the extra salt ions, are shown in Figs. 3 and 4. Again we see that when the temperature exceeds some critical value, the average charge of the macroion changes continuously (the left-hand curve in Fig. 3). However, in the case of added salt ions the critical temperature depends on the macroion concentration n (compare the left-hand curves in Figs. 3 and 4, which correspond to the same temperature but to different concentrations of the macroions).

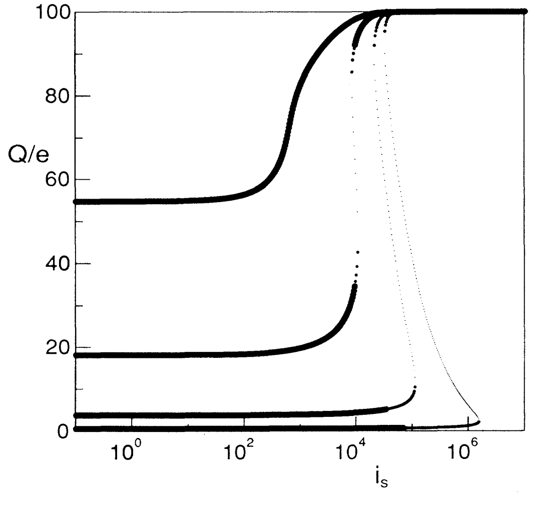

FIG. 3. Dependence of the average macroion charge $\bar{Q}/e$ versus partial ionic strength of the solution i_s associated with the added salt ions $i_s=\sum_a q_a^2 n_a/ne^2$, where n is the macroions concentration and n_a and q_a are, respectively, the concentrations and charges of salt ions of sort a. The number of active sites $\ell=100$. $\omega_0=10^{14}$ s^{-1}, $m=1.64\times10^{-24}$ g, and $E_0/kT_0=26$ at $T_0=300$ K. The curves from left to right correspond to $T=1.11T_0$, $1.03T_0$, $0.91T_0$, and $0.80T_0$, respectively. The macroions concentration $n=5\times10^{13}$ sm^{-3}. The designations are the same as in Fig. 1.

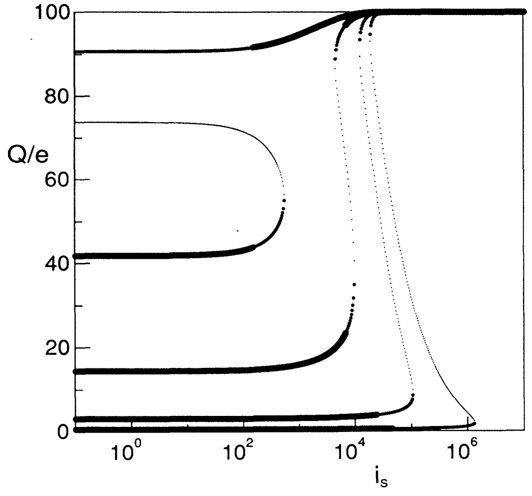

FIG. 4. Dependence of the average macroion charge $\bar{Q}/e$ versus partial ionic strength of the solution, associated with the added salt ions i_s. The number of active sites $\ell=100$. $\omega_0=10$ s^{-1}, $m=1.64\times10^{-24}$ g, and $E_0/kT_0=26$ at $T_0=300$ K. The curves from left to right correspond to $T=1.11T_0$, $1.03T_0$, $0.91T_0$, and $0.80T_0$, respectively. The macroions concentration $n=8\times10^{13}$ $\mathrm{s\,m}^{-3}$. The designations are the same as in Fig. 1.

