

Casimir and pseudo-Casimir interactions in confined polyelectrolytes

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We investigate the pseudo-Casimir force acting between two charged surfaces confining a single polyelectrolyte chain with opposite charge. We expand the exact free energy to the second order in the local electrostatic field as well as the replicated polymer density field around the mean-field (saddle-point) solution. The quadratic terms lead to a fluctuation interaction that is partly due to the (thermal) Casimir effect for the confined electrostatic field and partly due to the pseudo-Casimir effect due to the confined replicated polymer density field. We study the intersurface separation dependence of both effects and show that the pseudo-Casimir effect leads to a long range attraction between the surfaces that decays with an anomalous algebraic exponent of ~ 1.7 , smaller than the standard exponent of 2 in the case of Casimir interactions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1383052]

I. INTRODUCTION

Charged polymers have received much attention over the years for their indisputable importance in industrial applications as well as for their role in fundamental colloid science (for comprehensive introductions, see Refs. 1 and 2). Apart from the study of polymers in the bulk, their interactions with surfaces, as well as polymer-mediated interactions between surfaces have been studied on different levels.^{3,4} Though polyelectrolyte interaction with charged surfaces is quite similar to the general interaction of polymers with neutral surfaces,⁵ the long range nature of the Coulomb potential introduces additional features and difficulties that make these problems even more difficult to handle.

Most of the work on inhomogeneous polyelectrolytes was done on the mean-field level and the effect of thermal fluctuations has not been considered at all. The mean-field picture of the behavior of a polyelectrolyte chain confined between two oppositely charged surfaces that emerged from previous studies^{6,7} (see Fig. 1) lets one think that at small intersurface separations the polyelectrolyte mediated interactions are quite similar to those in the case of neutral polymers and decay algebraically with separation.^{3,4} At a critical value of the intersurface spacing there is a transition of the confined polyelectrolyte chain from a monomodal to a bimodal monomer density distribution. This means that at sufficiently large intersurface separations the polymer chain is on the average partly electrostatically adsorbed to both surfaces and the remaining part of the chain bridges the region between the surfaces. The consequence of these bridging inter-

actions is an exponentially decaying attraction between the surfaces that persists for all separations greater than the critical value.^{6,7} In this respect the charged chain between oppositely charged surfaces behaves on the mean-field level a lot like a neutral chain with a finite adsorption energy to the two bounding surfaces.

Recent theoretical studies⁸ however point to the conclusion that thermal fluctuation effects in Coulombic systems, ignored on the mean-field level, can hardly ever be considered as negligible. In the limit of small electrostatic coupling it has been known for a while that thermal fluctuations in an inhomogeneous Coulomb fluid lead to zero order van der Waals (or equivalently Casimir) forces.^{8,9} More recent studies of thermal effects in soft matter in general^{10,11} are very much consistent with these findings. It has been established that thermally driven fluctuations of order parameters of confined systems also lead to long range pseudo-Casimir forces,¹² quite similar in nature to ordinary Casimir forces except that instead of being due to electromagnetic field fluctuations they are a consequence of a general order parameter fluctuations (thus pseudo-Casimir interactions). In view of this we suspect that similar phenomena should also show up in the study of fluctuation effects of confined inhomogeneous polyelectrolytes.

In order to prove this conjecture we write the partition function for a polyelectrolyte chain confined between two oppositely charged planar surfaces in such a way that we were able to expand it to quadratic order in the relevant order parameters, in this case the local electric field and the replicated polymer density field (see below), around the mean-field profile and evaluate on this level the effect of thermal fluctuations. We note that thermal fluctuations decouple into two separate contributions: the Casimir contribution due to

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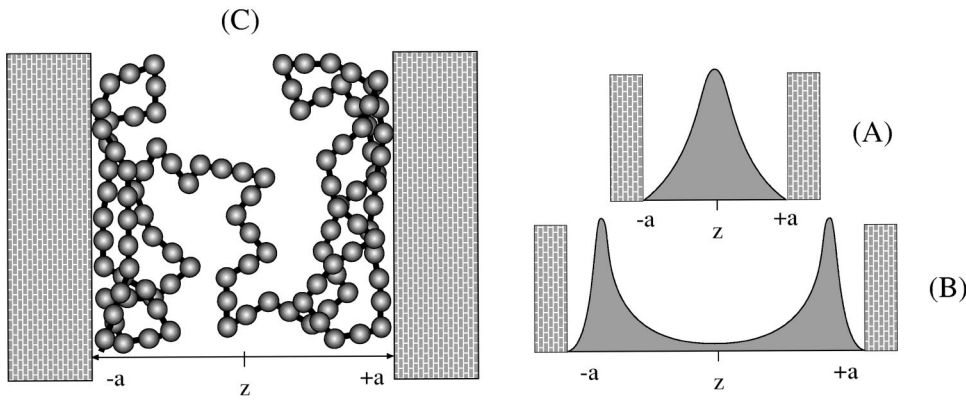


FIG. 1. Schematic representation of the mean-field solution. For separations between the surfaces smaller than the critical, the monomer density distribution is monomodal (A). For separations larger than critical the monomer density distribution is bimodal (B), corresponding to partial adsorption of the chain to the oppositely charged surfaces. Parts of the chain that are not adsorbed act as bridges between the surfaces (C).

electric field fluctuations and the pseudo-Casimir contribution due to the replicated polymer density field fluctuations. We show that the effect of thermal fluctuations depends on only one coupling parameter $\alpha_{MF} = (4\pi/3)(\sigma\ell/\tau)$, where σ is the surface charge density, τ is the line charge density of the polymer chain, and ℓ is the Kuhn's segment length. Depending on the value of this parameter the behavior of the system can be successfully described on the mean-field level ($\alpha_{MF} \gg 1$) or has to be amended by taking into account the fluctuation terms ($\alpha_{MF} \sim 1$). The most important consequence of the fluctuation effects seems to be the long range pseudo-Casimir force, with an anomalous algebraic dependence on the intersurface separations with an exponent 1.7, due to the confined fluctuations of the polymer density field that decays slower than the usual Casimir (or equivalently van der Waals) force.

