PHYSICAL REVIEW E **68**, 051104 (2003)

Weak nonlinear surface-charging effects in electrolytic films

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(Received 23 October 2002; published 20 November 2003)

A simple model of soap films with nonionic surfactants stabilized by added electrolyte is studied. The model exhibits charge regularization due to the incorporation of a physical mechanism responsible for the formation of a surface charge. We use a Gaussian field theory in the film but the full nonlinear surface terms which are then treated at a one-loop level by calculating the mean-field Poisson-Boltzmann solution and then the fluctuations about this solution. We carefully analyze the renormalization of the theory and apply it to a triple-layer model for a thin film with Stern layer of thickness h. For this model we give expressions for the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ and show their dependence on the parameters. The influence of image charges naturally arises in the formalism, and we show that predictions depend strongly on h because of their effects. In particular, we show that the surface charge vanishes as the film thickness $L\rightarrow 0$. The fluctuation terms in this class of theories contribute a Casimir-like attraction across the film. Although this attraction is well known to be negligible compared with the mean-field component for model electrolytic films with no surface-charge regulation, in the model studied here these fluctuations also affect the surface-charge regulation leading to a fluctuation component in the disjoining pressure which has the same behavior as the mean-field component even for large film thickness.

DOI: 10.1103/PhysRevE.68.051104 PACS number(s): 05.20.−y, 68.15.+e, 52.25.Kn

I. INTRODUCTION

Many situations in colloid, polymer, and interfacial science involve charged objects interacting in electrolyte solutions. In the case of two interacting membranes or soap films one encounters the electric double layer. The mean-field theory of such experimental configurations is the Poisson-Boltzmann theory [1,2] for which a surface boundary condition must be determined. For example, the surface charge or surface potential can be given, or a relation between the surface charge and surface potential may be specified. Such a relationship arises in a charge-regularized model where the surface-charging mechanism is derived from a microscopic description of the chemistry and geometry at the interface. Charge-regularized models have the property that, owing to the thermodynamic nature of the charging mechanism, the surface charge changes as the distance between the two surfaces varies. The variation of the surface charge with the intersurface distance will also change the effective interaction between the surfaces and consequently the disjoining pressure. Within the film, the mean-field Poisson-Boltzmann theory is only sensitive to the electrostatic properties of the electrolyte; the chemistry and effective sizes of the ions in the system only enter into the description of the surface-charging process. For example, experiment [3] shows that the disjoining pressure increases with increasing hydration radius of the counterions in ionic soap films. This effect can be explained by the fact that as the counterion radius increases the capacity for it to approach the surface and screen, the surface charge is reduced.

To take into account bulk surface tensions of electrolytes one must resort to a microscopic description of the physics at the interfaces. Depending on the nature of interface one may have specific adsorption due to chemical effects which can be taken into account via the law of mass action [4–8] or at a more statistical mechanical level by introducing an external potential at the surface which models the chemical liaison involved [9–11]. In addition, there are other forces which come into play which are not present in the standard Poisson-Boltzmann approach. These are effects due to fluctuations in the electromagnetic field which can be identified with van der Waals forces [12–14]. In bulk, the nonzero frequency van der Waals forces have little effect on the static ionic distributions since the relevant frequencies are too large and their contributions can be decoupled from those of zero frequency. However, it was pointed out in Ref. [15] that near interfaces the nonzero frequency van der Waals or dispersion forces can be important and depend strongly on the polarizability of the ions involved, and hence are ion specific. The zero frequency van der Waals forces, which correspond to thermal fluctuations in the electrostatic field, do strongly influence ionic distributions and so do modify the surface charge. When there are spatial variations in the dielectric constant image charges arise [16]. In the field-theoretic approach adopted in this paper image charges and their effects are naturally and systematically included by taking into account the fluctuations of the electrostatic field.

In this paper we use field-theoretic techniques to study the effects of nonlinear terms on the surface-charging mechanism and the disjoining pressure while retaining the free-field theory description for the bulk electrostatic fields. This corresponds to using linear Debye theory in the bulk with fugacity μ but with the fully interacting description of the sources for the charging mechanism of the surfaces. The effect of including nonlinear interactions in the bulk of the film will be addressed in a forthcoming paper. The model is ap-

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plied to a triple-layer thin film as an idealized model of the surfaces where there is a Stern layer of thickness h from which all ions are excluded. Calculations are performed to one-loop order in perturbation theory and an important outcome is that this extension of calculations beyond mean-field theory allows us to use the model as a paradigm for the analysis of the rôle of divergences which arise in the theory. There are three categories of divergence: (a) apparent ultraviolet divergences which can be shown to cancel when physical renormalization conditions are imposed; (b) ultraviolet divergences which are physical and are regulated by physical length scales which are typically the sizes of the ions involved; and (c) divergences associated with image charges induced by the dependence of the dielectric constant ϵ on z, the coordinate normal to the film. These appear in the self-energy contributions near to the surface and are regulated by the Stern layer thickness h. Of these, we discuss (a) and (c) in this paper since it can be shown that divergences of type (b), which must arise because the Sine-Gordon theory is not renormalizable in three dimensions, occur only in graphs at three-loop order and higher. Because divergences of type (c) are physical the charging mechanism for a realistic film cannot place charges directly on the surface because this would correspond to setting $h=0$. However, it should be emphasized that the mean-field theory is not singular as $h \rightarrow 0$, and we exploit this observation to set up the mean-field solution about which the fields are expanded so that the effects of field fluctuations can be analyzed.

In Sec. II we describe the field theory model we use in this study and how it is applied to the triple-layer thin film system discussed above. In Sec. III we discuss the mean-field solution to the field theory for the thin film for which the nonlinear interactions at the surface determine the source terms in the mean-field equation. In Sec. IV we give a detailed description of the effect of field fluctuations about the mean-field solution using the Schrödinger kernel approach developed in an earlier paper [24]. We give predictions for the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ as a function of film thickness L and show under reasonable assumptions that $\sigma(L) \rightarrow 0$ as $L \rightarrow 0$ and that the mean-field prediction for the large L tail of $P_d(L)$ is modified by one-loop corrections, which like the mean-field contribution also decay as $\exp(-mL)$ for large L, where m is the Debye mass. In Sec. V we present a number of example graphs and discuss their salient features. In particular, it is clear that the effects of image charges, which arise naturally and systematically in our formalism as terms in self-energies, are very strong and that qualitative predictions depend sensitively on the value of h, the thickness of the Stern layer. This demonstrates that a realistic model for the structure of the surface, and the width of the Stern layer in particular, is necessary for a quantitative study. We also present some conclusions in this section.

II. MODEL

We consider an idealized model of a thin film made with nonionic soap adapted to the experimental setup used to measure the disjoining pressure as a function of the film thickness [3,10,17–19]. The film shown in Fig. 1 consists of two parallel surfaces of area A, the interior of which is filled with a monovalent electrolyte solution such as NaCl in water with bulk dielectric constant ϵ. The exterior of the film is a dielectric medium of dielectric constant ϵ_0, for example, air. The perpendicular distance between the two surfaces is denoted by $L+2h$. The region of thickness h is the Stern layer from which the largest ions in the system are excluded, and h can be taken to be the radius of the largest ion type in the system, which is here chosen to be the anion (in most physical systems it is the cation with the largest radius due to hydration). If the radius of the cation in solution is h' and $h'<h$, then the cation is excluded from a region of width h' from the surface but can be present in the region $[-(h-h'),0]$ where there are no anions, thus leading to an effective surface charge in that region. Strictly speaking, just outside the film is the surfactant layer which in general will have a different dielectric constant to that of the exterior and the aqueous interior. Here for simplicity the presence of the nonionic surfactant is neglected. A version of this model with a single surface plus bulk is commonly used to model the surface properties of electrolyte solutions [15,20–22]. In experiments the thickness L of the film may be varied by applying an external pressure in the cell containing the film and its bulk.

