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Quenched charge disorder and Coulomb interactions

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We develop a general formalism to investigate the effect of quenched fixed charge disorder on effective electrostatic interactions between charged surfaces in a one-component (counterion-only) Coulomb fluid. Analytical results are explicitly derived for two asymptotic and complementary cases: (i) mean-field or Poisson-Boltzmann limit (including Gaussian-fluctuations correction), which is valid for small electrostatic coupling, and (ii) strong-coupling limit, where electrostatic correlations mediated by counterions become significantly large as, for instance, realized in systems with high-valency counterions. In the particular case of two apposed and ideally polarizable planar surfaces with equal mean surface charge, we find that the effect of the disorder is nil on the mean-field level and thus the plates repel. In the strong-coupling limit, however, the effect of charge disorder turns out to be additive in the free energy and leads to an enhanced long-range attraction between the two surfaces. We show that the equilibrium interplate distance between the surfaces decreases for elevated disorder strength (i.e., for increasing mean-square deviation around the mean surface charge), and eventually tends to zero, suggesting a disorder-driven collapse transition.

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I. INTRODUCTION

Electrostatic interactions usually provide the repulsion that stabilizies charged colloids and are one of the two essential ingredients in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability [1,2]. Electrostatic interactions in the presence of mobile counterions are standardly described by the Poisson-Boltzmann theory [1,3] that embodies the *mean-field* approach to Coulomb fluids and leads to pronounced repulsive interactions between like-charged macroions. It has recently been realized however [4–27] that, in the presence of polyvalent counterions, electrostatic interactions can mediate strong attractive interactions between like-charged macroions. This attraction cannot be captured by the mean-field approach and a paradigm dubbed the *strong-coupling limit* [24,25] was devised to describe the equilibrium properties of Coulomb fluids when the mobile counterion charges become large. The transition from the mean-field Poisson-Boltzmann description to the strong-coupling limit is governed by a single dimensionless electrostatic coupling parameter, being a ratio of two lengths, namely, the Bjerrum length, which identifies Coulombic interaction between ions themselves, and the Gouy-Chapman length, which describes electrostatic interaction between the ions and the charged macroion surface. This ratio involves the charge valency of counterions, the dielectric constant of medium and the surface charge density of interacting macroions [27]. The emerging picture of equilibrium properties of Coulomb fluids has thus become much richer than conveyed for many years by the DLVO paradigm.

The strong-coupling attraction is not just a refinement of the mean-field description. In fact it reverses the role of Coulomb interactions in the DLVO theory [27]. Instead of stabilizing the charged macroions they act more like Lifshitz–van der Waals interactions that tend to collapse them. Since Coulomb interactions in the strong-coupling limit are much stronger than the Lifshitz–van der Waals interactions, they themselves govern the destabilization of the colloids. The collapse of a highly charged polyelectrolyte, such as DNA, in the presence of polyvalent counterions is the most dramatic example of unexpected and counterintuitive features of the strong-coupling electrostatics [4,25]. Though other physical mechanisms, such as hydration layer complementarity [5], certainly contribute fine details to this collapse and account for its molecular specificity, electrostatic correlations involved in the strong-coupling limit provide the universal background for this intriguing phenomenon. The elucidation of this collapse in terms of the strong-coupling electrostatic interaction represents one of the major recent advances in the theory of colloid stability.

In what follows, we shall concentrate on yet another facet of Coulomb interactions in charged colloids, namely, the *quenched disordered* distribution of surface charges. Usually the charge on the surfaces of the macroions on the Poisson-Boltzmann or the strong-coupling level is assumed to be homogeneous and constant. This is in general quite a severe assumption and there are well known cases where this assumption is not realistic at all [28]. Random polyelectrolytes and polyampholytes present one such case [29–31]. There the sequence of charges can be distributed along the polymer backbone in a disordered manner. The Coulomb (self-)interactions of such polyelectrolytes are distinct and different from homogeneously charged polymers.

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A case even closer to the present line of reasoning are investigations of interactions between solid surfaces in the presence of charged surfactants. The aggregation of surfactants at solid surfaces in aqueous solutions was investigated with atomic force microscopy and shows structures consistent with half-cylinders on crystalline hydrophobic substrates for quaternary ammonium surfactants (above the critical micelle concentration), full cylinders on mica, and spheres on amorphous silica [32,33]. Such interfacial aggregates whose emergence and structural details depend on the method of preparation result from a compromise between the natural free curvature as defined by intermolecular interactions and the constraints imposed by specific surfactant-surface interactions and can pattern interacting surfaces at nanometer-length scales. Similar interfacial structures are also seen for interacting hydrophilic mica surfaces in the presence of cetyl-trimethyl-amonium bromide (CTAB) [34]. The surfaces appear to be covered by a mosaic of positively and negatively charged regions and experience a strong, *long-ranged attraction* which is comparable in magnitude to that between hydrophobic surfaces, and is orders of magnitude larger than that expected from Lifshitz–van der Waals forces [34]. The patterning of interacting surfaces described above is highly disordered, depends on the method of preparation, and has basic implications also for the forces that act between other types of hydrophilic surfaces with mixed charges, most notably the surfaces of cells and proteins, as well as in synthetic systems.

Motivated by these observations we set ourselves to investigate the effect of quenched disordered surface charge, specified by a constant mean value and mean-square deviation, on the interactions between charged surfaces in ionic solutions. We formulate the general partition function of a system of charged objects with a Gaussian-distributed quenched surface charge in a one-component Coulomb fluid using field-theoretical techniques and the standard replica trick. As a particular case, we focus on the effective interaction between two opposed, ideally polarizable planar surfaces of equal mean and mean-square deviation for disordered surface charge density. An explicit form for the interaction free energy can be obtained on the Poisson-Boltzmann level as well as on the strong-coupling level. The former, interestingly enough, shows no effect of the quenched charge disorder. The interaction free energy at the mean-field level plus quadratic (Gaussian) fluctuations around the mean-field solution is exactly the same as the one for a uniform charge distribution characterized solely by a constant mean surface charge. In the strong-coupling limit, the situation is altogether different. Here the quenched surface charge disorder contributes an additive *attractive* tail to the interaction determined by the mean surface charge. This attractive contribution is linear in the *disorder coupling strength*, which is proportional to the mean-square deviation of the charge distribution, and is a direct analogon of the electrostatic coupling parameter introduced in the case of no charge disorder [27]. This attractive tail can completely overwhelm the entropic repulsion due to counterion confinement on the strong-coupling level and can thus completely eliminate the finite equilibrium distance between the surfaces in this limit [24]. In other words, the introduction of charge disorder can destabilize the closely-packed bound state of two uniformly and like-charged surfaces [24,27], suggesting a collapse transition. This is an important result because especially in the biological context the surface charge disorder is ubiquitous, stemming not only or not at all from the method of preparation of the macroions, but from their intrinsic molecular disorder, dictated eventually by the evolutionary processes.

The outline of the paper is as follows. First we enunciate the result, which is indeed quite simple, but can only be derived by fairly detailed and rather involved technical arguments. The general formulation of the partition function for a one-component Coulomb fluid between charged planar surfaces is developed next in the form where the trace over the quenched disorder has already been evaluated exactly on the replica level. This very complicated partition function in the replica space can then be explicitly traced over local electrostatic field fluctuations on the Poisson-Boltzmann level as well as on the strong-coupling level. This can be accomplished by noting the properties of a certain type of symmetric matrices. The formalism developed in the present work is quite general and can be applied to investigate charge disorder effects in a variety of systems, including interactions between spherical and cylindrical macroions as well.

