

**Resummed two-loop calculation of the disjoining pressure of a symmetric electrolyte soap film**D. S. Dean<sup>1,2,\*</sup> and R. R. Horgan<sup>1,†</sup><sup>1</sup>*DAMTP, CMS, University of Cambridge, Cambridge, CB3 0WA, United Kingdom*<sup>2</sup>*IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 04, France*

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In this paper we consider the calculation of the disjoining pressure of a symmetric electrolytic soap film correct to two loops in perturbation theory. We show that the disjoining pressure is finite when the loop expansion is resummed using a cumulant expansion and requires no short distance cutoff in order to give a finite result. The loop expansion is resummed in terms of an expansion in  $g=l_B/l_D$  where  $l_D$  is the Debye length and  $l_B$  is the Bjerrum length. We show that there is a nonanalytic contribution of order  $g \ln(g)$ . We also show that the two-loop correction is greater than the one-loop term at large film thicknesses suggesting a nonperturbative correction to the one-loop result in this limit.

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**I. INTRODUCTION**

The determination of the effective interaction between two surfaces of a film-like structure is essential for the understanding of the conformational stability of a whole range of systems in soft-condensed matter physics. Examples are found in interactions between membranes and colloid physics [1]. The effective interaction between two semi-infinite dielectrics separated by a vacuum was calculated by Lifshitz [2] and the effect of an intervening dielectric was determined by Dzyaloshinski, Lifshitz, and Pitaevskii [3] and subsequently reformulated more simply in Ref. [4]. The effective interaction is due to van der Waals or dispersion forces and is given by the sum over the Matsubara modes of the problem; the nonzero frequency modes are a quantum effect and the contribution of zero modes correspond to a thermal Casimir type effect. In purely dielectric problems the contribution of each mode is described by a free Gaussian field theory and it has been shown how the input to these free field theories can be determined using dielectric data, see Ref. [5], and references therein.

In many situations, especially in biology, the middle slab of the system is filled with an electrolyte. For example, this is the case for a simple soap film connected to a bulk which is filled with an aqueous salt solution. It has been argued [6] that the presence of an electrolyte will not effect the nonzero frequency contribution to the interaction basically because the response time of the ions is too large to couple them to the these nonzero frequency modes. However the zero-frequency, or static, component of the interaction does couple to the ionic distribution and consequently its contribution is strongly affected by the presence of electrolyte. The field theory describing the zero frequency fluctuations of the electric field in the presence of ions is no longer a free field theory; the interactions are made up of two components: the basic thermal fluctuations of the electrostatic field and the induced Coulombic interactions between the ions. In the

presence of a neutral surface and a symmetric monovalent electrolyte the mean-field electrostatic potential is zero and the one-loop contribution about this trivial mean-field solution is equivalent to Debye-Hückel theory. The one-loop result is described and computed in Ref. [5] and has been rederived using a variety of different methods, for instance see Refs. [7,8]. In the absence of electrolyte the zero frequency contribution to the effective interaction, commonly known as the disjoining pressure  $P_d$ , behaves as  $P_d \approx -A/l^3$  for a film of thickness  $l$ . In the presence of electrolyte, at large film separations relative to the Debye length  $l_D$ , the disjoining pressure is screened at one loop and has the form  $P_d \approx -A \exp(-2l/l_D)/l$ . In both of these cases the constant  $A$  is positive and, hence, the effective force between the surfaces is attractive at one-loop order.

In this paper we calculate  $P_d$  to two-loop order. The naive two-loop calculation is in fact divergent when the dielectric constant of the film, or slab, is greater than that of the exterior [9], but we show here that the result can be resummed using a cumulant expansion similar to that used in Ref. [10] for the bulk to give a finite result which we argue is to be expected on physical grounds. The expansion we use can be controlled systematically, and the perturbative parameter is  $g=l_D/l_B$ , where  $l_B$  is the Bjerrum length. While the one loop or first term in the expansion in  $g$  is regular, the second order term in  $g$  is of the form  $g^2 \ln(g)$ , this singular behavior is found in the Onsager-Samaras limiting law for the excess surface tension of electrolyte solutions and has its origin in the image forces which repel the ions from the air/water interface. We also analyse the behavior of the  $O(g^2)$  term for large film thickness  $l$  and find that this term has the behavior  $-A' \ln(l/l_D) \exp(-2l/l_D)/l$ , which means that it becomes larger than the one-loop result for very thick films. We conjecture that this result suggests that it is the first term in a series which sums to give a contribution at large  $l$  to the disjoining pressure with behavior  $P_d \approx -A'' \exp(-2l/l_D)/l^\alpha$ , where the exponent  $\alpha$  has the form  $\alpha = 1 + \alpha_1 g + \alpha_2 g^2 \dots$ .

**II. TWO-LOOP CALCULATION**

The model of the soap film we shall consider is the following. The film body is a planar slab of thickness  $l$  sur-

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rounded on both sides by an external dielectric medium such as air. The interior of the film is filled with electrolyte and connected to a bulk reservoir of electrolyte. The electrolyte consists of a passive solvent of uniform dielectric constant containing monovalent anions and cations which are treated as point charges of charges  $-e$  and  $e$ , respectively. The electrolyte is symmetric in the sense that the anions and cations are identical in every respect other than that they have opposite electric charges.