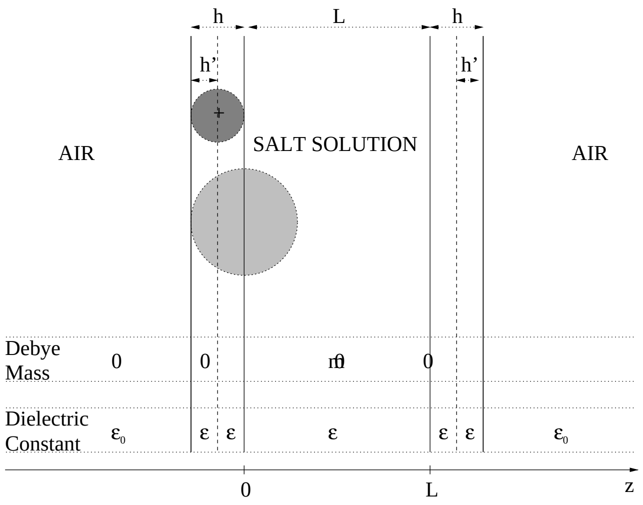


FIG. 1. Cross section through a model soap film. The distance of closest approach of the ions to the surfaces (at $z=0$ and $z=L$) is the effective radius of the ionic species in solution. The dielectric constants and Debye masses as a function of the distance perpendicular to the film surface, i.e., as a function of the position on the z axis are also shown.

The grand partition function for this model system may be expressed as a functional integral (the functional integral approach to slab geometries was introduced in Ref. [23])

$$\Xi = \int d[\phi]\exp(S[\phi]), \tag{1}$$

where

$$S[\phi]=-\frac{1}{2}\int_{(T+L+2h)\times A}\beta\epsilon(\mathbf{x})(\boldsymbol{\nabla}\phi)^2 d\mathbf{x}+2\mu\int_{L\times A}\cos(\beta e\phi)d\mathbf{x}+\mu_+^*\int_{L\times A}[\delta(z)+\delta(L-z)]\exp(i\beta e\phi)d\mathbf{x},\quad(2)$$

where e is the electron charge, A is the area of the film, and $\beta=1/k_BT$. The fugacities of the anions and cations are taken to be equal and denoted by μ, and for a monovalent electrolyte their densities in the bulk are also equal and are denoted by ρ. The total length in the z direction perpendicular to the film surfaces is $T+L+2h$, where T denotes the total length external to the film. In the region $z\in[-h,L+h]$ the dielectric constant, which is a function only of z, is given by $\epsilon(z)=\epsilon$ and outside the film $\epsilon(z)=\epsilon_0$.

The above field-theoretical formulation can be obtained directly from quantum electrodynamics [24] by retaining just the electrostatic potential field in the QED Lagrangian and coupling it to the distribution of ion charges. Alternatively, it can be obtained by standard field-theory techniques based on the Hubbard-Stratonovich transformation for a monovalent Coulomb gas. The formulation takes into account both the Coulomb interactions between the ions and the zero frequency van der Waals forces due to fluctuations in the electrostatic potential [24]. These zero frequency van der Waals forces are particularly relevant when there are variations in the dielectric constants of the system since they naturally and systematically include the effects of image charges. This is especially the case for aqueous soap films in air where $\epsilon/\epsilon_0\approx 80$. The density operators for the cations and anions can be shown to be

$$\rho_\pm(\mathbf{x})=\mu\exp[\pm ie\beta\phi(\mathbf{x})].\quad(3)$$

The last term in Eq. (2) represents a highly localized affinity for the cations to be at the surfaces $z=0$ and $z=L$ of the film, and is responsible for the generation of a surface charge. There are various mechanisms leading to affinities for ionic species at interfaces, ranging from chemical affinity to steric and entropic effects. Here this term arises in the following approximation. Since there can be cations in the region $[-(h-h'),0]$ and the corresponding region $[L,L+(h-h')]$, there is, in addition to the first two terms of the action Eq. (2), a surface term

$$\Sigma=\mu\int_{[-(h-h'),0]\times A}\exp(i\beta e\phi)d\mathbf{x}+\mu\int_{[L,L+(h-h')]\times A}\exp(i\beta e\phi)d\mathbf{x}.\quad(4)$$

This is the integral of the density operator given by Eq. (3) for the cations over the regions $[-(h-h'),0]$ and $[L,L+(h-h')]$. These are the regions in the Stern layers which may be occupied by the cations but from which the anions are excluded. If $h-h'\ll l_D$, where l_D is the Debye length which characterizes the scale of the electrostatic interactions, then we can approximate Σ by

$$\Sigma=\mu(h-h')\int_{L\times A}\delta(z)\exp(i\beta e\phi)d\mathbf{x}+\mu(h-h')\int_{L\times A}\delta(z-L)\exp(i\beta e\phi)d\mathbf{x}.\quad(5)$$

Comparing with the formula in Eq. (2) we see that $\mu_+^*=\mu(h-h')$. In general actions of the type of Eq. (2) can be used to describe various surface-charging mechanisms with the proviso that the region where the surface charge is localized has a width much smaller than the Debye length l_D. While this description acts as a motivation for the model it is clear that, in general, there will be specific adsorption for the different species near the air/water interface. To model a specific adsorption for the cations in the surface region $[-(h-h'),0]$ we take a surface cation fugacity μ_s in this region which is greater than the bulk cation fugacity μ. On shrinking the surface region to zero one would then have $\mu_+^*=\mu_s(h-h')$. In general, we will have that $\mu_+^*=\mu r$, where r is a parameter having the dimensions of length. There is some evidence for specific absorption of certain ionic species at seemingly chemically neutral interfaces; the famous and controversial Jones-Ray dip [25] in the surface tension of weak electrolyte solutions (with interfaces with air) can be explained by invoking a specific adsorption of anions at the interface [26], although the basic surface exclusion model introduced in Ref. [20] and used here cannot explain negative excess surface tensions. Recent experimental evidence points toward a specific adsorption of hydroxide ions at air/water and oil/water interfaces [22]. In what follows we treat μ_+^* as an independent variable to account for the more complex charging mechanisms which can occur at the interface.

It is important to note that the fugacity μ (and hence $\mu^*=\mu r$) is determined by the values of the physical bulk density ρ,

$$\rho=\mu\langle\cos\beta e\phi\rangle,$$

where the brackets stand for averaging over the bulk partition function. In mean-field theory or at the zero-loop level this implies $\rho=\mu$, but this is not true in general and the relationship must be calculated taking field interactions into account. In particular, it is important to note that final results must be expressed in terms of ρ which is a physically measurable quantity and not in terms of μ which is a parameter in the action tuned to achieve the value of ρ required. In order to calculate quantities to a given loop order we must expand μ as a series in ρ using Eq. (2) to the same order to obtain a consistent final result.

In Ref. [24] the field theory with the action of Eq. (2) was analyzed in the weak-coupling or Debye-Hückel limit which is a Gaussian approximation where the action is expanded to second order in the field ϕ. This amounts to the assumption that the mean-field densities of cations and anions throughout the film are small enough so that $8\pi\rho(z)l_B^3<1$, where l_B is the Bjerrum length $l_B=e^2\beta/4\pi\epsilon$. Another approach is to solve the full nonlinear mean-field equations and then calculate the one-loop correction which gives the effect of field fluctuations about this mean-field solution [28,29]. In Ref. [28] the resulting mean-field solution in the case of fixed surface charge was ingeniously expressed in terms of special functions which allowed an analytic calculation of the one-loop correction. In our case, however, the fact that the surface charge must be computed self-consistently leads to additional complications and we take a different approach. We assume that the Gaussian approximation is valid inside the film but not at the surface where, because of the increased charge density, the electrostatic interactions will be stronger, and we retain the full nonlinear surface operators. The resulting theory can be analyzed as before [24] but with an effective L-dependent surface source for the field. The theory is accurate to the same order in perturbation theory as before but, in addition, now includes nonperturbative surface effects. The corresponding Debye-Hückel action with nonlinear surface terms is

$$S^*[\phi]=-\frac{1}{2}\int_{(T+L+2h)\times A}\beta\epsilon(z)(\nabla\phi)^2 d\mathbf{x} -\frac{1}{2}\int_{L\times A}\beta\epsilon m^2\phi^2 d\mathbf{x}+\mu_+^*\int_{L\times A}[\delta(z) +\delta(L-z)]\exp(i\beta e\phi)d\mathbf{x}+2\mu AL, \tag{6}$$

where $m(\rho)=\sqrt{8\pi\rho l_B}\equiv 1/l_D$ is the bulk Debye mass, l_D is the Debye length, and l_B is the Bjerrum length defined above.

