

Field theoretic calculation of the surface tension for a model electrolyte systemD. S. Dean^{1,2,*} and R. R. Horgan^{1,†}¹*DAMTP, CMS, University of Cambridge, Cambridge CB3 0WA, United Kingdom*²*IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France*

(Received 7 November 2003; published 2 June 2004)

We carry out the calculation of the surface tension for a model electrolyte to first order in a cumulant expansion about a free-field theory equivalent to the Debye-Hückel approximation. In contrast with previous calculations, the surface tension is calculated directly without recourse to integrating thermodynamic relations. The system considered is a monovalent electrolyte with a region at the interface, of width h , from which the ionic species are excluded. In the case where the external dielectric constant ϵ_0 is smaller than the electrolyte solution's dielectric constant ϵ we show that the calculation at this order can be fully regularized. In the case where h is taken to be zero the Onsager-Samaras limiting law for the excess surface tension of dilute electrolyte solutions is recovered, with corrections coming from a nonzero value of ϵ_0/ϵ .

DOI: 10.1103/PhysRevE.69.061603

PACS number(s): 68.15.+e, 05.20.-y, 52.25.Kn

I. INTRODUCTION

The first experiments to measure the surface tension of electrolyte solutions show that the excess surface tension, denoted in this paper by σ_e , due to the presence of the electrolyte is positive [1]. This result has been confirmed by more recent experiments [2]. This effect was explained by Wagner [3] who pointed out that when the dielectric constant of the bulk solvent (here water) ϵ is greater than that of the exterior (here air) ϵ_0 then the image charges, due to the dielectric variation across the surface, repel the solute ions from the surface and thus lead to a reduction of the density of ions near the surface with respect to the bulk. Applying the Gibbs adsorption isotherm we then find that σ_e must be positive. In addition experimental results on systems at weak dilution for solutes of the same valency are very similar, suggesting a universal limiting law at weak dilution. Such a universal limiting law was subsequently obtained by Onsager and Samaras [4].

A series of experiments carried out in 1930s [5] caused a certain controversy as at very small electrolyte concentrations a negative excess surface tension was reported. It seems that these experiments have not been revisited using modern techniques, or at least have not been reproduced since. If a negative σ_e is found, then appealing to the Gibbs adsorption isotherm, there must be some mechanism causing ions to be positively adsorbed near the interface. Various authors have discussed ion-specific effects which could explain such a phenomenon [6–10], and also lead to the ion dependent variations seen in the measurements of σ_e at higher concentrations.

The calculation of the surface tension of electrolytes was recently revisited in a series of papers by Levin [11] and Levin and Flores-Mena [12]. Because of the thermodynamic equivalence of ensembles, an exact calculation of the surface tension should give the same result independent of the en-

semble chosen since the thermodynamic identities from which the surface tension is calculated are exact. However, Levin points out that calculations of the surface tension invariably rely on approximation schemes, notably the Debye-Hückel approximation, and that a given approximation scheme will generally yield different results for different choices of thermodynamic ensemble. For example, Levin applies a canonical approach whereas the original Onsager-Samaras result was obtained using the grand-canonical ensemble. In the approach of Levin σ_e is given by the excess Helmholtz free energy due to the presence of an interface. This free-energy excess is obtained by calculating the internal energy due to the presence of the interface and then integrating it via the Güntelberg charging process to obtain the free energy. In the limit of weak electrolytes the Onsager-Samaras limiting law is recovered, thus, as Levin remarks, suggesting that the Onsager-Samaras limiting law is indeed exact.

