

Electrostatic fluctuations in soap filmsD. S. Dean^{1,*} and R. R. Horgan^{2,†}¹IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France²DAMTP, CMS, University of Cambridge, Cambridge, CB3 0WA, United Kingdom

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A field theory to describe electrostatic interactions in soap films, described by electric multilayers with a generalized thermodynamic surface-charging mechanism, is studied. In the limit where the electrostatic interactions are weak, this theory is exactly soluble. The theory incorporates in a consistent way, the surface-charging mechanism and the fluctuations in the electrostatic field that correspond to the zero-frequency component of the van der Waals force. It is shown that these terms lead to a Casimir-like attraction that can be sufficiently large to explain the transition between the common black film to a Newton black film.

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I. INTRODUCTION

Soap films are naturally occurring examples of diffuse double layers [1,2]. They consist of two surfaces formed by hydrophobic surfactants that accumulate at the air-water interface due to the hydrophobic nature of the hydrocarbon chains of the surfactant molecule. In the classic experimental setup to measure the disjoining pressure in soap films, the film is placed in a cell in contact with a bulk solution, usually in a porous frit [3–5,7]. A capillary connecting the bulk solution to the outside of the cell allows the pressure in the cell to be varied and a direct measurement of the disjoining pressure P_d , generated by interactions within the film, is thus possible. The thickness of the film as a function of P_d , along with certain aspects of its structure such as the electronic density, can then be measured by x-ray or optical methods. The interface formed by the surfactant can lead to the formation of a surface charge and, in addition to the surfactant, the bulk can contain an electrolyte such as salt.

The simplest model of a soap film is of two charged surfaces separated by an electrolytic solution. Electrostatic interactions, therefore, play a fundamental role and can be taken into account at the simplest level of approximation by the mean-field Poisson-Boltzmann equation [1,2]. In the simplest of models, the surface charge or surface potential is taken to be fixed and is hence a fitting parameter of the theory. More elaborate theories take into account the mechanism of surface charging [5,6,8,9]. Steric effects between the counterions in the vicinity of the surface, known as the Stern layer, may also be incorporated [10]. Local modifications of the dielectric constant due to the presence of ions may also be incorporated [11,12]. In general, the disjoining pressure predicted in the mean-field formulations of such theories is repulsive (see later comments however). In a detailed experimental study of soap films formed by ionic surfactants such as sodium dodecyl sulfate (SDS) [5], it was shown that a modified Poisson-Boltzmann theory incorporating an energetic surface-charging mechanism, via an attractive free-energy potential at the film surface, can predict the surface

tension of the bulk solution. Then, with no free-fitting parameters remaining, the theory predicts the disjoining pressure of the films made from this bulk, just up to a pressure where the common black film (CBF) collapses and forms a Newton black film (NBF). The NBF is an extremely thin film where experiments [13] show that there is an extremely small separation between the two surfactant surfaces (about one layer of water molecules across). The CBF-NBF transition is experimentally interpreted as a first-order phase transition [7], and the body of theoretical work supports this interpretation. The rough picture, coming from the approximate theories that exist, is that at large distances the disjoining pressure is repulsive and stabilizes the CBF. At closer intersurface distances attractive van der Waals forces come into play, which are responsible for the eventual collapse to the NBF. Other important considerations in the physics of electric bilayers are the possibility of the ions in the surface charge forming a Wigner crystal [14] (at sufficiently low temperatures) and the role of film surface flexibility on the interaction between charged membranes [15].

The aim of this paper is to analyze the role of electrostatic fluctuations in the presence of generic surface-charging mechanisms and spatially varying dielectric constants in diffuse layer systems. Previous studies incorporating the fluctuations about the mean-field Poisson-Boltzmann theory in simpler models have revealed that these fluctuations lead to attractive interactions [16–18]. How these electrostatic fluctuations manifest themselves in terms of ion and counterion fluctuations has also been studied [19,20]. The analysis here is adapted to the limit of weak electrostatic interactions. We use a field theoretic formulation of the problem, which in addition to producing new results for fluctuating surface charges, allows one to recover, in a powerful and universal way, many results already established in the literature. In addition, our formulation is well adapted to develop a perturbative expansion that allows one to incorporate higher-order interactions.

The Poisson-Boltzmann theory may be supplemented by including the contribution of dispersion forces or van der Waals forces calculated from the Hamaker theory based on pairwise dipole interactions and, at a more sophisticated level, via the continuum Lifshitz theory [21]. The resulting Derjaguin-Landau-Verwey-Overbeek (DLVO) [1,2] theory

*Email address: dean@irsamc.ups-tlse.fr

†Email address: rrh@damtp.cam.ac.uk

has been very successful in describing the physics of electric double layers. However, the splitting of the overall interaction into a Poisson-Boltzmann static interaction and the van der Waals forces as two distinct and independent interactions is artificial from a global view point. The fluctuations of the full theory of the electrostatic interactions generate the zero-frequency van der Waals interaction. However, since the ion distributions do not respond to high-frequency fields, the nonzero frequency contributions to the van der Waals forces can be taken to be effectively independent of the ionic distribution. The zero-frequency contributions between neutral surfaces or surfaces with absorbed mobile ions or dipoles can be treated and one finds that the zero-frequency van der Waals forces become screened by the presence of an electrolyte [22]. In the context of the Debye-Hückel approximation these van der Waals forces have a formally identical origin to the Casimir effect, where the suppression of fluctuations of the electromagnetic field due to the presence of two surfaces leads to a net attractive force. The appearance of such generalized Casimir forces in soft condensed matter systems and many other contexts is now well established [23–25].

The theory proposed for electrolytic soap films in Ref. [5] can in fact be solved exactly in one dimension [26], via path integral techniques originally developed in Ref. [27]. In this exact theory one finds that the disjoining pressure is repulsive at large distances but attractive contributions come into play at smaller intersurface separations and can lead to a disjoining pressure isotherm predicting a collapse to a thinner film state at a certain thickness, as is seen in experiments. Attractive forces in the two-dimensional form of this model have also been found [28] at a particular critical temperature where the model is exactly soluble. In this paper we revisit the theory of Ref. [5] but in three dimensions. We use a field theory representation of the system in the weak coupling limit, equivalent to the region where the Debye-Hückel approximation is valid, where the field theory is free and one may decouple the Fourier components of the field and apply standard path integral results. This allows one to incorporate a thermodynamic or energetic surface-charging mechanism in a straightforward way and also allows one to take into account spatially varying dielectric constants. In principle the solution of the free-field theory can be written down in terms of a functional determinant that may be evaluated via functional techniques [11,22,29–33]; these functional techniques could also be applied here; however, the path integral method gives a very compact and rapid solution to the problem.

Recent experimental studies of the CBF-NBF transition have been carried out on nonionic soap films made with the surfactant $C_{12}E_6$ [7]. These films can be stabilized in the presence of small concentrations of electrolyte and are thus in a region where the linearized Poisson-Boltzmann equation can be used for the mean-field treatment and also where the free- or Gaussian-field theory we examine should be valid.

II. THE MODEL AND SURFACE-CHARGING MECHANISMS

Here we explain the derivation of the type of model proposed in Refs. [5,26] but with a generic surface-charging

mechanism or depletion interactions at the surface. We consider the case of a monovalent electrolyte for simplicity. In the presence of the surface, a surface charge may be generated by two basic mechanisms. First, as was taken to be the case in Refs. [5,9,26], there may be an affinity for one of the species to be on the surface. In the case of SDS, or other ionic films, this species is the soap tail as, due to the hydrophobic effect, the hydrocarbon tail lowers the free energy of the system by leaving the aqueous core and entering the air environment at the exterior of the film. The head of the surfactant, SO_4^- for SDS, is, however, negatively charged, thus leading to a surface charge. In the case of nonionic soap films the surface-charging mechanism is due to a difference in mobility of the ions. Hydration effects can make one species effectively larger than another, thus leading to a steric repulsion at the surface and hence an effective charge is induced by the un-neutralized presence of the other species. The enhancement of the repulsion between the surfaces of ionic Aerosol-OT films due to more hydrated counterions, e.g., LiCl instead of CsCl, has been experimentally demonstrated in Ref. [34]. Let us consider a model with one salt species (water is also partially dissociated and indeed plays an important role in the absence of salt), the generalization to several species is straightforward.