In what follows we shall use the standard field theoretic formulation for symmetric monovalent electrolyte systems [11]. The grand partition function for a film of electrolyte solution, surrounded on both sides by an external medium such as air, of thickness  $l$  is given by

$$\Xi_F(l) = \int d[\phi] \exp(S_F[\phi, l]), \quad (1)$$

where the action  $S_F$  of the film is given by

$$S_F[\phi, l] = -\frac{\beta\epsilon}{2} \int_{F_I} d\mathbf{x} (\nabla\phi)^2 + 2\mu \int_{F_I} d\mathbf{x} \cos(e\beta\phi) - \frac{\beta\epsilon_0}{2} \int_{F_E} d\mathbf{x} (\nabla\phi)^2. \quad (2)$$

The region inside the film is denoted by  $F_I$  and, if  $z$  is the coordinate perpendicular to the film surface, then  $F_I$  is the region  $z \in [0, l]$ . Inside  $F_I$ , the dielectric constant is  $\epsilon$  and is taken to be that of the solvent, in most cases water, and the fugacities for the cations and anions in this symmetric electrolyte are the same and are denoted by  $\mu$ . The region outside the film is denoted by  $F_E$ ; in  $F_E$  there is no electrolyte and the dielectric constant is denoted by  $\epsilon_0$ . In this paper we consider the physically relevant case where  $\epsilon > \epsilon_0$ .

For a bulk solution of thickness  $l$  the grand partition function is given by

$$\Xi_B(l) = \int d[\phi] \exp(S_B[\phi, l]), \quad (3)$$

where  $S_B$  is the bulk action

$$S_B = -\frac{\beta\epsilon}{2} \int_B d\mathbf{x} (\nabla\phi)^2 + 2\mu \int_B d\mathbf{x} \cos(e\beta\phi). \quad (4)$$

Here there is no contact with an exterior region and one can close the system by using periodic boundary conditions in the  $z$  direction. The value of the fugacity is determined by the bulk density  $\rho$  and is given by

$$\mu = \frac{\rho}{\langle \cos(e\beta\phi) \rangle_B} = Z\rho. \quad (5)$$

Here,  $Z^{-1} = \langle \cos(e\beta\phi) \rangle_B$  is a renormalization factor accounting for ion self-interactions, and the expectation is taken at an arbitrary position in an infinite bulk system, i.e., where  $l \rightarrow \infty$ . In experiments on planar systems or films the physical quantity which is measured is the disjoining pressure which is due to the effective interaction induced by the presence of the film surfaces. The disjoining pressure is the excess film

pressure  $P_F$  over the bulk pressure  $P_B$  and can be measured exactly using a pressure cell [12]:

$$P_d(l) = P_F(l) - P_B. \quad (6)$$

The film pressure depends explicitly on the film thickness and is given by

$$P_F(l) = \frac{1}{A} \frac{\partial}{\partial l} \ln[\Xi_F(l)]. \quad (7)$$

The bulk pressure is defined in the thermodynamic limit and is given by

$$P_B = \frac{1}{A} \lim_{l \rightarrow \infty} \frac{\partial}{\partial l} \ln[\Xi_B(l)]. \quad (8)$$

In order to develop a systematic expansion for the disjoining pressure we pass to the rescaled model in terms of the rescaled field

$$\phi \rightarrow \frac{\sqrt{g}}{e\beta} \phi, \quad (9)$$

and we measure length in terms of the Debye length  $l_D$ :

$$\mathbf{x} \rightarrow \mathbf{x}l_D, \quad (10)$$

where  $m = \sqrt{2\rho e^2\beta/\epsilon}$  is the Debye mass and  $l_D = 1/m$ . The dimensionless coupling  $g$  is given by  $g = l_B/l_D$  where  $l_B = e^2\beta/4\pi\epsilon$  is the Bjerrum length. In units of the Debye length we denote the thickness of the film by  $L = l/l_D$ .

The disjoining pressure  $P_d$  is obtained from the disjoining pressure of the rescaled model  $\mathcal{P}_d$  using

$$P_d = m^3 \mathcal{P}_d = 8\pi\rho g \mathcal{P}_d. \quad (11)$$

The effective action for the film in terms of the rescaled fields and lengths is

$$S_F = -\frac{1}{8\pi} \int_{F_I} d\mathbf{x} (\nabla\phi)^2 + \frac{Z(g)}{4\pi g} \int_{F_I} d\mathbf{x} \cos(\sqrt{g}\phi) - \frac{n}{8\pi} \int_{F_E} d\mathbf{x} (\nabla\phi)^2, \quad (12)$$

where  $n = \epsilon_0/\epsilon$  and the renormalization factor  $Z(g)$  simply becomes

$$Z(g) = \frac{1}{\langle \cos(\sqrt{g}\phi) \rangle_B}, \quad (13)$$

where again the expectation value in the equation above is for an infinite bulk system. The action  $S_F$  can be decomposed as

$$S_F = \frac{Z(g)}{4\pi g} V_F + S_F^{(0)} + \Delta S_F, \quad (14)$$

where  $V_F$  is the volume of the film and the first term is the ideal contribution. The term  $S_F^{(0)}$  is the action for a free or Gaussian field theory and is given by

$$\mathcal{S}_F^{(0)} = -\frac{1}{8\pi} \int_{F_I} d\mathbf{x} [(\nabla\phi)^2 + \phi^2] - \frac{n}{8\pi} \int_{F_E} d\mathbf{x} (\nabla\phi)^2. \quad (15)$$

The interacting part of  $\mathcal{S}_F$  is expressed as a perturbation

$$\Delta\mathcal{S}_F = \frac{1}{4\pi g} \int_{F_I} d\mathbf{x} \left\{ Z(g) [\cos(\sqrt{g}\phi) - 1] + \frac{g\phi^2}{2} \right\}, \quad (16)$$

and the action  $\mathcal{S}_B$  for the equivalent bulk system is given by

$$\mathcal{S}_B = -\frac{1}{8\pi} \int_B d\mathbf{x} (\nabla\phi)^2 + \frac{Z(g)}{4\pi g} \int_B d\mathbf{x} \cos(\sqrt{g}\phi). \quad (17)$$