The plan of the paper is as follows: In order to investigate the fluctuation effects we first write the free energy of a confined charged polymer chain between two surfaces in the form of an $\mathcal{O}(n)$ scalar field theory. From here the free energy is obtained via the standard $n \rightarrow 0$ replica trick.¹³ Since the mean-field is given by the saddle-point, we then expand this field theory to the second order around the saddle-point in both the electrostatic field and the replicated polymer density field. Calculation of the quadratic corrections to the mean-field free energy that can be performed exactly gives the Casimir and pseudo-Casimir interactions mediated by the confined electrostatic and confined replicated polymer density fields. We investigate the dependence of the regularized fluctuation interaction free energy on the intersurface separation in the limit of small and large spacings compared to the critical separation.

II. MEAN-FIELD THEORY

As a point of departure we shall take a model confined polyelectrolyte system, composed of two surfaces with a specified surface charge density (σ) and a confined, oppositely charged single polyelectrolyte chain of length $N\ell$, described with an Edwards Hamiltonian,

$$\mathcal{H}[\mathbf{r}(s)] = \frac{3}{2\ell} \int_0^{N\ell} \dot{\mathbf{r}}^2(s) ds + \frac{1}{2} \int_0^{N\ell} \int_0^{N\ell} V(\mathbf{r}(s), \mathbf{r}(s')) ds ds'. \quad (1)$$

We assume that the intersegment interactions are given by the unscreened Coulombic form $V(\mathbf{r}, \mathbf{r}') = \tau^2/4\pi\epsilon\epsilon_0 |\mathbf{r} - \mathbf{r}'|^{-1}$, where τ is the charge per unit length. This is a bit artificial since we completely ignore the presence of other mobile ionic species such as counterions and salt ions, but represents a clean, tractable model system where fluctuation effects can be studied in detail.

Performing now the Hubbard–Stratonovich transformation for the pair interaction potential, going to the grand canonical ensemble with a fixed chemical potential μ for the monomers and adequately removing the closed loop polymer configurations from the partition function *via* the $n \rightarrow 0$ limit of an $\mathcal{O}(n)$ scalar field theory with the field $\boldsymbol{\psi} = (\psi_1, \psi_2, \dots, \psi_n)$, we remain with the de Gennes–des Cloizeaux representation for the free energy of a charged polyelectrolyte chain,¹⁴

$$\begin{aligned} \mathcal{F}(\mu, \beta) &= \lim_{n \rightarrow 0} \frac{1}{n} \log \mathcal{Z}(\mu, \beta) \\ &= \lim_{n \rightarrow 0} \frac{1}{n} \log \int \mathcal{D}\phi(\mathbf{r}) \mathcal{D}\boldsymbol{\psi}(\mathbf{r}) \\ &\quad \times \exp\left(-\beta \int d^3\mathbf{r} \mathcal{H}[\phi(\mathbf{r}), \boldsymbol{\psi}_i(\mathbf{r})]\right), \end{aligned} \quad (2)$$

where

$$\begin{aligned} \beta\mathcal{H}[\phi(\mathbf{r}), \boldsymbol{\psi}_i(\mathbf{r})] &= \frac{1}{2} \frac{\ell^2}{6} \sum_i (\nabla\psi_i)^2 + \frac{1}{2} \mu \sum_i \psi_i^2 \\ &\quad + \frac{1}{2} \beta\epsilon\epsilon_0 (\nabla\phi)^2 + i\beta\tau \sum_i \phi\psi_i^2. \end{aligned} \quad (3)$$

In writing Eq. (2) we omitted the determinant $\det(\beta\epsilon\epsilon_0\nabla^2)$ from the denominator. As is usual on the one-loop expansion level, this term is exactly canceled by the zero order van der Waals term that one should add to the final total interaction free energy. This point is thoroughly explained in Refs. 9 and 15. See also below.

The path from here will be to obtain the mean-field solution of the model defined by Eq. (2) *via* the saddle-point of the $\mathcal{O}(n)$ scalar field theory along the lines of Ref. 16 and

then to evaluate the contribution of quadratic fluctuations around the saddle-point to the thermodynamic properties of the system.

Evaluation of the saddle-point from the field Hamiltonian Eq. (3) is trivial. One notices immediately that all the ψ_i satisfy the same saddle-point equation and thus $\psi_i \rightarrow \psi$. With this one can write the dependence of the Hamiltonian Eq. (3) on n explicitly¹⁷ and the limit $n \rightarrow 0$ can be obtained straightforwardly. One remains with

$$\beta\mathcal{F}_0 = - \lim_{n \rightarrow 0} \frac{1}{n} \log \mathcal{Z}_0 = \frac{1}{2} \int d^3\mathbf{r} \left(\frac{\ell^2}{6} (\nabla\psi)^2 + \mu\psi^2 + \beta\epsilon\epsilon_0 (\nabla\phi)^2 + i\beta\tau\phi\psi^2 \right), \tag{4}$$

where we introduced the mean polymer density field ψ so that the local monomer density is $\rho = \psi^2$ and the local electrostatic mean potential $\varphi = i\phi$. In the planparallel geometry considered here all the fields depend only on the transverse coordinate z , and the inhomogeneities are confined to this direction only $\psi = \psi(z)$, $\varphi = \varphi(z)$. The saddle-point equations of the Hamiltonian Eq. (3) can thus be written in the form,

