

# On the bulk modulus of the cell model of charged macromolecules suspensions

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We study theoretically the bulk modulus (inverse of the compressibility) of a suspension of charged objects (macroions), making use of a cell model to account for the finite density of macroions. The diffuse layer of charged microspecies around a macroion is described by a generic local density functional theory. Within this general framework, we obtain the condition for a positive bulk modulus, which is fulfilled by several proposals made in the literature and rules out the possibility of a critical point. We show that a sufficient condition for a positive compressibility also ensures that the same theory produces repulsive effective pair potentials. © 2003 American Institute of Physics. [DOI: 10.1063/1.1538604]

## I. INTRODUCTION

Macromolecules soluble in aqueous suspensions usually acquire an electric charge. Such systems are of considerable theoretical and experimental interest. Examples include proteins in living cells, dispersion paints, or superabsorbants. Their theoretical description is however a tremendous task, and operational approximate treatments are needed.

In this work, we consider a cell model to account for the macroions correlations,<sup>1</sup> in conjunction with a local density functional theory to describe the inhomogeneous electric double layer around a macroion.<sup>2,3</sup> This framework encompasses the standard mean-field Poisson–Boltzmann (PB) theory, but also more recent approaches proposed to account for microions excluded volume,<sup>4</sup> more general nonelectrostatic effects,<sup>5</sup> or to incorporate correlations between the screening microions,<sup>6,7</sup> that are neglected within PB theory. The cell model description may be considered as one of the simplest starting points, and provides an important benchmark against which experiments and more refined theories are tested. The resulting differential equations are however highly nonlinear, and even with the simplest of the approaches under consideration here (PB), can only be solved analytically in 1 or 2 dimensions without added salt (i.e., for the situation of a flat double layer in a confining slab, or for that of a rod-like macroion of infinite length enclosed in a concentric confining cylinder<sup>8</sup>). The linearized version of the above problem has therefore always been an important alternative, but is not free of internal inconsistencies. In particular, the linearized PB theory may lead to negative osmotic pressures<sup>9,10</sup> and negative bulk modulus (inverse of the compressibility),<sup>10</sup> whereas within the original nonlinear PB theory, it is straightforward to show that the osmotic pressure is necessarily positive. For the bulk modulus, the situation is

less clear: although this quantity is found positive in the numerical solution of PB equation, it seems that no formal proof exists concerning its sign. In this article, we derive such a proof and obtain the conditions under which a general local density functional theory leads to a positive compressibility within the cell model.

The article is organized as follows. The density functional theory formalism is presented in Sec. II, where a few useful identities are derived. The bulk modulus is then computed in Sec. III and cast in a form where a sufficient condition for its positivity clearly appears. Conclusions are drawn in the final section.

## II. GENERAL FORMALISM

### A. Density functional theory

We consider a  $\nu$ -dimensional colloid with spherical symmetry confined in its (concentric) Wigner–Seitz cell ( $\nu=2$  for a cylindrical colloid,  $\nu=3$  for a colloidal sphere). The cell is a spherical region  $\mathcal{R}$  of radius  $R$  and volume  $V = S_\nu R^\nu / \nu$  ( $S_\nu$  is the area of the unit radius  $\nu$ -dimensional sphere,  $S_2 = 2\pi$ ,  $S_3 = 4\pi$ ). The colloid (of fixed uniform surface charge density) is immersed in an electrolyte solution with several different species of ions with charges  $\{q_\alpha\}$ , and the local density of the species  $\alpha$  is denoted  $n_\alpha(\mathbf{r})$ . The system inside the cell is globally neutral. In what follows, we explicitly consider the semi-grand-canonical situation where the macroion's suspension is in osmotic equilibrium with a salt reservoir through a semipermeable membrane (permeable to microspecies only). We therefore consider the grand potential  $\Omega\{n_\alpha\}$ , which is a functional of microion densities that we write

$$\begin{aligned} \Omega\{n_\alpha\} = & \int_{\mathcal{R}} \omega(\{n_\alpha(\mathbf{r})\}) d\mathbf{r} + \frac{1}{2} \int_{\mathcal{R}} \rho(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \\ & + \lambda \int_{\mathcal{R}} \rho(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (2.1)$$