Clearly  $\mathcal{S}_B$  is invariant under  $\phi \rightarrow -\phi$  and, hence, from Eq. (13) one must have the expansion

$$Z(g) = 1 + z_1 g + z_2 g^2 + z_3 g^3 + \dots \quad (18)$$

Using the same decomposition for the bulk action as for the film action we obtain

$$\begin{aligned} \mathcal{S}_B &= \frac{Z(g)}{4\pi g} V_B - \frac{1}{8\pi} \int_B d\mathbf{x} [(\nabla\phi)^2 + \phi^2] + \frac{1}{4\pi g} \int_B d\mathbf{x} \left\{ Z(g) \right. \\ &\quad \left. \times (\cos(\sqrt{g}\phi) - 1) + \frac{g\phi^2}{2} \right\}, \end{aligned} \quad (19)$$

where  $V_B$  is the bulk volume. To order  $g$  the action  $\mathcal{S}_B$  may thus be written as

$$\begin{aligned} \mathcal{S}_B &= \frac{1 + z_1 g + z_2 g^2}{4\pi g} V_B - \frac{1}{8\pi} \int_B d\mathbf{x} [(\nabla\phi)^2 + \phi^2] \\ &\quad + \frac{g}{4\pi} \int_B d\mathbf{x} \left[ \frac{\phi^4}{4!} - \frac{z_1 \phi^2}{2} \right] + O(g^2). \end{aligned} \quad (20)$$

Hence, in order to calculate  $\ln(\Xi_B)$  to order  $g$  one needs to evaluate  $Z(g)$  to order  $g^2$ . We define

$$Z_n(g) = \frac{1}{\langle \cos(\sqrt{g}\beta\phi) \rangle_{n-1}}, \quad (21)$$

where the notation  $\langle O \rangle_n$  signifies the expectation value of  $O$  evaluated to  $n$ th order in the cumulant expansion. Then  $Z_n$  is an approximation to  $Z$  correct up to and including  $O(g^n)$ . Then we can write  $\mathcal{S}_B$  correct to order  $g$  as

$$\begin{aligned} \mathcal{S}_B &= \frac{Z_2(g)}{4\pi g} V_B - \frac{1}{8\pi} \int_B d\mathbf{x} [(\nabla\phi)^2 + \phi^2] + \frac{1}{4\pi g} \int_B d\mathbf{x} \left\{ Z_1(g) \right. \\ &\quad \left. \times [\cos(\sqrt{g}\phi) - 1] + \frac{g\phi^2}{2} \right\}. \end{aligned} \quad (22)$$

Clearly calculating with the action above gives the value of  $\ln(\Xi_B)$  correct to order  $g$  which includes the two-loop term in the loop expansion coming from the term  $g\phi^4/4!$  in the interaction term. We might go further and expand the interaction term and keep only terms of order  $g$ . However, when we consider the computation of the partition function  $\Xi_F$  for the film we shall see that the naive expansion of the interaction term in this manner is illegal because it gives rise to a

spurious divergence due to the image charge singularities. In the expansion for the disjoining pressure we must first identify the correct Boltzmann factor associated with the image charge potential, which is not expansible in  $g$ , and only then may we expand the remaining contributions to order  $g$  to obtain the two-loop divergence-free result for the disjoining pressure. We will find a term that behaves like  $g \ln(g)$  which indicates that some contributions are indeed not expansible in  $g$ . Therefore, at two-loop order we use the form for  $\mathcal{S}_B$  given in Eq. (22) and a similar form for  $\mathcal{S}_F$  which we discuss later. Then to  $O(g)$  we have

$$\ln(\Xi_B) = \frac{Z_2(g)}{4\pi g} V_B + \ln(\Xi_{B,0}) + \langle \Delta\mathcal{S} \rangle_{B,0} + O(g^2), \quad (23)$$

where

$$\Xi_{B,0} = \int d[\phi] \exp(\mathcal{S}_{B,0}), \quad (24)$$

with

$$\mathcal{S}_{B,0} = -\frac{1}{8\pi} \int_B d\mathbf{x} [(\nabla\phi)^2 + \phi^2], \quad (25)$$

and

$$\Delta\mathcal{S} = \frac{1}{4\pi g} \int_B d\mathbf{x} \left\{ Z_1(g) [\cos(\sqrt{g}\phi) - 1] + \frac{g\phi^2}{2} \right\}. \quad (26)$$

The last term is just the first term in the cumulant expansion about the free field theory with action  $\mathcal{S}_{B,0}$  and is given by

$$\langle \Delta\mathcal{S} \rangle_{B,0} = \frac{\int d[\phi] \exp(\mathcal{S}_{B,0}) \Delta\mathcal{S}}{\int d[\phi] \exp(\mathcal{S}_{B,0})}. \quad (27)$$

Inside the bulk we define

$$\langle \phi(\mathbf{x})\phi(\mathbf{x}) \rangle_{B,0} = G_B(0), \quad (28)$$

by translational invariance within the bulk. This now yields

$$Z_1(g) = \frac{1}{\langle \cos(\sqrt{g}\phi) \rangle_{B,0}} = \exp \left[ \frac{g}{2} G_B(0) \right], \quad (29)$$

and

$$\begin{aligned} \ln(\Xi_B) &= \frac{Z_2(g)}{4\pi g} V_B + \ln(\Xi_{B,0}) + \frac{V_B}{4\pi g} \left\{ 1 + \frac{g}{2} G_B(0) \right. \\ &\quad \left. - \exp \left[ \frac{g}{2} G_B(0) \right] \right\} + O(g^2). \end{aligned} \quad (30)$$