II. MAIN RESULTS

Since the derivation of our main result contains several rather subtle and highly non-trivial technical points we enunciate it first stripped of all technicalities. Our model system is composed of two ideally polarizable surfaces located at $z = \pm a$, with the intersurface spacing $D=2a$ (see Fig. 1). The mean surface charge density on both surfaces is the same with a magnitude equal to σ, while the mean-square deviation in surface charge density due to quenched disorder is given by g. The one-component Coulomb fluid between the two surfaces is composed of counterions of charge Ze_0, where Z is the counterion valency and e_0 is the elementary charge. For uniformly charged surfaces ($g=0$), the electrostatic coupling parameter that identifies the strength of electrostatic correlations in the system is given by [27]

$$\Xi = 2\pi Z^3 \ell_{\mathrm{B}}^2 \sigma = \frac{Z^2 \ell_{\mathrm{B}}}{\mu}, \tag{1}$$

where $\ell_{\mathrm{B}} = \beta e_0^2/(4\pi\epsilon\epsilon_0)$ is the Bjerrum length (with $\beta = 1/k_{\mathrm{B}}T$) and $\mu = e_0/(2\pi\ell_{\mathrm{B}} Z\sigma)$ is the Gouy-Chapman length associated with the mean charge. As was demonstrated by Netz [24] for the *undisordered case*, the partition function of the one-component Coulomb fluid has two different fixed points characterized by the value of Ξ. For $\Xi \ll 1$, the partition function is given by the Poisson-Boltzmann (mean-field) fixed point. Fluctuations around this fixed point may be accounted for by a systematic loop expansion [7,8,10,24]. At elevated coupling, the loop expansion scheme breaks down and the partition function for $\Xi \gg 1$ is determined by the asymptotic strong-coupling theory, which corresponds to the leading term of a virial expansion, and is in fact given by single-particle contributions.

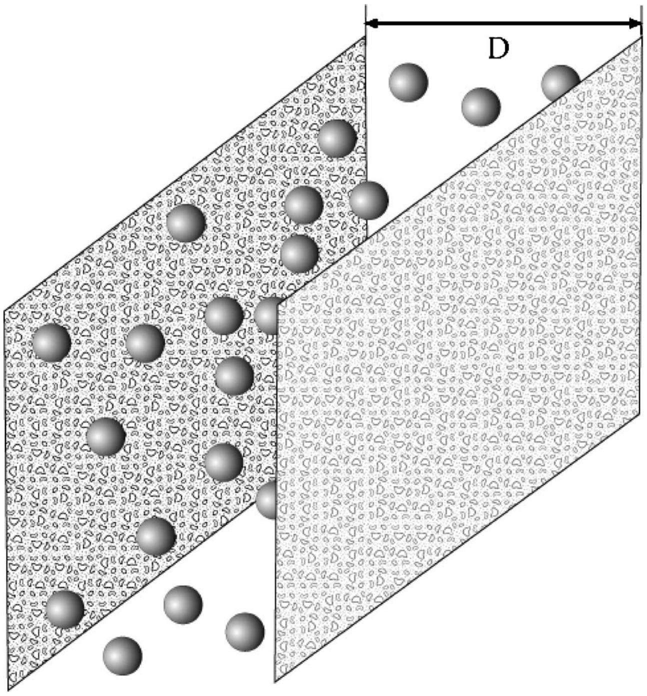

FIG. 1. Schematic representation of our model system: two ideally polarizable planar surfaces with quenched surface charge disorder at separation D with mobile (pointlike) counterions of charge Ze_0 confined in the intersurface space. The surface charge density is characterized by a Gaussian distribution with fixed mean value of magnitude σ and mean-square deviation g.

In the presence of quenched disorder ($g>0$), one can follow the same line of reasoning, by introducing the mean electrostatic coupling parameter Ξ in analogy with Eq. (1) but with σ now being the *mean* surface charge density. In the mean-field limit, characterized by $\Xi \ll 1$, we demonstrate that the disorder makes *no* contribution to the interaction free energy, if the bounding surfaces are ideally polarizable and thus do not allow the penetration of the field. The total interaction pressure in this limit is given by the standard mean-field (Poisson-Boltzmann) expression $P_{\mathrm{MF}}(D)$ and an additive contribution, $P_2(D)$, due to quadratic (Gaussian) fluctuations around the mean-field solution as

$$P(D) = P_{\mathrm{MF}}(D) + P_2(D). \tag{2}$$

Both terms depend only on the mean surface charge density σ and have been thoroughly analyzed before [1,7,10,16,19,24]. The Poisson-Boltzmann limit for ideally polarizable bounding interfaces is thus unaffected by the presence of disorder, i.e., it does not depend on g. This result is completely consistent with conclusions reached in Ref. [28] *via* an altogether different route.

In the strong-coupling limit, characterized by large mean electrostatic coupling parameter $\Xi \gg 1$, however, the interaction free energy is obtained to contain an essential contribution stemming from the quenched surface charge disorder. The total interaction pressure is given by the sum of the standard strong-coupling pressure $P_{\mathrm{SC}}(D)$ [24] that depends only on the mean charge density σ plus a disorder contribution, $P_\chi(D)$, depending on g, i.e.,

$$P(D) = P_{\mathrm{SC}}(D) + P_\chi(D), \tag{3}$$

where the disorder term in dimensionless representation reads

$$\frac{\beta P_\chi(D)}{2\pi \ell_{\mathrm{B}} \sigma^2} = -\chi\left(\frac{2\mu}{D}\right), \tag{4}$$

which is attractive and linear in χ defined as

$$\chi = \frac{Z^2(\beta e_0)^2 g}{8\pi(\epsilon\epsilon_0)^2} = 2\pi Z^2 \ell_{\mathrm{B}}^2 g. \tag{5}$$

Clearly by comparing Eq. (1) and Eq. (5), we can claim that χ represents the dimensionless *disorder coupling parameter*. $P_{\mathrm{SC}}(D)$ has been analyzed thoroughly before [24]. The disorder term in Eq. (3) incidentally has the same scaling form as the one-particle ideal entropy term in $P_{\mathrm{SC}}(D)$. It can change the sign of the interactions at small values of the intersurface spacing D, as will be shown later. The quenched charge disorder thus affects only the strong-coupling limit in a rather simple way, contributing an additive term to the free energy or the interaction pressure. After this introductory exposition, we next derive these results in full glory and all the relevant technical details.