Let us denote by $V_1(x)$ and $V_{-1}(x)$ the effective potential for the cations and anions, respectively, due to the surfaces of the film. The Hamiltonian for the electrolyte system is thus

$$H = \frac{1}{2} e \sum_i \psi(\mathbf{x}_i) q_i + \sum_i V_{q_i}(\mathbf{x}_i), \quad (1)$$

where the first term is the electrostatic energy with potential ψ , $q_i = \pm 1$ if particle i is a cation/anion, respectively, and \mathbf{x}_i its position. The second term is the boundary interaction. We denote by L the perpendicular distance between the two surfaces (in the direction z) and by A the surface area of the film [in the plane (x,y)]. We denote by $A \times L$ the region inside the film and by $A \times T$ the region outside the film. The total length of the system in the z direction is denoted by U and therefore $T = U - L$. To start with, we ignore the fact that just outside the surface one has a density of hydrocarbon tails (this will be taken into account very simply later on). The calculation for a triple layer in the absence of surface charging and electrolyte can be found in Refs. [35,37]. In this two-layer picture, therefore, the dielectric constant has the form $\epsilon(\mathbf{x}) = \epsilon$ for $\mathbf{x} \in A \times L$, where ϵ is the dielectric constant of the electrolyte solution, which in the dilute limit we shall consider to be the dielectric concentration of water. Outside the film we have $\epsilon(\mathbf{x}) = \epsilon_0$ ($\mathbf{x} \in A \times T$), where ϵ_0 is the dielectric constant of air. The difference between the internal and external dielectric constants means that one needs to take into account image charges and the zero-frequency terms of the Lifshitz theory, however, this is automatically incorporated in the field-theoretic formulation of the theory.

The electrostatic potential ψ satisfies the Poisson equation

$$\nabla \cdot \epsilon(\mathbf{x}) \nabla \psi(\mathbf{x}) = -e \sum_i q_i \delta(\mathbf{x} - \mathbf{x}_i). \quad (2)$$

We follow the standard method for converting a Coulomb system to a sine-Gordon-like field theory (see, for example, Ref. [11]) by performing a Hubbard-Stratonovich transformation with an auxiliary field ϕ to obtain the grand canonical partition function

$$\Xi = \int d[\phi] \exp(S[\phi]), \quad (3)$$

where

$$S[\phi] = -\frac{1}{2} \int_{(T+L) \times A} \beta \epsilon(\mathbf{x}) (\nabla \phi)^2 d\mathbf{x} + \mu \int_{L \times A} \exp(i\beta e \phi - \beta V_1(\mathbf{x})) d\mathbf{x} \mu \int_{L \times A} \exp[-ie\beta\phi - \beta V_{-1}(\mathbf{x})] d\mathbf{x} \quad (4)$$

and where μ is the fugacity of the cations and anions. It should be noticed that the Hubbard-Stratonovich transformation is over all space and hence the first, kinetic, term of the action is an integral over all space denoted $(T+L) \times A$ and the second two terms are the interaction terms restricted to the film region $L \times A$. We notice that the functional integral gives the ion-ion interaction upon performing the integral but, in addition, there is a term

$$\int d[\phi] \exp\left(\frac{\beta}{2} \int \phi \nabla \cdot \epsilon(\mathbf{x}) \nabla \phi d\mathbf{x}\right) = [\det(-\nabla \cdot \epsilon(\mathbf{x}) \nabla)]^{-1/2}. \quad (5)$$

This term is, however, the zero frequency contribution coming from the Lifshitz theory and in fact should be there [11]. This term naturally arises when one considers the full quantum electrodynamics (QED) of the system. If one fixes the positions of the ions and ignores the magnetic part of the Lagrangian, the time-independent (zero Matsubara frequency) purely electrostatic part of the Lagrangian is [38]

$$\mathcal{L}[\psi] = \frac{1}{2} \int \epsilon(\mathbf{x}) (\nabla \psi)^2 d\mathbf{x} - e \sum_i q_i \psi(\mathbf{x}_i), \quad (6)$$

hence the thermal field theory for the field ψ has a partition function [39]

$$Z = \int d[\psi] \exp(\beta \mathcal{L}[\psi]). \quad (7)$$

If one now takes a classical trace over the ion positions and passes to the grand canonical ensemble, one finds the expression for the grand potential above after changing the axis of the functional integration via $\psi \rightarrow -i\phi$. If one wishes to take into account the nonzero frequency Lifshitz terms one proceeds as above but keeping the full QED action and introducing the bosonic Matsubara frequencies $\omega_n = 2\pi n / \beta \hbar$ [39]. Hence the grand partition function Ξ contains the ionic interactions and zero frequency van der Waals contributions in the system. We define a Stern layer or depletion layer to be the region where either or both of the potentials $V_{\pm 1}$ are non-zero and take the width of this region to be δ , one can then say that δ sets a range for the depletion interactions. The action then has the form

$$S[\phi] = -\frac{1}{2} \int_{(T+L) \times A} \beta \epsilon(\mathbf{x}) (\nabla \phi)^2 d\mathbf{x} + 2\mu \int_{L \times A} \cos(\beta e \phi) d\mathbf{x} + \mu \int_{[0, \delta] \times A} \exp(i\beta e \phi) \{\exp[-\beta V_1(\mathbf{x})] - 1\} d\mathbf{x} + \mu \int_{[L-\delta, L] \times A} \exp(i\beta e \phi) \{\exp[-\beta V_1(\mathbf{x})] - 1\} d\mathbf{x} + \mu \int_{[0, \delta] \times A} \exp(-i\beta e \phi) \{\exp[-\beta V_{-1}(\mathbf{x})] - 1\} d\mathbf{x} + \mu \int_{[L-\delta, L] \times A} \exp(-i\beta e \phi) \{\exp[-\beta V_{-1}(\mathbf{x})] - 1\} d\mathbf{x}. \quad (8)$$

We now take δ to be small and take the limit $\delta \rightarrow 0$ choosing

$$\exp[-\beta V_{\pm 1}(\mathbf{x})] - 1 \rightarrow \mu_{\pm}^* [\delta(z) + \delta(L-z)] \quad (9)$$

where $\delta(z)$ is the one dimensional Dirac δ function. Clearly, μ_{\pm}^* is positive/negative for $V_{\pm 1}$ negative (attraction of the species towards the surface)/positive (repulsion of the species from the surface). Note that dimensionally $[\mu_{\pm}^*] = [\mu][\delta]$. In this simplified limit, the action is now

$$S[\phi] = -\frac{1}{2} \int_{(T+L) \times A} \beta \epsilon(\mathbf{x}) (\nabla \phi)^2 d\mathbf{x} + 2\mu \int_{L \times A} \cos(\beta e \phi) d\mathbf{x} + \mu_{+}^* \int_{L \times A} [\delta(z) + \delta(L-z)] \exp(i\beta e \phi) d\mathbf{x} + \mu_{-}^* \int_{L \times A} [\delta(z) + \delta(L-z)] \exp(-i\beta e \phi) d\mathbf{x}. \quad (10)$$

In the weak-coupling limit we proceed by expanding the action to quadratic order in all terms, yielding the Gaussian action

$$S_G[\phi] = -\frac{1}{2} \int_{(T+L) \times A} \beta \epsilon(z) (\nabla \phi)^2 d\mathbf{x} - \frac{1}{2} \int_{L \times A} \beta \epsilon m^2 \phi^2 d\mathbf{x} + i\lambda \left(\int_{z=0} \phi dx dy + \int_{z=L} \phi dx dy \right) - \frac{1}{2} \beta \epsilon m^2 \gamma \left(\int_{z=0} \phi^2 dx dy + \int_{z=L} \phi^2 dx dy \right) + 2\mu AL + 2(\mu_+^* + \mu_-^*)A. \quad (11)$$

Here $m = \sqrt{2\mu e^2 \beta / \epsilon}$ corresponds to the Debye mass (the inverse Debye length) in the dilute, weak-coupling limit, as in this limit $\mu \approx \rho$, where ρ is the bulk electrolyte concentration. In addition, we have

$$\lambda = e\beta(\mu_+^* - \mu_-^*) \equiv m^2 \bar{\gamma}, \quad \bar{\gamma} = \frac{\mu_+^* - \mu_-^*}{2\mu} \quad \gamma = \frac{\mu_+^* + \mu_-^*}{2\mu} \quad (12)$$

and we recall $\epsilon(z) = \epsilon$ for $z \in [0, L]$ and is equal to ϵ_0 elsewhere. We now express ϕ in terms of its Fourier decomposition in the $\mathbf{r} = (x, y)$ plane.