Note that since this phase transition occurs at fixed macroion concentration it resembles in some sense the counterion-condensation phenomenon, which is also observed at fixed macroion concentration when the counterion concentration is changed. The main difference between these phase transitions and the counterion-condensation phenomena is the possibility of coexistence in the former case of two phases with different average charges of the macroions. The counterion condensation occurs due to electrostatic instability of the counterion cloud in the field of its parental macroion [28]. At the same time the phase transition results from the interplay of different parts of the total free energy of the system. Whereas the free energy of the bound counterions per one counterion does not depend on concentration, the free energy per particle associated with electrostatic interactions of the free counterions depends on concentration. It gives a negative contribution to the total free energy and its absolute value increase with increasing concentration. That is why at high concentrations it becomes more favorable for the free energy (which tends to be minimized) to have the most of the counterions free. At some values of parameters these changes occur abruptly, so that the phase transition is observed.

This qualitative explanation of the effect follows the line of Stell and Wu [45], who discussed the physical reason of the liquid-gas-type transition in simple electrolytes, where the similar first-order phase transition (one can also call it a "weak-electrolyte–strong-electrolyte" transition [46,47]) is expected (see, e.g., [45,48] and references therein). Note also that liquid-liquid phase transitions were predicted for colloidal solutions [49–51] where the macroions were modeled as hard spheres with uniform surface charge density. In these studies the phase transition was established by observing the divergency of the osmotic compressibility associated with macroions. One can assume that on the microscopical level this occurs due to partial condensation of counterions on the macroions. One can also mention a recent experimental paper [52] where the liquid-gas-type phase transition as well as coexistence of two different phases were observed in solutions of ionizable colloidal particles.

The standard analysis for these first-order phase transitions [53] may be done to find the critical parameters, (α^*, T^*, n^*) for the $\alpha=\alpha(n,\ i_s$ fixed) dependence or (α^*, T^*, i_s^*) for the $\alpha=\alpha(i_s,\ n$ fixed) dependence. Unfortunately, it is not possible to treat these dependences analytically. Referring, for the detailed numerical analysis, to [54], we note here that critical parameters for the salt-free case are the following: For $\ell=100$ we obtain $n^* \simeq 6.3\times10^{13}$ sm^{-3}, $E_0/kT^* \simeq 23.75$, where $E_0/kT_0=26$ at $T_0=300$ K. For $\ell=500$, $n^* \simeq 1.1\times10^{11}$ sm^{-3}, $E_0/kT^* \simeq 28.5$, with $E_0/kT_0=31$ at $T_0=300$ K. In the calculations we use the following values of parameters: $m=1.64\times10^{-24}$ g (the mass of proton) and $\omega_0=10^{14}$ s^{-1}.

To make reasonable estimates for the value of E_0, note that for tightly bound counterions that are in direct contact with the macroion surface the energy of attractive Coulomb interaction is of the order of $10^2 kT$ (at $T=300$ K) for $r_0=1$ Å. If one takes into account the energy of effective repulsive interactions due to the presence of dielectric and use the estimates that give the continuum theory [40,41], one concludes that the total energy is approximately twice as small as the pure Coulomb one. Therefore the following estimate $E_0 \simeq 10-10^2 kT$ (at $T=300$ K) seems to be reasonable.

Since in the present study we consider the case of $nR^3 \ll 1$, where R is some characteristic length of the macroion, the latter value does not incorporate the theory. To confirm the self-consistency of the approach, we make some estimates. Let the colloidal particles have radius $R=350$ Å; then if $\ell=100$, the volume fraction $\Phi=\frac{4}{3}\pi R^3 n^*$ at critical density $n^*=6.3\times10^{13}$ is equal to 0.011 and thus $\Phi \ll 1$. At the same time, if the average charge of the macroion $\bar{Q} \simeq 10$, one obtains $\chi_D R \simeq 0.25$ and 0.025 for the case $\bar{Q} \simeq 1$. The average distance between the charged groups on the particle surface may be estimated as 70 Å. The latter value is much more than the Bjerrum length l_B, which for aqueous solutions is equal to 7.2 Å. The case of $\ell=500$ may be exemplified by the colloidal particles of radius $R=3000$ Å; for critical density one has $\Phi=0.012$ and $\chi_D R=0.09$ for $\bar{Q}=10$. The average distance between the active sites is equal to 270 Å, which again is much more than l_B. These estimates show that the restrictions imposed on our theory are satisfied and thus the self-consistency of the theory is confirmed.