In this paper we calculate σ_e in the grand-canonical ensemble by directly calculating the excess grand potential due to the presence of an interface. In this way we avoid the integration of differential thermodynamic identities such as the Gibbs adsorption isotherm or the Güntelberg charging process, and so provide another route for doing the calculation. In addition, we develop a controlled perturbation theory based on a cumulant expansion, similar to that used for bulk electrolytes by Netz and Orland [13]; this is a perturbation expansion in the coupling constant $g=l_B/l_D$, where l_D is the Debye length and l_B the Bjerrum length. We show that the Onsager-Samaras limiting law is the first term in this cumulant expansion, showing that it is indeed exact to this order. The limiting laws obtained in the literature are given in the limit where $\epsilon_0/\epsilon \rightarrow 0$, which is clearly a good approximation for aqueous solutions in air where $\epsilon_0/\epsilon \approx 1/80$. In this paper we generalize the Onsager-Samaras result and give the corresponding limiting law in the case where $\epsilon_0/\epsilon > 0$.

Our approach is also applied to a modified model of the interface where there is surface-exclusion layer for the ions of thickness h : a region at the surface from which the hydrated ions are forbidden [4,11,14]. Highly accurate numerical integration is used to investigate the importance of the

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

†Email address: rrh@damtp.cam.ac.uk

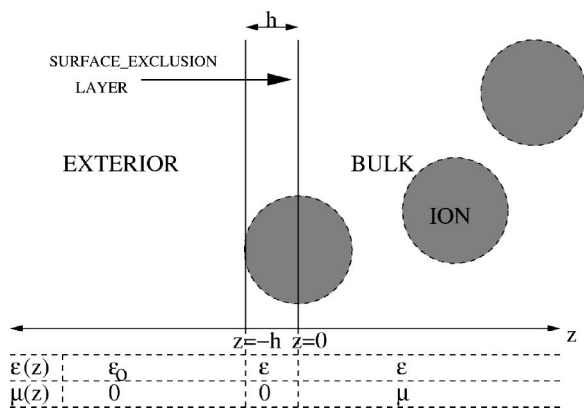


FIG. 1. Schematic image of the exterior bulk interface for the model considered here. The values of the local dielectric constants and fugacities as a function of the distance from the dividing surface are shown. The charges of the ions are taken to be at their centers which are excluded from the surface-exclusion layer of width h .

effect of this exclusion layer on the value of σ_e .

The techniques used in this paper are based on the field theoretic sine-Gordon representation of the grand partition function first introduced in this context in Ref. [15]. The perturbation theory about the free field or Debye-Hückel theory is carried out using a functional path integral technique introduced recently by the authors [16–18], which lends itself to the geometry of planar systems and gives a powerful alternative method for the calculation of the functional determinants involved.

We conclude with a discussion of our results and the possible advantages of our approach for calculating σ_e in more complex models where, for example, a surface charge exists due to a thermodynamic adsorption process for one of the ionic species at the surface or due to a difference in the hydrated radii between the cations and anions.

In this paper we use MKS units throughout.

II. THE MODEL

We consider a model consisting of a semi-infinite electrolyte bulk with monovalent salt in contact with a semi-infinite exterior, see Fig. 1. The bulk solvent's dielectric constant is denoted by ϵ and the exterior dielectric constant is denoted by ϵ_0 . There is a region of width h between the exterior and bulk which is filled with the bulk solvent but from where the salt ions are excluded, this is a standard surface-exclusion layer and was first introduced by Randles [14] in the context of electrolyte surface tensions. The width h of the surface-exclusion layer is the order of a hydrated ion radius. For simplicity both hydrated anions and cations are taken to be of the same size and are hence both excluded from this region and so there is no surface charging process. However, the model and approach can be generalized to ions of different radii which will lead to different ion-specific surface layer widths and so allowing a charging mechanism [17]. The interaction between the ions is taken to be the purely Coulombic interaction between point charges. In general, a

short-distance cutoff corresponding to a hard core interaction between ions of nonzero radius is necessary to regulate ultraviolet divergences in the model, but at the level of approximation used in this paper such divergences are absent and the assumption that the ions may be considered pointlike for the calculation of interior interactions is valid. In the bulk solution the fugacity of the cations and anions is equal and denoted by μ . The system up can be summarized in terms of a spatially dependent dielectric constant $\epsilon(z)$ and spatially dependent fugacity $\mu(z)$ which are defined as follows:

$$\begin{aligned} \epsilon(z) &= \epsilon_0, & z < -h, \\ \epsilon(z) &= \epsilon, & z > -h \end{aligned} \quad (1)$$

and

$$\begin{aligned} \mu(z) &= 0, & z < 0, \\ \mu(z) &= \mu, & z > 0. \end{aligned} \quad (2)$$

