

Electrostatic disorder-induced interactions in inhomogeneous dielectrics

R. PODGORNIK^{1,2} and A. NAJI^{3(*)}

¹ *Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana SI-1000 Ljubljana, Slovenia*

² *Department of Theoretical Physics, J. Stefan Institute - SI-1000 Ljubljana, Slovenia*

³ *Department of Physics, Technical University of Munich - D-85748 Garching, Germany*

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Abstract. – We investigate the effect of quenched surface charge disorder on electrostatic interactions between two charged surfaces in the presence of dielectric inhomogeneities and added salt. We show that in the linear weak-coupling regime (*i.e.*, when mean-field and Gaussian-fluctuations contributions are included), the image-charge effects lead to a non-zero disorder-induced interaction free energy between two surfaces of equal mean charge that can be repulsive or attractive depending on the dielectric mismatch across the bounding surfaces and the exact location of the disordered charge distribution.

Electrostatic interactions are one of the two fundamental components of the DLVO theory of colloidal stability [1, 2]. They are standardly described by the Poisson-Boltzmann (PB) theory [1, 3] embodying the *mean-field* approach to classical charged systems. Mean-field interactions between like-charged macroions are repulsive in nature and thereby tend to stabilize solutions of charged macroions. By contrast, in strongly coupled systems (*e.g.*, when multivalent counterions are present), electrostatic interactions induce strong attractive forces between like-charged macroions [4, 5], and thus act more like Lifshitz-van der Waals interactions that tend to destabilize charged solutions. This attraction cannot be captured by the mean-field approach and a new paradigm dubbed the *strong-coupling limit* [6, 7] was introduced to describe the equilibrium properties of Coulomb fluids when the mobile counterion charges become large. The crossover from the mean-field Poisson-Boltzmann description to the strong-coupling limit is governed by a single dimensionless electrostatic coupling parameter, which is given by the ratio of the Bjerrum length (identifying Coulombic interaction between ions themselves) and the Gouy-Chapman length (describing electrostatic interaction between ions and the charged macroion surface) [4]. Electrostatic interactions between charged macroions in the mean-field and the strong-coupling limit thus unfold into a much richer structure than conveyed for many years by the DLVO paradigm. The collapse of a highly charged polyelectrolyte, such as DNA,

(*) Present address: Department of Physics, and Department of Chemistry and Biochemistry, University of California - Santa Barbara, CA 93106, USA.

in the presence of multivalent counterions is the most dramatic example of unexpected and counter-intuitive features of the strong-coupling electrostatics [7, 8].

Recently, we added a new twist to the theory of electrostatic interactions in charged systems [9]: not only can electrostatic interactions between like-charged macroions turn from repulsive to attractive due to strong-coupling counterion-induced correlations, but we showed that in the case of no image interactions and no added salt (*i.e.*, only in the presence of neutralizing counterions), the *quenched disordered* distribution of surface charges on the macroions can induce an additive attractive interaction in the strong-coupling limit even if the mean charge of the macroions is *zero*. This effect is due to the nonlinear features of the average over quenched disorder of the distribution of charges on the macroion surfaces. Such quenched distributions of macroion charge have been invoked recently in experimental investigations of interactions between solid surfaces in the presence of charged surfactants [10, 11]. The patterning of interacting surfaces by quaternary ammonium surfactants in these experiments 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 in biological as well as in synthetic systems. Though the experimental situation is probably more complex and one cannot unequivocally differentiate between partly annealed and partly quenched cases, we were nevertheless motivated by these observations to develop the theory of electrostatic interactions in systems with purely quenched disordered macroion charge distributions further.

Here we will consider the effects of *added salt* and of *image interactions* due to dielectric inhomogeneities on the disorder-induced interaction between two charged walls of equal mean charge density. We shall focus only on the weak-coupling regime and evaluate interaction free energies up to the first-loop (Gaussian-fluctuations) contribution around the linearized mean-field (Debye-Hückel) solution. We will show that in general image interactions have a pronounced effect on the way disordered charge distributions bring about electrostatic interactions in salt solution, their most notable effect being that they can induce non-monotonic interactions as a function of the spacing between the interacting surfaces. These results markedly contrast the *weak-coupling* results obtained in the absence of added salt and image-charge effects [9], where the disorder contribution turns out to be nil.