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where

$$\rho(\mathbf{r}) = \sum_{\alpha} q_{\alpha} n_{\alpha}(\mathbf{r}) + \rho_{\text{col}}(\mathbf{r}) \quad (2.2)$$

is the total charge density including that of the colloid (denoted  $\rho_{\text{col}}$ ),  $\lambda$  is a Lagrange multiplier to ensure global electroneutrality ( $\partial\Omega/\partial\lambda = \int\rho = 0$ ), and  $\psi(\mathbf{r})$  is the electrostatic potential. Within PB theory, the local part of the functional (2.1) embodied in  $\omega$  is entirely of entropic origin. In other words, electrostatic interactions are taken into account at mean-field level only, through the term  $\int\rho\psi/2$ . This feature is shared by the theories of Refs. 4 and 5, but is not the case of the formalism put forward by Barbosa *et al.*,<sup>6,7</sup> where the term  $\omega$  contains electrostatic corrections to the mean-field Coulomb contribution. By comparison with the results of molecular dynamics simulations, this framework was shown to capture important correlations missed by the mean-field Poisson–Boltzmann.<sup>6</sup>

Within the standard Poisson–Boltzmann theory, the microions are treated as an ideal gas of charged particles reacting to the mean electrostatic potential. The free-energy density therefore reads  $f(\{n_{\alpha}\}) = f_{\text{id}}(\{n_{\alpha}\}) = \beta^{-1} \sum_{\alpha} n_{\alpha} \{\ln[\Lambda^3 n_{\alpha}] - 1\}$ , where  $\Lambda$  is an irrelevant length scale and  $\beta = 1/(k_B T)$  the inverse temperature. The grand potential functional describing the osmotic equilibrium with a salt reservoir is thus  $\Omega = \int f - \sum_{\alpha} \mu_{\alpha}^b \int n_{\alpha} + \int \rho\psi/2 + \lambda \int \rho$ , where the chemical potentials  $\mu_{\alpha}^b = \partial f_{\text{id}}(\{n_{\alpha}^b\})/\partial n_{\alpha}^b = \beta^{-1} \ln(\Lambda^3 n_{\alpha}^b)$  are defined from the bulk densities  $n_{\alpha}^b$  of microspecies in the reservoir. The local grand potential density finally takes the form

$$\begin{aligned} \omega(\{n_{\alpha}(\mathbf{r})\}) &= f(\{n_{\alpha}(\mathbf{r})\}) - \sum_{\alpha} \mu_{\alpha}^b n_{\alpha}(\mathbf{r}) \\ &= \beta^{-1} \sum_{\alpha} n_{\alpha}(\mathbf{r}) \left( \ln \frac{n_{\alpha}(\mathbf{r})}{n_{\alpha}^b} - 1 \right). \end{aligned} \quad (2.3)$$

As mentioned in the Introduction, other theories may be described by our formalism, such as those proposed to account for steric effects,<sup>4</sup> more general nonelectrostatic interactions,<sup>5</sup> or to go beyond mean field and include correlations.<sup>6,7</sup>

The mean-field Coulomb term  $\frac{1}{2} \int \rho(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}$  in Eq. (2.1) is actually quadratic in the densities if one writes the potential in term of the set  $\{n_{\alpha}\}$ . Introducing the proper Green’s function  $G(\mathbf{r}, \mathbf{r}')$  for the electrostatic problem in the region  $\mathcal{R}$ , it is always possible to write the electrostatic potential in the form (see the Appendix)

$$\psi(\mathbf{r}) = \int_{\mathcal{R}} \rho(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \quad (2.4)$$

with the cell boundary chosen as the potential reference,  $\psi(R) = 0$ .

The variational problem defined by the functional (2.1) leads to the stationary condition

$$\frac{\partial\omega(\{n_{\alpha}(\mathbf{r})\})}{\partial n_{\alpha}} + q_{\alpha}(\psi(\mathbf{r}) + \lambda) = 0, \quad (2.5)$$

which, in the Poisson–Boltzmann theory, reduces to

$$n_{\alpha}(\mathbf{r}) = n_{\alpha}^b e^{-\beta q_{\alpha}[\psi(\mathbf{r}) + \lambda]}. \quad (2.6)$$

Since the potential vanishes at the boundary of the cell, it can be seen in this equation that the Lagrange multiplier  $\lambda$  coincides with the so-called Donnan potential (potential drop across the interface of the cell and the bulk reservoir, which is formally at a potential  $-\lambda$ ).