$$\phi(\mathbf{r}, z) = \frac{1}{\sqrt{A}} \sum_{\mathbf{p}} \tilde{\phi}(\mathbf{p}, z) \exp(i\mathbf{p} \cdot \mathbf{r}) \quad (13)$$

where if $A = l \times l$ imposing periodic boundary conditions yields $\mathbf{p} \in (2\pi/l)(n_x, n_y)$ with $(n_x, n_y) \in Z^2$. In terms of the fields $\tilde{\phi}$, the action decouples and one obtains

$$S_G = S_0[\tilde{\phi}(0)] + \sum_{\mathbf{p} \neq 0} S_{\mathbf{p}}[\tilde{\phi}(\mathbf{p})] + 2\mu AL + 2(\mu_+^* + \mu_-^*)A, \quad (14)$$

where

$$S_0[\tilde{\phi}(0)] = -\frac{1}{2} \int_{T+L} \beta \epsilon(z) \left(\frac{\partial \tilde{\phi}(0, z)}{\partial z} \right)^2 dz - \frac{1}{2} \beta \epsilon m^2 \int_L \tilde{\phi}^2(0, z) dz + i\lambda \sqrt{A} [\tilde{\phi}(0, 0) + \tilde{\phi}(0, L)] - \frac{1}{2} \beta \epsilon \gamma m^2 [\tilde{\phi}^2(0, 0) + \tilde{\phi}^2(0, L)] \quad (15)$$

and

$$S_{\mathbf{p}}[\tilde{\phi}(\mathbf{p})] = -\frac{1}{2} \int_{T+L} \beta \epsilon(z) \left(\frac{\partial \tilde{\phi}(\mathbf{p}, z)}{\partial z} \frac{\partial \tilde{\phi}(-\mathbf{p}, z)}{\partial z} + \mathbf{p}^2 \tilde{\phi}(\mathbf{p}, z) \tilde{\phi}(-\mathbf{p}, z) \right) dz - \frac{1}{2} \beta \epsilon m^2 \int_L \tilde{\phi}(\mathbf{p}, z) \tilde{\phi}(-\mathbf{p}, z) dz. \quad (16)$$

The system therefore decomposes into a system of simple harmonic oscillators and

$$\Xi = \mathcal{N} \exp[2\mu AL + 2A(\mu_+^* + \mu_-^*)] \int d[\tilde{\phi}(0)] \exp[S_0] \prod_{\mathbf{p} \neq 0} d[\tilde{\phi}(\mathbf{p})] \exp[S_{\mathbf{p}}], \quad (17)$$

wherein the following \mathcal{N} will be used to note L -independent normalization factors. Each oscillator (labeled by \mathbf{p}) has a time-dependent Hamiltonian

$$H_{\mathbf{p}} = -\frac{1}{2M(z)} \frac{d^2}{dX^2} + \frac{1}{2} M(z) \omega^2(\mathbf{p}, z) X^2 \quad (18)$$

where $M(z) = \beta \epsilon(z)$ and $\omega(\mathbf{p}, z) = \sqrt{\mathbf{p}^2 + m^2}$ for $z \in [0, L]$ and $\omega(\mathbf{p}, z) = |\mathbf{p}| = p$ for $z \notin [0, L]$. Here X represents the field $\phi(\mathbf{p})$ and z corresponds to the temporal coordinate. The mode $\mathbf{p} = 0$ is slightly more complicated due to the presence of a linear source term. One may write

$$\int d[\tilde{\phi}(0)]\exp[S_0]=\mathcal{N}_0\text{Tr}\exp[-(U-L)H_E]\exp\left(i\lambda\sqrt{A}X-\frac{1}{2}\beta\epsilon m^2\gamma X^2\right)\exp(-LH_F)\exp\left(i\lambda\sqrt{A}X-\frac{1}{2}\beta\epsilon m^2\gamma X^2\right), \quad (19)$$

where H_E is the Hamiltonian outside the film with mass $M_E=\beta\epsilon_0$ and $\omega_E=0$ and H_F is the Hamiltonian in the film with $M_F=\beta\epsilon$ and $\omega_F=m$ (subscripts E and F will be used to denote the masses and frequencies external and internal to the film, respectively). In the limit where $U\rightarrow\infty$, only the eigenstate of H_E of the lowest energy survives the thermodynamic limit (we shall see later that this is compatible with the constraint of electroneutrality within the film at mean-

field level). We recall that the ground-state wave function of the simple harmonic oscillator is given up to a normalization by

$$\psi_0(X,M,\omega)=\exp\left(-\frac{M\omega X^2}{2}\right) \quad (20)$$

and the corresponding ground-state energy is $\frac{1}{2}\omega$. In the case where $\mathbf{p}=0$ one has the ground-state wave function $\psi_0(X,M_E,0)=1$. Using this in Eq. (19) thus yields

$$\int d[\tilde{\phi}(0)]\exp[S_0]=\mathcal{N}_0\int\exp\left(i\lambda\sqrt{A}X-\frac{1}{2}M_F m^2\gamma X^2\right)K(X,Y,L,\omega_F,M_F)\exp\left(i\lambda\sqrt{A}Y-\frac{1}{2}M m^2\gamma Y^2\right)dXdY, \quad (21)$$

where $K(X,Y,L,\omega,M)$ is the Feynman kernel for the simple harmonic oscillator [38] and is given by

$$K(X,Y,L,\omega,M)=\left(\frac{M\omega}{2\pi\sinh(\omega L)}\right)^{1/2}\exp\left(-\frac{1}{2}M\omega\coth(\omega L)[X^2+Y^2-2XY\text{sech}(\omega L)]\right). \quad (22)$$

Performing the above integral yields a term extensive in A coming from the linear source term and a nonextensive fluctuation term, that we shall absorb into the normalization term, yielding

$$\frac{\ln\left(\int d[\tilde{\phi}(0)]\exp[S_0]\right)}{A}=-\frac{\lambda^2[m\gamma\sinh(mL)+\cosh(mL)+1]}{\beta\epsilon m[(m^2\gamma^2+1)\sinh(mL)+2m\gamma\cosh(mL)]}. \quad (23)$$

This term can be simplified slightly giving the zero-momentum contribution to the grand potential per area of the film. Writing $J=-\ln(\Xi)/(\beta A)=J_c+\sum_{\mathbf{p}}J_{\mathbf{p}}$, where

$$J_c=-\frac{2}{\beta}(\mu L+\mu_+^*+\mu_-^*), \quad (24)$$

is the ideal part of the grand potential, we find

$$\beta J_0=2m\mu\bar{\gamma}^2\frac{\cosh\left(\frac{mL}{2}\right)}{\sinh\left(\frac{mL}{2}\right)+m\gamma\cosh\left(\frac{mL}{2}\right)}. \quad (25)$$

In fact we shall see later, as should be expected, that this term is the mean-field contribution to the theory.

The nonzero momentum modes only contribute to the fluctuations but summed together give an extensive contribution. The contribution to the grand partition function of one of these modes is

$$\int d[\tilde{\phi}(\mathbf{p})]\exp[S_{\mathbf{p}}]=\mathcal{N}_{\mathbf{p}}\text{Tr}\left[\exp\left(-\frac{M_E\omega_E X^2}{2}\right)\exp[-(U-L)H_E]\exp\left(-\frac{1}{2}\beta\epsilon m^2\gamma X^2\right)\exp(-LH_F)\right. \\ \left.\times\exp\left(-\frac{1}{2}\beta\epsilon m^2\gamma X^2\right)\exp\left(-\frac{M_E\omega_E X^2}{2}\right)\right]. \quad (26)$$

Note that there is no undercounting in this contribution as the field ϕ was real and hence $\tilde{\phi}(p)=\tilde{\phi}(-p)$. One thus obtains

$$\int d[\tilde{\phi}(\mathbf{p})] \exp[S_{\mathbf{p}}] = \mathcal{N}_{\mathbf{p}} \exp\left(-\frac{U-L}{2} \omega_E\right) \int \exp\left(-\frac{M_E \omega_E X^2}{2} - \frac{1}{2} M_F m^2 \gamma X^2\right) K(X, Y, L, \omega_F, M_F) \\ \times \exp\left(-\frac{M_E \omega_E Y^2}{2} - \frac{1}{2} M_F m^2 \gamma Y^2\right) dX dY. \quad (27)$$