Note that the term neglected in passing from the full action, Eq. (2), to Eq. (6) to the order of ϕ^4 is

$$\Delta S^*=\int_{L\times A}\left[\beta\epsilon[m^2(\rho)/2-m^2(\mu)/2]\phi^2+\frac{2\mu e^4\beta^4\phi^4}{4!}\right]d\mathbf{x}. \tag{7}$$

Using the effective action S^* as a starting point for a perturbation theory it can be shown that the dimensionless perturbative parameter is $g=ml_B$. It can also be shown that in the bulk the term ΔS^* only contributes to observables at $O(g^2)$, and we thus neglect it in our current one-loop analysis along with the higher-order terms in the expansion of the cosine.

From the discussion above, the weak-coupling limit corresponds to $g=ml_B<1$, and the Gaussian approximation will be valid throughout the film so long as the local or effective mean-field Debye mass $m(\rho(z))=\sqrt{8\pi\rho(z)l_B}$ does not become so large that this weak coupling condition is violated. This condition is $8\pi\rho(z)l_B^3<1$ as stated earlier. We note that since $\rho(z)>\rho_{bulk}$, this necessarily requires that $8\pi\rho_{bulk}l_B^3<1$.

Proceeding with the approximation scheme described above we have the expression

$$\Xi\approx\int d[\phi]\exp(S^*[\phi]) \tag{8}$$

for the grand partition function. The mean-field Poisson-Boltzmann equation is obtained from the saddle point of the action S^*:

$$\frac{\delta}{\delta\phi(\mathbf{x})}S^*|_{\phi_c}=0, \tag{9}$$

with μ substituted by ρ in the final mean-field results deduced from the solution since $\mu=\rho$ at the zero-loop order. We should emphasize that, as already discussed above, when calculating to a given loop order, the mean-field expressions should be evaluated with μ expressed as a series in ρ determined by Eq. (2) to the same order. This is the usual procedure for perturbative loop expansions in field theory and ensures the removal of nonphysical divergences in the results.

Taking into account the Gaussian fluctuations about the mean-field solution gives the perturbative correction to one-loop for which we have

$$\Xi\approx\exp(S^*[\phi_c])\int d[\phi'] \times\exp\left(\frac{1}{2}\int d\mathbf{x}d\mathbf{y}\frac{\delta^2 S^*}{\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})}\bigg|_{\phi_c}\phi'(\mathbf{x})\phi'(\mathbf{y})\right). \tag{10}$$

All other terms are treated as interactions to be analyzed by perturbation theory and yield corrections at two-loop and higher order.

The grand-potential per unit area of film J can be separated into a mean-field contribution plus the zero frequency van der Waals contribution coming from the fluctuations. We write

$$J=J^{MF}+J^{vdW}, \tag{11}$$

where

$$J^{MF}=-\frac{1}{A\beta}S[\phi_c] \tag{12}$$

and

$$J^{vdW}=\frac{1}{2A\beta}\mathrm{Tr}\ln\left(-\frac{\delta^2 S^*}{\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})}\bigg|_{\phi_c}\right). \tag{13}$$

The stability of the mean-field solution and validity of the one-loop approximation is ensured if the Hessian operator $H=-\delta^2S^*/\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})|_{\phi_c}$ is positive definite.

III. MEAN-FIELD THEORY

The mean-field equation is obtained as usual by looking for an imaginary solution to Eq. (9), $\phi_c=i\psi$, where ψ is real and corresponds to the mean-field electrostatic potential [24]. The resulting equation for ψ is

$$\beta\nabla\cdot\epsilon\nabla\psi-m^2\beta\epsilon\psi+\mu_+^*\beta e[\delta(z)+\delta(L-z)]\exp(-\beta e\psi) =0 \tag{14}$$

within the film, and outside the film we have

$$\beta\nabla\cdot\epsilon_0\nabla\psi=0. \tag{15}$$

This mean-field equation has the form of a standard linearized Poisson-Boltzmann equation but with nonlinear boundary terms.

An important fact to note is that in mean-field theory the limit $h,h'\to 0$ discussed in Sec. II and implicit in Eq. (14) is nonsingular. This is because image charge contributions are first seen in the one-loop self-energies contributions which arise from an analysis of the field fluctuations about the solution to the mean-field equations (14) and (15). These contributions are discussed in detail in the following section.

The solution for ψ is by symmetry only dependent on z and symmetric about the midplane of the film at $z=L/2$, and so we choose the solution $\psi(z)=C(L)\cosh[m(z-L/2)]$ inside the film. Outside the film Eq. (15) gives $d\psi/dz=0$, which is the condition of electroneutrality of the mean-field solution within the film. Integrating the mean-field equation between $z=0^-$ and $z=0^+$, and using the condition of electroneutrality, we find

$$\epsilon\frac{d\psi}{dz}\Big|_{z=0^+}=-e\mu_+^*\exp[-\beta e\psi(0)]. \tag{16}$$

Defining $D(L)=C(L)\beta e\cosh(mL/2)$ gives the nonlinear self-consistent equation determining D to be

$$D(L)=\alpha\coth\left(\frac{mL}{2}\right)\exp[-D(L)], \tag{17}$$

where $\alpha=m\mu_+^*/2\mu=mr/2$ is dimensionless. In the Stern layer model $\alpha=m(h-h')/2=(h-h')/2l_D$. As stated in Sec. II it is when $l_D\gg(h-h')$ that the formulation in terms of a surface charge is valid. In the study of this particular model we have $\alpha\ll 1$, which also implies small surface charges compatible with the use of the quadratic approximation within the film. Then Eq. (17) may be formally solved as a power series in $\alpha\coth(mL/2)$ using standard series inversion techniques from complex analysis. We find that

$$D(L)=\alpha\coth\left(\frac{mL}{2}\right)\sum_{n=0}^{\infty}(-1)^n\left[\alpha\coth\left(\frac{mL}{2}\right)\right]^n\frac{(n+1)^{n-1}}{n!}. \tag{18}$$

It is useful for what follows to define the running variable

$$\alpha'(L)=D(L)\tanh\left(\frac{mL}{2}\right)=\frac{m\mu_+^*\exp[-\beta e\psi(0)]}{2\mu}. \tag{19}$$

From Eq. (18) we then have

$$\alpha'(L)=\alpha\sum_{n=0}^{\infty}(-1)^n\left[\alpha\coth\left(\frac{mL}{2}\right)\right]^n\frac{(n+1)^{n-1}}{n!}. \tag{20}$$

We can regard $\alpha'(L)$ as a variable encoding the effective fugacity which controls the surface-charging mechanism. Many observable quantities are most appropriately expressed in terms of $\alpha'(L)$ rather than α. This is a common phenomenon in quantum field theory where the physical expansion parameter is a running coupling which is an explicit function of a physical scale appropriate to the system under study. For example, in particle physics the scale will be the center-of-mass energy of a scattering process and in critical phenomena it is the diverging correlation length of the system. Series expansions in the effective, running, parameter are more stable and convergent than in the original bare parameter which parametrizes the action of the theory. Here, as in other cases, the running coupling $\alpha'(L)$ is expressed as an infinite series in the corresponding bare parameter α. We can immediately see from Eq. (20) why $\alpha'(L)$ is a better expansion parameter. As $L\to\infty$, α' takes its bulk surface value $\alpha^*=\lim_{L\to\infty}\alpha'(L)$. As mentioned previously we are using a Gaussian field theory inside the film and so the mechanism generating the surface charge cannot be taken to be too strong, implying that $\alpha\ll 1$, which gives $\alpha^*\approx\alpha$. As L decreases $\alpha'(L)$ decreases. However, since the expansion in Eq. (20) is in $\alpha\coth(mL/2)$, the nonlinear terms in this series must be taken into account when varying L. Indeed, for small L one can show that $\alpha'(L)\sim -mL\ln(L)/2$, which tends to zero as L tends to zero.