III. GENERAL FORMALISM: THE REPLICA METHOD FOR QUENCHED AVERAGING

The partition function of a one-component (counterion-only) Coulomb fluid in the field of an external fixed charge characterized by the volume charge density $\rho(\mathbf{r})$ can be derived in the form of a functional integral over the fluctuating electrostatic field $\phi(\mathbf{r})$ as [7,8]

$$\mathcal{Z} = e^{-(1/2)\ln\det \beta v(\mathbf{r},\mathbf{r}')} \int \mathcal{D}[\phi(\mathbf{r})] e^{-\beta\mathcal{H}[\phi(\mathbf{r})]}, \tag{6}$$

where the field-action is given by

$$\beta\mathcal{H}[\phi(\mathbf{r})] = \frac{1}{2}\beta \int\int d\mathbf{r}\, d\mathbf{r}'\, \phi(\mathbf{r}) v^{-1}(\mathbf{r},\mathbf{r}') \phi(\mathbf{r}') - \tilde{\lambda} \int d\mathbf{r}\, \Omega(\mathbf{r}) e^{-i\beta Z e_0 \phi(\mathbf{r})} + i\beta \int d\mathbf{r}\, \rho(\mathbf{r}) \phi(\mathbf{r}). \tag{7}$$

Here the geometry function $\Omega(\mathbf{r})$ specifies the volume accessible for counterions in space (it, for instance, takes into account the presence of hard walls). The rescaled absolute activity (fugacity), $\tilde{\lambda}$ (connected to the chemical potential, μ, via $\mu = \ln \lambda$), is defined as

$$\tilde{\lambda} = \lambda e^{(1/2)e_0^2 \beta v(\mathbf{r},\mathbf{r})}. \tag{8}$$

The Coulomb interaction potential $v(\mathbf{r},\mathbf{r}') = 1/(4\pi\epsilon\epsilon_0|\mathbf{r}-\mathbf{r}'|)$ is a solution of

$$-\epsilon\epsilon_0 \nabla^2 v(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{9}$$

and thus obviously the inverse Coulomb operator is given by

$$v^{-1}(\mathbf{r},\mathbf{r}') = -\epsilon\epsilon_0 \nabla^2 \delta(\mathbf{r}-\mathbf{r}'). \qquad (10)$$

We assume in what follows that the external charge distribution has a quenched disordered component and is in fact distributed with a Gaussian probability distribution around its mean $\rho_0(\mathbf{r})$ as

$$\text{const} \times e^{-(1/2)\int d\mathbf{r}\, g^{-1}(\mathbf{r})[\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2}. \qquad (11)$$

Here the width of the charge disorder distribution, i.e., the mean-square charge density, is given by $g(\mathbf{r})$. Though it is difficult to argue for or against this particular form of the disorder model it has two important features: it is analytically solvable, as we shall demonstrate below, and it leads to highly nontrivial results [35].

This model of the disorder, approximate as it may be, contains two important parameters that are valuable apart from the details of the model: the average charge and the average square deviations from this charge.

The average over quenched charge disorder is obtained by applying the standard Edwards-Anderson replica ansatz [36] in the form

$$\mathcal{F} = -k_B T \overline{\log \mathcal{Z}} = -k_B T \lim_{n\to 0} \frac{\overline{\mathcal{Z}^n} - 1}{n}, \qquad (12)$$

where the disorder average is defined with respect to the external charge density distribution, Eq. (11), as

$$\overline{(\ldots)} = \int \mathcal{D}[\rho(\mathbf{r})](\cdots) e^{-(1/2)\int d\mathbf{r}\, g^{-1}(\mathbf{r})[\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2}. \qquad (13)$$

The quenched average over the charge density disorder affects only the source term in Eq. (7). Thus we only need to evaluate

$$\overline{e^{-i\beta\int d\mathbf{r}\, \rho(\mathbf{r})\phi(\mathbf{r})}} = \int \mathcal{D}[\rho(\mathbf{r})] e^{-i\beta\Sigma_\alpha \int d\mathbf{r}\, \rho(\mathbf{r})\phi_\alpha(\mathbf{r}) - (1/2)\int d\mathbf{r}\, g^{-1}(\mathbf{r})[\rho(\mathbf{r}) - \rho_0]^2} = \text{const} \times e^{-(1/2)\beta^2 \int d\mathbf{r}\, g(\mathbf{r})\Sigma_{\alpha,\beta}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) - i\beta\Sigma_\alpha \int d\mathbf{r}\, \rho_0(\mathbf{r})\Sigma_\alpha \phi_\alpha(\mathbf{r})} \qquad (14)$$

for $\alpha,\beta = 1,\ldots,n$ being the replica labels. Taking this into account, the final form of the replicated partition function $\overline{\mathcal{Z}^n}$ can be obtained as

$$\overline{\mathcal{Z}^n} = e^{-(1/2)n \ln \det \beta v(\mathbf{r},\mathbf{r}')} \int \mathcal{D}[\phi_\alpha(\mathbf{r})] e^{-\beta\tilde{\mathcal{H}}[\phi_\alpha(\mathbf{r})]}, \qquad (15)$$

with

$$\beta\tilde{\mathcal{H}}[\phi_\alpha(\mathbf{r})] = \tfrac{1}{2}\sum_{\alpha\beta} \int\int d\mathbf{r}\, d\mathbf{r}' \mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) - V[\phi_\alpha(\mathbf{r})] + i\beta \int d\mathbf{r}\, \rho_0(\mathbf{r}) \sum_\alpha \phi_\alpha(\mathbf{r}), \qquad (16)$$

where

$$V[\phi_\alpha(\mathbf{r})] = \tilde{\lambda} \int d\mathbf{r}\, \Omega(\mathbf{r}) \sum_\alpha e^{-i\beta Z e_0 \phi_\alpha(\mathbf{r})}. \qquad (17)$$

Above we introduced the following matrix in the replica space:

$$\mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = (\beta v^{-1}(\mathbf{r},\mathbf{r}') + \beta^2 g(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'))\delta_{\alpha\beta} + \beta^2 g(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')(1-\delta_{\alpha\beta}). \qquad (18)$$

The expression (15) together with Eq. (12) represents the starting formulation for the free energy in the presence of quenched charge disorder. There are two separate problems with the above replicated partition function (15) that we have to resolve. First of all there is the nonlinear term in the field action that precludes direct integration. On top of that we have to evaluate the functional integral in the replica space for arbitrary number of replicas, n, and then take the limit of $n \to 0$.

The way we will approach this rather formidable task is to combine the methods developed for the one component (counterion-only) Coulomb fluid without disorder [24] and modify them as we proceed to incorporate appropriately the disorder effects. We shall start with the Poisson-Boltzmann or the saddle-point limit, which is exact for $\Xi \to 0$ [24], and then proceed to the strong-coupling limit.