One now carries out exactly the same calculation in the film where within a film of thickness  $L$  we define

$$\langle \phi(\mathbf{x})\phi(\mathbf{x}) \rangle_{F,0} = G_F(z, L), \quad (31)$$

where the field correlator at coinciding points now depends on the distance  $z$  from the surface of the film and  $L$ , its thickness;  $\langle \phi(\mathbf{x})\phi(\mathbf{y}) \rangle_{F,0}$  is the propagator for the action  $\mathcal{S}_{F,0}$ . We then obtain to  $O(g)$ :

$$\ln(\Xi_F) = \frac{Z_2(g)}{4\pi g} V_F + \ln(\Xi_{F,0}) + \frac{1}{4\pi g} \int_{V_F} d\mathbf{x} \left( \exp \left\{ -\frac{g}{2} [G_F(z,L) - G_B(0)] \right\} + \frac{g}{2} G_F(z,L) - \exp \left[ \frac{g}{2} G_B(0) \right] \right) + O(g^2). \quad (32)$$

In the limits  $L \rightarrow \infty, z \rightarrow \infty, z/L \rightarrow 0$ , we recover the expression for  $\ln(\Xi_B)$  in Eq. (30). We note that the exponent of the first exponential under the integral sign in Eq. (32) contains the repulsive image charge potential which is singular as  $z \rightarrow 0$ . Evidently, it is illegal to expand this exponential as it stands and it is clear that it contains the correct Boltzmann factor for the potential due to the image charges. In terms of the rescaled system the disjoining pressure is then given by

$$\beta P_d = \frac{\partial}{\partial L} B_0(L) + \frac{\partial}{\partial L} B_1(L), \quad (33)$$

where

$$G_R(z,L) = \int_1^\infty dP \left\{ \frac{2\Gamma^2(P)\exp(-2PL) + \Gamma(P)\exp[-2P(L-z)] + \Gamma(P)\exp(-2Pz)}{1 - \Gamma^2(P)\exp(-2PL)} \right\}, \quad (37)$$

where

$$\Gamma(P) = \frac{P - n\sqrt{P^2 - 1}}{P + n\sqrt{P^2 - 1}}. \quad (38)$$

We can compare the result in Eq. (35) with the result of Netz [9] where he computes the two-loop contribution to the free energy of the film. When normalized with respect to the bulk free energy, the result of Netz agrees with Eq. (35) expanded to and truncated at  $O(g)$ . In the case where  $\Delta=0$  the expression of Netz is indeed the disjoining pressure correct to two loops. However, in the case where  $\Delta=(1-n)/(1+n)>0$ , i.e., when there is dielectric discontinuity in the system, the expression truncated at  $O(g)$  is divergent. As already remarked, this is due to the presence of image charges which repel charge away from the surface into the film when  $\Delta>0$  as is the case of air/water films, for example. Netz obtains a finite result using this truncated expansion by introducing an ultraviolet (UV) cutoff in the  $P$  integration defining  $G_R(z,L)$  in Eq. (37). The UV cutoff is associated with a microscopic length scale such as the ionic radius of the solute, and at three loop order and above it can be shown that it is necessary to impose such an UV cutoff in order to obtain a finite result; the physical nature of the divergence in this case is the collapse of opposite charged ions onto each other which is then regulated by a hard-core repulsion. At two loops there is no such effect and the UV cutoff is not needed to obtain a finite result. Expanding the exponential in the expression for

$$B_0(L) = \frac{1}{A} \left\{ \ln[\Xi_{F,0}(L)] - L \lim_{L' \rightarrow \infty} \frac{\ln[\Xi_{B,0}(L')]}{L'} \right\}, \quad (34)$$

is the one-loop or  $O(1)$  contribution in the expansion in  $g$ , and  $A$  is the area of the film. The two-loop term, or term to  $O(g)$ , is given by

$$B_1(L) = \frac{1}{4\pi g} \int_0^L dz \left\{ \exp \left[ -\frac{g}{2} G_R(z,L) \right] - 1 + \frac{g}{2} G_R(z,L) \right\}, \quad (35)$$

with

$$G_R(z,L) = G_F(z,L) - G_B(0). \quad (36)$$

We note that there is no need to calculate  $Z_2(g)$ , the approximation to  $Z(g)$  accurate to  $O(g^2)$ , in order to compute the disjoining pressure, since this term is the same in both the film and the bulk and hence cancels identically. We find

$B_1$  amounts to an illegal expansion of a Boltzmann weight which keeps charge away from the surface. This term needs to be treated with care as in the Onsager-Samaras [13] calculation of the excess surface tension of ionic solution where a similar term also arises. Any divergence arising from such an illegal expansion is spurious.

We write

$$\beta P_d = \beta P_d^{(0)} + \beta P_d^{(1)}, \quad (39)$$

where  $\mathcal{P}_d^{(n)}$  is the  $O(g^n)$  contribution to  $\mathcal{P}_d$ . The one-loop,  $O(1)$ , contribution to the disjoining pressure has been worked out by many authors and is given by

$$\beta P_d^{(0)} = -\frac{1}{2\pi} \int_1^\infty P^2 dP \frac{\Gamma^2(P)\exp(-2PL)}{1 - \Gamma^2(P)\exp(-2PL)}. \quad (40)$$

From the above equation we find the two-loop contribution to be given by

$$\beta P_d^{(1)} = \frac{1}{4\pi g} \left\{ \exp \left[ -\frac{g}{2} G_R(L/2,L) \right] + \frac{g}{2} G_R(L/2,L) - 1 \right\} + \frac{1}{4\pi} \int_0^{L/2} dz \frac{\partial}{\partial L} G_R(z,L) \left\{ 1 - \exp \left[ -\frac{g}{2} G_R(z,L) \right] \right\}. \quad (41)$$

We emphasize that this expression is finite for all  $L>0$  and requires no UV regularization.