Finally, discriminating between the optimal density profiles fulfilling Eq. (2.5) and the generic arguments of the grand potential functional leads to unnecessary heavy notations and will not be useful for the subsequent analysis.

### B. A few useful identities

Consider a functional  $\mathcal{Q}$  of the density profiles  $n_{\alpha}(\mathbf{r})$  having an explicit dependence on the volume  $V$  of the cell and the potential drop  $\lambda$  (later, we shall be interested in  $\mathcal{Q} = \Omega$ ). The total derivative  $d\mathcal{Q}/dV$  of  $\mathcal{Q}$  when the volume of the cell varies is<sup>10</sup>

$$\frac{d\mathcal{Q}}{dV} = \frac{\partial\mathcal{Q}}{\partial V} + \int_{\mathcal{R}} \sum_{\alpha} \frac{\delta\mathcal{Q}}{\delta n_{\alpha}(\mathbf{r})} \frac{dn_{\alpha}(\mathbf{r})}{dV} d\mathbf{r} + \frac{\partial\mathcal{Q}}{\partial\lambda} \frac{d\lambda}{dV}, \quad (2.7)$$

where the first term is the variation due to the explicit dependence of  $\mathcal{Q}$  on  $V$ , the second is due to the variation of the density profiles when the volume changes, and the last is due to the variation of the potential drop with the volume. Computing  $dn_{\alpha}(\mathbf{r})/dV$  and  $d\lambda/dV$  would require to solve the variational problem (2.5) subject to the neutrality condition for a cell of volume  $V+dV$  and for a cell of volume  $V$ , before computing the difference of the two solutions. However, this will not be necessary for our purposes.

We will be interested most of the time in quantities defined by a local density. In general, the partial derivative with respect to the volume (explicit dependence) of such a quantity may be computed by means of the dilatation method

$$\begin{aligned} \frac{\partial}{\partial V} \left[ \int_{\mathcal{R}} g(\mathbf{r}) d\mathbf{r} \right] &= \frac{\partial}{\partial V} \left[ V \int_{\tilde{\mathcal{R}}} g(V^{1/\nu} \tilde{\mathbf{r}}) d\tilde{\mathbf{r}} \right] \\ &= \frac{1}{V} \int_{\mathcal{R}} g(\mathbf{r}) d\mathbf{r} + \frac{1}{V\nu} \int_{\mathcal{R}} \mathbf{r} \cdot \frac{\partial g(\mathbf{r})}{\partial \mathbf{r}} d\mathbf{r} \\ &= \frac{1}{V} \int_{\mathcal{R}} g(\mathbf{r}) d\mathbf{r} + \frac{1}{V\nu} \int_{\partial\mathcal{R}} g(\mathbf{r}) \mathbf{r} \cdot d\mathbf{S} \\ &\quad - \frac{1}{V\nu} \int_{\mathcal{R}} \nu g(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2.8)$$

$$= \frac{1}{V\nu} \int_{\partial\mathcal{R}} g(\mathbf{r}) \mathbf{r} \cdot d\mathbf{S}. \quad (2.9)$$

We first made a change of variable  $\mathbf{r} = V^{1/\nu} \tilde{\mathbf{r}}$  to show explicitly the volume dependence of the integral. After computing the derivatives and returning to the unscaled variable  $\mathbf{r}$  we made an integration by parts ( $\nu$  is the dimensionality of the cell  $\nu = 2, 3$ ). For the spherical isotropic geometry we are interested in, this result reduces to

$$\frac{\partial}{\partial V} \left[ \int_{\mathcal{R}} g(\mathbf{r}) d\mathbf{r} \right] = g(R). \quad (2.10)$$