We note that in general surface-charge-regulated models [7], even if there is an exact solution to the Poisson-Boltzmann equation (or its linearized form) in the bulk, one must determine the surface potential via a transcendental equation relating the surface charge to the surface potential. In general, this equation must be solved numerically by iteration [4] or by linearizing the boundary equation [5]. Fortunately in the case studied here we have an explicit series solution to the boundary equation. The disjoining pressure of the film $P_d(L)$ is the difference between the film and bulk pressures. In the grand canonical ensemble

$$P_d(L)=P(L)-P_{\text{bulk}}=-\frac{\partial J(L)}{\partial L}+\lim_{L\to\infty}J(L)/L, \tag{21}$$

where J is the film grand-potential per unit area. We can decompose the disjoining pressure into a contribution coming from the mean-field solution and a contribution coming from the field fluctuations which corresponds to the zero frequency van der Waals interaction,

$$P_d^{MF}(L)=-\frac{\partial J^{MF}(L)}{\partial L}+\lim_{L\to\infty}J^{MF}(L)/L, \tag{22}$$

$$P_d^{vdW}(L)=-\frac{\partial J^{vdW}(L)}{\partial L}+\lim_{L\to\infty}J^{vdW}(L)/L. \tag{23}$$

After some straightforward but laborios algebra we find that

$$P_d^{MF}(L)=\mu k_BT\frac{D^2(L)}{\cosh^2\left(\frac{mL}{2}\right)}$$

$$=\rho k_BT\frac{D^2(L)}{\cosh^2\left(\frac{mL}{2}\right)}, \tag{24}$$

where the last line above is the mean-field result with μ evaluated at zero-loop order for consistency. The zero-loop mean-field value of the density within the film is given by

$$\rho_{MF}(\mathbf{x})=2\rho\cosh[e\beta\psi(\mathbf{x})], \tag{25}$$

and in the linearized theory within the film this becomes

$$\rho_{MF}(\mathbf{x})=2\rho+\rho e^2\beta^2\psi(\mathbf{x})^2. \tag{26}$$

At the midplane $z=L/2$ of the film one has

$$\rho_{MF}\left(z=\frac{L}{2}\right)-\rho_{\text{bulk}}=\rho\frac{D^2(L)}{\cosh^2\left(\frac{mL}{2}\right)}. \tag{27}$$

The midplane pressure formula [1,2], for Poisson-Boltzmann theories with fixed surface charges or potentials, relates the disjoining pressure to the midplane mean-field density by

$$P_d^{MF}=k_BT\left[\rho_{MF}\left(z=\frac{L}{2}\right)-\rho_{\text{bulk}}\right]. \tag{28}$$

In fact, in theories of the type considered here with external potentials at or near the film surface, one can show quite generally that the midplane formula holds generically as long as these external potentials are zero in a finite interval containing the midplane $z=L/2$ (and hence when the two surface potentials do not overlap). One can see directly, comparing Eqs. (24) and (28) with the linearized approximation, Eq. (27), that the midplane formula is respected here.

The mean-field, zero-loop surface charge $\sigma_{MF}(L)$ may be written in terms of $\alpha'(L)$ defined in Eq. (19). We have

$$\sigma_{MF}(L)=e\mu^*\frac{\partial}{\partial\mu^*}\beta J_{MF}, \tag{29}$$

which gives

$$\sigma_{MF}(L)=\frac{2\rho e\alpha'(L)}{m}. \tag{30}$$

As remarked in the preceding section it is clear that $\alpha'(L)$ is the appropriate expansion parameter for physical observables.

The mean-field disjoining pressure in terms of $\alpha'(L)$ is

$$P_d^{MF}=\rho k_BT\frac{\alpha'^2(L)}{\sinh^2\left(\frac{mL}{2}\right)}, \tag{31}$$

which, in terms of the mean-field surface charge, reads

$$P_d^{MF}=\frac{\sigma_{MF}^2(L)}{2\epsilon\sinh^2\left(\frac{mL}{2}\right)}. \tag{32}$$

For the linearized Poisson-Boltzmann equation with constant surface charge σ_c one finds [8,27]

$$P_d^{MF}=\frac{\sigma_c^2}{2\epsilon\sinh^2\left(\frac{mL}{2}\right)}. \tag{33}$$

Hence, at the mean-field level, fitting the disjoining pressure at each value of L with an L-dependent σ_c will reproduce the behavior of $\sigma_{MF}(L)$ in the current theory. This result is also true for full nonlinear mean-field theory and is not dependent on the quadratic field approximation in the bulk used here.

IV. FLUCTUATION EFFECTS

In this section we give the expression for the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ correct to one loop and shall explicitly explain the rôle of divergences. We demonstrate that the ultraviolet divergences arising at one loop cancel when the physical renormalization condition determining the density ρ is imposed, and that the divergences as $h\to 0$ appearing in surface self-energy graphs are physical and correspond to image charge effects.

Evaluating the fluctuations about our mean-field solution yields

$$\frac{1}{2}\int d\mathbf{x}d\mathbf{y}\left.\frac{\delta^2 S_{DH}}{\delta\phi'(\mathbf{x})\delta\phi'(\mathbf{y})}\right|_{\phi_c}\phi'(\mathbf{x})\phi'(\mathbf{y})$$

$$=-\frac{1}{2}\int_{(T+L)\times A}\beta\epsilon(z)(\boldsymbol{\nabla}\phi')^2d\mathbf{x}-\frac{1}{2}\int_{L\times A}\beta\epsilon m^2\phi'^2d\mathbf{x}$$

$$-\frac{1}{2}\beta\epsilon m\alpha'(L)\int_{L\times A}[\delta(z)+\delta(L-z)]\phi'^2d\mathbf{x}, \tag{34}$$

where $\alpha'(L)$ is defined in Eq. (19).

The main difference in Eq. (34) from the pure Gaussian theory of Ref. [24] is that the surface term $\alpha'(L)$ is now a function of the film thickness, whereas in the pure Gaussian theory it is a constant. The fluctuation term, Eq. (34), may be evaluated using functional techniques [14,28,30–32] as it is a functional determinant, or by path integral techniques [24]. In the calculation of this functional determinant, it is easily verified that the eigenvalues of the Hessian operator H are indeed positive, thus ensuring the stability of the mean-field solution and hence the validity of the one-loop approximation.