We may attempt to expand Eq. (41) to  $O(g)$  to get

$$\beta\mathcal{P}_d^{(1)} = \frac{g}{32\pi}G^2(L/2,L) + \frac{g}{8\pi}\int_0^{L/2} dz G_R(z,L) \frac{\partial}{\partial L} G_R(z,L) + O(g^2), \quad (42)$$

thus giving what naively looks like the two-loop contribution.

The function  $G(z,L)$  can be shown to be finite every where for  $z \in [0, L/2]$  except at  $z=0$ . It is straightforward to isolate the divergent part of  $G_R(z,L)$  near  $z=0$ , and we find that

$$G_R(z,L) = \Delta \frac{\exp(-2z)}{2z} + G'_R(z,L), \quad (43)$$

where  $G'_R(z,L)$  is finite for all  $z \in [0, L/2]$ . Hence, the first term of Eq. (42) is finite but the second has a logarithmic divergence at  $z=0$  when  $\Delta > 0$ . Introducing a large  $P$  cutoff in the integral in Eq. (37) defining  $G_R(z,L)$ , as was done in Ref. [9], eliminates the  $1/z$  singularity in  $G(L,z)$  but has no physical basis, in fact it is eliminating a physical effect which should be there due to the presence of image charges; the divergent term of  $G_R(z,L)$  should be kept in the exponential (which is just the Boltzmann factor due to the image charges). We can now carry out a legal expansion in  $g$  for the terms which give finite contributions, and obtain

$$\beta\mathcal{P}_d^{(1)} = \frac{g}{32\pi}G_R^2(L/2,L) + \frac{g}{8\pi}\int_0^{L/2} dz G'_R(z,L) \frac{\partial}{\partial L} G'_R(z,L) + \frac{1}{4\pi}\int_0^{L/2} dz \frac{\partial}{\partial L} G'_R(z,L) \left[ 1 - \exp\left(-\frac{g\Delta e^{-2z}}{4z}\right) \right]. \quad (44)$$

We now write the two-loop contribution to the disjoining pressure as the sum of these three terms

$$\beta\mathcal{P}_d^{(1)} = \beta\mathcal{P}_d^{(1a)} + \beta\mathcal{P}_d^{(1b)} + \beta\mathcal{P}_d^{(1c)}. \quad (45)$$

The first two terms can be immediately written down and a careful asymptotic analysis of the last term of Eq. (44) gives a finite resummed two-loop contribution

$$\beta\mathcal{P}_d^{(1a)} = \frac{g}{32\pi}G_R^2(L/2,L), \quad (46)$$

$$\beta\mathcal{P}_d^{(1b)} = \frac{g}{8\pi} \left( \int_0^{L/2} dz \left\{ G_R(z,L) \left[ \frac{\partial}{\partial L} G'_R(z,L) - \frac{\partial}{\partial L} G'_R(0,L) \right] + G'_R(z,L) \frac{\partial}{\partial L} G'_R(0,L) \right\} \right), \quad (47)$$

$$\beta\mathcal{P}_d^{(1c)} = \frac{g\Delta}{16\pi} \left\{ \frac{\partial}{\partial L} G'_R(0,L) \left[ -\ln\left(\frac{g\Delta}{2}\right) + 1 - 2\gamma \right] \right\}, \quad (48)$$

where  $\gamma=0.577\ 215\dots$  is Euler's constant. We see from the third term a contribution proportional to  $g \ln(g)$  signifying

that the assumption that  $\mathcal{P}_d$  can be naively expanded in  $g$  is incorrect.

### III. LARGE $L$ ASYMPTOTICS

In this section we will analyze the asymptotic behavior of the disjoining pressure of thick films. We start by recalling the one loop result. At large  $L$  the behavior of the integral determining  $\mathcal{P}_d^{(0)}$  in Eq. (40) is dominated by small  $P$ , i.e., the contribution to the integration coming from near  $P=1$ . The leading term for large  $L$  is [5]:

$$\beta\mathcal{P}_d^{(0)} \approx -\frac{\exp(-2L)}{4\pi L}. \quad (49)$$

We see that the thick film disjoining pressure at one loop is attractive and exponentially screened with characteristic length  $l_D$ . Interestingly, the value of  $\Delta$  does not appear in the leading term of this expression which is therefore independent of the strength of the dielectric discontinuity between the film and exterior. For large  $L$  we find that

$$G_R(L/2,L) \approx 2\frac{\exp(-L)}{L}, \quad (50)$$

and thus

$$\beta\mathcal{P}_d^{(1a)} \approx \frac{g}{8\pi} \frac{\exp(-2L)}{L^2}, \quad (51)$$

which is clearly negligible with respect to the one-loop contribution at large  $L$ .