$$\frac{\ell^2}{6} \frac{d^2\psi(z)}{dz^2} = \mu\psi(z) + 2\beta\tau\varphi(z)\psi(z), \tag{5}$$

$$-\epsilon\epsilon_0 \frac{d^2\varphi(z)}{dz^2} = \tau\psi^2(z).$$

These mean-field equations are exactly equivalent to those derived previously^{6,7} if one takes into account that the polyelectrolyte chain is the only mobile charge in the system (no counterions and no salt). The first equation of Eq. (5) is the equation for the density field $\psi(z)$ of the polymer in an inhomogeneous external field $\varphi(z)$, while the second one is a Poisson–Boltzmann equation for the mean electrostatic potential $\varphi(z)$ of a charged polymer chain with charge density $\rho(z) = \tau\psi^2(z)$.

The second equation of Eq. (5) can be solved explicitly and its solution can be manipulated⁶ to yield a limiting form valid close to the boundaries at $z = \pm a$, where the potential is largest,

$$\epsilon\epsilon_0\varphi(z) = -\tau \int_{-a}^{+a} |z-z'| \psi^2(z') dz' \approx -\tau|z| + \mathcal{O}(z^2). \tag{6}$$

This expression can be obtained rather straightforwardly by Taylor expanding the solution around $z = \pm a$. In the opposite limit, $z \approx 0$, we can derive

$$\epsilon\epsilon_0\varphi(z) \approx -\tau \int_{-a}^{+a} |u| \psi^2(u) du - \tau\psi^2(0)z^2 + \mathcal{O}(z^4).$$

Since the mean-field is largest close to the boundaries we will use the approximate expression valid strictly only close to $z = \pm a$ in the whole interval. This approximation works

extremely well everywhere⁶ except close to the origin where z is small anyway. The reason for introducing this additional but inessential approximation is that it also helps in transforming the first of Eqs. (5) from a nonlinear Landau–Ginzburg-type equation into a linear equation, which can be solved analytically and explicitly in terms of Airy’s functions.⁶

The electroneutrality demands that at the bounding surfaces ($z = \pm a$) we have $-\epsilon\epsilon_0(\partial\varphi/\partial\mathbf{n}) = \tau(N/S) \equiv \sigma$, where \mathbf{n} is the boundary surface normal. Because of the impenetrability of the boundaries to the polymer chain we should also have $\psi(z = \pm a) = 0$. The unnormalized solution of the first mean-field equation Eq. (5) can now be obtained explicitly in the form,

$$\psi(x) \sim Ai(y_0 - x)Bi'(y_0) - Bi(y_0 - x)Ai'(y_0), \tag{7}$$

where we introduced the dimensionless variables $x = \lambda_B^{1/3}z$, $x_0 = \lambda_B^{1/3}a$, $y_0 = 6\mu\lambda_B^{-2/3}/\ell^2$, $\lambda_B = (12\beta\tau^2/\epsilon\epsilon_0\ell^2)$ and $Ai(x)$ and $Bi(x)$ are the standard Airy functions. The dependence $y_0 = y_0(x_0)$ is obtained from the vanishing density field boundary conditions at the two bounding surfaces. We derive⁶ that $y_0(x_0)$ grows linearly with x_0 for large x_0 , and therefore $u_0 = y_0 - x_0$ asymptotically approaches a constant $u_0^\infty \approx -2.34$, while for small x_0 , y_0 is negative and behaves approximately like $y_0 \approx -(\pi/2x_0)^2$.

The main consequence of the mean-field equations is that for very small intersurface separations the chain is desorbed with a monomodal density distribution.^{6,7} In this regime of intersurface separations the interactions between the surfaces are repulsive, decaying algebraically with plate separation. At a critical value of the intersurface separation $x_0 = 1.986$ the electrostatic attraction between the monomers and the surfaces, or more appropriately the repulsion of the monomers and the electroneutrality condition for the whole system, causes the chain to adsorb to both surfaces creating a polymer bridge leading in its turn to bridging attraction between the surfaces. This attraction, though exponentially small, persists for all separations between the surfaces larger than the critical. The intersurface pressure is thus repulsive for $x_0 < 1.986$ and attractive for $x_0 > 1.986$. For details, see Ref. 6.

III. FLUCTUATIONS

We now turn to the contribution of fluctuations around the saddle point to the free energy. First we expand the Hamiltonian Eq. (3) to the second order in deviations from the mean-fields Eq. (5). Our treatment of the fluctuation effect will thus be based on a quadratic (one-loop) expansion. The second functional derivatives of the field Hamiltonian can be assembled into a Hessian of the fields of Eq. (3),

$$\mathbb{H} = \begin{bmatrix} -\frac{\ell^2}{6}\nabla^2 + \mu + 2i\beta\tau\phi & 2i\beta\tau\psi_n \\ 2i\beta\tau\psi_n & -\beta\epsilon\epsilon_0\nabla^2 \end{bmatrix}, \tag{8}$$

where φ and ψ_n are the solutions of the mean-field equations Eq. (5). While integrating out the mean replicated polymer density field and the mean electrostatic field fluctuations we notice that the functional integral over ψ_i fluctuations can be

evaluated directly, giving an explicit dependence of the fluctuational partition function on n . This is similar to the general case treated by Emery.¹⁷ The limit $n \rightarrow 0$ can now be evaluated explicitly leading to the following contribution of the fluctuations around the mean-fields in the quadratic order to the free energy,