IV. THE MEAN-FIELD (POISSON-BOLTZMANN) LIMIT

Let us first investigate the saddle-point limit of the functional integral (15). The saddle-point equation for the $\phi_\alpha(\mathbf{r})$ field is given obviously by

$$\int d\mathbf{r}' \sum_\beta \mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\beta(\mathbf{r}') - \frac{\partial V[\phi_\alpha(\mathbf{r})]}{\partial \phi_\alpha(\mathbf{r})} + i\beta\rho_0(\mathbf{r}) = 0. \qquad (19)$$

Taking into account Eq. (18), this amounts to

$$-\beta\epsilon\epsilon_0 \nabla^2 \phi_\alpha(\mathbf{r}) + \beta^2 g(\mathbf{r}) \sum_\beta \phi_\beta(\mathbf{r}) - \frac{\partial V[\phi_\alpha(\mathbf{r})]}{\partial \phi_\alpha(\mathbf{r})} + i\beta\rho_0(\mathbf{r}) = 0. \qquad (20)$$

In the replica formulation we have to take the limit $n \to 0$, which implies that

$$\lim_{n\to 0}\sum_{\beta} \phi_\beta(\mathbf{r}) \to 0. \qquad (21)$$

By furthermore making the substitution $\phi_\alpha(\mathbf{r}) \to i\phi_\alpha(\mathbf{r})$ and noting that in the limit $n\to 0$, the index α becomes irrelevant, and denoting the corresponding potential as $\phi_{\rm MF}(\mathbf{r})$, we are left with

$$\epsilon\epsilon_0 \nabla^2 \phi_{\rm MF}(\mathbf{r}) + \tilde{\lambda} Z e_0 \Omega(\mathbf{r}) e^{-\beta Z e_0 \phi_{\rm MF}(\mathbf{r})} = -\rho_0(\mathbf{r}). \qquad (22)$$

This is of course nothing but the Poisson-Boltzmann equation for the fixed mean charge density $\rho_0(\mathbf{r})$ and the mean-field Poisson-Boltzmann potential $\phi_{\rm MF}(\mathbf{r})$ [7,24]. The corresponding mean-field (saddle-point) action can be written as

$$\begin{aligned}\beta\tilde{\mathcal{H}}[\phi_{\rm MF}(\mathbf{r})] = {} & -\tfrac{1}{2}\epsilon\epsilon_0\beta \int d\mathbf{r} (\nabla\phi_{\rm MF}(\mathbf{r}))^2 \\ & - \tilde{\lambda}\int d\mathbf{r}\, \Omega(\mathbf{r}) e^{-\beta Z e_0 \phi_{\rm MF}(\mathbf{r})} \\ & + \beta \int d\mathbf{r}\, \rho_0(\mathbf{r})\phi_{\rm MF}(\mathbf{r}). \qquad (23)\end{aligned}$$

The effect of the quenched charge disorder on the mean potential is thus nil. Obviously the saddle-point action can be taken out of the functional integral since it is simply multiplicative in the number of replicas.

We now discuss the fluctuations around the mean-field, or the saddle-point, fields. Expanding $\beta\tilde{\mathcal{H}}[\phi_\alpha(\mathbf{r})]$ in Eq. (16) to the second order in the deviations from $\phi_{\rm MF}(\mathbf{r})$, we are left with

$$\overline{\mathcal{Z}^n} = e^{-(1/2)n \ln \det \beta v(\mathbf{r},\mathbf{r}') - n\beta\tilde{\mathcal{H}}_{\rm MF}[\phi_{\rm MF}(\mathbf{r})]} \int \mathcal{D}[\phi_\alpha(\mathbf{r})] e^{-\beta\tilde{\mathcal{H}}_2[\phi_\alpha(\mathbf{r})]}, \qquad (24)$$

where $\tilde{\mathcal{H}}_{\rm MF}[\phi_{\rm MF}(\mathbf{r})] = \tilde{\mathcal{H}}[\phi_{\rm MF}(\mathbf{r})]$,

$$\beta\tilde{\mathcal{H}}_2[\phi_\alpha(\mathbf{r})] = \tfrac{1}{2}\sum_{\alpha\beta} \int\int d\mathbf{r}\, d\mathbf{r}'\, \phi_\alpha(\mathbf{r}) \mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\beta(\mathbf{r}), \qquad (25)$$

and

$$\mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}') - \left.\frac{\partial^2 V[\phi_\alpha(\mathbf{r})]}{\partial\phi_\alpha^2(\mathbf{r})}\right|_{\phi_{\rm MF}} \delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}'). \qquad (26)$$

In the above expression the second term has to be evaluated at the saddle point and thus yields

$$\left.\frac{\partial^2 V[\phi_\alpha(\mathbf{r})]}{\partial\phi_\alpha^2(\mathbf{r})}\right|_{\phi_{\rm MF}} = -\tilde{\lambda}(\beta Z e_0)^2 \Omega(\mathbf{r}) e^{-\beta Z e_0 \phi_{\rm MF}(\mathbf{r})}. \qquad (27)$$

Thus we obtain explicitly

$$\begin{aligned}\mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = {} & \Big[\beta v^{-1}(\mathbf{r},\mathbf{r}') + \Big(\tilde{\lambda}(\beta Z e_0)^2\Omega(\mathbf{r}) e^{-\beta Z e_0\phi_{\rm MF}(\mathbf{r})} \\ & + \beta^2 g(\mathbf{r})\Big)\delta(\mathbf{r}-\mathbf{r}')\Big]\delta_{\alpha\beta} + \beta^2 g(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \\ & \times (1-\delta_{\alpha\beta}). \qquad (28)\end{aligned}$$

Since $\beta\tilde{\mathcal{H}}_2[\phi_\alpha(\mathbf{r})]$ is Gaussian in $\phi_\alpha(\mathbf{r})$ the functional integral, Eq. (24), can be evaluated explicitly yielding

$$\overline{\mathcal{Z}^n} = e^{-(1/2)n \ln \det \beta v(\mathbf{r},\mathbf{r}') - n\beta\tilde{\mathcal{H}}_{\rm MF}[\phi_{\rm MF}(\mathbf{r})] - (1/2)\ln \det \mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}')}. \qquad (29)$$

The task now is to evaluate the determinant $\det \mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ explicitly as a function of n and then use this to evaluate the $n\to 0$ limit. This can be done with the help of the following matrix identity. Take a symmetric $n\times n$ matrix of the general form

$$M_{\alpha\beta} = \begin{bmatrix} b & s & s & \dots \\ s & b & s & \dots \\ s & s & b & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} = b\ \delta_{\alpha\beta} + s(1-\delta_{\alpha\beta}). \qquad (30)$$

It is rather straightforward to show *via* induction that

$$\det M_{\alpha\beta} = (b-s)^n\left(1 + \frac{ns}{b-s}\right). \qquad (31)$$

In order to exploit this matrix identity we first define the operator $G(\mathbf{r},\mathbf{r}')$ as

$$\begin{aligned}& \int d\mathbf{r}''\Big(\beta v^{-1}(\mathbf{r},\mathbf{r}'') + \tilde{\lambda}(\beta Z e_0)^2\Omega(\mathbf{r}) e^{-\beta Z e_0 \phi_{\rm MF}(\mathbf{r})} \\ & \quad \times \delta(\mathbf{r}-\mathbf{r}'')\Big) G(\mathbf{r}'',\mathbf{r}') \\ & = \delta(\mathbf{r}-\mathbf{r}'), \qquad (32)\end{aligned}$$

or equivalently

$$\Big(-\beta\epsilon\epsilon_0\nabla^2 + \tilde{\lambda}(\beta Z e_0)^2 \Omega(\mathbf{r}) e^{-\beta Z e_0\phi_{\rm MF}(\mathbf{r})}\Big) G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \qquad (33)$$

With this definition and by using the Tr log formula, the determinant $\det \mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ can be obtained explicitly as

$$\begin{aligned}\tfrac{1}{2}\ln \det \mathcal{G}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = {} & -\tfrac{n}{2}\ln \det G(\mathbf{r},\mathbf{r}') + \frac{1}{2}\mathrm{Tr}\ln\big(\delta(\mathbf{r}-\mathbf{r}') \\ & + n\beta^2 g(\mathbf{r}) G(\mathbf{r},\mathbf{r}')\big). \qquad (34)\end{aligned}$$