This yields an L -dependent contribution to the grand potential per unit area of

$$J_{\mathbf{p}} = -\frac{1}{A\beta} \left[\frac{1}{2} L(p - \sqrt{p^2 + m^2}) - \frac{1}{2} \ln \left\{ 1 - \left(\frac{\epsilon_0 p + \epsilon m^2 \gamma - \epsilon \sqrt{p^2 + m^2}}{\epsilon_0 p + \epsilon m^2 \gamma + \epsilon \sqrt{p^2 + m^2}} \right)^2 \exp(-2L\sqrt{p^2 + m^2}) \right\} \right]. \quad (28)$$

The total contribution from the modes $\mathbf{p} \neq 0$ is the grand potential associated with the static electrostatic fluctuations, or the zero-frequency van der Waals force, hence we write $J_{vdW} = \sum_{\mathbf{p} \neq 0} J_{\mathbf{p}}$. We should remark, however, given the unified treatment used here, this notation is slightly arbitrary as with the definition used here J_{vdW} contains terms coming from the ionic fluctuations. The first term in the expression (28) will clearly lead to an ultraviolet divergence in the grand potential, however, the disjoining pressure $P_d(L)$ is given by the difference between the film and bulk pressures

$$P_d(L) = P(L) - P_{\text{bulk}} = -\frac{\partial J(L)}{\partial L} + \lim_{L \rightarrow \infty} J(L)/L = -\frac{\partial J^*(L)}{\partial L}. \quad (29)$$

After summing over all values of \mathbf{p} , by passing to the continuum for large A , we obtain the divergence-free result

$$\beta J^*(L) = \frac{1}{4\pi} \int_0^\infty dp p \ln \left[1 - \left(\frac{\epsilon_0 p + \epsilon m^2 \gamma - \epsilon \sqrt{p^2 + m^2}}{\epsilon_0 p + \epsilon m^2 \gamma + \epsilon \sqrt{p^2 + m^2}} \right)^2 \exp(-2L\sqrt{p^2 + m^2}) \right] + 2m\mu\bar{\gamma}^2 \frac{\cosh\left(\frac{mL}{2}\right)}{\sinh\left(\frac{mL}{2}\right) + m\gamma \cosh\left(\frac{mL}{2}\right)} \\ = \beta J_{vdW}^*(L) + \beta J_0(L). \quad (30)$$

From Eq. (29) it is clear that $J^*(L)$ is the effective interaction potential between the two surfaces.

The bulk grand potential contains the extensive contribution that itself contains the divergence. By taking the difference, we have concentrated on the part relevant to the calculation of the disjoining pressure. However, it is instructive to remark that the extensive term in Eq. (28) is the term in the bracket that is explicitly proportional to L . It can be shown that on integration this term does indeed give the standard Debye-Hückel expression for the pressure. It is, in fact, the one-loop contribution similar to that explicitly discussed in the one-dimensional (1D) model in Ref. [26]. The difference in the 3D case is that the integral is divergent and so must be renormalized. The divergence for this integral is due to the self-energy of the charge distribution included in the original definition of the partition function. It can be removed by imposing the renormalization condition that the fugacity μ be chosen so that the density is given by

$$\rho V = -\frac{\mu}{\beta} \frac{\partial \ln \Xi}{\partial \mu},$$

where V is the system volume. μ is then a bare quantity that is a function of the ultraviolet cutoff. It can be shown that when the appropriate one-loop calculations are performed, the bulk pressure is finite and is given by

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

Where they are important the UV divergences will ultimately be regulated by the finite size of the ions. However, these contributions will be corrections and it will be possible to estimate their importance using perturbative methods. The details will be postponed to a further paper that will report on the perturbative approach in general. The renormalization of μ is not of relevance to what follows but is central to higher-order corrections.

III. VARIOUS LIMITS

To demonstrate the generality of the formalism here and its compatibility with well-established results in the literature derived by other means, we shall consider various limits of the formulas derived above.

A. Mean field limit

The mean-field theory for the action (11) is obtained from the equation

$$\frac{\delta}{\delta \phi(\mathbf{x})} S_G[\phi] = 0. \quad (31)$$

This yields the equation

$$\begin{aligned} & \beta \nabla \cdot \epsilon \nabla \phi - m^2 \beta \epsilon \phi + i\lambda [\delta(z) + \delta(z-L)] \\ & - \beta \epsilon m^2 \gamma \phi [\delta(z) + \delta(z-L)] = 0 \end{aligned} \quad (32)$$

within the film. Outside the film one has

$$\beta \nabla \cdot \epsilon_0 \nabla \phi = 0. \quad (33)$$

As is usual for Euclidean Sine-Gordon field theories, the physical saddle point is imaginary, one writes $\phi = i\psi$ and it turns out that ψ is the mean-field electrostatic potential, this is also clear from the static QED formulation (7). In addition, the mean-field solution depends only on the coordinate z . From Eq. (33) one finds that outside the film $d\psi/dz = 0$, which is simply the condition of electroneutrality in the film. Inside the film (strictly away from $z=0$ and $z=L$) one has therefore

$$\beta \epsilon \left(\frac{d^2}{dz^2} \psi - m^2 \psi \right) = 0, \quad (34)$$

which is simply the linearized Poisson-Boltzmann equation. The solution to this equation, which gives a potential symmetric about the film's midpoint $z=L/2$, is

$$\psi(z) = C \cosh \left[m \left(z - \frac{L}{2} \right) \right]. \quad (35)$$

Integrating the mean-field equation between $z=0^-$ and $z=0^+$, and using the condition of electroneutrality, one finds

$$\beta \epsilon \left. \frac{d\psi}{dz} \right|_{z=0^+} - \beta \epsilon m^2 \gamma \psi(0) + \lambda = 0. \quad (36)$$

This allows one to solve for C giving

$$C = \frac{\lambda}{\beta \epsilon m \left[\sinh \left(\frac{mL}{2} \right) + m \gamma \cosh \left(\frac{mL}{2} \right) \right]}. \quad (37)$$

Substituting this mean-field solution into the expression (11) for S_G , yields the mean-field action that is exactly the expression (25) obtained from the zero-momentum contribution in the previous analysis.

B. No electrolyte, no surface charging

This amounts to calculating the zero van der Waals forces across a slab of dielectric constant ϵ while the dielectric constant of the external media is given by ϵ_0 . Here one has

$$J^*(L) = \frac{k_B T}{4\pi} \int_0^\infty dp p \ln \left[1 - \left(\frac{\epsilon_0 - \epsilon}{\epsilon_0 + \epsilon} \right)^2 \exp(-2Lp) \right]. \quad (38)$$

The integral above is easily evaluated by expanding the logarithm leading to

$$J^*(L) = - \frac{k_B T}{16\pi L^2} \sum_{n=1}^\infty \frac{1}{n^3} \left(\frac{\epsilon - \epsilon_0}{\epsilon + \epsilon_0} \right)^{2n}. \quad (39)$$

This yields the attractive, Casimir-like, disjoining pressure [22,32]

$$P_d(L) = - \frac{k_B T}{8\pi L^3} \sum_{n=1}^\infty \frac{1}{n^3} \left(\frac{\epsilon - \epsilon_0}{\epsilon + \epsilon_0} \right)^{2n}. \quad (40)$$

C. No surface charging

If one considers the limit where there is no interaction between the ions and the surface one has $\mu_+^* = \mu_-^* = 0$ and hence $\gamma = 0$. This is the case of an electrolyte confined by two neutral surfaces (in both the electrostatic and chemical sense) but with a medium of dielectric constant ϵ_0 outside the film and dielectric constant ϵ inside the film. One thus obtains

$$\begin{aligned} J^*(L) &= \frac{k_B T}{4\pi} \int_0^\infty dp p \ln \left[1 - \left(\frac{\epsilon_0 p - \epsilon \sqrt{p^2 + m^2}}{\epsilon_0 p + \epsilon \sqrt{p^2 + m^2}} \right)^2 \right. \\ &\quad \left. \times \exp(-2L\sqrt{p^2 + m^2}) \right]. \end{aligned} \quad (41)$$

This thus recovers the result of Ref. [22] demonstrating the screening of the zero-frequency van der Waals interaction in the presence of an electrolyte.