IV. CONCLUSION

In the present study the problem of an average charge of variably ionizable particles in solutions is investigated. Contrary to the ordinary counterion condensation theories where only the interaction of the macroion with its own counterion cloud is considered, all types of interactions, i.e., macroion-counterion, macroion-macroion, and counterion-counterion, are taken into account. We develop a mean-field theory for the case of site-bound counterions, so that the one-site partition function of bound counterions is explicitly incorporated into the theory. For tightly bound counterions the partition function is calculated with the use of harmonic approximation for the potential well of the macroion-counterion interactions. For nontightly bound counterions the Bjerrum approach is used.

We find out that a first-order phase transition of the type weakly charged macroion–strongly charged macroion occurs in the salt-free case when the concentration of the macroions is changed. We analyze also the salt-added case when some extra salt ions are present in the solution. We observe that the similar first-order phase transition occurs when the concentration of extra salt ions is changed while the concentration of macroions is fixed. Contrary to the ordinary counterion condensation phenomena, the first-order phase transition implies that two phases with different average charges of the macroions may coexist in the system.

ACKNOWLEDGMENTS

The author is thankful to Professor A. Khokhlov and Professor R. Klein for useful and stimulating discussions, to Dr. A. Ferrante for drawing my attention to Refs. [45,48,49–51], and to Dr. A. Pikovsky for critical comments and invaluable help in the preparation of the manuscript. Special thanks are due to Dr. J. Kurths for his warm hospitality and for creative atmosphere in the working group of "Nonlinear Dynamic." I also acknowledge support from the Max-Planck-Gesellschaft.

APPENDIX

In this appendix we show that more rigorous considerations give the same results as those derived in Sec. II, where the reasonable "physical" arguments were used.

Let $F(N_f)$ be conditional free energy of the system with the condition that the number of free counterion is equal to N_f, so that $N_b=\ell N-N_f$ is a number of bound counterions. Let these N_b counterions be distributed over the N macroions and $a_1, a_2, \ldots, a_N$ be the numbers of counterions bound to the 1st,2nd,…,Nth macroion $(a_1+a_2+\cdots+a_N=N_b)$. These a_i counterions may be distributed over ℓ sites in a number of different ways. Let $\{a_i\}$ denote some particular distribution of counterions. The active surface site occupied by the counterion together with the corresponding bound counterion form a dipole, and for the tightly bound counterions one can neglect interactions between this dipole and other nonoccupied active sites on the macroions and with the free counterions. Then one can write for the conditional free energy

$$\beta F(N_f)=-\ln\left\{\frac{1}{2\pi i}\oint\frac{d\xi}{\xi^{N_b+1}}(N_b!)^{-1}(Z_{\mathrm{id}M}Z_{\mathrm{idc}})\times\sum_{\{a_1\}}\cdots\sum_{\{a_N\}}\frac{N_b!}{a_1!a_2!\cdots a_N!}\int d\omega_1\cdots\int d\omega_N Z(\{a_1\})\xi^{a_1}\cdots Z(\{a_N\})\xi^{a_N}\times Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})\right\}. \tag{A1}$$