We will need also to compute the derivative of some terms given by a double integral. Following the same steps as above, this derivative is given by

$$\begin{aligned} \frac{\partial}{\partial V} \left[ \int_{\mathcal{R}} g(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \right] \\ = \int_{\mathcal{R}} g(\mathbf{R}, \mathbf{r}') d\mathbf{r}' + \int_{\mathcal{R}} g(\mathbf{r}, \mathbf{R}) d\mathbf{r}. \end{aligned} \quad (2.11)$$

The key assumption here is that both quantities  $\int g(\mathbf{r}, \mathbf{R}) d\mathbf{r}$  and  $\int g(\mathbf{R}, \mathbf{r}) d\mathbf{r}$  only depend on the modulus  $R = |\mathbf{R}|$ . Another important point to notice is that the volume total derivative is taken at constant total electric charge because the system is neutral. Applying Eq. (2.7) to  $\sum_{\alpha} q_{\alpha} N_{\alpha} = \int \sum_{\alpha} q_{\alpha} n_{\alpha}(\mathbf{r}) d\mathbf{r}$  then gives

$$\sum_{\alpha} q_{\alpha} \frac{dN_{\alpha}}{dV} = 0 = \rho(R) + \int_{\mathcal{R}} \sum_{\alpha} q_{\alpha} \frac{dn_{\alpha}(\mathbf{r})}{dV} d\mathbf{r}. \quad (2.12)$$

### III. THE COMPRESSIBILITY

#### A. Derivation from the grand potential

Applying formula (2.7) to the grand potential once gives minus the pressure. However, as noticed in Ref. 10, the second and third terms vanish at the solution of the variational problem. Making use of Eqs. (2.10) and (2.11), we consequently have

$$\frac{\partial \Omega}{\partial V} = \omega(\{n_{\alpha}(R)\}) + \rho(R) [\psi(R) + \lambda] \quad (3.1a)$$

$$= \omega(\{n_{\alpha}(R)\}) + \lambda \rho(R). \quad (3.1b)$$

The last equality follows from  $\psi(R) = 0$  [see the property (A10)] and is valid in general for arbitrary isotropic densities *even* if they differ from the optimal ones solving the variational problem. This will be used later. Note that the symmetry property of the Green's function [ $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r})$ ] is an important ingredient in obtaining the above equations.<sup>12</sup>

Using the stationary condition (2.5) one finds the usual result<sup>1,3,10</sup>

$$p = \sum_{\alpha} n_{\alpha}(R) \frac{\partial \omega}{\partial n_{\alpha}(R)} - \omega(\{n_{\alpha}(R)\}), \quad (3.2)$$

which reduces to  $p = k_B T \sum_{\alpha} n_{\alpha}(R)$  within PB theory (see Ref. 13 for a general derivation of this result, valid beyond PB).

When computing the second total derivative with respect to the volume of  $\Omega$  to obtain the bulk modulus, one should not disregard the second and third terms of Eq. (2.7) too early.

$$\frac{d^2 \Omega}{dV^2} = \frac{\partial^2 \Omega}{\partial V^2} \quad (3.3a)$$

$$+ 2 \int_{\mathcal{R}} \sum_{\alpha} \frac{\delta}{\delta n_{\alpha}(\mathbf{r})} \left[ \frac{\partial \Omega}{\partial V} \right] \frac{dn_{\alpha}(\mathbf{r})}{dV} d\mathbf{r} \quad (3.3b)$$

$$+ 2 \frac{\partial^2 \Omega}{\partial V \partial \lambda} \frac{d\lambda}{dV} \quad (3.3c)$$

$$+ \int_{\mathcal{R}^2} \sum_{\alpha\gamma} \frac{\delta^2 \Omega}{\delta n_{\alpha}(\mathbf{r}) \delta n_{\gamma}(\mathbf{r}')} \frac{dn_{\alpha}(\mathbf{r})}{dV} \frac{dn_{\gamma}(\mathbf{r}')}{dV} d\mathbf{r} d\mathbf{r}' \quad (3.3d)$$

$$+ 2 \int_{\mathcal{R}} \sum_{\alpha} \frac{\delta}{\delta n_{\alpha}(\mathbf{r})} \left[ \frac{\partial \Omega}{\partial \lambda} \right] \frac{dn_{\alpha}(\mathbf{r})}{dV} \frac{d\lambda}{dV} d\mathbf{r} \quad (3.3e)$$

$$+ \frac{\partial^2 \Omega}{\partial \lambda^2} \left[ \frac{d\lambda}{dV} \right]^2. \quad (3.3f)$$