$$\begin{aligned} \beta \mathcal{F}_2 &= \lim_{n \rightarrow 0} \frac{1}{n} \log Z_2 \\ &= \frac{1}{2} \ln \det(-\nabla^2) + \frac{1}{2} \ln \det \left(-\nabla^2 + \frac{6}{\ell^2} \mu + 12 \frac{\beta \tau}{\ell^2} \varphi(\mathbf{r}) \right) \\ &\quad + 12 \frac{(\beta \tau^2)}{\epsilon \epsilon_0 \ell^2} \int \int d^3 \mathbf{r} d^3 \mathbf{r}' \mathcal{G}(\mathbf{r}, \mathbf{r}') \mathcal{G}_0(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}) \psi(\mathbf{r}'), \end{aligned} \quad (9)$$

where $\varphi(\mathbf{r})$ and $\psi(\mathbf{r})$ are the solutions of the mean-field equations Eq. (5). The two Green's functions $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ and $\mathcal{G}_0(\mathbf{r}, \mathbf{r}')$ are the functional inverses defined as

$$\begin{aligned} \left(-\nabla^2 + \frac{6}{\ell^2} \mu + 12 \frac{\beta \tau}{\ell^2} \varphi(\mathbf{r}) \right) \mathcal{G}(\mathbf{r}, \mathbf{r}') &= \delta^3(\mathbf{r} - \mathbf{r}'), \\ (-\nabla^2) \mathcal{G}_0(\mathbf{r}, \mathbf{r}') &= \delta^3(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (10)$$

The first term in Eq. (9) comes from the confined electric field fluctuations and is in fact the standard zero-order Casimir interaction energy¹⁸ (see below). The second and the third terms are due to the confined polymer density field fluctuations and thus correspond to the pseudo-Casimir interactions. The free energy Eq. (9) is obtained already *after* the cancellation referred to in the discussion following Eq. (3) and thus represents the total interaction free energy including the zero order van der Waals contribution. The latter is evaluated for a slab of thickness $2a$ with boundaries impenetrable to electrostatic fields.

Let us first deal with the two functional determinants in Eq. (9). Since the mean-field solution depends only on the transverse coordinate z we need to investigate the functional determinant of an operator of the type $-(d^2/dz^2) + V(z)$ that can be evaluated in two different ways. One can first of all find the eigenvalues λ_n of this operator with the boundary condition $f_n(z = \pm a) = 0$. The functional determinant comes out as the product of these eigenvalues $\prod_n \lambda_n$. The other approach would take into account the van Vleck identity¹⁹ involving $f_0(z)$, the eigenfunction with zero eigenvalue and with boundary conditions $f_0(z = -a) = 0$ and $f_0'(z = -a) = 1$. The logarithm of the functional determinant can thus be written equivalently (up to an irrelevant—in this context—additive constant) in two different ways¹⁹

$$\ln \det \left(-\frac{d^2}{dz^2} + V(z) \right) = \sum_n \ln \lambda_n = \ln [f_0(z = a)]. \quad (11)$$

In what follows we will use both representations together with the Fourier decomposition in the (x, y) plane and will find both equally inadequate when approaching the critical

intersurface separation $x_0 = 1.986$, either from above or below, where the mean polymer density field goes through a monomodal to bimodal transition.

Of the first two terms in Eq. (9) the first one is trivial to evaluate either *via* the van Vleck relation or the eigenvalue product representation. First of all we introduce the Fourier decomposition in the (x, y) plane with a wave vector \mathbf{Q} , since we only need to take into account the boundaries in the z direction. This leads to the standard zero-order (thermal) Casimir interaction in the form

$$\begin{aligned} \frac{1}{2} k_B T \sum_{\mathbf{Q}} \ln \det \left(-\frac{d^2}{dz^2} + Q^2 \right) \\ = \frac{S k_B T}{4\pi} \int_0^\infty Q dQ \ln \left(\frac{\cosh Qa \sinh Qa}{Q} \right), \end{aligned} \quad (12)$$

where S is the total area of the interacting boundary surfaces.

The second term is trickier. First of all we again introduce the Fourier decomposition in the (x, y) plane with a wave vector \mathbf{Q} and invoke the approximate solution Eq. (6). Using again the van Vleck identity we derive

$$\begin{aligned} \frac{1}{2} k_B T \sum_{\mathbf{Q}} \ln \det \left(-\frac{d^2}{dz^2} + Q^2 + \frac{6}{\ell^2} \mu + 12 \frac{\beta \tau}{\ell^2} \varphi(z) \right) \\ = \frac{S k_B T}{4\pi} \int_0^\infty Q dQ \ln (C(Q, a) S(Q, a)), \end{aligned} \quad (13)$$

where we decomposed the determinant of the operator into two separate contributions stemming from symmetric and antisymmetric modes,

$$\begin{aligned} C(Q, z) &= Bi'(y(Q)) Ai(y(Q) - \lambda_B^{1/3} z) \\ &\quad - Ai'(y(Q)) Bi(y(Q) - \lambda_B^{1/3} z), \\ S(Q, z) &= Bi(y(Q)) Ai(y(Q) - \lambda_B^{1/3} z) \\ &\quad - Ai(y(Q)) Bi(y(Q) - \lambda_B^{1/3} z), \end{aligned} \quad (14)$$

where $y(Q) = \lambda_B^{-2/3} (Q^2 + (6\mu/\ell^2))$ while $Ai(x)$ and $Bi(x)$ are the standard Airy functions.²⁰ The Airy function solutions are of course a consequence of the approximation Eq. (6) for the mean electrostatic potential. The free energy Eq. (13) still needs to be properly regularized by subtracting the infinite bulk and surface terms, see below.