Assume (see fig. 1) a monovalent salt solution confined between two charged surfaces at $z = \pm a$. Assume furthermore that the surface charges are small such that the linearization approximation is valid. The corresponding grand canonical partition function in the field of

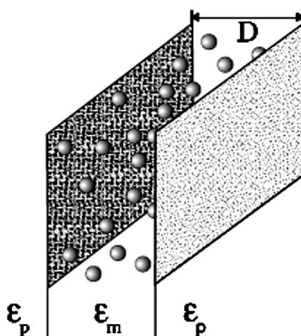


Fig. 1 – Geometry of a system composed of two surfaces with disordered charge distribution at separation $D = 2a$ with different dielectric constants for the interior region (where salt ions are present), ϵ_m , and for the exterior region, ϵ_p .

a fixed charge distribution, $\rho(\mathbf{r})$, is given in the functional integral representation as

$$\mathcal{Z} = \int \mathcal{D}[\phi(\mathbf{r})] e^{-\mathcal{S}[\phi(\mathbf{r})]}, \quad (1)$$

where $\phi(\mathbf{r})$ is a fluctuating potential field and the linearized effective Hamiltonian reads [12]

$$\mathcal{S}[\phi(\mathbf{r})] \cong \frac{\beta\epsilon_0}{2} \int d\mathbf{r} \epsilon(\mathbf{r}) \left[(\nabla\phi(\mathbf{r}))^2 + \kappa^2(\mathbf{r})\phi^2(\mathbf{r}) \right] + i\beta \int d\mathbf{r} \rho(\mathbf{r})\phi(\mathbf{r}). \quad (2)$$

Here we assume that the dielectric constant $\epsilon = \epsilon(\mathbf{r})$ have the value ϵ_p in the two semi-infinite regions $|z| > a$, which may in general be different from, ϵ_m , assumed for the region between the charged surfaces (see fig. 1). Accordingly, the inverse Debye screening length is $\kappa(\mathbf{r}) = \kappa = \sqrt{8\pi\ell_B n}$ in between the two surfaces (with $\ell_B = e^2/(4\pi\epsilon_0\epsilon k_B T)$ being the Bjerrum length and n the salt concentration), and zero otherwise. We assume that the surface charge distribution, $\rho(\mathbf{r})$, has a quenched disordered component. The average over quenched disorder is done as

$$\mathcal{F} = -k_B T \overline{\ln \mathcal{Z}} \quad (3)$$

in order to calculate the free energy \mathcal{F} , where the disorder average is defined here *via* a Gaussian⁽¹⁾ probability distribution

$$\overline{(\dots)} = \int \mathcal{D}[\rho(\mathbf{r})] (\dots) e^{-\frac{1}{2} \int d\mathbf{r} g^{-1}(\mathbf{r}) (\rho(\mathbf{r}) - \rho_0(\mathbf{r}))^2}, \quad (4)$$

over all different disorder realizations. This self-averaging *ansatz* precludes a direct comparison with single realization disorder effects [13]. Note that $\rho_0(\mathbf{r})$ represents the mean charge density and $g(\mathbf{r})$ gives the disorder variance around the mean value. Since all the functional integrals in the expression for the disorder-averaged free energy are Gaussian, the free energy follows straightforwardly as

$$\mathcal{F} = -k_B T \overline{\ln \mathcal{Z}} = \frac{\beta}{2} \text{Tr} g(\mathbf{r}) \mathcal{G}(\mathbf{r}, \mathbf{r}') + \frac{k_B T}{2} \text{Tr} \ln \mathcal{G}^{-1}(\mathbf{r}, \mathbf{r}') + \frac{\beta}{2} \iint d\mathbf{r} d\mathbf{r}' \rho_0(\mathbf{r}) \mathcal{G}(\mathbf{r}, \mathbf{r}') \rho_0(\mathbf{r}'). \quad (5)$$