Using the results of Ref. [24] we find that the terms depending explicitly on α' and L that will contribute to the disjoining pressure and the surface charge are

$$\begin{aligned}\beta J^{vdW}(L,\alpha')&\\ &=\beta J^{vdW}_{\text{bulk}}L+\frac{m^2}{2\pi}\int dkk\,\ln[B(km)k+\alpha'(L)+\sqrt{k^2+1}]\\ &\quad+\frac{m^2}{4\pi}\int dkk\,\ln\Bigg[1-\left(\frac{B(km)k+\alpha'(L)-\sqrt{k^2+1}}{B(km)k+\alpha'(L)+\sqrt{k^2+1}}\right)^2\\ &\quad\times\exp(-2Lm\sqrt{k^2+1})\Bigg],\end{aligned} \tag{35}$$

where

$$B(p)=\frac{1+\Delta\,\exp(-2ph)}{1-\Delta\,\exp(-2ph)}, \tag{36}$$

with $\Delta=(\epsilon_0-\epsilon)/(\epsilon_0+\epsilon)$. The term $\beta J^{vdW}_{\text{bulk}}$ in Eq. (35) is the van der Waals contribution to the bulk grand-potential per unit volume and is given by

$$\beta J^{vdW}_{\text{bulk}}=\frac{m^2}{4\pi}\int dkk(\sqrt{k^2+1}-k). \tag{37}$$

The mean-field contribution to the bulk grand-potential per unit volume is simply $\beta J^{MF}_{bulk}=-2\mu$ since the mean-field solution in the bulk is just $\psi=0$; there are no surfaces to set up a mean-field potential. At this point we may not replace μ by ρ because we need to work to one loop for consistency. The total bulk grand-potential per unit volume is thus given by

$$\begin{aligned}\beta J_{\text{bulk}}&=-2\mu+\frac{m^2}{4\pi}\int dkk(\sqrt{k^2+1}-k)\\ &=-2\mu-\frac{m^3}{12\pi}+\frac{1}{8\pi}\Lambda m^2+O\left(\frac{m^4}{\Lambda}\right)\\ &=-2\mu-g\frac{2\rho}{3}\left(1-\frac{3\Lambda}{2m}\right),\end{aligned} \tag{38}$$

where Λ is a momentum space cutoff corresponding to a short distance cutoff $a\sim 1/\Lambda$, and $g=m^3/8\pi\rho=ml_B$. We see that indeed the expansion is in the dimensionless coupling g as asserted in Sec. II. The bulk density of electrolyte is given by

$$2\rho=-\mu\frac{\partial}{\partial\mu}\beta J_{\text{bulk}}=2\mu+\frac{m^3}{8\pi}-\frac{1}{8\pi}\Lambda m^2,$$

which can be written as

$$\mu=Z\rho,\quad Z=1-\frac{g}{2}\left(1-\frac{\Lambda}{m}\right).$$

From its definition in Sec. II we then also have, to this order in g, that $\mu^*_+=Z\rho^*_+$.

Substituting this result into Eq. (38) gives the well-known Debye expression for the bulk pressure

$$\beta P_{\text{bulk}}=-\beta J_{\text{bulk}}=2\rho-\frac{m^3}{24\pi}. \tag{39}$$

In addition, the above results can be used to show that the term ΔS^*, defined by Eq. (7) and which is neglected in our theory, is $O(g^2)$ in the bulk as stated previously.

In the field-theoretic formulation used here the surface charge (on one surface) per unit area, σ, is given by

$$\sigma=e\mu^*_+\langle\exp[ie\beta\phi(z=0)]\rangle. \tag{40}$$

From this expression it is clear that $\sigma\geqslant 0$ since we take $e\mu^*>0$ in what follows. However, for the purposes of this paper and to the order of accuracy of the present treatment we expand this operator to quadratic order and use the approximation

$$\begin{aligned}\sigma=e\mu^*_+\exp[-e\beta\psi(z=0)]\langle 1+ie\beta\phi'(z=0)&\\ -\tfrac{1}{2}e^2\beta^2\phi'^2(z=0)\rangle,&\end{aligned} \tag{41}$$

where the average $\langle\cdots\rangle$ in the above equation is over the fluctuations ϕ'. Since the one-loop action in ϕ' is quadratic, it follows that our result for σ in this approximation will be the first terms in an exponential series which can be immediately reexponentiated to give a result that is manifestly non-negative. Where this approximation breaks down can then be easily inferred from this fact and we shall remark on this later in the section. However, the aim of this paper is to demonstrate how observables can be calculated consistently to one loop and how all divergences can be accounted for and their role understood; this approximation is sufficient for this objective.

A consequence of the one-loop action in ϕ' being of quadratic form is that the average of the term linear in ϕ' in Eq. (41) is zero and we may then write

$$\sigma=\frac{2\mu e\alpha'(L)}{m}-\frac{e\alpha'(L)}{2}\frac{\partial\beta J^{vdW}}{\partial\alpha'(L)}\Big|_{\alpha'=0}+O(\alpha'^2), \tag{42}$$

where we have used that $\alpha=m\mu^*_+/2\mu$ and where we have kept only the leading-order behavior of the surface charge in α'. We note that the first term in Eq. (42) is simply the mean-field contribution σ_{MF}. The next order terms can be calculated and are finite though one needs to eliminate certain artificial divergences [34]. The formula, Eq. (42), gives the surface charge in terms of the conjugate variable α'. We note that the first term on the right-hand side of Eq. (42) is simply the mean-field contribution to the surface charge σ_{MF} but we do not replace μ by ρ since μ must be expanded in terms of ρ to one-loop order for consistency. To $O(\alpha')$ we obtain

$$\sigma(L)=\frac{2e\alpha'(L)}{m}\left(\mu-\frac{m^3}{8\pi}\int\frac{kdk}{D_+(k,m)}+\frac{m^3}{4\pi}\int kdk\frac{D_-(k,m)\sqrt{k^2+1}}{D_+(k,m)[D_+(k,m)^2\exp(2Lm\sqrt{k^2+1})-D_-(k,m)^2]}\right)+O(\alpha'^2), \tag{43}$$

where $D_{\pm}(k,m)=kB(km)\pm\sqrt{k^2+1}$. There is, however, a divergence in the first integral term in Eq. (43). This term corresponds to the van der Waals contribution to the charge of a bulk surface, $\sigma_{\text{bulk}}=\lim_{L\to\infty}\sigma$. This divergence can be regularized by choosing the fugacity μ to give the desired bulk electrolyte density ρ correct at one-loop order (as alluded to previously). We define

$$\Gamma=\int kdk\left(\frac{1}{kB(km)+\sqrt{k^2+1}}-\frac{1}{2k}\right) \tag{44}$$

and then

$$\sigma_{\text{bulk}}=\frac{2e\alpha^*}{m}\left(\mu-\frac{m^3}{8\pi}\Gamma-\frac{m^2\Lambda}{16\pi}\right), \tag{45}$$

where Λ is the ultraviolet cutoff introduced in the bulk calculation above. Note that for weak charging $\alpha^*\sim\alpha$. Hence in terms of the physical variable ρ we obtain the divergence-free formula for σ_{bulk},

$$\sigma_{\text{bulk}}=\frac{2e\alpha^*}{m}\left(\rho-\frac{m^3}{16\pi}-\frac{m^3}{8\pi}\Gamma\right). \tag{46}$$