In the grand-canonical ensemble the grand partition function for the system is given by the functional integral over the Wick rotated electrostatic potential ϕ ,

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

with the action S given by

$$S[\phi] = -\frac{\beta}{2} \int d\mathbf{x} \epsilon(\mathbf{x}) (\nabla \phi)^2 + 2 \int d\mathbf{x} \mu(\mathbf{x}) \cos(e\beta\phi), \quad (4)$$

where e is the electron charge and β is the inverse temperature. We note that with this action carrying out the functional integral over ϕ induces the Coulomb interaction with image charges between the ions in the system. In addition, this partition function includes the effect of the thermal fluctuations of the electrostatic field which are present even in the absence of ions, namely, at $\mu=0$, which is due to the contribution of fluctuations in the presence of an interface. When $\mu=0$ the partition function which yields this contribution is

$$\Xi(\mu=0) = \det[-\nabla \epsilon(\mathbf{x}) \cdot \nabla]^{-1/2}. \quad (5)$$

This gives a contribution to the surface tension even in the absence of ions. It should be noted that it is incorrect to impose the condition $\Xi(\mu=0)=1$ on $\Xi(\mu)$ since this contribution is then wrongly omitted. For a detailed discussion of this point in terms of quantum electrodynamics we refer the reader to Ref. [16]. The fugacity $\mu(\mathbf{x})$ is determined by the ion density $\rho(\mathbf{x})$. In the system under study ρ is the ion density in the bulk reservoir and thus we have

$$\mu = \frac{\rho}{\langle \cos e\beta\phi \rangle} = Z\rho. \quad (6)$$

The renormalization constant $Z^{-1} = \langle \cos e\beta\phi \rangle$ explicitly accounts for the ion self-interaction effects. Here we have used the fact that at a point \mathbf{x} in the system, the average density of cations/anions is given by

$$\rho_{\pm}(\mathbf{x}) = \mu \langle \exp[\pm ie\beta\phi(\mathbf{x})] \rangle \quad (7)$$

and for \mathbf{x} in the bulk $\rho_{\pm}(\mathbf{x}) = \rho$.

We take the area of the system across the interface to be A and the length (in the z direction) of the exterior to be L' and of the bulk to be L . If one considers just the exterior system without any interface, its grand partition function is given by

$$\Xi_E = \int d[\phi] \exp(S_E[\phi]) \quad (8)$$

with S_E given by

$$S_E[\phi] = -\frac{\beta}{2} \int d\mathbf{x} \epsilon_0 (\nabla \phi)^2, \quad (9)$$

the integration being over the region $L' \times A$. For a pure bulk system with no interface the grand partition function is given by

$$\Xi_B = \int d[\phi] \exp(S_B[\phi]), \quad (10)$$

where S_B is given by

$$S_B[\phi] = -\frac{\beta}{2} \int d\mathbf{x} \epsilon (\nabla \phi)^2 + 2 \int d\mathbf{x} \mu \cos(e\beta\phi), \quad (11)$$

the integration being over the region $L \times A$. The surface tension is then given by the difference in the grand potential of the system with the interface and that of the sum of the two individual (exterior and bulk) systems divided by the total area, i.e.,

$$\sigma = \frac{1}{A} [J(L', L) - J^{(B)}(L) - J^{(E)}(L')], \quad (12)$$

where $J(L', L)$ is the grand potential for the system shown in Fig. 1, and where $J^{(E)} = -\ln(\Xi_E)/\beta$ and $J^{(B)} = -\ln(\Xi_B)/\beta$ denote the grand potentials for a bulk system of electrolyte and exterior system of the same volumes $[L \times A]$ and $[L' \times A]$, respectively, but with no interfaces. The definition of Eq. (12) for the surface tension is, of course, also in agreement with various other methods for calculation. For example, it is the same as that obtained from the Gibbs adsorption equation as originally used by Onsager and Samaras. The expression, Eq. (12), for the surface tension can also be obtained from the formula