Here $\sum_{\{a_i\}}$ designates summation over all values of a_i from $a_i=0$ to ℓ and over all particular distributions of counterions $\{a_i\}$. For convenience we use in Eq. (A1) a well-known relation $(2\pi i)^{-1}\oint d\xi/\xi^{k+1}=\delta_{k0}$, where integration of the complex variable ξ is carried out over a zero-containing circuit (see, e.g., [40]). Therefore only the terms satisfying the condition $a_1+a_2+\cdots+a_N=N_b=\ell N-N_f$ give nonzero contribution to the sum. $Z(\{a_i\})$ is the partition function for macroion with a particular counterion distribution $\{a_i\}$. $\int d\omega_i$ means integration over orientational coordinates of the ith macroion. $Z_{\mathrm{id}M}$ and Z_{idc} are the ideal-gas partition functions for macroions and free counterions, respectively. Namely

$$Z_{\mathrm{idc}}=V^{N_f}(N_f!\Lambda_c^3)^{-1}, \tag{A2}$$

where $\Lambda_c=h(2\pi mkT)^{-1/2}$ is the de Broglie thermal wavelength of the counterions, with the analogous expression for the corresponding macroion ideal-gas partition function. $Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})$ is a configuration integral for a system consisting of free counterions and macroions with a given set of macroions orientations $\omega_1,\ldots,\omega_N$ and a given set of the counterions distributions $\{a_1\},\ldots,\{a_N\}$:

$$Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})=\frac{1}{V^{N+N_f}}\int dR^N dr^{N_f}\exp\{-\beta U_l(R^N,r^N)-\beta U_s(R^N,r^N)\}, \tag{A3}$$

where $dR^N=dR_1\cdots dR_N$ and $dr^{N_f}=dr_1\cdots dr_{N_f}$ means integration over macroions and free counterions coordinates, respectively, and $U_l(R^N,r^N)$ denotes the long-range Coulomb interactions whereas $\beta U_s(R,r)$ denotes other types of interactions, i.e., short-range repulsive, van der Waals interactions, etc. It is convenient to consider the macroion particles that differ by orientations and by the counterion distributions as particles of different "sorts" (as well as it was suggested by Onsager for particles of different orientations [55]). Then one can apply the usual methods of calculation of the configurational integral for many-sort systems (see, e.g., [40]).

Let N_a be the number of particles of the sort a, including free counterions, and U_l^{ab} and U_s^{ab} are correspondingly the Coulomb and short-range interactions between the particles of the sort a and b, so that $U_l(R^N,r^{N_f})=\sum_{a,b}U_l^{ab}$ and $U_s(R^N,r^{N_f})=\sum_{a,b}U_s^{ab}$. One can calculate the configurational integral with the use of standard technique, transforming the integration in Eq. (A3) over R^N,r^{N_f} to integration over collective variables ρ_{ka},ρ_{kb}^* with the help of the Jacobian $J(R^N,r^{N_f},\rho_{ka},\rho_{kb}^*)$ [40]. Using then a Gaussian approximation for the Jacobian (random-phase approximation) and performing on this basis an expansion with respect to the short-range interactions, one finally obtains for the many-sort system [40]

$$Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})=Q_G(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})\exp(B_2+B_3+\cdots), \tag{A4}$$

where Q_G is Gaussian (random-phase) approximation for the configurational integral [40]:

$$Q_G=\exp\left\{\tfrac{1}{2}\sum_{\mathbf{k}}{}'(\mathrm{Sp}D(\mathbf{k})-\ln\{\det[1+\mathbf{D}(\mathbf{k})]\})\right\} \tag{A5}$$

where the summation over the wave vectors $\mathbf{k}$ is carried in the upper half-space $k_Z>0$, and matrix $\mathbf{D}(\mathbf{k})$ is defined as follows [40]:

$$\mathbf{D}_{ab}(\mathbf{k})=V^{-1}\beta(N_aN_b)^{1/2}U_l^{ab}(\mathbf{k})=V^{-1}\beta(N_aN_b)^{1/2}\int d\mathbf{R}\exp(i\mathbf{k}\cdot\mathbf{R})U_l^{ab}(\mathbf{R}). \tag{A6}$$