Here we have defined the inverse of the operator $\beta\epsilon\epsilon_0(-\nabla^2 + \kappa^2)$ as the Green function that satisfies

$$\beta\epsilon_m\epsilon_0(-\nabla^2 + \kappa^2)\mathcal{G}(\mathbf{r}, \mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}') \quad (6)$$

with the appropriate boundary conditions of the continuity of derivatives multiplied by the dielectric constants at the surfaces with dielectric discontinuity. The disorder-averaged partition function could also be obtained through the replica formalism [9] but the direct integration approach is much more straightforward in the case of linearized effective Hamiltonian, eq. (2). In the second and third terms of eq. (5), we recognize the usual fluctuational and linearized mean-field Debye-Hückel (DH) contributions, respectively. The first term therefore stems from the effects of the disorder. Let us evaluate it explicitly and analyze its consequences.

Because of transverse isotropy, the following Fourier decomposition for the Green function is valid:

$$\mathcal{G}(\mathbf{r}, \mathbf{r}') = \int \frac{d^2 Q}{(2\pi)^2} \mathcal{G}(\mathbf{Q}; z, z') e^{-i\mathbf{Q}\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')} \quad (7)$$

with z and z' denoting the normal coordinate to the surfaces and $\boldsymbol{\rho} = (x, y)$, the transverse coordinates. We now evaluate two Green functions corresponding to the cases

⁽¹⁾Though it is difficult to argue for or against this particular (Gaussian) form of the disorder, it has two important features: it is analytically solvable as we demonstrate here, and it leads to highly non-trivial results.

- i) when the disordered charge distribution is contained within the medium ε_m , and
- ii) when the disordered charge distribution is contained within the medium ε_p .

These Green functions can be derived straightforwardly by using the methods described in ref. [14] as

$$\mathcal{G}(\mathbf{Q}; z, z') = \frac{1}{2\beta\varepsilon_m\varepsilon_0 u} \left[e^{-u|z-z'|} + \frac{2\alpha e^{-4ua}}{1-\alpha^2 e^{-4ua}} (e^{2ua} \cosh u(z+z') + \alpha \cosh u(z-z')) \right] \quad (8)$$

for the case i), and

$$\mathcal{G}'(\mathbf{Q}; z, z') = \frac{1}{2\beta\varepsilon_p\varepsilon_0 Q} \left[e^{-Q|z-z'|} - \frac{\alpha(1-e^{-4ua})}{1-\alpha^2 e^{-4ua}} (e^{-Q|a+z'|+Q(a+z)}) \right], \quad (9)$$

for the case ii). Here, we have defined

$$\alpha(Q) = \frac{\varepsilon_m u(Q) - \varepsilon_p Q}{\varepsilon_m u(Q) + \varepsilon_p Q} \quad \text{with} \quad u^2(Q) = Q^2 + \kappa^2. \quad (10)$$

Furthermore, we assume that the disorder variance is surface distributed,

$$g(\mathbf{r}) = g(\boldsymbol{\rho}, z) = G \delta(z+a) + G \delta(z-a), \quad (11)$$

where the constant G implies a negligibly small lateral disorder correlation length. For finite disorder correlation length, *i.e.* $G = G(\boldsymbol{\rho})$, one could in principle compare the self-averaged disorder free energy, eq. (3), with single realization disorder effects [15]. They would necessarily be different.