The final expression for the replicated partition function becomes

$$\begin{aligned}\ln\overline{\mathcal{Z}^n} = {} & -\tfrac{n}{2}\ln \det \int d\mathbf{r}'\, \beta v(\mathbf{r},\mathbf{r}') G^{-1}(\mathbf{r}',\mathbf{r}'') - n\beta\tilde{\mathcal{H}}_{\rm MF}[\phi_{\rm MF}(\mathbf{r})] \\ & - \tfrac{1}{2}\mathrm{Tr}\ln\big(\delta(\mathbf{r}-\mathbf{r}') + n\beta^2 g(\mathbf{r}) G(\mathbf{r},\mathbf{r}')\big). \qquad (35)\end{aligned}$$

We have thus evaluated the partition function on the Poisson-Boltzmann level plus Gaussian-field fluctuations *exactly* as a function of n. The replica trick now leads directly to the free energy, Eq. (12), of the form

$$\mathcal{F}_\lambda = -k_BT\lim_{n\to 0}\frac{\overline{\mathcal{Z}^n}-1}{n} = \tilde{\mathcal{H}}_{\rm MF}[\phi_{\rm MF}(\mathbf{r})] + \frac{k_BT}{2}\ln\det\int d\mathbf{r}'\beta v(\mathbf{r},\mathbf{r}')G^{-1}(\mathbf{r}',\mathbf{r}'') + \frac{\beta}{2}\mathrm{Tr}\; g(\mathbf{r})G(\mathbf{r},\mathbf{r}'). \tag{36}$$

These three terms have a straightforward physical interpretation [9,24]. The first term is the standard mean-field result, the second is the one-loop correction around the mean field, and the third one is the contribution of the disorder. Obviously the latter is linear in the strength of the quenched charge disorder g.

We now go back from the grand-canonical to the canonical partition function *via* the Legendre transform [24]

$$\mathcal{F}_N = \mathcal{F}_\lambda + k_BT\, N\ln\lambda, \tag{37}$$

where N is the total number of counterions, which can be expressed through the absolute activity, λ, as

$$N = -\lambda\frac{\partial\mathcal{F}_\lambda}{\partial\lambda} = -\tilde{\lambda}\frac{\partial\mathcal{F}(\tilde{\lambda})}{\partial\tilde{\lambda}}. \tag{38}$$

(This simply means that the log of the absolute activity is defined up to an additive constant.) To the lowest order, and on the saddle-point level, we obtain straightforwardly

$$N = \tilde{\lambda}\int d\mathbf{r}\,\Omega(\mathbf{r})e^{-\beta Ze_0\phi_{\rm MF}(\mathbf{r})}. \tag{39}$$

This relation is nothing but the normalization condition for the mean-field density profile of counterions, $\tilde{\lambda}\,\Omega(\mathbf{r})e^{-\beta Ze_0\phi_{\rm MF}(\mathbf{r})}$, that can be connected with the electroneutrality condition *via* $2\sigma S = NZe_0$, where S is the total area and σ the surface charge density of macroions. Thus we finally are left with

$$\mathcal{F}_N = \mathcal{F}_\lambda - k_BT\,N\ln\int d\mathbf{r}\,\Omega(\mathbf{r})e^{-\beta Ze_0\phi_{\rm MF}(\mathbf{r})} + k_BT\,N\ln N. \tag{40}$$

For two charged planar surfaces, for instance, the interaction pressure can be obtained by differentiating the free energy $\mathcal{F}_N$ with respect to the separation D.

Since the contribution of the quenched charge disorder to the grand canonical free energy Eq. (36) is additive, it follows straightforwardly that the canonical free energy Eq. (37) can be also decomposed into a sum of two terms: one that does not depend on the presence of the quenched charge disorder and the other one that does:

$$\mathcal{F}_N = \mathcal{F}_N(g=0) + \frac{\beta}{2}\mathrm{Tr}\; g(\mathbf{r})G(\mathbf{r},\mathbf{r}'). \tag{41}$$

The first term can be furthermore rewritten as a sum of the mean field (saddle-point) term and the term corresponding to Gaussian fluctuations around the mean field

$$\mathcal{F}_N(g=0) = \mathcal{F}_N^{\rm MF}[\phi_{\rm MF}(\mathbf{r})] + \mathcal{F}_N^{(2)}, \tag{42}$$

where

$$\mathcal{F}_N^{\rm MF}[\phi_{\rm MF}(\mathbf{r})] = -\tfrac{1}{2}\epsilon\epsilon_0\int d\mathbf{r}(\nabla\phi_{\rm MF}(\mathbf{r}))^2 + \int d\mathbf{r}\,\rho_0(\mathbf{r})\phi_{\rm MF}(\mathbf{r}) - k_BT\,N\ln\int d\mathbf{r}\,\Omega(\mathbf{r})e^{-\beta Ze_0\phi_{\rm MF}(\mathbf{r})} + k_BT(N\ln N - N) \tag{43}$$

is the mean-field Poisson-Boltzmann free energy, and

$$\mathcal{F}_N^{(2)} = \frac{k_BT}{2}\ln\det\int d\mathbf{r}'\beta v(\mathbf{r},\mathbf{r}')G^{-1}(\mathbf{r}',\mathbf{r}'') \tag{44}$$

is the contribution of Gaussian fluctuations around the mean-field solution. These terms have already been introduced and evaluated elsewhere [7] and will not be analyzed again here.

V. MEAN-FIELD RESULTS FOR TWO CHARGED PLATES

Let us assume now that our system is composed of two planar surfaces, located at $z=\pm a$, with mean surface charge density $-\sigma$. It is thus obviously homogeneous in directions $\rho=(x,y)$. The mean volume charge distribution therefore reads

$$\rho_0(\mathbf{r}) = \rho_0(z,\rho) = -\sigma\delta(z-a) - \sigma\delta(z+a). \tag{45}$$

The mean-square charge density due to disorder is analogously written as

$$g(\mathbf{r}) = g(z,\rho) = g\,\delta(z-a) + g\,\delta(z+a). \tag{46}$$

Note also that since counterions are confined to the intersurface space (Fig. 1), the geometry function $\Omega(\mathbf{r})$ reads

$$\Omega(\mathbf{r}) = \Omega(z) = \begin{cases} 1 & -a<z<a, \\ 0 & \text{otherwise}. \end{cases} \tag{47}$$

From Eq. (41) where we set the disorder-independent terms apart, we derive the canonical free energy in this particular geometry in the form

$$\mathcal{F}_N = \mathcal{F}_N(g=0) + \tfrac{1}{2}\beta\, g\int d^2\rho[G(a,a;\rho,\rho) + G(-a,-a;\rho,\rho)]. \tag{48}$$

If we assume furthermore that the mean electrostatic field is confined solely to the region between the surfaces, that is assuming that the surfaces are ideally polarizable, then the last term in Eq. (48) describing the effects of the disorder is identically zero since it is straightforward to show that in this case

$$G(a,a;\rho,\rho) = G(-a,-a;\rho,\rho) = 0.$$

Therefore, with ideally polarizable bounding surfaces, the effect of the disorder on the electrostatic interactions is zero also on the one-loop level. Evaluating the interaction pressure between the two opposed surfaces from Eq. (48), we thus find

$$P(D) = P_{\mathrm{MF}}(D) + P_2(D). \tag{49}$$

The first component of pressure is obtained from the mean field Poisson-Boltzmann free energy (Eq. (43), which is always repulsive. For two planar equally charged surfaces at large separations and in dimensionless units, one has [1,7]

$$\tilde{P}(D) = \frac{\beta P_{\mathrm{MF}}(D)}{2\pi \ell_{\mathrm{B}} \sigma^2} \simeq \left(\frac{\pi\mu}{D}\right)^2. \tag{50}$$