Virial coefficients $B_2,B_3,\ldots$ in Eq. (A4) arising in expansion may be expressed in terms of the short-range potentials U_s^{ab} and the equilibrium correlation functions of the pure Coulomb system in the RPA [40,43]. Their values are of the order of $nR^3,(nR^3)^2,\ldots$ [40] and will not be considered here (in the present study we deal only with the dilute solutions). Note that

$$U_l^{ab}(\mathbf{R})=\sum_{\alpha\in\{a\},\omega}\ \sum_{\beta\in\{b\},\omega'}(q_\alpha q_\beta/\epsilon)|\mathbf{R}+\mathbf{r}_\alpha-\mathbf{r}_\beta|^{-1}, \tag{A7}$$

where q_α and r_α are, respectively, the charge and the position (with the respect to macroion center) of the αth active site and R is the intercenter distance for the macroions. The summation over active sites α and β is carried out for the particular distribution of bound counterions $\{a\}$ and $\{b\}$ and its orientations ω and ω', which correspond to the sort a and sort b. Therefore we obtain for $U_l^{ab}(\mathbf{k})$

$$U_l^{ab}(\mathbf{k})=\frac{4\pi\beta}{\mathbf{k}^2\epsilon}e^2S_a(\mathbf{k})S_b^*(\mathbf{k}) \ , \tag{A8}$$

where $eS_a(\mathbf{k})=\sum_{\alpha\in\{a\}},\sum_{\alpha\in\{a\},\omega}q_\alpha\exp(-i\mathbf{k}\cdot\mathbf{r}_\alpha)$. Note that in Eq. (A8) ϵ may also be considered a $\mathbf{k}$-dependent value. When the sort a corresponds to the counterion, i.e., when $a=c$, one obviously has $eS_c(\mathbf{k})=q_c$, where q_c is the counterion charge. One can also write the matrix $\mathbf{D}(\mathbf{k})$ in a diadic form:

$$\mathbf{D}_{ab}(\mathbf{k})=\mathbf{d}(\mathbf{k})\mathbf{d}^*(\mathbf{k}) \ , \tag{A9}$$

where the ath component of the vector $\mathbf{d}(\mathbf{k})$ is defined by the relation

$$\mathbf{d}_a(\mathbf{k})=\left[\frac{4\pi\beta}{\mathbf{k}^2\epsilon}e^2\frac{N_a}{V}\right]^{1/2}S_a(\mathbf{k}) \ . \tag{A10}$$

It can be easily shown that for the matrix of the form (A9) the following relation holds true: $\det(1+\mathbf{dd})=1+\mathrm{Sp}(\mathbf{dd})$. Thus one can write for the Gaussian configuration integral Q_G

$$Q_G=\exp\left\{\tfrac{1}{2}\sum_{\mathbf{k}}{}'\left[\frac{\chi^2(\mathbf{k})}{\mathbf{k}^2}-\ln\left[1+\frac{\chi^2(\mathbf{k})}{\mathbf{k}^2}\right]\right]\right\} , \tag{A11}$$

where $\chi^2(\mathbf{k})$ is defined by the relation

$$\begin{aligned}\chi^2(\mathbf{k})&=4\pi\beta e^2V^{-1}\epsilon^{-1}\sum_a N_aS_a(\mathbf{k})S_a^*(k)\\&=4\pi\beta q_c^2n_f/\epsilon+\frac{4\pi\beta ne^2}{\epsilon}\sum_{\{a_1\},\omega_1}\cdots\sum_{\{a_N\},\omega_N}\frac{1}{N}[S_a(\mathbf{k},\{a_1\})S_a^*(\mathbf{k},\{a_1\})+\cdots+S(\mathbf{k},\{a_N\})S^*(\mathbf{k},\{a_N\})] \ ,\end{aligned} \tag{A12}$$

where $n=N/V$ and $n_f=N_f/V$. Note that in Eq. (A12) integration over ω_i is assumed. Let us now notice that summation over $\{a_i\}$ and integration over $d\omega_i$ in Eq. (A1) may be represented in the following form:

$$\begin{aligned}&\int d\omega_1\sum_{\{a_1\}}Z(\{a_1\})\frac{\xi^{a_1}}{a_1!}\cdots\int d\omega_N\sum_{\{a_N\}}Z(\{a_N\})\frac{\xi^{a_N}}{a_N!}Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})\\&\qquad=(Z_{\mathrm{BC}})^N\prod_{i=1}^N\int d\omega_i\sum_{\{a_i\}}P(\{a_i\},\omega_i)Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\}) \ ,\end{aligned} \tag{A13}$$

where $P(\{a_i\},\omega_i)=(4\pi Z_{\mathrm{BC}}a_i!)^{-1}Z(\{a_i\})\xi^{a_i}$ may be interpreted as a "probability" for the macroion to have distribution of bound counterions $\{a_i\}$ and orientation $\{\omega_i\}$ and $Z_{\mathrm{BC}}=\sum_{\{a\}}Z(\{a\})\xi^a/a!$. Due to symmetry of its arguments the function $Q(\omega_1,\{a_1\};\ldots;\omega_N,\{a_N\})$ may be always represented in a form $Q=Q(\phi_1,\phi_2,\ldots)$, where functions $\phi_1,\phi_2,\ldots$ are the following: $\phi_i=[\phi_i(\omega_1,\{a_1\})+\cdots+\phi_i(\omega_N,\{a_N\})]/N$, $i=1,2\ldots$ In the thermodynamic limit, $n=N/V=\mathrm{const}, N\to\infty$, $V\to\infty$, it may be easily shown [making the same considerations that are usually made deriving the central limit theorem (see, e.g., [56])] that the following relation holds true:

$$\lim_{N\to\infty}\prod_{i=1}^N\int d\omega_i\sum_{\{a_i\}}P(\{a_i\},\omega_i)Q(\phi_1,\phi_2,\ldots)=Q(\bar{\phi}_1,\bar{\phi}_2,\ldots) \ , \tag{A14}$$

where the functions $\bar{\phi}_1,\bar{\phi}_2,\ldots$ are functions averaged over the probability distribution $P(\{a_i\},\omega_i)$, i.e.,

$$\bar{\phi}_i=\int d\omega\sum_{\{a\}}P(\{a\},\omega)\phi_i(\omega,\{a\}) \ . \tag{A15}$$

Therefore one can rewrite Eq. (A1) as follows:

$$\begin{aligned}&\exp[-\beta F(N_f)]\\&\quad=\frac{1}{2\pi i}\oint d\xi\exp[-(N_B+1)\ln(\xi)-\beta F_{\mathrm{id}}(N_f)\\&\qquad\qquad-\beta\Omega_b(\xi)-\beta\widetilde{F}_{\mathrm{RPA}}(\xi,N_f)] \ ,\end{aligned} \tag{A16}$$

where $\beta F_{\mathrm{id}}(N_f)=-\ln[Z_{\mathrm{id}M}Z_{\mathrm{idc}}(N_f)]$, $\beta\Omega_B(\xi)=-N\ln[Z_{BC}(\xi)]$, and $\beta\widetilde{F}_{\mathrm{RPA}}(\xi,N_f)=-\ln[\bar{Q}_G(\xi,N_f)]$, with

$$\bar{Q}_G(\xi,N_f)=\exp\left[\frac{1}{2}\frac{V}{8\pi^3}\int d\mathbf{k}\left\{\frac{\overline{\chi^2(\mathbf{k})}}{\mathbf{k}^2}-\ln\left[1+\frac{\overline{\chi^2(\mathbf{k})}}{\mathbf{k}^2}\right]\right\}\right] , \tag{A17}$$

$$\begin{aligned}\overline{\chi^2(\mathbf{k})}&=\overline{\chi^2(\mathbf{k},\xi,N_f)}\\&=(4\pi\beta/V\epsilon)[N_fq_c^2+Ne^2\overline{S(\mathbf{k})S^*(\mathbf{k})}] \ .\end{aligned} \tag{A18}$$