D. Localized surface charge fluctuations

It is easy to see that the term proportional to γ in the action (11) is a term proportional to the surface charge fluctuation about its mean value. The effect of surface charge fluctuations in the limit where the counterions are highly localized about the surface was considered in Refs. [32] and [6]. In Ref. [32] the problem was considered in the strong- and weak-coupling Debye-Hückel regime, in this regime the electrostatic fluctuations lead to the computation of a mathematically identical determinant in both Refs. [32] and [6] and the electrostatic fluctuations in our model also have the same mathematical structure. The differences between [6,32] and our model are in terms of the physical interpretation at this level. In the case of nonvarying dielectric constant (for instance, the case of two membranes interacting in water) the contribution to the disjoining pressure coming from the electrostatic fluctuations or the zero-frequency van der Waals term $P_d^{(vdW)}(L)$ is given by taking $m=0$ within the film. Immediately one obtains

$$P_d^{(vdW)}(L) = - \frac{k_B T}{2\pi} \int dp \frac{p^2}{[\exp(2pL)(1+p\bar{\lambda})^2 - 1]} \quad (42)$$

where $\bar{\lambda} = 2/m^2\gamma$. The expression (42) is up to the definition of $\bar{\lambda}$ the same as obtained in Refs. [32] and [6].

In Ref. [32] the problem of localized surface charging but with varying dielectric constant, that outside the film being different to that within the film, was also considered. In Ref. [36] the model of Ref. [6] was studied incorporating the same dielectric constant variation. However, at a mathemati-

cal level the calculation of the electrostatic fluctuations in Refs. [32,36] and here is again identical. Here we find that the contribution from the electrostatic fluctuations is

$$P_d^{(vdw)}(L) = -\frac{k_B T}{2\pi} \times \int dp \left[\frac{p^2}{\exp(2pL) \left(\frac{(\epsilon + \epsilon_0)p + \epsilon m^2 \gamma}{(\epsilon - \epsilon_0)p + \epsilon m^2 \gamma} \right)^2 - 1} \right]. \quad (43)$$

This equation agrees with the result of Ref. [32] (in the Debye-Hückle regime) which is obtained there by calculating the contribution of the ionic fluctuations and then adding the contribution coming from the zero-frequency Lifshitz terms. In Ref. [36] only the ionic fluctuations were included and hence the result differs from ours and that of Ref. [32] by the zero-frequency Lifshitz term.

E. Including the nonzero frequency van der Waals contribution

Let us mention that if one wanted to now take into account nonzero-frequency contributions from the Lifshitz

theory, which are in principle uncoupled or very weakly coupled to the static ionic fluctuations, one should use a total potential

$$J_T(L) = J^*(L) + \sum_{\omega \neq 0} J_{\text{Lif}}(\omega, L) \quad (44)$$

where $J_{\text{Lif}}(\omega, L)$ is the contribution to the dispersion potential coming from the Matsubara frequency ω in the absence of an electrolyte. As mentioned previously, in the formulation here, the zero-frequency Lifshitz and ionic components are treated together in the grand partition function Ξ .

IV. THE TRIPLE LAYER

As mentioned earlier, the change in the dielectric constant due to the presence of the hydrocarbon layer formed just outside the surface of the soap film by the surfactant should also be taken into account. If one considers this to be a region of size h at either interface, but inaccessible to the aqueous solution, one now has a different Hamiltonian H_H (where the subscript H denotes the hydrocarbon region) in these regions characterized, for a mode \mathbf{p} , by $\omega_H = p$ and $M_H = \beta \epsilon_1$, where ϵ_1 is the dielectric constant of this hydrocarbon region (strictly this is a mixture of air-hydrocarbon chains). Using the formalism developed here one finds that the mode \mathbf{p} yields a contribution

$$\int d[\tilde{\phi}(\mathbf{p})] \exp[S_{\mathbf{p}}] = \mathcal{N}_{\mathbf{p}} \exp \left[- \left(\frac{U-L-2h}{2} \right) \omega_E \right] \int \exp \left(- \frac{M_E \omega_E X^2}{2} \right) K(X, Y, h, \omega_H, M_H) \exp \left(- \frac{1}{2} M_F m^2 \gamma Y^2 \right) \times K(Y, Z, L, \omega_F, M_F) \exp \left(- \frac{1}{2} M_F m^2 \gamma Z^2 \right) K(Z, W, h, \omega_H, M_H) \exp \left(- \frac{M_E \omega_E W^2}{2} \right) dX dY dZ dW \quad (45)$$

to the grand partition function.

The $\mathbf{p}=0$ mode or mean-field contribution is unchanged by the addition of the hydrocarbon layer and after some algebra one finds that

$$\beta J^*(L) = \frac{1}{4\pi} \int_0^\infty dp p \ln \left[1 - \left(\frac{\epsilon_1 B(p)p + \epsilon(m^2 \gamma - \sqrt{p^2 + m^2})}{\epsilon_1 B(p)p + \epsilon(m^2 \gamma + \sqrt{p^2 + m^2})} \right)^2 \exp(-2L\sqrt{p^2 + m^2}) \right] + 2m\mu\bar{\gamma}^2 \frac{\cosh\left(\frac{mL}{2}\right)}{\sinh\left(\frac{mL}{2}\right) + m\gamma \cosh\left(\frac{mL}{2}\right)}, \quad (46)$$

where

$$B(p) = \frac{1 + \Delta \exp(-2ph)}{1 - \Delta \exp(-2ph)} \quad (47)$$

with

$$\Delta = \frac{\epsilon_0 - \epsilon_1}{\epsilon_0 + \epsilon_1}. \quad (48)$$

Note that if $\epsilon_0 = \epsilon_1$, we recover the double-layer result obtained earlier. In the limit $h \rightarrow 0$ we obtain $\epsilon_1 B(p) \rightarrow \epsilon_0$ and when $h \rightarrow \infty$ one has $\epsilon_1 B(p) \rightarrow \epsilon_1$ as it should. A key, physically illuminating step in the algebra mentioned above is the evaluation of the term

$$\psi^*(Y) = \int \exp \left(- \frac{1}{2} M_E \omega_E X^2 \right) K(X, Y, h, M_H, \omega_H) dX. \quad (49)$$

One finds that

$$\psi^*(Y) = \left(\frac{M_H \omega_H}{M_E \omega_E \sinh(\omega_H h) + M_H \omega_H \cosh(\omega_H h)} \right)^{1/2} \times \exp \left[-\frac{1}{2} Y^2 \left(\frac{M_E \omega_E M_H \omega_H \coth(\omega_H h) + M_H^2 \omega_H^2}{M_E \omega_E + M_H \omega_H \coth(\omega_H h)} \right) \right]. \quad (50)$$

The normalization here is unimportant for the calculation of the disjoining pressure (as h is taken to be fixed). We can now interpret ψ^* as the new effective ground-state wave function associated with the mode \mathbf{p} entering the film. As there is no electrolyte in the hydrocarbon region one has that $\omega_H = \omega_E = p$ (the case where electrolyte was present could be easily handled by the same formalism) and hence one finds that the effective or renormalized ground-state wave function entering the film is

$$\psi_0(X) = \exp \left[-\frac{1}{2} X^2 \omega_H M_H \left(\frac{M_E \coth(ph) + M_H}{M_E + M_H \coth(ph)} \right) \right]. \quad (51)$$

Clearly, this leads to a renormalization of M_H with respect to what it would be if the region of hydrocarbons was in fact of infinite size, and consequently one finds a p dependent renormalization of the dielectric constant ϵ_1 as

$$\epsilon_1^R(p) = \epsilon_1 B(p) = \epsilon_1 \left(\frac{\epsilon_0 \coth(ph) + \epsilon_1}{\epsilon_0 + \epsilon_1 \coth(ph)} \right), \quad (52)$$

which is easily seen to be in agreement with the definition of $B(p)$ above. This calculation can easily be generalized to an arbitrary number of electrolyte free layers simply by calculating recursively the value of $B(p)$ generated by the composition of all the layers before arriving at the penultimate layer before the film. In the case of no surface interaction and no electrolyte this result agrees with the calculation of the zero-frequency contribution to the van der Waals force in Refs. [8,37].

In what concerns the momentum dependence of $\epsilon^R(p)$ one finds that

$$\epsilon^R(p) \approx \epsilon_0 \quad \text{for} \quad \frac{1}{p} \gg h, \quad (53)$$

$$\epsilon^R(p) \approx \epsilon_1 \quad \text{for} \quad \frac{1}{p} \ll h. \quad (54)$$

Hence the long-wavelength modes entering the film behave as if the hydrocarbon layer was not there and the short-wavelength modes behave as if there was only the hydrocarbon layer present.

V. BEHAVIOR OF THE DISJOINING PRESSURE

In this section we shall examine how the disjoining pressure is affected by changing the various physical parameters of the theory. We write

$$P_d = P_d^{(0)} + P_d^{(vdW)}, \quad (55)$$

where the first term is the mean-field or zero-mode contribution $P_d^{(0)} = -\partial J_0 / \partial L$ and $P_d^{(vdW)} = -\partial J_{vdW}^* / \partial L$ is the zero-frequency van der Waals contribution coming from the modes \mathbf{p} such that $|\mathbf{p}| \neq 0$.