In what follows we introduced also these dimensionless variables: $q^2 = \lambda_B^{-2/3} Q^2$ and $u(q, x, x_0) = y(q, x_0) - x = q^2 + y_0(x_0) - x = u_0(x_0) + q^2 + x_0 - x$. Here $y_0(x_0)$ is the largest zero of the symmetric function $C(y_0(x_0), x_0)$ which corresponds exactly to the zero of the mean-field solution Eq. (7) at the two bounding surfaces.⁶

The third term in Eq. (9) appears to be the most difficult one to evaluate but fortunately it is possible to prove that within the approximation Eq. (6) its contribution to the fluctuation free energy \mathcal{F}_2 is in fact negligible compared to the other two, i.e., Eqs. (13) and (14). Taking into account the approximate form for the mean electrostatic potential Eq. (6) the last term in Eq. (9) can be evaluated explicitly leading to

$$12 \frac{(\beta\tau^2)}{\epsilon\epsilon_0} \int \int d^3\mathbf{r} d^3\mathbf{r}' \mathcal{G}(\mathbf{r},\mathbf{r}') \mathcal{G}_0(\mathbf{r},\mathbf{r}') \psi(\mathbf{r})\psi(\mathbf{r}') = \frac{\lambda_B}{(\epsilon\epsilon_0)} \int_{-a}^{+a} dz |z| \mathcal{G}(z,z',Q=0), \quad (15)$$

where we took into account that the mean-field solution $\psi(\mathbf{r})$ depends only on the transverse coordinate z and that again we can introduce the Fourier decomposition in the (x,y) plane with a wave vector \mathbf{Q} . The magnitude of the coupling contribution Eq. (15) turns out to be much smaller than the other two, Eqs. (12) and (13), and can thus be safely ignored in numerical computations.

The fluctuation free energy, \mathcal{F}_2 which is thus composed only of the contributions from the fluctuational determinants of the electrostatic field and the replicated polymer density field, still contains the divergent bulk and surface parts together with the interaction terms.^{9,18} \mathcal{F}_2 is thus formally infinite. This infinity can be regularized by subtracting the infinite bulk and surface contributions¹⁸ and thus in forming the regularized fluctuation free energy,

$$\mathcal{W}_2(a) = \mathcal{F}_2(a) - \mathcal{F}_2^\infty(a).$$

Here $\mathcal{F}_2^\infty(a)$ stands for the form of the fluctuation free energy for large values of the argument but evaluated at a finite a .¹⁸

Using now the standard form for the mean-field pressure⁷ and adding to it the fluctuation contribution, one can write for the total pressure between the boundary surfaces,

$$\mathcal{W}_2(x_0) = \frac{Sk_B T}{4\pi} \int_{u_0}^{\infty} du \ln \left(\frac{(Bi'(u+x_0)Ai(u) - Ai'(u+x_0)Bi(u))(Bi(u+x_0)Ai(u) - Ai(u+x_0)Bi(u))}{(Bi'_L(u+x_0)Ai(u) - Ai'_L(u+x_0)Bi(u))(Bi_L(u+x_0)Ai(u) - Ai_L(u+x_0)Bi(u))} \right), \quad (18)$$

where Ai_L , Bi_L , Ai'_L , and Bi'_L are the lowest order asymptotic expressions for the Airy functions.²⁰ The next order in the asymptotic expansion of the Airy function is $Ai_{L2}(t) \approx -0.07(\frac{2}{3}t^{3/2})^{-1}Ai_L(t)$ and in order for it to be negligible, t has to be large enough, typically larger than 1.5. This leads to the condition $u_0(x_0) + x_0 > 1.5$, which yields roughly that x_0 has to be larger than ≈ 3 if our calculation is to be accurate to within a few percent. For smaller values of the intersurface separation the form of the regularized interaction free energy Eq. (18) does not work.

Figure 2 shows the dependence of the dimensionless fluctuational free energy \mathcal{W}_2 on the dimensionless separation x_0 . As already stated the regularization procedure Eq. (18) can only be used for sufficiently large intersurface spacing. The log-log plot (see the inset of Fig. 2) reveals that asymptotically the fluctuational contribution with an algebraic decay prevails. From the inset of Fig. 2 we read that the free energy decays asymptotically as $x_0^{-1.7}$ and we also show how fast this asymptote is approached. The free energy stays on the asymptote essentially for all x_0 larger than about 6.

$$p(a) = p_{MF} + p_{FL}[\delta\phi] + p_{FL}[\delta\psi] = \frac{1}{2}k_B T \mu \psi^2(z=0) - \frac{k_B T \zeta(3)}{8\pi(2a)^3} + p_{FL}(a), \quad (16)$$

where the first term on the r.h.s. derives from the mean-field solution, the second one derives from the Casimir term stemming from the electrostatic field fluctuations, first term in Eq. (9) and the third one derives from the pseudo-Casimir terms stemming from the replicated density field fluctuations, second term in Eq. (9), with

$$p_{FL}(a) = -\frac{1}{S} \left(\frac{\partial \mathcal{W}_2(a)}{\partial (2a)} \right). \quad (17)$$

The next section deals with the evaluation and regularization of the fluctuation terms in Eq. (16).

IV. RESULTS: LARGE INTERSURFACE SEPARATION

We will first have to regularize the divergent expression Eq. (13) by subtracting the divergent terms explicitly in the limit of large x_0 (to be quantified below). When x_0 is large enough the argument $y = u + x_0$ of the Airy functions in Eq. (14) becomes large too and we can use the asymptotic expansion formulas²⁰ for the Airy functions to explicitly find the divergent terms in $\mathcal{F}_2^\infty(a)$. The regularized free energy is then

The algebraic decay of the free energy and concomitantly of the pressure, indicates that the fluctuation induced force has a much longer range than the mean field force which decays approximately exponentially.^{6,7} Also it has a longer range than the zero-order Casimir (or equivalently the zero order van der Waals) interaction free energy that decays as x_0^{-2} .