At the solution of the variational problem most of these terms vanish, as it will be shown below. The first term (3.3a) is obtained taking the partial derivative of (3.1b) with respect to  $V$

$$\begin{aligned} \frac{\partial}{\partial V} [\omega(\{n_{\alpha}(R)\}) + \lambda \rho(R)] \\ = \frac{1}{S_{\nu} R^{\nu-1}} \left\{ \sum_{\alpha} \frac{\partial n_{\alpha}(R)}{\partial R} \left[ \frac{\partial \omega}{\partial n_{\alpha}(R)} + q_{\alpha} \lambda \right] \right\} = 0. \end{aligned} \quad (3.4)$$

We have used the variational equation (2.5) at  $\mathbf{r} = \mathbf{R} \in \partial \mathcal{R}$  and the fact that  $\psi(R) = 0$ . The second term (3.3b) is obtained replacing the expression (3.1b) for  $\partial \Omega / \partial V$  into (3.3b)

$$2 \sum_{\alpha} \left[ \frac{\partial \omega}{\partial n_{\alpha}(R)} + q_{\alpha} \lambda \right] \frac{dn_{\alpha}(R)}{dV} = 0, \quad (3.5)$$

where we have once more used Eq. (2.5) at  $\mathbf{r} = \mathbf{R} \in \partial \mathcal{R}$ .

The third term (3.3c) is equal to

$$2\rho(R) \frac{d\lambda}{dV}, \quad (3.6)$$

and with the fifth term (3.3e)

$$\begin{aligned} 2 \frac{\partial}{\partial \lambda} \int_{\mathcal{R}} \sum_{\alpha} \left[ \frac{\partial \omega}{\partial n_{\alpha}} + q_{\alpha} (\psi(\mathbf{r}) + \lambda) \right] \frac{dn_{\alpha}(\mathbf{r})}{dV} \frac{d\lambda}{dV} d\mathbf{r} \\ = 2 \int_{\mathcal{R}} \sum_{\alpha} q_{\alpha} \frac{dn_{\alpha}(\mathbf{r})}{dV} \frac{d\lambda}{dV} d\mathbf{r} = -2\rho(R) \frac{d\lambda}{dV}, \end{aligned} \quad (3.7)$$

gives a vanishing contribution. We have used in the preceding equation the relation (2.12). The last term (3.3f) is zero since  $\Omega$  is linear on  $\lambda$ . Finally, the inverse compressibility may be cast in the form

$$\begin{aligned} \chi^{-1} &= -V \left( \frac{\partial p}{\partial V} \right)_{T, \mu_i} \\ &= V \frac{d^2 \Omega}{dV^2} \\ &= V \int_{\mathcal{R}^2} \sum_{\alpha\gamma} \frac{\delta^2 \Omega}{\delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}')} \frac{dn_\alpha(\mathbf{r})}{dV} \frac{dn_\gamma(\mathbf{r}')}{dV} d\mathbf{r} d\mathbf{r}'. \end{aligned} \tag{3.8}$$

From Eq. (2.1) we have

$$\begin{aligned} \frac{\delta^2 \Omega}{\delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}')} &= \frac{\partial \omega(\{n_\delta(\mathbf{r})\})}{\partial n_\alpha \partial n_\gamma} \delta(\mathbf{r} - \mathbf{r}') \\ &\quad + q_\alpha q_\beta G(\mathbf{r}, \mathbf{r}'). \end{aligned} \tag{3.9}$$