We show explicitly the dependence on ξ of functions in Eqs. (A16)–(A18) since the averaging is performed with the use of ξ-dependent probabilities $P(\{a_i\},\omega_i)$, namely

$$\overline{S(\mathbf{k})S^*(\mathbf{k})}=\int d\omega\sum_{\{a\}}(Z_{BC}a!)^{-1}Z(\{a\})\xi^a\times S(\mathbf{k},\{a\})S^*(\mathbf{k},\{a\}) \ . \tag{A19}$$

The averaging of the virial coefficients B_2,B_3 may be done in the same way as averaging of the Gaussian configurational integral. Since all the terms in the exponent power on the right-hand side of Eq. (A16) are of the order of $N\to\infty$ (note that N_b and N_f also tend to infinity), one can use an asymptotic estimate for the integral in Eq. (A16), which yields

$$F(N_f)=\beta^{-1}N_b\ln(\xi^*)+F_{\mathrm{id}}(N_f)+\Omega_b(\xi^*)+\tilde{F}_{\mathrm{RPA}}(\xi^*,N_f)+\mathrm{const}\ , \tag{A20}$$

where ξ^* being the extremum point of the function in the exponent power in Eq. (A16) is the solution of the following equation:

$$N_b=\ell N-N_f=\beta\xi\frac{\partial}{\partial\xi}\Omega_b(\xi)+\beta\xi\frac{\partial}{\partial\xi}\tilde{F}_{\mathrm{RPA}}(\xi,N_f)\ . \tag{A21}$$

Thus one can write $\xi^*=\xi^*(N_f)$. Introducing the value μ (chemical potential), $\xi=\exp(\beta\mu)$, one can see that Eq. (A21) may be written as

$$N_b=\ell N-N_f=\frac{\partial}{\partial\mu}\Omega_b(\mu)+\frac{\partial}{\partial\mu}\tilde{F}_{\mathrm{RPA}}(\mu,N_f)\ . \tag{A22}$$

This equation defines the value of $\mu=\mu(N_f)$. Similarly, one can write Eq. (A20):

$$F(N_f)=\Omega_b(\mu)+\mu N_b+F_{\mathrm{id}}(N_f)+\tilde{F}_{\mathrm{RPA}}(\mu,N_f)\ . \tag{A23}$$

Minimizing $F(N_f)$ with respect to N_f one obtains the relation

$$\mu(N_f)=\frac{\partial}{\partial N_f}F_{\mathrm{id}}+\frac{\partial}{\partial N_f}F_{\mathrm{RPA}}+\left[\frac{\partial\mu}{\partial N_f}\right]\left[\frac{\partial}{\partial\mu}\right]F_{\mathrm{RPA}}\ . \tag{A24}$$

Equations (A22)–(A24) are the basic equations of the problem of the average charge of the variably ionizable particles. The functions used in these equations are defined by Eqs. (A17)–(A19) where the value ξ is substituted by $\exp(\beta\mu)$, namely

$$e^2\overline{S(\mathbf{k})S^*(\mathbf{k})}=\sum_{\{a\}}(Z_{BC}a!)^{-1}Z(\{a\})e^{\beta\mu a}\times\sum_{\alpha,\gamma\in\{a\}}q_\alpha q_\gamma\frac{\sin(kl_{\alpha\gamma})}{kl_{\alpha\gamma}}\ , \tag{A25}$$

where the integration over the angular variables has been performed and $l_{\alpha\gamma}=|\mathbf{r}_\alpha-\mathbf{r}_\gamma|$ is the distance between αth and γth active site on the macroion surface.