We remark here that in the case $\Delta\neq 0$, if the Stern layer thickness h is taken to zero, then the term Γ in Eq. (46) diverges. It is clear however that one cannot have a surface charge exactly at the interface between two media of different dielectric constants due to the presence of arbitrarily close image charges which would lead to an infinite energy cost. The divergence in h as $h\to 0$ in Eq. (46) is thus a physical divergence and any model using a surface charge must place this surface charge away from a discontinuity in the dielectric constant, ϵ. As emphasized in Sec. III, there is no divergence as $h\to 0$ in mean-field theory and so the result that no charge can be situated precisely at the surface cannot be deduced from the mean-field solution but rather arises through well-understood image charge effects first arising at one-loop order. Of course, if the change in ϵ is not abrupt but takes a smooth functional form, then this statement will be moderated accordingly. However, in such more complicated, and perhaps more realistic circumstances, the potential energy related to image charge effects is still calculable in our formalism from self-energy terms evaluated in the region where ϵ varies strongly. When $\Delta=0$ no such divergence is present and $B(km)=1$ leading to the simple formula

$$\sigma_{\text{bulk}}=\left(1-\frac{g}{6}\right)\sigma_{MF}(\infty). \tag{47}$$

We notice that from Eq. (39) that, to this order, this equation may be written as

$$\sigma_{\text{bulk}}=\frac{\beta P_{\text{bulk}}e\alpha^*}{m}. \tag{48}$$

In the absence of dielectric discontinuities (when $\epsilon=\epsilon_0$), from Eq. (47) we see that the effect of electrostatic interactions is to reduce the surface charge from the value it would have had without interactions. This is because the excess anions left in the bulk pull the cationic surface charge into the bulk. The case where $\Delta>0$ (i.e., $\epsilon_0>\epsilon$) leads to $B(km)\geqslant 1$ for all k and, examining the integrand in the formula defining Γ, we find that $\Gamma<0$ and hence that positive Δ increases the surface charge above that of the case $\Delta=0$. This is to be expected physically as the image charges in this case attract the ions toward the medium of higher dielectric constant [16]. In the case where $hm\ll 1$ we may evaluate the integral defining Γ since the leading divergence as $hm\to 0$ comes from the large k integration. We find

$$\sigma_{\text{bulk}}=\left(1-\frac{g}{6}+\frac{g\Delta}{4mh}\right)\sigma_{MF}(\infty). \tag{49}$$

Again, we see that for $\Delta>0$ ($\Delta<0$) there is an enhancement (reduction) of the surface charge. This enhancement (reduction) can be physically attributed to the presence of image charges.

Finally the L dependence of the surface charge at $O(\alpha')$ is given by

$$\sigma(L)=\sigma_{MF}(L)[1+g\Sigma(mL,mh)], \tag{50}$$

where

$$\Sigma(mL,mh)=-\frac{1}{2}-\Gamma+2\int kdk\,\frac{D_-(k,m)\sqrt{k^2+1}}{D_+(k,m)[D_+(k,m)^2\exp(2Lm\sqrt{k^2+1})-D_-(k,m)^2]}, \tag{51}$$

where $D_{\pm}(k,m)=kB(km)\pm\sqrt{k^2+1}$. As remarked earlier the surface charge must be non-negative because in our model the expectation value of the charge operator given in Eq. (40) is the exponential of a function of (ρ,L,h). Our approximation has considered so far the quadratic expansion of this operator but we can easily now infer the full exponential result from these last two equations to be

$$\sigma(L)=\sigma_{MF}(L)e^{g\Sigma(mL,mh)}. \tag{52}$$

To replace our result by the exponentiated expression is to perform a selective resummation of higher-order graphs in the expansion for σ which respects the physical constraint that σ is non-negative. This exponentiation is also clearly consistent at the level of accuracy of the present one-loop approach as the terms introduced are of order g^2. Indeed, if one did not use the expansion of the exponential as done in Eq. (41), but rather calculated the expectation value of σ using the Gaussian form of the action of the fluctuations ϕ', we would clearly recover the same formula. The result in Eq. (49) can be similarly exponentiated. We remark that corrections from interactions within the film bulk,which have been omitted in this model, will give a multiplicative factor of the form $1+ag^2+\cdots$.

Because $\alpha'(L)\rightarrow 0$ as $L\rightarrow 0$, we find that σ_{MF}, and hence the surface charge σ, vanishes as the film becomes thin. This is a physical result as clearly two surface charges lying on each other will have an infinite electrostatic energy and this situation will be thermodynamically suppressed. This vanishing of the surface charge as $L\rightarrow 0$ is not picked up by a purely Gaussian theory [24].

As previously stated the total disjoining pressure is composed of a mean-field contribution and a contribution coming from the fluctuations. We find that the total of these two terms gives

$$P_d(L)=\frac{\sigma_{MF}^2(L)}{2\epsilon\sinh^2\left(\frac{mL}{2}\right)}\left(1+2g\frac{\Sigma(mL,mh)}{\left[1+\alpha'(L)\coth\left(\frac{mL}{2}\right)\right]}\right)$$
$$-4g\rho k_BT\left(\int dkk\sqrt{k^2+1}\right)\frac{f^2(k)}{1-f^2(k)}, \tag{53}$$

where

$$f(k)=\frac{kB(km)+\alpha'(L)-\sqrt{k^2+1}}{kB(km)+\alpha'(L)+\sqrt{k^2+1}}\exp(-Lm\sqrt{k^2+1}). \tag{54}$$

In order to simplify the calculation in terms of quantities already computed we have simply used the decomposition

$$\frac{\partial J}{\partial L}=\left(\frac{\partial J}{\partial L}\right)_{\alpha'}+\frac{\partial\alpha'}{\partial L}\frac{\partial J}{\partial\alpha'}, \tag{55}$$

where first partial derivative is computed at constant α'. The second term may be written in terms of the mean field and one-loop surface charges σ_{MF} and σ using Eq. (42). Also in the derivation of this formula the divergences which arise at intermediate stages of the calculation can, as in the case of the surface charge, be shown to cancel in the final result. The reader should note that we have used the small α' expansion in Eq. (53) as with the surface-charge calculation. However the term $\alpha'(L)\coth(mL/2)$ cannot be expanded for small L as it diverges as $L\rightarrow 0$.

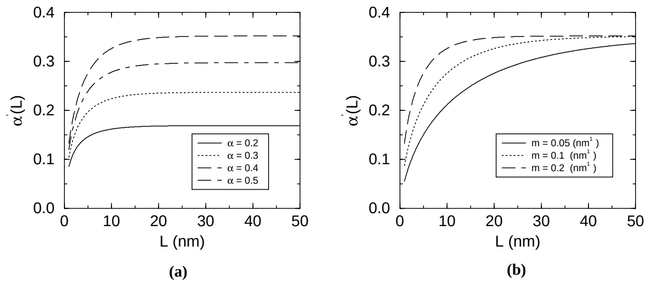
The first term in Eq. (53) is simply the mean-field contribution to P_d, the second (in the same bracket) is the contribution coming from the dependence of J^{vdW} on L via the L dependence of α'. The last term is a form of screened zero frequency van der Waals contribution. In the absence of electrolyte we find that this last term gives a $1/L^3$ Casimir attraction across the film. This can be seen by making the change of variables $p=km$ in the expression for f in Eq. (54) and then taking the limit $m\rightarrow 0$. Clearly when $m=0$ we see that α is also zero since there is no surface charging when there is no electrolyte, and the only length scale in the system is L.

In the presence of electrolyte this interaction is screened [14] and decays exponentially as $\exp(-2mL)$, which is twice as quick as the mean-field contribution to the disjoining pressure which decays as $\exp(-mL)$ for large L. However in the theory presented here, the fluctuation effects contribute an additional term which decays also as $\exp(-mL)$ and hence the fluctuations modify the long distance behavior of P_d. We note that in theories with a fixed surface charge, the long-range component of the disjoining pressure is not altered at one-loop level. The renormalization of the long-range component of the disjoining pressure, as demonstrated here, is specific to charge-regularized models. The strength and sign of this long-range modification of P_d is controlled by $g\Sigma(mL,mh)$, defined in Eq. (51), which can be interpreted as the deviation of $\ln[\sigma(L)]$ from its mean-field value. If the fluctuation effects enhance (reduce) the surface charge, then the long-range value of P_d is increased (decreased) from its mean-field value. The Casimir term is, however, always attractive.

It should be remarked at this stage that to this order, $O(g)$, there will be L-dependent contributions from the non-Gaussian interaction term in ϕ'^4. These contributions can be shown to vanish as $L\rightarrow\infty$ but their effect for finite L must be calculated. However, such a calculation requires the apparatus for the general perturbation theory which we shall present in a forthcoming paper [34].