The second term, stemming from Gaussian fluctuations around the mean field (Eq. (44), in fact corresponds to zero-frequency (static) Lifshitz–van der Waals interaction [9]. For two plates, this term contributes an attractive component that scales as [7,8,10,16,19]

$$\tilde{P}_2(D) = \frac{\beta P_2(D)}{2\pi \ell_{\mathrm{B}} \sigma^2} \simeq -\pi^2 \left(\frac{\mu}{D}\right)^3 \ln(D/\mu). \tag{51}$$

The result derived above, that the effect of quenched charge disorder on the interactions in planar geometry is nil, is pleasingly consistent with a previous study of quenched disorder on the weak-coupling level [28], which also shows no disorder contribution to the density profile of counterions at a single charged surface.

VI. THE STRONG-COUPLING LIMIT

Now we address the strong-coupling limit, $\Xi \gg 1$, which was shown to correspond to the first order term in the expansion of the partition function in terms of the absolute activity [24]. Expanding Eq. (15) in terms of $\tilde{\lambda}$ we obtain to the lowest order

$$\begin{aligned}\overline{\mathcal{Z}^n} &= \overline{\mathcal{Z}_0^n} + \tilde{\lambda}\overline{\mathcal{Z}_1^n} + \mathcal{O}(\tilde{\lambda}^2) \\ &= e^{-(1/2)n \ln \det \beta v(\mathbf{r},\mathbf{r}')} \left(\int \mathcal{D}[\phi_\alpha(\mathbf{r})] e^{-\beta \tilde{\mathcal{H}}_0[\phi_\alpha(\mathbf{r})]} \right. \\ &\quad \left. + \tilde{\lambda} \int d\mathbf{R}\, \Omega(\mathbf{R}) \sum_{\gamma=1}^{n} \int \mathcal{D}[\phi_\alpha(\mathbf{r})] e^{-\beta \tilde{\mathcal{H}}_1[\phi_\alpha(\mathbf{r}),\phi_\gamma(\mathbf{R})]} \right),\end{aligned} \tag{52}$$

with

$$\begin{aligned}\beta\tilde{\mathcal{H}}_0[\phi_\alpha(\mathbf{r})] &= \tfrac{1}{2}\sum_{\alpha\beta} \int\int d\mathbf{r}\, d\mathbf{r}' \mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) \\ &\quad + i\beta \int d\mathbf{r}\, \rho_0(\mathbf{r}) \sum_\alpha \phi_\alpha(\mathbf{r})\end{aligned} \tag{53}$$

and

$$\begin{aligned}\beta\tilde{\mathcal{H}}_1[\phi_\alpha(\mathbf{r})] &= \tfrac{1}{2}\sum_{\alpha\beta} \int\int d\mathbf{r}\, d\mathbf{r}' \mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) \\ &\quad - i\beta \int d\mathbf{r}\, \rho_0(\mathbf{r}) \sum_\alpha \phi_\alpha(\mathbf{r}) + i\beta Z e_0 \phi_\gamma(\mathbf{R}).\end{aligned} \tag{54}$$

$\mathcal{D}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ was defined already in Eq. (18). The first functional integral in Eq. (52) can be evaluated straightforwardly by noting that it is equivalent to Eq. (15) for $V[\phi_\alpha]=0$. Since in this limit obviously

$$\beta G(\mathbf{r},\mathbf{r}') = v(\mathbf{r},\mathbf{r}')$$

we obtain immediately

$$\begin{aligned}\mathcal{F}_0 &= -k_{\mathrm{B}}T \lim_{n\to 0} \frac{\overline{\mathcal{Z}_0^n} - 1}{n} = \tfrac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}' \rho_0(\mathbf{r}) v(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r}') \\ &\quad + \tfrac{1}{2}\mathrm{Tr}\ g(\mathbf{r}) v(\mathbf{r},\mathbf{r}')\end{aligned} \tag{55}$$

corresponding to the zeroth-order term of the virial expansion. The first term is the standard electrostatic interaction energy between external charges and the second term is the contribution of the disorder. We note here again that with the ansatz (46), the disorder term does not depend on the separation between the bounding surfaces because $v(z=a, z'=a:\rho,\rho)$ does not depend on a.

The second term in Eq. (52) is a bit trickier but can be again straightforwardly reduced to

$$\overline{\mathcal{Z}_1^n} = \overline{\mathcal{Z}_0^n} \int d\mathbf{R}\, \Omega(\mathbf{R}) \sum_{\gamma=1}^{n} e^{\beta u_\gamma(\mathbf{R})}, \tag{56}$$

where

$$\begin{aligned}\beta u_\gamma(\mathbf{R}) &= \beta^2 Z e_0 \int d\mathbf{r}' \sum_\alpha \mathcal{D}^{-1}_{\alpha\gamma}(\mathbf{r}',\mathbf{R})\rho_0(\mathbf{r}') \\ &\quad - \tfrac{1}{2}(\beta Z e_0)^2 \mathcal{D}^{-1}_{\gamma\gamma}(\mathbf{R},\mathbf{R}).\end{aligned} \tag{57}$$

The task now is to evaluate the expressions $\Sigma_\alpha \mathcal{D}^{-1}_{\alpha\beta}(\mathbf{r}',\mathbf{R})$ and $\mathcal{D}^{-1}_{\alpha\alpha}(\mathbf{R},\mathbf{R})$ explicitly as a function of n. This can be done just as before by considering the following identity valid for a symmetric $n\times n$ matrix of the general form

$$M_{\alpha\beta} = b\ \delta_{\alpha\beta} + s(1-\delta_{\alpha\beta}). \tag{58}$$

One can derive *via* induction that

$$M^{-1}_{\alpha\alpha} = \frac{1}{(b-s)}\left[1 + \frac{s}{(b-s)}\left(1 + \frac{ns}{b-s}\right)^{-1}\right] \tag{59}$$

and

$$\sum_\beta M^{-1}_{\alpha\beta} = \frac{1}{(b-s)}\left(1 + \frac{ns}{b-s}\right)^{-1}. \tag{60}$$

With the help of these matrix identities we can derive that

$$\mathcal{D}^{-1}_{\gamma\gamma}(\mathbf{R},\mathbf{R}) = \int d\mathbf{r}\, G(\mathbf{R},\mathbf{r}) T(\mathbf{r},\mathbf{R}), \tag{61}$$

where

$$\begin{aligned}T(\mathbf{r},\mathbf{r}') &= \delta(\mathbf{r}-\mathbf{r}') - \beta^2 \int d\mathbf{r}'' g(\mathbf{r}'') G(\mathbf{r}'',\mathbf{r})\big[\delta(\mathbf{r}-\mathbf{r}') \\ &\quad + n\beta^2 g(\mathbf{r}) G(\mathbf{r},\mathbf{r}')\big]^{-1}.\end{aligned} \tag{62}$$