These equations may be significantly simplified in some special cases. If $l_{\alpha\beta}\gg l_B$, where l_B is the Bjerrum length, and one can use the approximation $Z(\{a\})=(Z_b)^a$, which means that interactions between bound ions are neglected, then the partition function for the particular counterion distribution $\{a\}$ depends only on the number of bound counterions a. The charge structure factor for the single macroion $e^2\overline{S(\mathbf{k})\,S^*(\mathbf{k})}$ may be calculated if one notices that the following relation, which may be obtained from a simple combinatorics, holds true:

$$\sum_{\substack{\{a\}\\ a\ \text{fixed}}}\sum_{\alpha,\gamma\in\{a\}}q_\alpha q_\gamma\frac{\sin(kl_{\alpha\gamma})}{kl_{\alpha\gamma}}=a!\begin{bmatrix}\ell\\ a\end{bmatrix}e^2\left[\sum_{\substack{\alpha,\gamma\\ \alpha\neq\gamma}}\frac{\sin(kl_{\alpha\gamma})}{kl_{\alpha\gamma}}\frac{(\ell-a)(\ell-a-1)}{\ell(\ell-1)}+(\ell-a)\right]\ , \tag{A26}$$

where "a fixed" means that the summation over the counterion distributions $\{a\}$ are performed with a fixed number of counterions. With the use of Eqs. (A25) and (A26) we finally obtain

$$e^2\overline{S(\mathbf{k})S^*(\mathbf{k})}=[(1-\ell^{-1})^{-1}f(k)+(1-\ell)^{-1}]((\overline{Q}^2-\overline{Q}e)+\overline{Q}e\ , \tag{A27}$$

where $\overline{Q}$ is the average charge, $\overline{Q^2}$ is the average square charge of the macroions, and the function $f(k)$ is defined as follows; $f(k)=\ell^{-2}\sum_{\alpha,\gamma}\sin(kl_{\alpha\gamma})/kl_{\alpha\gamma}$. Since $Z(\{a\})=(Z_b)^a$ and

$$\sum_{\substack{\{a\}\\ a\ \text{fixed}}}Z(\{a\})=(Z_b)^a a!\begin{bmatrix}\ell\\ a\end{bmatrix}\ , \tag{A28}$$

one obtains $Z_{BC}=\sum_{a=1}^{\ell}\binom{\ell}{a}(Z_b)^a e^{\beta\mu a}$. Therefore we conclude that $\Omega_b(\mu)$, for this case, coincides with $\Omega_b(\mu)$, obtained previously [see Eq. (5)]. Similarly the expressions for $\overline{Q}$ and $\overline{Q^2}$ also coincide with the previously obtained relations [Eqs. (9) and (10)]. Both of these values may be expressed in terms of the average number of bound counterions per one macroion $\overline{a}$ [see Eq. (10)] and thus only in terms of n_f. Therefore, we come to the conclusion that for this particular case the value of $\tilde{F}_{\mathrm{RPA}}(\mu,N_f)$ actually depends only on N_f and not on μ, i.e., $\tilde{F}_{\mathrm{RPA}}(\mu,N_f)=F_{\mathrm{RPA}}(N_f)$ [see Eqs. (A17), (A18), and (A27)]. As a result one obtains, instead of Eqs. (A22) and (A24),

$$N_b=\ell N-N_f=\frac{\partial}{\partial\mu}\Omega_b(\mu)\ , \tag{A29}$$

$$\mu=\frac{\partial}{\partial N_f}F_{\mathrm{id}}+\frac{\partial}{\partial N_f}F_{\mathrm{RPA}}\ . \tag{A30}$$

Equations (A29), (A30), and (A23) [with $\tilde{F}_{\mathrm{RPA}}(\mu,N_f)$ substituted by $F_{\mathrm{RPA}}(N_f)$] are just the same equations as Eqs. (21)–(24), which were derived on the basis of reasonable physical argumentation. Now, however, it is shown what kind of approximations were implicitly used in deriving these equations.

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