A. The mean-field contribution

The mean-field contribution to the disjoining pressure is

$$P_d^{(0)}(L) = \frac{\mu m^2 \bar{\gamma}^2}{\beta \left[\sinh\left(\frac{mL}{2}\right) + m \gamma \cosh\left(\frac{mL}{2}\right) \right]^2}, \quad (56)$$

which is clearly always positive. This repulsive component is generated by an effective surface charge that is present when $\mu_+^* - \mu_-^* \neq 0$, that is, there is an asymmetry between the cation/anion affinities or repulsions at the surface. At large intersurface separations one finds

$$P_d^{(0)}(L) \approx \frac{4 \mu m^2 \bar{\gamma}^2}{\beta \mu (1 + m \gamma)^2} \exp(-mL), \quad (57)$$

which has the standard Poisson-Boltzmann exponential decay with the characteristic length scale of the Debye length $l_D = 1/m$. If γ is negative $\gamma = -\gamma'$ (with $\gamma' > 0$) the magnitude of the repulsion is enhanced. Here there is a critical value L_c where the mean-field component to the disjoining pressure diverges. One finds that

$$L_c = \frac{1}{m} \ln \left(\frac{1 + m \gamma'}{1 - m \gamma'} \right). \quad (58)$$

The divergence here is not physical as it can be avoided by keeping higher-order terms in the expansion of the surface terms in the full action (10). However, it does indicate an enhancement of the repulsion due to the presence of a Stern layer of effective length $\delta' = \gamma'$ from the considerations in Sec. II. If the theory were applicable for large L and L_c were small, then one finds

$$L_c \approx 2 \delta', \quad (59)$$

that is, the pressure should rise rapidly when the two effective Stern layers come into contact, thus giving a large repulsive term in the disjoining pressure before the surfactant surfaces actually come into contact. This image is valid in the range where $m \delta' \ll 1$, that is, the width of the Stern layer is much smaller than the Debye length. It is clear that the limit taken in Eq. (9) is only valid in this case. In the case where $m \delta' \geq 1$ one must treat the Stern layer as a continuum and introduce two new layers of finite thickness.

In the case $\gamma > 0$ the magnitude of the repulsive part of the disjoining pressure is decreased as γ increases. At $L = 0$ one finds the disjoining pressure

$$P_d^{(0)}(0) = \mu k_B T \left(\frac{\bar{\gamma}}{\gamma} \right)^2. \quad (60)$$

Therefore at small interface separations one needs to incorporate steric repulsion between the surfactants in the two surfaces to prevent a collapse to a zero film thickness. We point out here that an attractive contribution to the disjoining pressure from mean-field theory has been found in a model with finite depletion force range (where $\delta > 0$) but at interfacial separations where the depletion layers overlap (i.e., $L < 2\delta$). In the model studied here we have taken the limit $\delta \rightarrow 0$ and hence do not observe this effect. In the context of SDS soap films [5], δ was estimated, from considering the hydrophobic nature of the soap tails, to be about 1.5 nm. In these systems the collapse from a CBF to NBF is seen at generically larger film thicknesses and it seems that, in this case, depletion forces at the mean-field level are too short-range to explain the CBF-NBF transition. In other experimental situations, however, it is possible that such depletion forces at the mean-field level play a determining role in the intersurface attraction.

B. The zero-frequency van der Waals contribution

As mentioned previously, the presence of an electrolyte in the film leads to a screening of the zero-frequency van der Waals interaction and simple expressions for $P_d^{(vdW)}$ as a function of L do not exist due to the presence of a second length scale, the Debye length ($= 1/m$). In the absence of a surface charging mechanism this contribution to the disjoining pressure has been studied qualitatively in detail in a wide variety of geometries and dielectric structures [11,22,33]. For simplicity, we consider just the bilayer model. In the case $L \gg 1/m$, the disjoining pressure is dominated by modes such that $p \ll 1$ and one obtains to leading order

$$P_d^{(vdW)} \sim -\frac{k_B T m^3}{4\pi m L} \left(\frac{m\gamma - 1}{m\gamma + 1} \right)^2 \exp(-2mL). \quad (61)$$

We see that the prefactor controlling the strength of the long-distance attraction depends crucially on the value of γ and hence the surface-charging mechanism. The exponential decay is, however, twice as rapid as that of the mean-field contribution, meaning that in the thick film regime the zero-frequency van der Waals attraction is dominated by the mean-field repulsion term.

In the limit $L \ll 1/m$ one finds

$$P_d^{(vdW)} \sim -\frac{k_B T}{8\pi L^3} \sum_{n=1}^{\infty} \frac{1}{n^3} \left(\frac{\epsilon - \epsilon_0}{\epsilon + \epsilon_0} \right)^{2n}, \quad L \ll 1/m. \quad (62)$$

This expression is independent of γ and consequently coincides with that given in Ref. [22] and Eq. (40). Hence we see that it is only in the regime of very thin films that the zero-frequency van der Waals force takes the Hamaker form $P_d^{(vdW)} \sim -1/L^3$.

VI. ORDERS OF MAGNITUDE AND COMPARISON WITH EXPERIMENTAL DATA

The theory presented so far is the linearized version that is equivalent to the Gaussian approximation and corresponds to

the free field formulation. We should expect that a detailed comparison with experiment will not be wholly successful since we have yet to include nonlinear effects. However, it is instructive to show qualitatively how well the model performs and to this end we study one case for which the parameters are typical of experiments. We consider a soap film in air consisting of ionic liquid bounded by two thin hydrocarbon layers of hydrophobic surfactant. We idealize the model to be a bilayer system where we do not account for the nonzero thickness of the hydrocarbon layers. The liquid is composed of water with a dissolved salt, such as NaCl. The hydrophobic surfactant is of one charge only and so we set $\mu_+^* \equiv \mu^*$, $\mu_-^* = 0$. The fugacity μ of the cations and anions is chosen by the experimenter and determines the Debye mass m through $m^2 = 2\mu e^2/kT$. For the free energy we use Eq. (28) that we recast in terms of dimensionless variables as

$$F_0(l) = -\frac{\cosh(l/2)}{\sinh(l/2) + \alpha \cosh(l/2)},$$

$$F_{(vdW)}(l) = \frac{1}{4\pi} \int dk k \ln \left[1 - \left(\frac{k\epsilon_0/\epsilon + \alpha - \sqrt{k^2 + 1}}{k\epsilon_0/\epsilon + \alpha + \sqrt{k^2 + 1}} \right)^2 \right] \times \exp(-2l\sqrt{k^2 + 1}),$$

$$P_d = 2kT\mu\bar{\alpha}^2 \frac{d}{dl} F_0(l) + kTm^3 \frac{d}{dl} F_{(vdW)}(l), \quad (63)$$

where $l = Lm$, $\alpha = m\gamma$, $\bar{\alpha} = m\bar{\gamma}$ with $\gamma = \bar{\gamma} = \mu^*/2\mu$. Typical values for these parameters are

$$kT = 4 \times 10^{-21} \text{ J}, \quad \mu \sim 0.2 \text{ mM} \Rightarrow m \sim 0.05 \text{ nm}^{-1},$$

$$\alpha = \bar{\alpha} = 2.0.$$

The coefficients in Eq. (63) are then

$$c_0 = 2k_B T \mu \bar{\alpha}^2 = 4000 \text{ Pa}, \quad c_1 = k_B T m^3 = 500 \text{ Pa},$$

$$\epsilon/\epsilon_0 = 80,$$

where the ratio ϵ/ϵ_0 is for water to air. The disjoining pressure P_d is given in pascals. For these values a plot of P_d is shown in Fig. 1. The solid curve is the total value of P_d while the dashed curve gives the repulsive contribution from F_0 and the attractive contribution from $F_{(vdW)}$ is shown as the dotted curve. The theory predicts a collapse certainly by $L = 8 \text{ nm}$ and since the collapse corresponds to a first-order phase transition the Maxwell construction will predict that collapse will be observed at larger L . Since we do not have a theory for the short-range repulsive force that eventually stabilizes the NBF we cannot use the Maxwell construction to give an accurate value for where the film becomes metastable but $8 \text{ nm} < L < 20 \text{ nm}$ would be a reasonable range. However, if one considers that a short-range steric interaction comes into play for small intersurface separations, this