There is also no obvious connection between this result and the behavior of the fluctuation part of the interaction free energy of a system composed of unconnected counterions treated on the same level of approximation.²¹ In that case the fluctuation free energy decays as $x_0^{-2} \ln x_0$, which is much faster than $x_0^{-1.7}$.

V. RESULTS: SMALL INTERSURFACE SEPARATION

For small plate separations the above procedure cannot work because in that case we cannot write down explicitly the asymptotic form of the Airy functions that would be valid in the whole range of integration in Eq. (13). We found out that the best way to approach the evaluation of the fluctua-

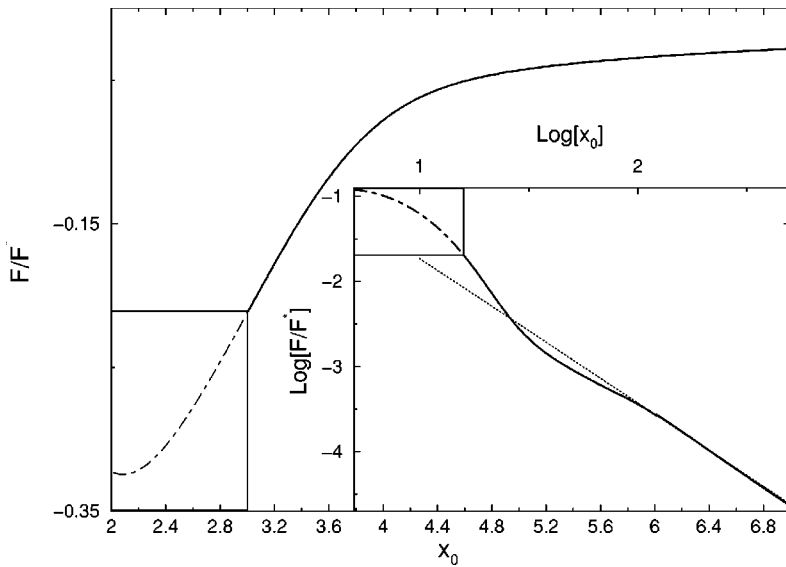


FIG. 2. The regular part of the fluctuational free energy $F = \mathcal{W}_2$ in the limit of large separations (see main text) plotted with respect to the dimensionless separation x_0 . The region around the critical separation $x_0 = 1.986$, where the approximations are doubtful, is marked with a box. On the inset there is the same plot in the logarithmic scale ($\log|F/F^*|$). One can read from the inset that the dependence of the free energy on the separation is algebraic with the exponent around 1.7 ($\mathcal{W}_2 \propto x_0^{-1.7}$). This power law asymptote is depicted with a dotted line. The constant F^* is defined as $F^* = Sk_B T \lambda_B^{2/3} / 16\pi$.

tion determinant in this limit is via a perturbation analysis using the eigenvalue representation of the functional determinant Eq. (11).

The perturbative treatment of the evaluation of Eq. (13) can be introduced as follows. The differential equation we have to solve is

$$\left(-\frac{d^2}{dx^2} + q^2 + y_0(x_0) + |x - x_0| \right) \psi = 0. \tag{19}$$

The last term can be treated as a linear perturbation potential $V(x) = |x - x_0|$. What we will do now is to evaluate the determinant of the operator in Eq. (19) in the form of a perturbation expansion in $V(x)$ up to and including the first order. The order zero of the perturbation expansion of the determinant of the operator Eq. (19) gives

$$\det \left(-\frac{d^2}{dx^2} + q^2 + y_0 \right) = \psi_0^0(x_0) = \frac{\sinh 2\sqrt{q^2 + y_0}x_0}{2\sqrt{q^2 + y_0}}. \tag{20}$$

The final integration over the wave vector \mathbf{Q} has to be divided into two parts because y_0 is negative, leading to

$$\mathcal{W}_2^0 = \frac{Sk_B T \lambda_B^{2/3}}{16\pi x_0^2} \left[\int_0^\pi w dw \ln \frac{\sin w}{w} - \frac{\zeta(3)}{4} \right]. \tag{21}$$

To obtain the first order term in the perturbation expansion we shall use the product of the eigenvalues representation of the determinant of the operator which leads to the following first order form of the free energy:

$$\mathcal{F}_2^1 = \frac{k_B T \lambda_B^{2/3} S}{4\pi} \int_0^\infty q dq \sum_N \ln \lambda_N^1, \tag{22}$$

where λ_N^1 represents the first order correction to the eigenvalue of the differential equation Eq. (19). This correction can be evaluated by standard formulas of the perturbation theory²² leading to the following result:

$$\begin{aligned} \lambda_N^1 &= \lambda_N^0 - \frac{\langle N|V(x)|N \rangle}{\langle N|N \rangle} \\ &= \lambda_N^0 - \frac{\int_0^{2x_0} |x - x_0| \sin^2(N\pi/2x_0)x dx}{\int_0^{2x_0} \sin^2[(N\pi/2x_0)x] dx} = \lambda_N^0 + \frac{x_0}{2}, \end{aligned} \tag{23}$$

so the sum of the first order corrections to the log of the determinant of the operator Eq. (22) is

$$\begin{aligned} \sum_N \ln \lambda_N^1 &\approx \sum_N \ln \lambda_N^0 \\ &+ \frac{x_0^3}{\pi^2} \sum_N \frac{1}{N^2 - 1 + (2x_0/\pi)^2 [q^2 + (x_0/2)]}. \end{aligned} \tag{24}$$