The second term, the Coulomb contribution, when replaced into Eq. (3.8), gives

$$\begin{aligned} &\int_{\mathcal{R}^2} \sum_{\alpha\gamma} q_\alpha q_\gamma G(\mathbf{r}, \mathbf{r}') \frac{dn_\alpha(\mathbf{r})}{dV} \frac{dn_\gamma(\mathbf{r}')}{dV} d\mathbf{r} d\mathbf{r}' \\ &= -\frac{1}{S_\nu} \int_{\mathcal{R}} \phi(\mathbf{r}) \Delta \phi(\mathbf{r}) d\mathbf{r} \end{aligned} \tag{3.10a}$$

$$= -R^{\nu-1} \phi(R) \partial_n \phi(R) + \frac{1}{S_\nu} \int_{\mathcal{R}} |\nabla \phi(\mathbf{r})|^2 d\mathbf{r}, \tag{3.10b}$$

where we have defined the “electric potential” created by the charge variation

$$\phi(\mathbf{r}) = \int_{\mathcal{R}} G(\mathbf{r}, \mathbf{r}') \sum_\alpha q_\alpha \frac{dn_\alpha(\mathbf{r}')}{dV} d\mathbf{r}', \tag{3.11}$$

and performed an integration by parts. The boundary term in (3.10b) vanishes because, from Eq. (A10), one has

$$\phi(R) = \int_\alpha \sum_\alpha q_\alpha \frac{dn_\alpha(\mathbf{r}')}{dV} G(\mathbf{R}, \mathbf{r}') d\mathbf{r}' = 0, \tag{3.12}$$

thus showing that the Coulomb contribution term is always positive, and

$$\begin{aligned} \chi^{-1} &= V \int_{\mathcal{R}} \sum_{\alpha\gamma} \frac{\partial^2 \omega}{\partial n_\alpha \partial n_\gamma} \frac{dn_\alpha(\mathbf{r})}{dV} \frac{dn_\gamma(\mathbf{r})}{dV} \\ &\quad + \frac{V}{S_\nu} \int_{\mathcal{R}} \left| \nabla_{\mathbf{r}} \left[ \int_{\mathcal{R}} G(\mathbf{r}, \mathbf{r}') \sum_\alpha q_\alpha \frac{dn_\alpha(\mathbf{r}')}{dV} d\mathbf{r}' \right] \right|^2 d\mathbf{r}. \end{aligned} \tag{3.13}$$

### B. Discussion

From Eq. (3.13), the positive definiteness of the integral operator whose kernel is defined by

$$\frac{\partial^2 \omega(\{n_\delta(\mathbf{r})\})}{\partial n_\alpha \partial n_\gamma} \delta(\mathbf{r} - \mathbf{r}') \tag{3.14}$$

ensures that the compressibility is positive (this is a sufficient but not necessary condition). This is the case for Poisson–Boltzmann theory, where  $\omega$  is simply the ideal gas grand potential density, and it may be checked that it also holds for the theories presented in Refs. 4–6.

More generally, in any well-constructed approximate theory for the colloid based on density functionals for the grand potential of the form (2.1) (that is, a local density term plus an “interaction term” given by the mean-field Coulomb electrostatic energy), the solution of the variational problem should be a minimum, i.e., the quadratic form

$$\frac{\delta^2 \Omega}{\delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}')}, \tag{3.15}$$

should be positive definite to ensure thermodynamic stability. From expression (3.8), it then follows that the compressibility will always be positive in such a theory.

Equation (3.8) for the compressibility can be seen as a generalization for nonuniform fluids of the compressibility sum rule for uniform fluids<sup>13,14</sup>

$$\beta(n\chi)^{-1} = 1 - n \int c^{(2)}(r) dr, \tag{3.16}$$

written here for a one-component system. In this relation,  $c^{(2)}(r)$  is the direct correlation function defined, in the more general situation of a mixture, from

$$\frac{\delta^2 \Omega}{\delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}')} = \frac{\delta^2 \mathcal{F}_{id}}{\delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}')} - k_B T c_{\alpha\gamma}^{(2)}(\mathbf{r}, \mathbf{r}'), \tag{3.17}$$

where  $\mathcal{F}_{id}$  is the ideal gas contribution to the free-energy functional. When one replaces (3.17) into (3.8) for a uniform fluid [ $c_{\alpha\gamma}^{(2)}(\mathbf{r}, \mathbf{r}') = c_{\alpha\gamma}^{(2)}(|\mathbf{r} - \mathbf{r}'|)$ ], and knowing that for a uniform fluid  $dn_\alpha(\mathbf{r})/dV = -N_\alpha/V^2 = -n_\alpha/V$ , one recovers the compressibility sum rule

$$\beta\chi^{-1} = \sum_\alpha n_\alpha - \int_{\mathcal{R}} \sum_{\alpha\gamma} n_\alpha n_\gamma c_{\alpha\gamma}^{(2)}(r) d\mathbf{r}. \tag{3.18}$$