The disordered surface charge can reside either inside the slab (*e.g.*, at $z = \pm|a - \delta|$) or outside the slab (*e.g.*, at $z = \pm|a + \delta|$ for arbitrarily small $\delta > 0$). The only difference in the calculation is whether expression (8) or (9) is used when evaluating the first trace in eq. (5). Subsequently, one obtains the disorder-induced part of the free energy for the two aforementioned cases of the location of the disordered charge distribution as

$$\frac{\beta}{2} \text{Tr} g(\mathbf{r})\mathcal{G}(\mathbf{r}, \mathbf{r}') = \frac{GS}{4\pi \varepsilon_m \varepsilon_0} \int_0^\infty Q dQ \frac{\alpha (1+\alpha)^2 e^{-4ua}}{u(1-\alpha^2 e^{-4ua})} = \frac{GS \kappa}{4\pi \varepsilon_m \varepsilon_0} F_{(i)}(\kappa a), \quad (12)$$

for the case i), and

$$\frac{\beta}{2} \text{Tr} g(\mathbf{r})\mathcal{G}'(\mathbf{r}, \mathbf{r}') = \frac{GS}{4\pi \varepsilon_p \varepsilon_0} \int_0^\infty Q dQ \frac{\alpha (1-\alpha^2) e^{-4ua}}{Q(1-\alpha^2 e^{-4ua})} = \frac{GS \kappa}{4\pi \varepsilon_p \varepsilon_0} F_{(ii)}(\kappa a), \quad (13)$$

for the case ii), where S is the total area of the two bounding surfaces. In both of the above expressions we have subtracted the part of the free energy that does not depend on the surface separation a since we are only interested in the interaction free energy.

It is thus immediately obvious that some asymmetry should exist in the system (either different dielectric constants in between and outside the surfaces, or salt in between and no salt outside, etc.) in order that the disorder contribution to the free energy becomes non-zero. Also obviously in both cases i) and ii), if $\alpha = 0$, there is no disorder-induced interaction. If $\alpha = -1$, then in the case i), the interaction is zero, but not in the case ii).

The dependence of the disorder part of the free energy, that is eqs. (12) and (13), on the dimensionless separation between the surfaces, κa , is evaluated numerically and shown in fig. 2. The most interesting feature of the disorder-induced interaction free energy is that the interaction can be non-monotonic and that it depends critically on the ratio of the two

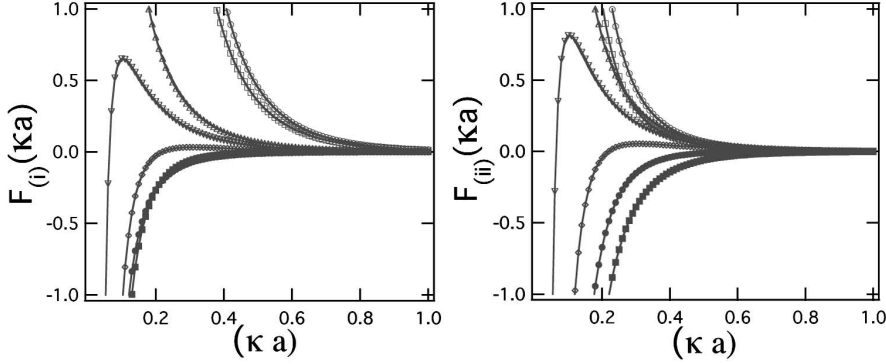


Fig. 2 – The disorder-induced contribution to the interaction between two charged surfaces, $F_{(i)}(\kappa a)$ (left) and $F_{(ii)}(\kappa a)$ (right) from eqs. (12) and (13), respectively, for $0 < \kappa a < 1$ and the ratios $\varepsilon_m/\varepsilon_p = 0.2, 0.4, 0.6, 0.8, 1.0, 5.0$ and 10.0 (from top to bottom). The non-monotonic character of the disorder-induced interaction is clearly discernible. Its details depend crucially on the ratio $\varepsilon_m/\varepsilon_p$.

dielectric constants. For small and large values of κa , the disorder interaction free energy assumes simple limiting forms as we show later.