Since the first term in this expression has already been calculated, we now focus on the second one. This term is obviously divergent. If we calculated the bulk contribution, there would be an integral over N instead of the discrete sum, which is a consequence of the boundary conditions. The regularized free energy is thus¹⁸ obtained as the difference between the sum and the integral of the same expression. After some algebra the result of this manipulation is

$$\begin{aligned} \mathcal{W}_2^1 &= \frac{Sk_B T \lambda_B^{2/3} x_0}{16\pi} \left[\frac{1}{2} \int_0^{\sqrt{1 - (2x_0^3/\pi^2)}} dw \left(\pi(\coth \pi w \right. \right. \\ &\quad \left. \left. - \cot \pi w - 1) - \ln \frac{1+w}{1-w} + 2 \arctan \frac{1}{w} \right) \right. \\ &\quad \left. + \frac{1}{2} \int_{\sqrt{1 - (2x_0^3/\pi^2)}}^\infty dw \left(\pi(\coth \pi w - 1) \right. \right. \\ &\quad \left. \left. + 2 \left(\arctan \frac{1}{w} - \frac{1}{w} \right) \right) \right]. \end{aligned} \tag{25}$$

Even without really calculating the second order we can nevertheless say something about its magnitude. The maximal

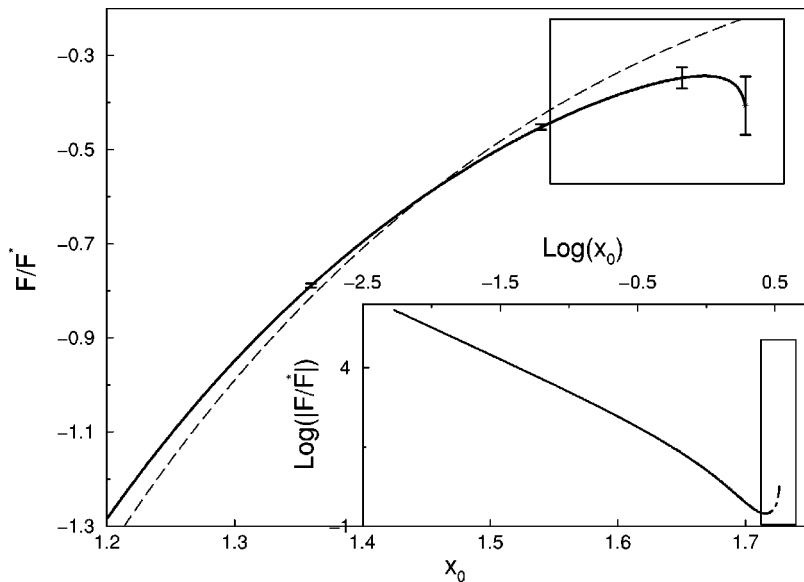


FIG. 3. The regular part of the fluctuational free energy $F = \mathcal{W}_2$ in the limit of small separations. The region around the critical separation $x_0 = 1.986$, where the approximations are doubtful, is again marked with a box. The zero-order approximation is shown dashed and the result up to the first order solid. The error bars represent the maximal possible error of the first order result. The inset represents the log-log plot of the free energy, wherefrom we deduce that for small separations the fluctuation free energy scales as x_0^{-2} . The constant F^* is defined in Fig. 2.

difference between the first and the second order perturbation terms can be obtained in standard notation as²²

$$\delta\lambda_N^1 \leq \frac{1}{\Delta\lambda} [\langle N|V(x)^2|N \rangle - (\langle N|V(x)|N \rangle)^2], \quad (26)$$

where $\Delta\lambda$ is the minimal difference between λ_N and any other λ_M . A short calculation then yields $\delta\lambda^1/\lambda^1 \leq x_0^3/14.8$. As expected, the reliability of the first order result drops as we move towards larger x_0 , i.e., towards the mean field phase transition from below.

Figure 3 shows the first and the second perturbation order of the regularized fluctuation free energy at small intersurface separations. The pressure obviously changes sign for sufficiently large separation (x_0 larger than ~ 1.68 in Fig. 3). For small enough separations the free energy scales approximately as x_0^{-2} which is the same scaling form as for the mean-field part. It seems to us that the change in sign of the pressure close to the transition point $x_0 = 1.986$ is not due entirely to artifacts of the first order perturbation theory for

sufficiently large intersurface separations, but could conceivably survive all higher order perturbation terms. Unfortunately all approximation schemes that we could think of broke down close to the transition point and we thus have to leave the important question about the behavior of the fluctuation component of the pressure close to the transition unanswered.

VI. DISCUSSION

We have described all the contributions to the fluctuational free energy of the system. To evaluate the fluctuational part of the pressure between the two surfaces the derivatives of the regularized free energy with respect to x_0 have been performed numerically. The total pressure can thus be obtained by simply taking the sum of mean-field and fluctuational contributions Eq. (16). Figure 4 shows the dimensionless total pressure as a function of the dimensionless separation x_0 which can be written, Eq. (16), as