The behavior of  $G'(z,L)$  at large  $L$  is given to leading order by

$$G'_R(z,L) \approx \exp(-2L) \left[ \frac{1}{L} + \frac{1}{2L-z} \exp(2z) + \frac{1}{2L+z} \exp(-2z) \right] + H(z), \quad (52)$$

where

$$H(z) = \int_1^\infty dP [(\Gamma(P) - \Delta)] \exp(-2Pz). \quad (53)$$

Hence,

$$\frac{\partial}{\partial L} G'_R(z,L) \approx -2 \exp(-2L) \left[ \frac{1}{L} + \frac{1}{2L-z} \exp(2z) + \frac{1}{2L+z} \exp(-2z) \right]. \quad (54)$$

Using this result we find that for large  $L$  the leading behavior is

$$\beta\mathcal{P}_d^{(1b)} \approx -\frac{g}{16\pi} \frac{\exp(-2L)}{L} \left\{ \ln(L) + \gamma + \frac{8}{1-n^2} [\ln(1+n) - n \ln(2)] + O\left(\frac{1}{L^{1/2}}, \frac{\ln(L)}{L}\right) \right\}, \quad (55)$$

and for the special case  $n=0$  the nonleading  $O(1/L^{1/2})$  correction is absent and this result becomes

$$\beta\mathcal{P}_d^{(1b)} \approx -\frac{g}{16\pi} \frac{\exp(-2L)}{L} \left[ \ln(L) + \gamma + \frac{1}{2L} \ln(L) + O\left(\frac{1}{L}\right) \right]. \quad (56)$$

It can be shown that the coefficient of  $\exp(-2L)\ln(L)/L$  is independent of  $n$  in the general case and is therefore given for any value of  $n$  by this result. Hence, as in the case of  $\mathcal{P}_d^{(0)}$ , the leading contribution to  $\mathcal{P}_d^{(1)}$  at large  $L$  is also independent of  $\Delta$ .

We also find

$$\beta\mathcal{P}_d^{(1c)} \approx -\frac{g\Delta \exp(-2L)}{4\pi L} [-\ln(g\Delta/2) + 1 - 2\gamma]. \quad (57)$$

We notice that if we take the contribution of the one-loop term with the leading two-loop term then we have

$$\beta\mathcal{P} \approx -\frac{\exp(-2L)}{4\pi L} \left[ 1 + \frac{g}{4} \ln(L) \right], \quad (58)$$

which suggests the speculative resummation

$$\beta\mathcal{P} \approx -\frac{\exp(-2L)}{4\pi L^{1-g/4}}. \quad (59)$$

If valid, the terms leading to this resummation must come from higher-order terms in the cumulant expansion. It can be verified that they do not arise from higher-order terms in  $g$  in the expansion of Eq. (41).

Examining the contributions to  $\beta\mathcal{P}^{(1)}$  as defined by Eq. (45) at large  $L$  we see that  $\beta\mathcal{P}^{(1a)}$  is clearly subdominant, but although  $\beta\mathcal{P}^{(1b)}$  is clearly the leading term at very large  $L$  we must bear in mind that this expansion is valid for small  $g$ . Comparing Eq. (56) with Eq. (57) we see that there exists a crossover length  $L^*$  defined by

$$L^* \sim 1/g^4, \quad (60)$$

such that for  $1 \ll L \ll L^*$  we have  $\beta\mathcal{P}^{(1)} \approx \beta\mathcal{P}^{(1c)}$  and thus in this region  $\beta\mathcal{P}^{(1)}$  has the same functional form as the one-loop result. Thus only for  $L \gg L^*$  does one see the modification of the functional form of  $\beta\mathcal{P}$  with respect to the one-loop result.

#### IV. NUMERICAL RESULTS

The major result of this paper for the large- $L$  asymptotic behavior of  $\mathcal{P}_d$  is the expression Eq. (55). In Fig. 1 we show data points for

$$R_d^{(1b)}(L) = \frac{16\pi L}{g} e^{2L} \beta\mathcal{P}_d^{(1b)} \quad (61)$$

vs  $L$  computed numerically using Eqs. (37), (43), and (47) for  $n=0$ . The solid line is the asymptotic form derived for  $R_d^{(1b)}(L)$  from the expression in Eq. (56) but including a term proportional to  $1/L$  whose coefficient we determine by a fit to the data. This fit curve is

$$R_d^{(1b)}(L) = -\gamma - \ln(L) - \frac{1}{2L} \ln(L) - \frac{1.45354}{L}. \quad (62)$$

It is not useful to directly plot  $\mathcal{P}_d^{(1)}$  given in Eq. (41) since it is a rapidly changing function of  $L$ . However, the impor-

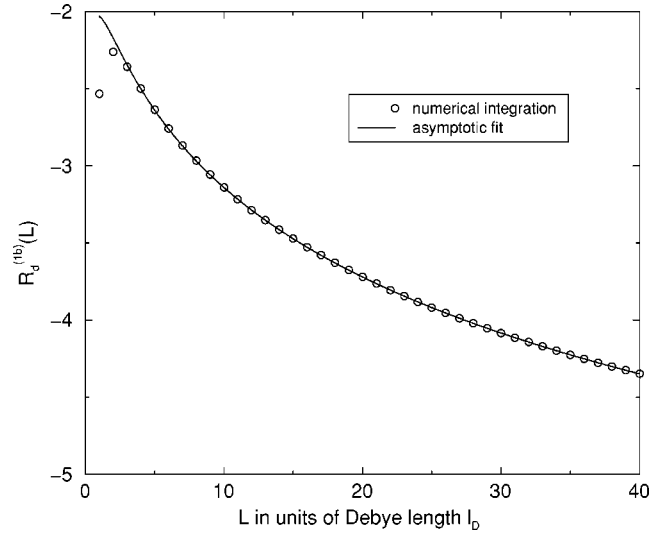


FIG. 1. Computed data for  $R_d^{(1b)}(L)$  given in terms of  $\mathcal{P}_d^{(1b)}$  in Eq. (61). The solid curve is the prediction for the asymptotic  $L$  dependence from Eq. (55) with an additional fitted term proportional to  $1/L$ . The equation for this curve is given in Eq. (62).