Similarly

$$\sum_{\alpha} \mathcal{D}^{-1}_{\alpha\gamma}(\mathbf{r}',\mathbf{R}) = \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')\big[\delta(\mathbf{r}-\mathbf{r}') + n\beta^2 g(\mathbf{r}) G(\mathbf{r},\mathbf{r}')\big]^{-1}. \tag{63}$$

Neither of the above two equalities depends on the index γ, and the γ terms in Eq. (56) are thus additive leading to

$$\overline{\mathcal{Z}^n_1} = n\overline{\mathcal{Z}^n_0} \int d\mathbf{R}\, \Omega(\mathbf{R}) e^{\beta u_\gamma(\mathbf{R})}. \tag{64}$$

Since this is already first order in n, we only need Eq. (57) up to the zeroth order in n, thus obtaining

$$\overline{\mathcal{Z}^n} = \overline{\mathcal{Z}^n_0}\left(1 + \tilde{\lambda} n \int d\mathbf{R}\, \Omega(\mathbf{R}) e^{\beta u(\mathbf{R})}\right), \tag{65}$$

where

$$\beta u(\mathbf{R}) = \beta Z e_0 \int d\mathbf{r}' v(\mathbf{r}',\mathbf{R}) \rho_0(\mathbf{r}') + \tfrac{1}{2}(\beta Z e_0)^2 \int d\mathbf{r}\, g(\mathbf{r}) v^2(\mathbf{r},\mathbf{R}), \tag{66}$$

and hence *in extenso*

$$\overline{\mathcal{Z}^n} = \overline{\mathcal{Z}^n_0}\left(1 + \lambda\ n \int d\mathbf{R}\, \Omega(\mathbf{R}) e^{\beta Z e_0 \int d\mathbf{r}' v(\mathbf{r}',\mathbf{R}) \rho_0(\mathbf{r}') + (1/2)(\beta Z e_0)^2 \int d\mathbf{r}\, g(\mathbf{r}) v^2(\mathbf{r},\mathbf{R})}\right). \tag{67}$$

Note that in this formula we have the original fugacity λ and not the rescaled value $\tilde{\lambda}$ (see Eq. (8)). The divergent self-interaction is cancelled by an equal and opposite term in $\beta u(\mathbf{R})$. The total free energy can now be obtained from

$$\mathcal{F}_\lambda = -k_B T \lim_{n\to 0} \frac{\overline{\mathcal{Z}^n} - 1}{n} = \tfrac{1}{2} \int\int d\mathbf{r}\, d\mathbf{r}' \rho_0(\mathbf{r}) v(\mathbf{r},\mathbf{r}') \rho_0(\mathbf{r}') + \tfrac{1}{2}\mathrm{Tr}\ g(\mathbf{r}) v(\mathbf{r},\mathbf{r}') - k_B T\ \lambda \int d\mathbf{R}\, \Omega(\mathbf{R}) e^{\beta u(\mathbf{R})}. \tag{68}$$

If we now go back from the grand-canonical to the canonical partition function [24] again *via* a Legendre transform as given in Eqs. (37) and (38), we finally are left with

$$\mathcal{F}_N = \tfrac{1}{2} \int\int d\mathbf{r}\, d\mathbf{r}' \rho_0(\mathbf{r}) v(\mathbf{r},\mathbf{r}') \rho_0(\mathbf{r}') + \tfrac{1}{2}\mathrm{Tr}\ g(\mathbf{r}) v(\mathbf{r},\mathbf{r}') - N k_B T \ln \int d\mathbf{R}\, \Omega(\mathbf{R}) e^{\beta u(\mathbf{R})}. \tag{69}$$

The three terms in the above free energy have the following interpretation: the first one is the direct Coulomb interaction between the fixed charged surfaces (macroions) of mean charge density ρ_0. The second one, very similar to an analogous term in the weak coupling limit, represents the direct effect of the disorder and is proportional to the mean-square disorder charge density g. The third term embodies the disorder effect on the strong coupling level: It depends in an exponential fashion on the mean-square disorder strength g and has a nontrivial dependence on Coulomb interaction potential $v(\mathbf{r},\mathbf{r}')$ [see Eq. (66)].

VII. STRONG-COUPLING RESULTS FOR TWO CHARGED PLATES

Assuming again that our system is composed of two planar surfaces, located at $z = \pm a$, and with surface charge density $-\sigma$, we have

$$\rho_0(\mathbf{r}) = -\sigma\delta(z-a) - \sigma\delta(z+a), \tag{70}$$

where because of the electroneutrality

$$2S\sigma = NZe_0 \tag{71}$$

(with S being the area for each surface). The strength of the disorder is assumed to be of the form

$$g(\mathbf{r}) = g\,\delta(z-a) + g\,\delta(z+a), \tag{72}$$

and the geometry function $\Omega(\mathbf{R})$ is given by Eq. (47). We can now compute all the terms in the expression for the free energy, Eq. (69), explicitly. We obtain

$$\frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}' \rho_0(\mathbf{r}) v(\mathbf{r},\mathbf{r}') \rho_0(\mathbf{r}') = -\tfrac{1}{2}\frac{\sigma^2 S(2a)}{\epsilon\epsilon_0} + \text{const.}, \tag{73}$$

where the term const again stands for all the terms that are independent of the separation between the surfaces. Furthermore

$$\beta u(\mathbf{R}) = \beta Z e_0 \int d\mathbf{r}' v(\mathbf{r}',\mathbf{R}) \rho_0(\mathbf{r}') + \tfrac{1}{2}(\beta Z e_0)^2 \int d\mathbf{r}' g(\mathbf{r}') v^2(\mathbf{r}',\mathbf{R}) = -\beta Z e_0 \frac{\sigma(2a)}{2\epsilon\epsilon_0} - \tfrac{1}{2}\frac{(\beta Z e_0)^2 2\pi g}{(4\pi\epsilon\epsilon_0)^2}\ln(a^2 - z^2) + \text{const.} \tag{74}$$

The last term is again independent of the separation between the surfaces and contributes an additive constant to the free energy. Inserting all these expressions back into Eq. (69), we obtain

$$\frac{\beta \mathcal{F}_N}{N} = \tfrac{1}{2}\frac{\beta Z e_0 \sigma}{2\epsilon\epsilon_0} D + (\chi - 1)\ln D - I(\chi)$$

$$= \tfrac{1}{2}\frac{D}{\mu} + (\chi - 1)\ln D - I(\chi), \tag{75}$$

where $D=2a$ is the separation between the surfaces, $\mu = e_0/(2\pi\ell_B Z\sigma)$ is just the Gouy-Chapman length for mean surface charge density, and

$$\chi = \frac{Z^2(\beta e_0)^2 g}{8\pi(\epsilon\epsilon_0)^2} = 2\pi Z^2 \ell_B^2 g \tag{76}$$

is the dimensionless *disorder coupling parameter*. Note that it is very similar to the electrostatic coupling parameter for mean charge Ξ, Eq. (1), except that it scales with counterion valency as Z^2 instead of Z^3. Furthermore,

$$I(\chi) = \ln\frac{1}{D}\int_{-D/2}^{+D/2}\left(\frac{(D/2)^2 - z^2}{D^2}\right)^{-\chi/2} dz = {}_2F_1\left(\tfrac{1}{2}, \tfrac{\chi}{2}, \tfrac{3}{2}, 1\right), \tag{77}$$

which is independent of the interplate distance D. The effect of disorder on the interactions between disordered charged surfaces in the strong-coupling limit is thus contained in the second term in Eq. (75). Its behavior depends crucially on whether the dimensionless disorder coupling strength is smaller than, equal to, or larger than one. Evaluating the interaction pressure, $P(D)$, from the free energy, Eq. (75), we find, in dimensionless representation,

$$\widetilde{P}(D) \equiv \frac{\beta P(D)}{2\pi\ell_B \sigma^2} = \widetilde{P}_{SC}(D) - \chi\left(\frac{2\mu}{D}\right), \tag{78}$$

where the first term is the standard strong-coupling pressure [24]

$$\widetilde{P}_{SC}(D) = -1 + \frac{2\mu}{D}, \tag{79}$$

while the second additive term represents the effects of the disorder (see Fig. 2).