Putting the above results together with the fluctuational and mean-field contributions in eq. (5) and assuming that the surface charge distribution has a mean value given by

$$\rho_0(\mathbf{r}) = \sigma \delta(z+a) + \sigma \delta(z-a), \quad (14)$$

we obtain the following expressions for the interaction free energy

$$\frac{\mathcal{F}}{S} = \frac{G}{4\pi\varepsilon_m\varepsilon_0} \int_0^\infty \frac{QdQ\alpha(1+\alpha)^2 e^{-4ua}}{u(1-\alpha^2 e^{-4ua})} + \frac{k_B T}{4\pi} \int_0^\infty QdQ \ln(1-\alpha^2 e^{-4ua}) + \frac{\sigma^2}{\varepsilon_m\varepsilon_0\kappa} (\coth \kappa a - 1) \quad (15)$$

for the case i), and

$$\frac{\mathcal{F}'}{S} = \frac{G}{4\pi\varepsilon_p\varepsilon_0} \int_0^\infty \frac{QdQ\alpha(1-\alpha^2) e^{-4ua}}{Q(1-\alpha^2 e^{-4ua})} + \frac{k_B T}{4\pi} \int_0^\infty QdQ \ln(1-\alpha^2 e^{-4ua}) + \frac{\sigma^2}{\varepsilon_m\varepsilon_0\kappa} (\coth \kappa a - 1) \quad (16)$$

for the case ii). These are the final results of our calculation. We note here that the only approximation involved in the derivation of the above results is the linearization approximation in the Coulomb field action, eq. (2), that makes them valid only in the weak-coupling limit, *i.e.*, for small mean surface charge density σ and low counterion valency.

Let us assess the importance of the disorder-induced interaction by considering a few illuminating limiting cases, the general form being given numerically in fig. 2. In the case of vanishing salt or small separations, $\kappa a \rightarrow 0$, one gets in the case i)

$$\frac{\beta}{2} \text{Tr } g(\mathbf{r})\mathcal{G}(\mathbf{r}, \mathbf{r}') = \frac{G S \varepsilon_m(\varepsilon_m - \varepsilon_p)}{4\pi\varepsilon_0(\varepsilon_m + \varepsilon_p)^3 a} f\left(\frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m + \varepsilon_p}\right), \quad (17)$$

where

$$f(\alpha) \equiv \int_0^\infty \frac{du e^{-u}}{(1-\alpha^2 e^{-u})}. \quad (18)$$

The above limiting form is valid only if $\varepsilon_m \neq \varepsilon_p$. Otherwise higher-order terms come into play. The case ii) leads to exactly the same free energy and thus in this limit, there is no difference in the disorder-induced interaction whether the disordered charge distribution is within medium ε_m or ε_p . Obviously in this limit, the disorder-induced part of the interaction

falls off inversely with the first power of the separation, $D = 2a$, which is to be compared with the inverse-square decay in the case of the zero-frequency van-der-Waals (fluctuational) term. Its sign depends on the values of both dielectric constants. One should also note that in this limit, the disorder and the mean-field term combine, yielding

$$\frac{\mathcal{F}}{S} \simeq \frac{\sigma^2}{\varepsilon_m \varepsilon_0 \kappa^2 a} \left(1 + \frac{G \varepsilon_m^2 (\varepsilon_m - \varepsilon_p) \kappa^2}{4\pi \sigma^2 (\varepsilon_m + \varepsilon_p)^3} f\left(\frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m + \varepsilon_p}\right) \right). \quad (19)$$

It would thus seem that the disorder merely renormalizes the square of the charge density. But since the disorder term can be either positive or negative, depending on the value of $\varepsilon_m - \varepsilon_p$, one cannot claim that the only effect of disorder in this limit is the disorder-renormalization of the mean surface charge, since the whole expression, eq. (19), cannot be written as proportional to $(\sigma_R)^2 = (\sigma - \sigma')^2$, which is by definition always positive, where σ' would indicate the disorder-dependent terms. An important consequence of the disorder effects in this limit is that it induces interactions even between nominally uncharged surfaces with a mean charge density $\sigma = 0$. These interactions have the same dependence on the separation as the mean-field DH term in this limit, except that they can be either repulsive or attractive depending again on the difference $\varepsilon_m - \varepsilon_p$. Nominally neutral surfaces thus exhibit electrostatic-like interactions induced *solely* by the variance of the charge distribution, not its mean value!