tant comparison is with the one-loop result  $\mathcal{P}_d^{(0)}$ , which corresponds to the attractive Casimir force and which is present even as  $\rho \rightarrow 0$ , that is,  $g \rightarrow 0$ . In this limit  $\mathcal{P}_d^{(0)}$  arises solely from the thermal fluctuations of the electrostatic field in the presence of interfaces of dielectric discontinuity. In the limit  $g \rightarrow 0$  the two-loop contribution must vanish since the one-loop result is exact; this can be seen in the expressions given earlier. However, for  $g > 0$  we see that  $\mathcal{P}_d^{(1)}$  is of the same sign as  $\mathcal{P}_d^{(0)}$  and so corresponds to an increase in the attractive force. In Fig. 2 we plot the ratio  $\mathcal{P}_d^{(1)}/\mathcal{P}_d^{(0)}$  for various values of  $g$ :  $g=0.1, 0.3, 0.5$ . We see that  $\mathcal{P}_d^{(1)}$  is comparable with  $\mathcal{P}_d^{(0)}$  for  $g \sim 0.5$  over a wide range of values of the film thickness  $L$ . For small enough  $L$  ( $L \leq 2$ ) the one-loop result eventually dominates. It is clear that  $\mathcal{P}_d^{(1)}$  scales, as expected, approximately linearly with  $g$  in the small range considered. The value  $g \sim 0.5$  corresponds to a solute density in water of about 50 mM at room temperature. This result shows that a quantitative analysis of the collapse phenomenon in a thin electrolyte soap film must take account of higher-order effects for solute densities greater than 10 mM. An important point to note is that both  $\mathcal{P}_d^{(0)}$  and  $\mathcal{P}_d^{(1)}$  are negative for all  $L > 0$ , and so the two-loop contribution adds to the attractive force between the interfaces.

In Fig. 3 we plot the ratio  $\mathcal{P}_d^{(1)}/\mathcal{P}_d^{(1c)}$  where the denominator is the approximation to  $\mathcal{P}_d^{(1)}$  given in Eq. (57). This approximation arises from the resummed terms which properly account for the Boltzmann factor associated with the image charges. It is clear that this approximation is a good one over a wide range of film thickness  $L$  and shows that the dominant contribution in this range behaves as  $g \ln(g)$ . It is clear that this should be the case in this range as in the case  $g=0.5$ , from Eq. (3)  $L^* \sim 16$ .

#### V. CONCLUSION

In this paper we have carefully calculated the two-loop contribution,  $\mathcal{P}_d^{(1)}$ , to the disjoining pressure for a thin elec-

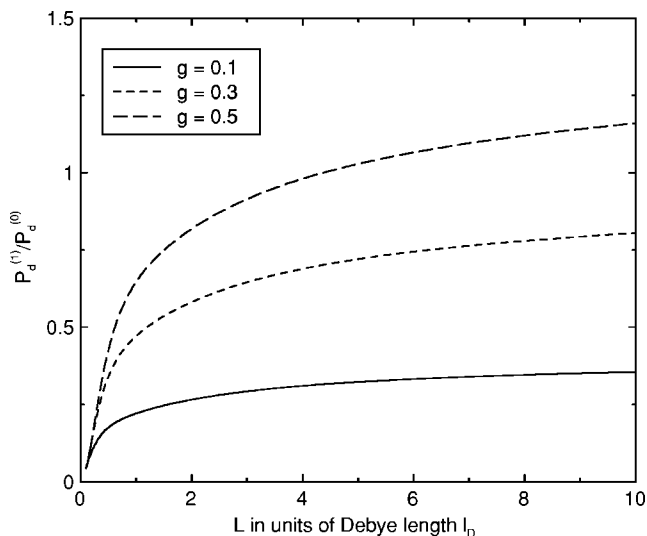


FIG. 2. The ratio of the two-loop contribution,  $\mathcal{P}_d^{(1)}$ , and the one-loop contribution,  $\mathcal{P}_d^{(0)}$ , to the disjoining pressure is plotted for different values of  $g=l_D/l_B$ :  $g=0.1, 0.3, 0.5$ . We see that  $\mathcal{P}_d^{(1)}$  is comparable with  $\mathcal{P}_d^{(0)}$  for  $g \sim 0.5$  over a wide range of values of the film thickness  $L$ . For small enough  $L$  ( $L \leq 2$ ) the one-loop result eventually dominates. It is clear that  $\mathcal{P}_d^{(1)}$  scales, as expected, approximately linearly with  $g$  in the small range considered. The value  $g \sim 0.5$  corresponds to a solute density of about 50 mM at room temperature.

trolite soap film of thickness  $l$  and monovalent solute density  $\rho$ . The surfaces of the film are the interfaces of dielectric discontinuity separating the film interior of dielectric constant  $\epsilon$  from the exterior which consists of nonionic medium of dielectric constant  $\epsilon_0$ . The length scales in the problem are set by the Bjerrum length  $l_B = e^2 \beta / (4\pi\epsilon)$  and the Debye length  $l_D^{-1} = m = \sqrt{2\rho e^2 \beta / \epsilon}$ . The model used for the ionic interactions is the Sine-Gordon field theory extensively dis-