Although Eq. (3.8) is a natural generalization of the compressibility sum rule and similar expressions exist in the literature (see, for instance, Ref. 14), we included here the derivation of this result in the context of the Poisson–Boltzmann and other generic local density functional theories because these theories are approximate (nonexact) and nothing guarantees in advance the validity of Eq. (3.8) for nonexact theories.

### IV. CONCLUSION

Within the cell model and a generic local density functional theory, we have considered a suspension of charged spherical macromolecules of arbitrary dimension. We have cast the corresponding compressibility in a form where the sign of this quantity is positive under a (weak) sufficient condition: the grand potential  $\omega$  appearing in Eq. (2.1) should be a convex-up function on densities  $\{n_\alpha\}$ . This proves that the stability requirement of a positive compressibility is fulfilled by Poisson–Boltzmann theory as well as several improvements upon this mean-field approach.<sup>4–7</sup> Our results show that such theories yield stable suspensions, and cannot exhibit a critical point associated with a gas–liquid phase separation.

This result should be put in perspective with the recent proofs that within PB theory, the effective interactions be-

tween two identical colloids confined in a cylinder of infinite length is necessarily positive.<sup>15,16</sup> This proof has been extended to the more general family of local density functional theories (2.1) in Refs. 3 and 17. It was shown that the positive definiteness of the local free-energy density (or equivalently of the grand potential density in the semi-grand-canonical situation) was a sufficient condition for repulsive interactions. The results derived in this article show that under the same circumstances exactly, the bulk modulus within a cell model is also a positive quantity.

We explicitly considered the semi-grand-canonical situation where the macroions suspension is dialyzed against an electrolyte reservoir. Our results may, however, be extended to other electrostatic situations, such as the canonical one where the mean salt content in the suspension is fixed, or to the situation where the macroions are held at constant potential rather than constant charge.

## APPENDIX: ON THE CHOICE OF THE GREEN'S FUNCTION

We consider the Green's function  $G(\mathbf{r}, \mathbf{r}')$  satisfying

$$\nabla_{\mathbf{r}}^2 G(\mathbf{r}, \mathbf{r}') = -S_\nu \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{A1})$$

with yet unspecified boundary conditions. From a standard identity (Green second identity), the solution of Poisson's equation  $\nabla_{\mathbf{r}}^2 \psi = -S_\nu \rho(\mathbf{r})$  obeys the relation<sup>11</sup>

$$\begin{aligned} \psi(\mathbf{r}) &= \int_{\mathcal{R}} \rho(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ &+ \frac{1}{S_\nu} \int_{\partial\mathcal{R}} \frac{\partial \psi(\mathbf{r}')}{\partial n'} G(\mathbf{r}, \mathbf{r}') dS' \\ &- \frac{1}{S_\nu} \int_{\partial\mathcal{R}} \psi(\mathbf{r}') \frac{\partial G}{\partial n'}(\mathbf{r}, \mathbf{r}') dS', \end{aligned} \quad (\text{A2})$$

where  $\partial_n \equiv \partial/\partial n$  denotes the normal derivative and  $\partial\mathcal{R}$  is the surface delimiting the region  $\mathcal{R}$ .

The Dirichlet  $G_D$  and Neumann  $G_N$  Green's function satisfy the boundary conditions

$$G_D(\mathbf{r}, \mathbf{r}') = 0 \quad \text{and} \quad \partial_n G_N(\mathbf{r}, \mathbf{r}') = -1/R^{\nu-1} \quad \text{for } \mathbf{r}' \in \partial\mathcal{R}. \quad (\text{A3})$$

For Dirichlet boundary conditions, we therefore have

$$\begin{aligned} \psi(\mathbf{r}) &= \int_{\mathcal{R}} \rho(\mathbf{r}') G_D(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ &- \frac{1}{S_\nu} \int_{\partial\mathcal{R}} \psi(\mathbf{r}') \frac{\partial G_D}{\partial n'}(\mathbf{r}, \mathbf{r}') dS'. \end{aligned} \quad (\text{A4})$$