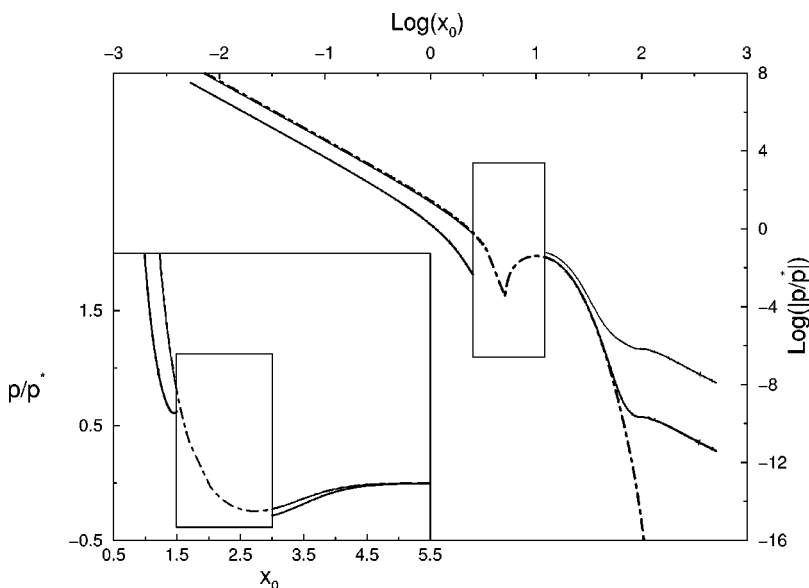


FIG. 4. The mean field pressure (dotted-dashed line) and the total pressure ($\alpha_{MF}=4$, thick line and $\alpha_{MF}=100$, thin line) between two plates as a function of the separation in the logarithmic scale. The uncertain region around $x_0 = 1.986$, where the approximations are doubtful, is marked by a box. The box contains only the mean-field results which can be evaluated for the whole range of x_0 values. One can clearly observe the long range tail stemming from the thermal fluctuations of the monomer density field. Inset shows the total pressure—mean field plus fluctuational—between two plates as a function of the separation for different values of parameter $\alpha_{MF}=4100$. A large deviation from the mean field result is obtained for $\alpha_{MF}=4$, whereas fluctuations hardly matter for $\alpha_{MF}=100$. The constant p^* is defined as $p^* = \sigma^2/2\epsilon\epsilon_0$.

$$\begin{aligned}
p(x_0) &= p_{\text{MF}} + p_{\text{FL}}[\delta\phi] + p_{\text{FL}}[\delta\psi] \\
&= \frac{k_B T}{2} \frac{\lambda_B \ell^2 \sigma}{8 \tau} y_0(x_0) \tilde{\psi}^2(0) - \frac{k_B T \zeta(3) \lambda_B}{64 \pi x_0^3} \\
&\quad - \lambda_B^{1/3} \frac{d}{d(2x_0)} \left(\frac{\mathcal{W}_2(x_0)}{S} \right) \\
&= p^* \left[y_0(x_0) \tilde{\psi}^2(0) - \frac{\zeta(3)}{4 \alpha_{\text{MF}} x_0^3} + \frac{f(x_0)}{\alpha_{\text{MF}}} \right], \quad (27)
\end{aligned}$$

where $f(x_0)$ is a function of x_0 only, $\tilde{\psi}(0)$ is the normalized dimensionless ψ , $\alpha_{\text{MF}} = (4\pi/3)(\sigma\ell/\tau)$, and $p^* = k_B T \lambda_B \alpha_{\text{MF}} / 16\pi = \sigma^2 / 2\epsilon\epsilon_0$. The parameter α_{MF} depends on the charge density on the plates σ , the linear charge density on the polyelectrolyte chain τ and on the segment length of the polyelectrolyte ℓ . If we put in experimentally reasonable values of $\sigma \approx e_0 / 1.35 \text{ nm}^2$, then α_{MF} is about 100 for DNA (a relatively stiff polyelectrolyte) and around 4 for hyaluronic acid (a relatively flexible polyelectrolyte). Obviously the larger α_{MF} the less important will the fluctuation effects be and the more accurate will be the mean-field result.

Figure 4 shows the complete pressure Eq. (27) as a function of the dimensionless separation for different values of the coupling parameter α_{MF} . As already stated we were unable to analyze the behavior of the interaction pressure close to the mean-field transition point. Our failure could indicate that close to the transition point our harmonic approach to the fluctuations breaks down. This would not be totally unexpected since we are dealing with a continuous transition in the distribution of the polyelectrolyte density that apparently has all the attributes of a second order phase transition, with large fluctuations close to the transition point. We will however not pursue this line of thought here.

It is clear from Fig. 4 that the effect of the fluctuations on the intersurface force can be profound. First of all the fluctuations modify the force at small separations making it less repulsive if compared to the mean-field case. Since both the mean-field as well as the fluctuation contribution to the free energy scale as x_0^{-2} (but with a different sign) it appears that the effect of the fluctuations is simply to renormalize the magnitude of the pressure but not its scaling form. If one would thus try to fit the complete $p(a)$ with $p_{\text{MF}}(a)$ one would have to introduce a smaller effective charge on the surfaces for the fit to make sense.

At large separations the behavior of $p(a)$ is completely different from the behavior of $p_{\text{MF}}(a)$. What the fluctuations do is that they provide a long range algebraic tail to the interactions, which overwhelms the exponentially screened mean-field attraction at large intersurface separation. The algebraic fluctuation tail decays with an anomalous exponent of 1.7, that makes the polyelectrolyte mediated fluctuation interactions even longer ranged than the standard van der Waals interactions. This in itself is one of the main conclusions of our work. It is also this long ranged tail that is

probably most amenable to experimental observation and verification. Since the fluctuation effects are stronger for smaller α_{MF} we predict that they should be easier to measure for very flexible polyelectrolytes, such as hyaluronic acid as opposed to DNA.

The main drawback of this work is that the fluctuation effects have been treated on a harmonic level which *a priori* assumes that they are small. However what saves us here is that the mean-field interactions decay exponentially whereas the fluctuation interactions decay algebraically. This is different than in the case of a simple, i.e., unconnected, Coulomb fluid such as an inhomogeneous electrolyte. In that case both the mean-field as well as the fluctuation interactions decay exponentially but the mean-field interactions have a range twice as long as the fluctuation interactions.⁹ The case of polyelectrolytes is in this respect fundamentally different: the range of fluctuation interactions is *larger* than the range of mean-field interactions and the use of harmonic approach to fluctuations is probably better grounded in this case.²³⁻²⁷

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