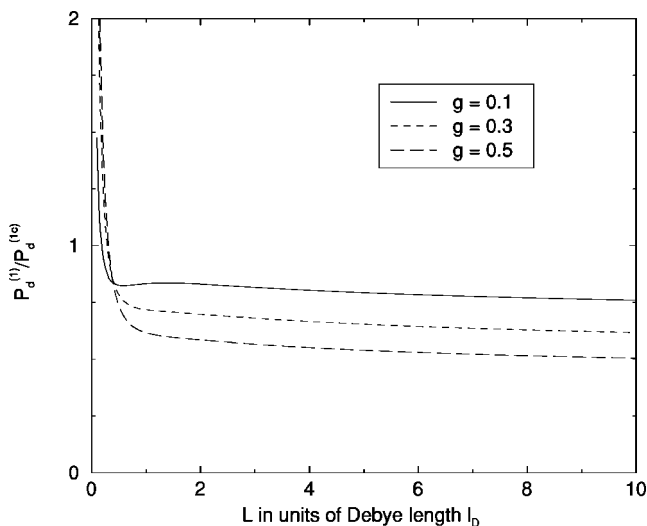


FIG. 3. The ratio of the exact two-loop result,  $\mathcal{P}_d^{(1)}$  for the disjoining pressure and the approximate result  $\mathcal{P}_d^{(1c)}$  given in Eq. (57).  $\mathcal{P}_d^{(1c)}$  is seen to be a good approximation until  $L$  becomes small or larger than  $L^*$  as defined by Eq. (60) ( $L^* \sim 16$  for  $g=0.5$ ).

cussed in earlier work [8]. All quantities can be expressed in dimensionless form in terms of the coupling constant  $g = l_B/l_D$  and  $n = \epsilon_0/\epsilon$ , with overall dimensions carried by the Debye mass  $m$ . By naive power counting the  $N$ -loop contribution is the  $O(g^{N-1})$ . The self-energy divergences are included in the explicit renormalization constant  $Z(g)$  defined in Eq. (5).

We have computed  $\mathcal{P}_d^{(1)}$  in the cumulant expansion of the film free energy  $\ln(\Xi_F)$  given in terms of the effective action  $S_F(\phi, L)$  defined in Eq. (12). Although, we are naively working to  $O(g)$  it is clear that it is illegal to expand all terms to this order since the effect of image charges is to introduce a spurious ultraviolet divergence in this case. As an ion at distance  $z$  from an interface approaches the interface the image potential is repulsive and diverges like  $\beta V_I(z) \approx g\Delta/2z$ , where  $\Delta = (1-n)/(1+n)$ . It is necessary to keep the Boltzmann factor  $\exp[-\beta V_I(z)]$  intact for this otherwise divergent contribution, which is then regulated in the proper way. The resulting expression for  $\mathcal{P}_d^{(1)}$  is given in Eq. (44). The outcome is that the naive expectation that this contribution is  $O(g)$  is incorrect and the asymptotic analysis of the expression for  $\mathcal{P}_d^{(1)}$  gives the term  $\mathcal{P}_d^{(1c)}$  shown in Eq. (48) which contains a term of order  $g \ln(g)$ . Moreover, in Fig. 3 we see that the approximate expression  $\mathcal{P}_d^{(1c)}$  contributes the major part of the full result for small  $L = l/l_D$ , and so the collapse phenomenon observed in thin electrolytic soap films may be modified significantly by such nonanalytic terms. From Fig. 2 we observe that the two-loop and one-loop contributions are comparable for  $g \sim 0.5$ , corresponding to solute densities  $\rho \sim 50$  mM. For  $L \ll 1$  we would still expect the one-loop contribution,  $\mathcal{P}_d^{(0)}$ , to dominate all others on physical grounds; the image charges will ensure that all ions are expelled from the film leaving a nonionic water-filled film. The only, and therefore exact, contribution is the Casimir term due purely to the presence of the dielectric discontinuities.

The question arises how large  $g$  can be taken before the loop expansion breaks down. The only evidence is from the calculation of the bulk Debye pressure where the Debye-Hückel correction to the ideal value  $P_0$  is

$$P_B = P_0 \left( 1 - \frac{g}{6} \right). \quad (63)$$

This suggests that the expansion parameter might be as small as  $g/6$ . However, we know that the two-loop term is  $O[g \ln(g)]$  and that our calculation deals with the effects of an interface whose physics is completely different from that of the bulk. Nevertheless, we may take this result as an indication of what we might expect.

We might have expected that the leading large- $L$  contribution from  $\mathcal{P}_d^{(1)}$  behaves in a similar manner to that of the one-loop contribution, namely

$$\mathcal{P}_d^{(0)} \approx -\frac{A}{L} \exp(-2L). \quad (64)$$

However, the analysis of the large  $L$  behavior shows a departure from expectations because of subtle contribution

from the image charges; we see from Eq. (56) and from Fig. 1 that the leading large- $L$  term behaves as

$$\mathcal{P}_d^{(1)} \approx -gA' \frac{\ln(L)}{L} \exp(-2L). \quad (65)$$

This result implies that for sufficiently large  $L$  the loop-expansion fails to converge since  $\mathcal{P}_d^{(1)}$  will become larger than  $\mathcal{P}_d^{(0)}$ . We suggest that higher-order loop contribution can be resummed to give an anomalous exponent as shown in Eq. (59); this point requires further investigation. However, for physically relevant conditions the loop expansion will be valid.

The conclusion of this paper is that the naive loop expansion of the free energy for these systems is invalid in the presence of a dielectric discontinuity, and a careful resummation of higher loop-order terms must be employed to properly take into account the Boltzmann weight of image charges. Furthermore, at two-loop order as generated by the cumulant expansion, the disjoining pressure is finite without the need for the introduction of an ultraviolet regulator. In addition, we have shown that the two-loop disjoining pressure is negative for  $L > 0$  and so enhances the attraction between the interfaces predicted at one-loop order.

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