For the isotropic situation considered here and from Gauss law, the last term in Eq. (A4) may be written as

$$-\psi(R) \frac{1}{S_\nu} \int_{\partial\mathcal{R}} \frac{\partial G_D}{\partial n'}(\mathbf{r}, \mathbf{r}') dS' = \psi(R). \quad (\text{A5})$$

So far, the choice  $G_D(\mathbf{r}, \mathbf{r}') = 0$  for  $\mathbf{r}' \in \partial\mathcal{R}$  does not ensure that  $\psi(R) = 0$ . We chose to fix the zero of the electric poten-

tial at the boundary of the cell  $\psi(R) = 0$  so that we recover Eq. (2.4).

For Neumann boundary conditions

$$\begin{aligned} \psi(\mathbf{r}) &= \langle \psi \rangle_S + \int_{\mathcal{R}} \rho(\mathbf{r}') G_N(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ &+ \frac{1}{S_\nu} \int_{\partial\mathcal{R}} \frac{\partial \psi(\mathbf{r}')}{\partial n'} G_N(\mathbf{r}, \mathbf{r}') dS', \end{aligned} \quad (\text{A6})$$

where the first term  $\langle \psi \rangle_S = \psi(R)$  is the average of the electric potential on the surface of the cell and we chose it to vanish. The last term in Eq. (A6) is

$$\begin{aligned} \frac{1}{S_\nu} \partial_n \psi(R) \int_{\partial\mathcal{R}} G_N(\mathbf{r}, \mathbf{r}') dS' &= -\frac{1}{R^{\nu-1}} \int_{\mathcal{R}} \rho(\mathbf{r}') d\mathbf{r}' \\ &\times \int_{\partial\mathcal{R}} G_N(\mathbf{r}, \mathbf{r}'') dS''. \end{aligned} \quad (\text{A7})$$

We have used Gauss law:  $-\partial_n \psi(R) = \int \rho(\mathbf{r}') d\mathbf{r}' / R^{\nu-1}$ . A proper choice of the Green's function ensures that the surface integral on the right-hand side of (A7) is independent of  $\mathbf{r}$ , and vanishes (one can shift  $G_N$  by an arbitrary constant). Explicitly, in the three-dimensional case, the choice

$$\begin{aligned} G_N(\mathbf{r}, \mathbf{r}') &= -\frac{1}{R} + \frac{1}{r_>} + \sum_{\ell=1}^{\infty} \left[ \frac{r_<^\ell}{r_>^{\ell+1}} + \frac{\ell+1}{\ell} \frac{(rr')^\ell}{R^{2\ell+1}} \right] \\ &\times P_\ell(\cos \theta), \end{aligned} \quad (\text{A8})$$

with  $r_> = \max(r, r')$  and  $r_< = \min(r, r')$ ,  $\theta$  the angle between  $\mathbf{r}$  and  $\mathbf{r}'$  and  $P_\ell$  the Legendre polynomial of order  $\ell$ , makes the term (A7) vanish. Finally, with this choice for the Green's function and for the reference potential, we have in both cases of boundary conditions

$$\psi(\mathbf{r}) = \int_{\mathcal{R}} \rho(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad \text{and} \quad \psi(R) = 0. \quad (\text{A9})$$

A useful property that follows from these considerations is that for *any* isotropic charge distribution  $\rho(r)$  (eventually nonglobally neutral) we have in both cases of boundary conditions

$$\int_{\mathcal{R}} \rho(r') G(\mathbf{R}, \mathbf{r}') d\mathbf{r}' = 0, \quad (\text{A10})$$

where  $\mathbf{R} \in \partial\mathcal{R}$ . This follows directly in the Dirichlet boundary conditions case from  $G(\mathbf{R}, \mathbf{r}') = 0$  and in the Neumann boundary conditions case from the particular choice (A8). Finally, we emphasize that the symmetry property  $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r})$  is not necessarily fulfilled by a generic Green's function,<sup>12</sup> but may be imposed as a separate requirement, and holds for the functions considered here.

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