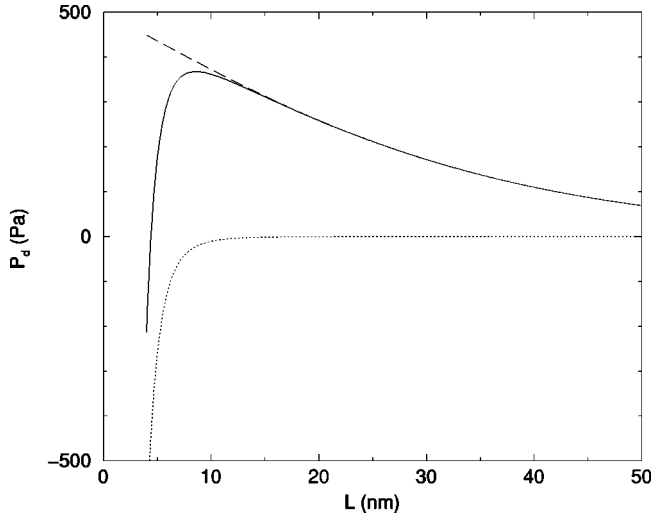


FIG. 1. The disjoining pressure P_d for the linearized theory using typical parameter values: $\mu_{\text{NaCl}}=0.2$ mM, $m_{\text{Debye}}=0.05$ nm $^{-1}$, $\alpha=2.0$. The solid line is the full result, the dashed line is the repulsive contribution and the dotted line the attractive, van der Waals contribution.

should dominate the van der Waals attraction thus causing the disjoining pressure to rise rapidly. In Ref. [7] the experimentally measured thin film repulsion was for example fitted with a Lennard-Jones potential. The $P_d(L)$ isotherm will then have the usual van der Waals gas form with, on decreasing L , first a maximum and then a minimum. The maximum of P_d will correspond to the spinodal point and the point of coexistence between CBF and NBF determined via the Maxwell construction as mentioned above. Interestingly, in the one-dimensional form of this model [26] the thin film can be stabilized by purely electrostatic interactions and several maxima and minima seen on the disjoining pressure isotherm, indicating the possibility of a sequence of collapses.

The attractive van der Waals contribution $P_d^{(vdW)}$ above can be compared with the Hamaker form at short distances predicted by Eq. (62). However, numerical study of the case of interest here shows that the values of L for which this behavior holds are too small to be relevant to the collapse described above.

For $L \gg 1/m$ the leading term is given by Eq. (61) and the value of α is crucial in determining the overall coefficient. Indeed, for $\alpha \sim 1$ the behavior will be given by nonleading terms not shown here. In Fig. 2 we plot $P_d^{(vdW)}$ vs L . It is seen that while the large L asymptotic form (61) is a good approximation for $L > 1/m = 20$ nm, in the region important to the collapse, $5 \text{ nm} < L < 20$ nm, the full result deviates strongly from this form. Thus we find that the full expression for $P_d^{(vdW)}$ must be used in the region of interest.

The surface-charging mechanism is very important to the prediction of the collapse transition. If a fixed surface charge is used we should omit the quadratic term in ϕ in the expansion of the source in Eqs. (9), (65). This corresponds to setting $\alpha=0$ where it occurs explicitly in the expressions for F_0 and $F_{(vdW)}$ in Eq. (63) while not changing the values of the coefficients c_0, c_1 . In this case for the parameters above there is no collapse.

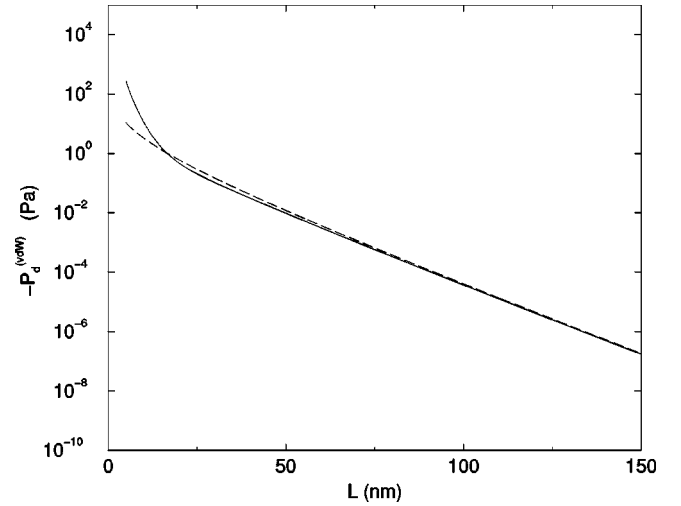


FIG. 2. The van der Waals contribution $P_d^{(vdW)}$ for the linearized theory plotted against L using typical parameter values: $\mu_{\text{NaCl}}=0.2$ mM, $m_{\text{Debye}}=0.05$ nm $^{-1}$, $\alpha=2.0$. The dashed line is the asymptotic formula Eq. (61) which is seen to be accurate until $L \leq 1/m = 20$ nm. The standard Hamaker form $\propto L^{-3}$ is not applicable for the relevant values of L .

In a more general case with both μ_+^*, μ_-^* nonzero the same expressions as in Eq. (63) apply but with the generalization $\alpha \neq \bar{\alpha}$. The effect of choosing fixed $\bar{\alpha}=2.0$ but varying α can be seen in Fig. 3 where the values used above, $c_0=4000$ Pa, $c_1=500$ Pa, are adopted but different values of $\alpha=1.0, 1.5, 2.0, 3.0$ are used. The term most affected is the repulsive mean-field term and even in the linearized theory this is very sensitive, as we should expect, to the charging mechanism for the surfaces. We see that the predicted properties of the collapse transition are strongly dependent on the choice of $\bar{\alpha}$ and α and therefore on the details of the film being studied.

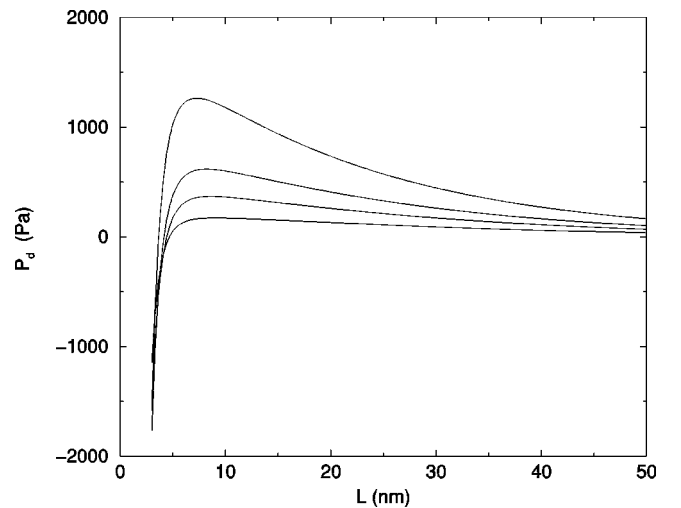


FIG. 3. The disjoining pressure P_d for the linearized theory using typical parameter values: $\mu_{\text{NaCl}}=0.2$ mM, $m_{\text{Debye}}=0.05$ nm $^{-1}$, $\bar{\alpha}=2.0$ but for different values of α occurring explicitly in Eq. (63). The curves from top down are for $\alpha=0.5, 1.0, 1.5, 2.0$, and 3.0 .

VII. BEHAVIOR OF THE SURFACE CHARGE

In the limit $\delta \rightarrow 0$ the surface charge (on one surface) per unit area σ can be seen to be

$$\sigma = -\frac{e}{2} \left(\mu_+^* \frac{\partial}{\partial \mu_+^*} - \mu_-^* \frac{\partial}{\partial \mu_-^*} \right) \beta J = -\frac{e}{2} \left(\gamma \frac{\partial}{\partial \gamma} + \bar{\gamma} \frac{\partial}{\partial \bar{\gamma}} \right) \beta J, \quad (64)$$

where $\gamma, \bar{\gamma}$ are defined in Eq. (12).

Even in the Gaussian approach the source terms encode the nontrivial charging properties of the surfaces bounding the ionic liquid. From Eq. (9) we have used the approximation for the source

$$\begin{aligned} & \mu_+^* \exp(i\beta e \phi) + \mu_-^* \exp(-i\beta e \phi) \\ & = i\lambda \phi - \frac{1}{2} \beta \epsilon m^2 \gamma \phi^2 + \dots \end{aligned} \quad (65)$$

The term linear in ϕ represents a fixed surface charge but the term in ϕ^2 corresponds to surface charge fluctuations.