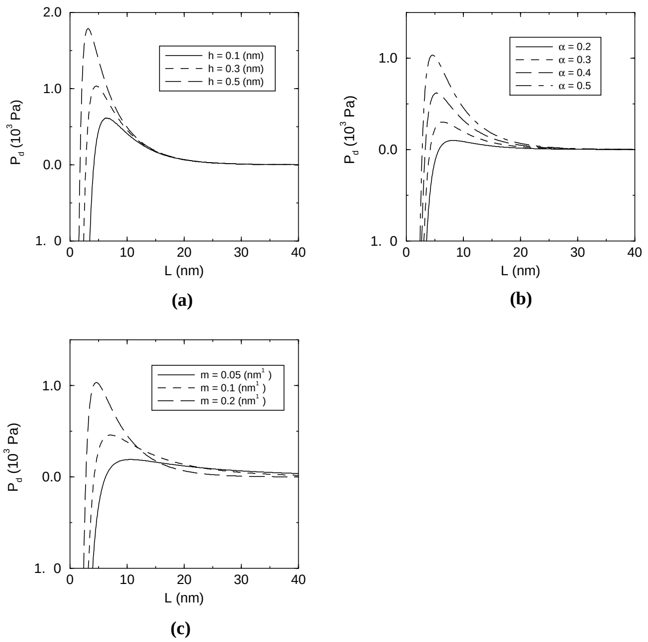
V. DISCUSSION AND CONCLUSION

We have systematically developed a theory for a thin film with a full nonlinear surface-charging mechanism while retaining the free-field theory description for the bulk electrostatic fields. This corresponds to using linear Debye theory in the bulk with fugacity μ but with the fully interacting description of the sources for the charging mechanism of the surfaces. We have applied the theory to a model consisting of a triple-layer system, shown in Fig. 1, in which there is adsorption of cations onto the surface modeled by a surface fugacity μ_+^* and encoded in the dimensionless surface absorption strength parameter $\alpha=m\mu_+^*/2\mu$. At the surface there is a Stern layer of thickness h' from which all ions are excluded, and the film is of thickness L. The dielectric con-



(a) (b)

FIG. 2. The dependence of $\alpha'(L)$ on (a) α and (b) the Debye mass m for the values shown. $\alpha'(L)$ controls the strength of the surface-charging adsorption.



(a) (b) (c)

FIG. 3. The dependence of the disjoining pressure P_d, in units of (10^3 pascal), given in Eq. (53) on (a) the Debye mass m for $h=0.3$ nm, $\alpha=0.5$, (b) α for $h=0.3$ nm, $m=0.2$ nm^{-1}, and (c) the surface layer thickness h for $\alpha=0.5$, $m=0.2$ nm^{-1}. The sensitive dependence of P_d on h shown in (a) is evident as we should expect since the influence of the image charges increases rapidly as h decreases.

stants in what follows will be those for air/water systems where $\epsilon \sim 80\epsilon_0$ in the film and ϵ_0 outside the film. This model for a real surface is too simple but it encodes the important feature that the thermodynamic properties of the film are very strongly dependent on the detailed nature of the surface and its properties. This is due to two features: the charging mechanism which allows the surface charge to remain in equilibrium with the interior charges and the effect of image charges due to the discontinuity in the dielectric constant at the surface. First, we determine the mean-field solution $\phi_c(z)$ using the nonlinear surface operators as the source and then we use the Schrödinger kernel approach to calculate the partition function as an expansion in α and $g=ml_B$, where l_B is the Bjerrum length. Much of the details of this approach have been discussed in an earlier paper [24]. In this paper, we concentrate on the effects of the nonlinear surface-charging mechanism which leads us to introduce an effective, or running, surface-charging parameter $\alpha'(L)$ and we analyze how the behavior of the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ depend on h, α, and m. The formulas summarizing our findings are Eqs. (19) and (50)–(53). Examples of the solutions to these equations are shown in Figs. 2 –7 and we now briefly discuss the salient features of these results.

In Figs. 2(a) and 2(b), and we show $\alpha'(L)$ as a function of L for various values of α and m, respectively. The effective parameter $\alpha'(L)$ controls the strength of the surface-charging mechanism, and from Eq. (17) and what follows, it is clear that $\alpha'(L)\to 0$ as $L\to 0$ which in turn causes σ_{MF} and σ to vanish also in this limit.

In Figs. 3(a), 3(b), and 3(c) we show the dependence of P_d on L given in Eq. (53) for various values of h, α, and m, respectively. From all these figures we see that the characteristic collapse transition is evident but that its strength is very sensitive to the parameter values. In particular, from Fig. 3(a) we see that P_d decreases as h decreases, as we should expect, since the image charges at the surface are repelling the cations and so reducing the surface charge; this effect can be seen directly in Fig. 6(a). The effect on P_d is due to the Σ-dependent term in Eq. (53) which arises because of the implicit L dependence of the free energy through its dependence on $\alpha'(L)$. Note that $\sigma_{MF}(L)$ is independent of h as in this formulation the effect of image charges first comes in at the one-loop level. The dependences of P_d on α and m are shown in Figs. 3(b) and 3(c) and have the expected trends, but again the height of the peak in $P_d(L)$ is strongly dependent on the parameters which have been chosen to take values that can typically be achieved in experiment. In Fig. 4 we show the mean-field and one-loop contributions to $P_d(L)$ for typical parameter values $h=0.3$ (nm), $\alpha=0.5$, and $m=0.2$ (nm^{-1}). In Fig. 5 we compare $P_d(L)$ for the nonlinear theory of this paper, given in Eq. (53), with the linearized theory from Ref. [24] for these same parameter values. Al-

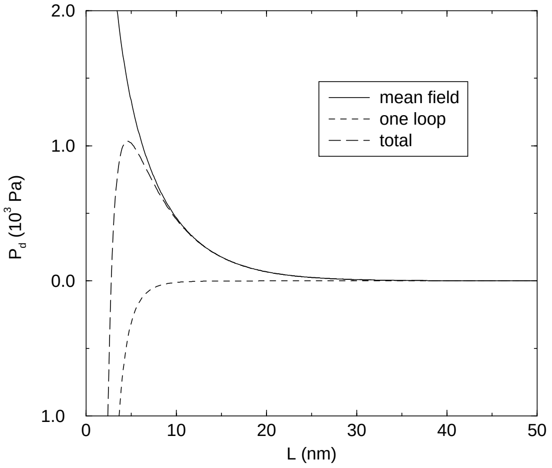


FIG. 4. The disjoining pressure P_d, in units of (10^3 pascal), as a function of L given in Eq. (53) showing the mean-field contribution and the one-loop [$O(g)$] contributions for $h=0.3$ nm, $\alpha=0.5$, and $m=0.2$ nm^{-1}.

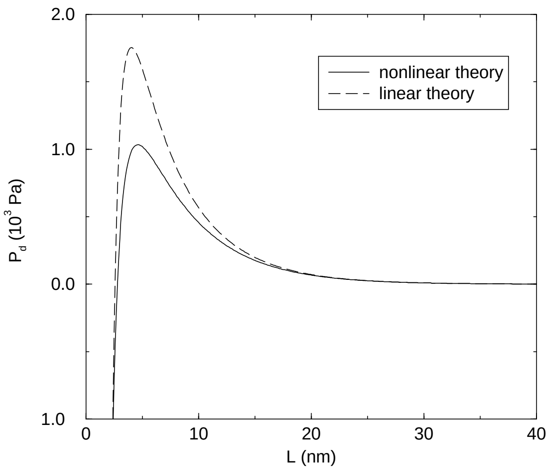


FIG. 5. The disjoining pressure P_d, in units of (10^3 pascal) for the nonlinear theory given in Eq. (53) compared with the linearized theory from Ref. [24] for $h=0.3$ nm, $\alpha=0.5$, and $m=0.2$ nm^{-1}. Although the peak in P_d occurs for much the same value of L, it is lower in the nonlinear theory for this value of h. Since the peak height is strongly dependent on h, we see that a quantitative prediction requires a realistic model for the surface.