From Eq. (75), we can derive also the equilibrium distance D^* between the two surfaces, corresponding to zero interaction pressure. It is obtained as

$$D^* = 2(1-\chi)\mu. \tag{80}$$

In the undisordered case, $\chi=0$, this reduces to the known form as obtained in Ref. [24], that is an equilibrium distance equal to twice the Gouy-Chapman length. From this value the equilibrium distance then continuously approaches zero for increasing χ; it reaches zero for the critical value $\chi_c=1$ and remains at zero thereafter. This behavior has all the features of a second-order, quenched-disorder-driven collapse transition (see Fig. 2, inset).

For $\chi=1$ the interaction pressure between the surfaces is obviously constant in the whole range of separations D right down to zero. For $\chi \geqslant 1$, the counterion entropy, i.e., the $-\ln D$ term in Eq. (75), is completely wiped out by the surface charge disorder. It thus appears that the quenched charge disorder and the counterion entropy for large values of the disorder coupling strength in some sense counteract one another.

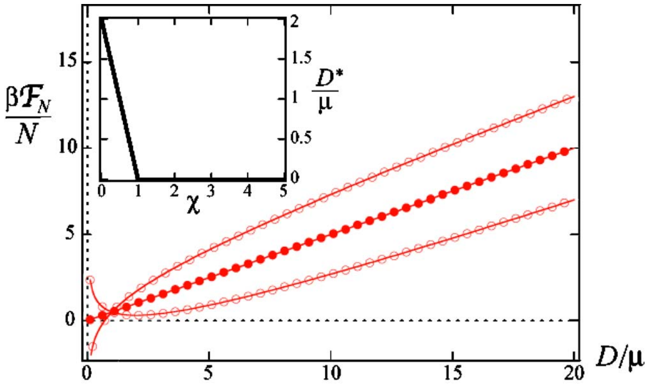

FIG. 2. (Color online) Free energy per particle, Eq. (75), as a function of dimensionless interplate distance D/μ for $\chi=0$, 1, and 2 (bottom line, middle line, and top line). $\mu=e_0/(2\pi\ell_B Z\sigma)$ is the Gouy-Chapman length for mean surface charge density. Inset: dimensionless equilibrium distance D^*/μ as a function of the disorder coupling parameter χ.

VIII. DISCUSSION

We have assessed the effect of the quenched macroion charge disorder in the case of interactions between two opposed surfaces in a one-component Coulomb fluid. We assumed a Gaussian ansatz for the quenched surface charge density distribution, with finite mean and a constant mean-square width. Though the final results within these assumptions are very simple they are highly nontrivial and difficult to derive.

In the case of two ideally polarizable surfaces at separation D, we find that in the weak-coupling or the Poisson-Boltzmann level, $\Xi \ll 1$ (where $\Xi=2\pi Z^3\ell_B^2\sigma$ is the electrostatic coupling due to the mean charge σ), the quenched surface charge disorder has no effect on the interactions. This is strictly true only for ideally polarizable surfaces. In the general case, electrostatic images would contribute to the disorder-driven part of the interaction, making it nonzero and dependent on the dielectric mismatch between the dielectric material of the surfaces and that of the aqueous solution bathing the electrolyte in between. The disorder-driven part of the interaction in this general case can be either attractive or repulsive, depending on the sign of the dielectric mismatch [37].

On the strong-coupling level $\Xi \gg 1$, the disorder effects are always present even in the case of ideally polarizable bounding surfaces. The disorder-driven part of the interaction free energy turns out to be additive and is linear in the disorder coupling parameter $\chi=2\pi Z^2\ell_B^2 g$, which is analogous to the mean charge coupling parameter Ξ introduced in Ref. [24], and scales with the square counterion valency Z and the mean-square width of the disorder distribution g. For increasing disorder coupling parameter χ, we find that the equilibrium distance is gradually displaced towards smaller values if compared to the case with no disorder, $\chi=0$. At a critical value $\chi_c=1$, the equilibrium distance becomes zero and remains zero for even larger values of the disorder coupling parameter. Thus one could think of the disorder effects in terms of a disorder-driven second-order collapse phase transition. We are unsure at this point how general this interpretation might be. In order to assess its validity additional cases of disorder modified Coulomb interactions should be investigated.

In our analysis we avoided the issues associated with the size of the counterions. Because the strong-coupling free energy includes only up to the single-particle interaction terms, assuming *hard-core* finite-size counterions leads formally to a renormalized geometry function Ω implying simply a different closest-approach distance between counterions and the walls. In this limit, excluded-volume interactions between particles enter only in the subleading correction terms [24,27].

Since quenched disorder is ubiquitous in the context of charged biological macroions, our analysis should be of fundamental value especially in this context. In understanding the electrostatic interactions between charged membranes, polyelectrolytes, and cells, sufficient attention should thus be given to disorder effects that obviously contribute in a nontrivial manner to the electrostatic interactions in aqueous electrolyte solutions. Pronounced attraction stemming from the strong-coupling electrostatics can thus be made even stronger due to charge disorder effects.

From our general formulation it follows that even for net-neutral macroions, i.e., $\sigma=0$, but with nonzero charge disorder, $g\neq 0$, the total interaction can show electrostatic effects. This is indeed the most nonintuitive and striking feature of our theory. Persistent observations of electrophoretic potentials [38] of net uncharged particles might thus have an elegant explanation in terms of the disorder effects invoked in this contribution. These might enhance the effects of other charging mechanisms such as Lifshitz–van der Waals–interactions driven adsorption or might in fact, if proper source of the quenched disorder is identified, be the sole cause of electrostatic effects with nominally uncharged macroions. Concurrent measurements of the electrophoretic potentials with an estimation of the local macroion charge disorder could substantiate or disprove the explanation tentatively proposed above.

Numerical simulations of counterions in the presence of disordered surface charge distributions will be valuable to examine the present predictions, in particular, for large mean electrostatic coupling $\Xi \gg 1$ and large disorder strength, where the disorder-driven collapse transition is predicted. Simulations with disorder effects are however difficult and time consuming and we leave them for a subsequent publication [37]. We have also not given appropriate attention to the image effects in this contribution. They would add additional details to the disorder-driven interaction that would tend to obscure our main points. For reasons of clarity we will thus relegate the image effects to a subsequent publication [37].

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