We decompose σ in terms of the mean-field contribution and the van der Waals contribution $\sigma = \sigma_0 + \sigma_{vdW}$. The term coming from the mean-field (and constant or ideal) contributions to the grand potential is

$$\begin{aligned} \sigma_0(L) &= \frac{e\mu}{m} \frac{\bar{\alpha}}{\alpha + \tanh\left(\frac{mL}{2}\right)} \\ &\times \left[2 \tanh\left(\frac{mL}{2}\right) + \frac{\bar{\alpha}^2}{\alpha + \tanh\left(\frac{mL}{2}\right)} \right]. \end{aligned} \quad (66)$$

The contribution from the van der Waals term is independent of $\bar{\gamma}$ and can be written as

$$\sigma_{vdW} = -\frac{e}{2} \bar{\alpha} \frac{\partial}{\partial \alpha} \beta J_{vdW}. \quad (67)$$

We find

$$\begin{aligned} \sigma_{vdW} &= \frac{\bar{\alpha} e m^2}{2\pi} \int dk k \frac{f(k)}{1 - f^2(k)} \frac{\sqrt{k^2 + 1}}{(k\epsilon_0/\epsilon + \alpha + \sqrt{k^2 + 1})^2} \\ &\times \exp(-l\sqrt{k^2 + 1}), \end{aligned} \quad (68)$$

where f is given by

$$f(k) = \left(\frac{k\epsilon_0/\epsilon + \alpha - \sqrt{k^2 + 1}}{k\epsilon_0/\epsilon + \alpha + \sqrt{k^2 + 1}} \right) \exp(-l\sqrt{k^2 + 1}). \quad (69)$$

For the parameters given in the previous section, $\mu = 0.2$ mM, $m = 0.05$ nm⁻¹, $\alpha = \bar{\alpha} = 2.0$, the behavior of σ is shown versus L in Fig. 4. One notices that the surface charge is regularized on varying L , though not drastically (about 10% over 40 nm) just up to the film thickness L

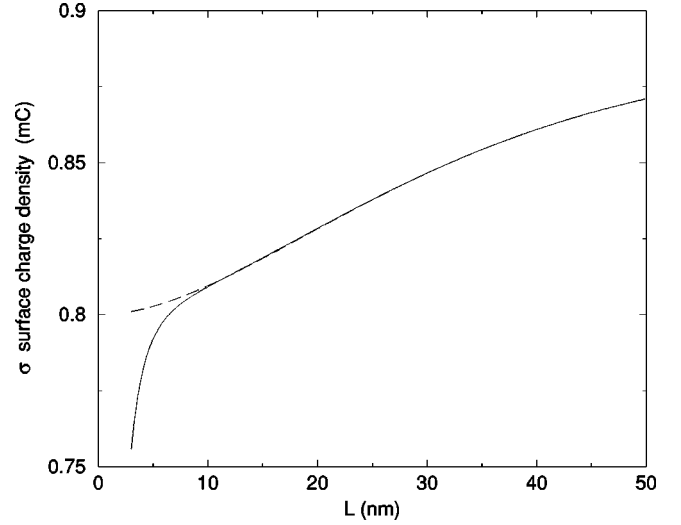


FIG. 4. The surface charge σ in mC plotted versus L for $\mu_{\text{NaCl}} = 0.2$ mM, $m_{\text{Debye}} = 0.05$ nm⁻¹, $\alpha = 2.0$. The solid line is the full result, the dashed line is the mean-field contribution σ_0 . The van der Waals contribution, $\sigma_{(vdW)}$ is negligible until $L \leq 10$ nm where it is responsible for the rapid decrease in σ .

~ 10 nm. One sees that in this case the effect of the van der Waals term is to decrease the value of σ from its mean-field value.

VIII. CONCLUSIONS AND OUTLOOK

In this paper we have presented a field theoretic formulation of the electrostatic interactions in soap-film-like systems, which treats on the same footing the zero-frequency van der Waals or Lifshitz terms and the contributions coming from ionic fluctuations. The basic idea is to use the static part of the QED Lagrangian coupled to the charge density coming from the ions in the system and then integrating over the electrostatic potential ψ and the positions of the ions (which are treated classically). The time-dependent and magnetic field terms in the full QED Lagrangian are thus neglected, this is equivalent to the nonretarded limit where the velocity of light $c \rightarrow \infty$. Retardation effects can be taken into account by summing over the nonzero Matsubara frequencies; however, the coupling of these terms with the ionic distribution is weak. The incorporation of retardation effects requires in addition the frequency dependence of the electric permittivities.

This treatment is easily applicable to systems with spatially varying dielectric constants and elegantly avoids calculations of the arising image effects. The formalism also allows the incorporation of surface charges induced by equilibrium processes. In the grand canonical ensemble one obtains a Sine-Gordon field theory. Linearizing this theory leads to a soluble Gaussian field theory and is equivalent to the Debye-Hückel approximation, which should be valid for weak ionic concentrations. In this form the evaluation of the grand potential is carried out by using the Feynman kernel for simple harmonic oscillators. The use of the Feynman kernel in the field theoretic formalism allows us to reproduce a wide range of results established in the literature via other

methods. The effect of surface charge fluctuations can also be taken into account and it was also shown how many different layers of varying dielectric constant simply lead to a renormalization of the simple bilayer result.

Preliminary investigation of the relevant experimental soap film parameters shows that the van der Waals contributions lead to a weak (screened) attraction at large intersurface separations. For thinner films there is an increased attraction, which can overcome the mean-field repulsion present in the models considered here. However, in the region where the film collapses, the attraction does not have the simple Hamaker $1/L^3$ form and is strongly dependent on the Debye mass m and the surface-charging parameters. Indeed an essential ingredient is the inclusion of the surface-charging mechanism which, although treated here in the Gaussian approximation, nevertheless predicts an L -dependent surface charge density that is important to the details of the collapse. A linear approximation to the surface charge source is inadequate since it leads to a fixed surface charge and hence a diverging mean-field repulsive pressure P_0 as L decreases. By including the term in ϕ^2 in the expansion of the sources, the surface charge is shown to decrease as L decreases and so the divergence in the mean-field repulsion P_0 is regulated.

Although not necessary for the theory presented here, it is interesting to compare the outcome with our work on the 1D Coulomb gas model for a soap film [26]. The mechanism in 1D for the collapse was the changing balance of contributions to P_d between the even and odd eigenfunctions of the Mathieu equation as the film thickness L varied. The important states were the lowest-lying ones including the ground state. In the Gaussian approximation used in the present work we can ask which are the important eigenfunctionals of the theory in 3D that play a similar role. In this model the eigenfunctionals are products of harmonic oscillator eigenfunctions for each of the transverse momentum modes separately for which the coordinate is $\tilde{\phi}(\mathbf{p})$. The source term is, however, only a function of the zero mode $\tilde{\phi}(0)$ and the important corresponding term in the wave functional from Eq. (18) is [$\mathbf{p}=0$, $X \equiv \tilde{\phi}(0)$],

$$\Psi_n(X) = h_n(X) \exp(-mX^2/2),$$

where n is the oscillator excitation number. For large n the Hermite polynomial has an oscillatory factor,

$$h_n(X) \sim \cos(\sqrt{nm}X - (n-1)\pi/2).$$

The relevant coefficient is the overlap of this wave function with the source term in Eq. (21) $\exp(i\sqrt{A}\mu^*\beta eX)$ and it is clear that this will not be large unless the oscillatory factors match. This will be the case when

$$\sqrt{nm} \sim \sqrt{A}\mu^*\beta e,$$

and the corresponding energy values are of order $E \sim (n+1/2)m \sim A\mu^{*2}(\beta e)^2/m$ giving an extensive contribution to the free energy as we must expect. Hence the important states are not the ground state and those that are nearby but highly excited states that carry the extensive nature of the system.

By taking experimentally reasonable values for the parameters in our formulas we obtain acceptable predictions for the collapse phenomenon and surface charging for simple description of the film. However, to make accurate predictions will require the film to be modeled as a multiple layer with the correct permittivities for each layer and possible charging potentials included. We must also include the contributions of nonlinear and non-Gaussian operators and to do this involves three ingredients. The first is to solve the nonlinear mean-field equations, the second is to develop the perturbation theory for the non-Gaussian source operators within the Gaussian field theory, and the third to use perturbation theory for the non-Gaussian interactions given by the sine-Gordon theory in the film interior. Because the system is not translation invariant these perturbation theories are not standard but it has been developed and will be presented in a succeeding paper together with the nonlinear mean-field formulas.

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