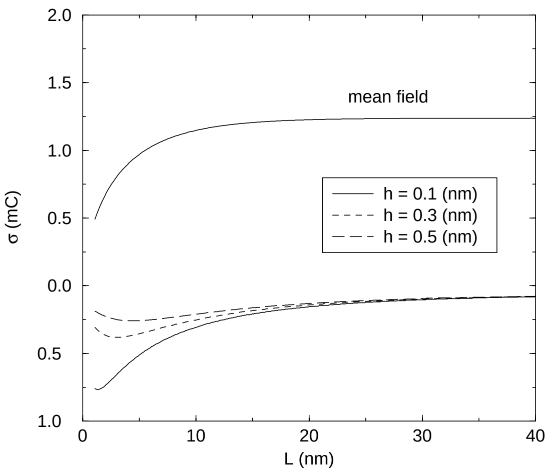
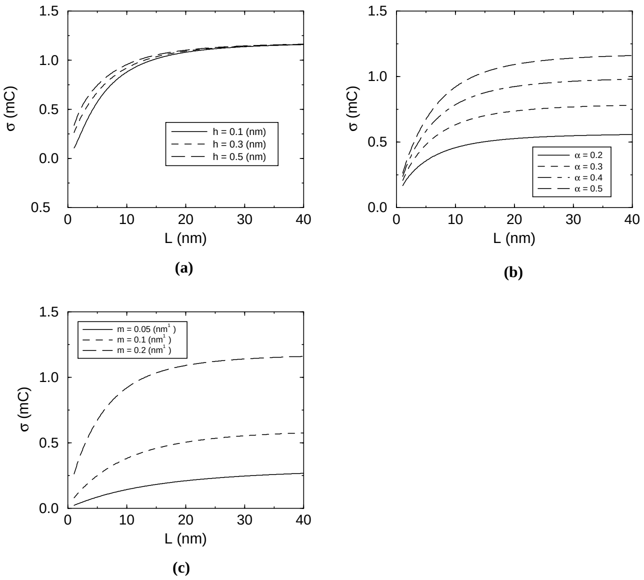


FIG. 7. The surface charge σ in millicoulombs in Eq. (52) showing the mean-field contribution $\sigma_{MF}(L)$ and the one-loop $[O(g)]$ contribution given by $\sigma_{MF}(L)\times g\Sigma(mL,mh)$, where $\Sigma(mL,mh)$ is defined in Eq. (51) for values of h shown and $\alpha=0.5$, $m=0.2$ nm^{-1}. The one-loop contribution is negative and has a minimum before turning to zero as it must since $\alpha'(L)$ [Eq. (19)] and hence $\sigma_{MF}(L)$ vanishes as $L\rightarrow 0$.

though the peak in P_d occurs in much the same place, it is lower in the nonlinear theory for this value of h. Since the peak height is strongly dependent on h, we see that a quantitative prediction requires a realistic model for the surface.

In Figs. 6(a), 6(b), and 6(c) the behavior of the surface charge $\sigma(L)$ given in Eq. (52) as a function of L is shown for various values of h, α, and m, respectively. The behavior of $\sigma(L)$ is dominated by the behavior of the mean-field surface charge $\sigma_{MF}(L)$ to which it is proportional. The important fact is that when the nonlinear surface-charging mechanism is incorporated in the model we find that $\sigma_{MF}(L)$ vanishes as $L\rightarrow 0$ since from Eq. (30) it is proportional to $\alpha'(L)$, the effective strength of the charging mechanism, which vanishes itself in this limit, Eq. (19). We see this effect in Fig. 6(a) where $\sigma(L)$ decreases very strongly with L for small L, but also note that as h decreases the rate of decrease to zero increases so that for $L<1/m_D$ there is a factor of 2 between the values of σ for $h=0.1$ (nm) and $h=0.5$ (nm). However, this is the region in the neighborhood of the collapse, as can be seen from Fig. 3(a), and so it is possible that the model is not accurate in this region. The dependences of $\sigma(L)$ on the bare charging strength α and on the Debye mass m are shown in Figs. 6(b) and 6(c) where the trends based on the above discussion are as expected but, as in the case of P_d the magnitude of $\sigma(L)$ is very sensitive to parameter values. The overall prediction is that $\sigma(L)$ is strongly dependent on L and vanishes as $L\rightarrow 0$. The mean-field and one-loop contributions, which are the first and second terms in Eq. (50), are shown in Fig. 7 for various values of h and $\alpha=0.5$, $m=0.2$ (nm^{-1}), where the insensitivity of σ_{MF} to h is obvious, and the dominance of divergence as $h\rightarrow 0$ for small L in the one-loop contribution is very clear.



(a)

(b)

(c)

FIG. 6. The dependence of the surface charge σ in millicoulombs from Eq. (50) on (a) the Debye mass m for $h=0.3$ nm, $\alpha=0.5$, (b) α for $h=0.3$ nm, $m=0.2$ nm^{-1}, and (c) the surface layer thickness h for $\alpha=0.5$, $m=0.2$ nm^{-1}. We see that σ decreases with L and from (a) that this effect is enhanced as h becomes smaller as we should expect since the image charge repulsion has a greater influence. In our model σ is constrained to vanish as $L\rightarrow 0$ since it is proportional to σ_{MF}, Eq. (52), which vanishes in this limit as discussed in Sec. III.

An important feature of these calculations to note is that the results are expressed as a series in both $\alpha'(L)$ and $g=ml_B$ with resummations where possible. As already noted, the coupling $\alpha'(L)$ is an effective, or running, coupling since it depends on L, whereas α can be considered as a bare coupling which describes the strength of the interaction at the surface. Using $\alpha'(L)$ corresponds to summing an infinite series in α in perturbation theory in Eq. (18). This is crucial for the region $L<l_D$ since the series in α will develop very

large terms as coth($mL/2$) becomes large and so is badly behaved. In contrast, using $\alpha'(L)$ gives an important contribution to the L dependence of the calculated quantities which is well behaved. In addition, we have not expanded the final result as a series in $\alpha'(L)$ since the closed forms presented arise from the evaluation of the field determinant which naturally corresponds to an infinite sum of one-loop diagrams. Such resummations are well known in quantum field theory and renormalization group theory [33]. The coupling g is the strength of the nonlinear interactions and a diagrammatic expansion for perturbation theory generated by the interaction terms in the field ϕ gives a power series in g. The major approximation in this current work is to use the free-field theory within the bulk. This is because the object was to study the effects of the nonlinear surface-charging mechanism and we have shown that these effects are indeed strong and it is clear that any approach which omits them or assumes a constant surface charge will be incorrect. We also conclude that for such finite-size systems characterized by a length scale L we must expect that approximations may break down and some terms become large as L takes an extreme value: $L\rightarrow 0$ in our model. Another example is the surface charge $\sigma(L)$ which physically is non-negative for all L but in the Gaussian approximation clearly changes sign for L small enough, Eq. (50), but where an obvious resummation of an infinite series of selected tadpole graphs, corresponding to exponentiation, ensures that this physical condition is not violated, Eq. (52). The resummation of tadpole subgraphs can still be done at higher orders in perturbation theory and it is the aim of work in hand to systematically study how the perturbative series can be ordered using these ideas.

A consistent control over spurious and artificial infinities must await the full perturbation theory. An example is eluded to in Eq. (42) and what follows. We have indicated how to control such quantities here to the one-loop level and see that even here the analysis is rather delicate. There are, in principle, $O(g)$ terms from interactions (in the term ΔS^*) within the bulk which, as we have shown, vanish as $L\rightarrow\infty$ but contribute finite L effects to P_d and σ, but these terms are not expected to be large. We shall present an analysis of all these topics in a forthcoming paper [34] in which the full nonlinear theory and its perturbation expansion will be studied.

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