In the opposite limit of large salt or large separations, $\kappa a \rightarrow \infty$, one remains with

$$\frac{\mathcal{F}}{S} = \frac{G e^{-4\kappa a}}{\pi \varepsilon_0 \varepsilon_m 4a} - \frac{k_B T \kappa^2}{16\pi (\kappa a)} e^{-4\kappa a} + 2 \frac{\sigma^2}{\varepsilon_m \varepsilon_0 \kappa} e^{-2\kappa a} \quad (20)$$

for the case i). The disorder-induced component (first term) has the same separation dependence as the standard screened zero-frequency van-der-Waals (vdW) interaction (second term), but is shorter ranged than the corresponding mean-field DH term (third term). Also in this limit, the disorder-induced interaction is always *repulsive*, which means that the overall interaction can change sign upon increase of the separation, as is already apparent from fig. 2. The interesting point now is that the disorder-induced term clearly renormalizes the fluctuational (van-der-Waals) contribution, since it has the same separation dependence as the zero-frequency van-der-Waals term but with the opposite sign.

For the second case ii) and in the same limit of $\kappa a \rightarrow \infty$, we obtain

$$\frac{\mathcal{F}'}{S} = \frac{G}{\pi \varepsilon_0 \varepsilon_m} \sqrt{\frac{\pi}{8\kappa a}} e^{-4\kappa a} - \frac{k_B T \kappa^2}{16\pi (\kappa a)} e^{-4\kappa a} + 2 \frac{\sigma^2}{\varepsilon_m \varepsilon_0 \kappa} e^{-2\kappa a}. \quad (21)$$

Again the disorder part of the interaction (first term) has almost the same functional dependence on the intersurface separation as the van-der-Waals part (second term).

One can thus make a general conclusion that in the limit $\kappa a \rightarrow 0$, the disorder-induced component of the interaction free energy effectively behaves like the mean-field contribution, while in the limit $\kappa a \rightarrow \infty$, it behaves like the fluctuational (vdW) contribution. In a certain sense, the disorder-induced interaction thus *interpolates* between mean-field and fluctuational interactions. All this is of course valid only in the weak-coupling limit and one cannot apply these conclusions to the disordered strong-coupling regime [9]. The analysis of the interplay between disorder-induced effects and image-charge effects in the strong-coupling limit will be left for a separate exercise.

The results derived above, apart from the effects due to finite salt concentration in between the apposed charged surfaces, clearly differ from those obtained in the absence of dielectric inhomogeneities [9], where the mean-field contribution was shown to be decoupled from the disorder effects. The conclusion reached in ref. [9] is thus limited to disordered charge distributions immersed in a single dielectric medium without any inhomogeneities in the corresponding static dielectric constant.

Note that if the mean surface charge is zero ($\sigma = 0$), then according to eqs. (20) and (21), the equilibrium spacing between surfaces is given by the competing disorder-induced and fluctuational interaction parts for large κa . In case i), eq. (20) obviously implies no finite equilibrium surface separation. The interaction is monotonic and its sign depends on whether the ratio $4G/(\kappa\epsilon_m\epsilon_0k_B T)$ is bigger or smaller than one. In case ii), eq. (21) implies an optimal surface separation since the disorder and fluctuational contributions do not have exactly the same separation dependence.

In all the limiting cases addressed above, the disorder-induced part of the interaction can be masked by either mean-field or fluctuational terms in the total interaction, which would make its effects particularly difficult to pinpoint experimentally but they would be nevertheless identifiable *via* a thorough, but unfortunately very time consuming, quenched disorder simulation. The most important features of the quenched charge disorder seem to be the presence of electrostatic interactions between nominally electroneutral surfaces and the non-monotonic character of the interaction at intermediate separations between charged surfaces (see fig. 2). Both features may be important for the stability of planar charged macromolecular assemblies such as lipid bilayers.

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