$$2\sigma = - \int_0^{\infty} P_d(L) dL, \quad (13)$$

where $P_d(L)$ is the disjoining pressure for a film of external medium of thickness L surrounded by bulk electrolyte [19]. This system consists of two bulk surfaces a distance L apart, and so twice the surface tension is given by the work needed to create an infinitely thick film: $L \rightarrow \infty$. As mentioned in the Introduction, the approach here is different from previous techniques since here the grand potential difference corresponding to the surface tension is calculated directly.

The excess surface tension σ_e for a system with bulk electrolyte concentration ρ is defined by

$$\sigma_e(\rho) = \sigma(\rho) - \sigma(0), \quad (14)$$

where $\sigma(0)$ is the surface tension of the system with no added electrolyte. This definition means that σ_e is free of the ultraviolet or short-distance divergences found in calculations of the surface tension between two media of differing dielectric constants [19,20].

In electrostatic problems where the chemical potential and dielectric constants depend only on the coordinate z , the field theory can be formulated as a functional path integral for a dynamical field $\phi(\mathbf{r}, z)$ which evolves in a temporal coordinate z [18]. The functional Hamiltonians are denoted by H_E in the exterior region, H_B in the bulk and H_S in the surface-exclusion layer. In three dimensions this functional problem cannot be solved exactly but in one dimension it can be and leads to an explicit solution for the one-dimensional Coulomb gas [21]. The free Debye-Hückel theory can be also solved in this formulation [16] and one can develop a perturbation theory about it as we shall show here. For the moment we will use the Hamiltonian formulation explicitly in order to find a formal expression for the excess surface tension. For a globally electroneutral system with no interfaces and Hamiltonian H and length L in the z direction, one may write the grand partition function as [18]

$$\Xi = \text{Tr} \exp(-LH), \quad (15)$$

that is, we take the system to be periodic in the z direction. Hence for the pure bulk of electrolyte density ρ one has that for large L ,

$$\Xi^{(B)} = \langle \Psi_0^{(B)}(\rho) | \exp[-LH_B(\rho)] | \Psi_0^{(B)}(\rho) \rangle \quad (16)$$

and for the exterior region

$$\Xi^{(E)} = \langle \Psi_0^{(E)} | \exp(-L'H_E) | \Psi_0^{(E)} \rangle, \quad (17)$$

where $|\Psi_0^{(B)}(\rho)\rangle$ and $|\Psi_0^{(E)}\rangle$ are the normalized ground-state wave functionals for the bulk and exterior functional Hamiltonians $H_B(\rho)$ and H_E , respectively. Note that the wave functionals must be normalized so that the corresponding grand potential is zero for a system of zero volume, that is, zero length in the z direction. If the corresponding ground-state energies are $E_0^{(B)}(\rho)$ and $E_0^{(E)}$, then we have

$$\beta J^{(B)}(L) = LE_0^{(B)}(\rho), \quad (18)$$

$$\beta J^{(E)}(L') = L'E_0^{(E)}, \quad (19)$$

and the corresponding bulk pressures are given by

$$\beta P^{(B)} = -\frac{E_0^{(B)}(\rho)}{A}, \quad (20)$$

$$\beta P^{(E)} = -\frac{E_0^{(E)}}{A}. \quad (21)$$

For the system with interface we find

$$\Xi = \langle \Psi_0^{(E)} | \exp(-L'H_E) \exp(-hH_S) \exp[-(L-h)H_B] | \Psi_0^{(B)} \rangle \times (\rho), \quad (22)$$

this is easily seen by joining two such systems together with periodic boundary conditions. We thus obtain

$$\beta J(L, L') = \{L'E_0^{(E)} + (L-h)E_0^{(B)}(\rho) - \ln[\langle \Psi_0^{(E)} | \exp(-hH_S) | \Psi_0^{(B)}(\rho) \rangle]\}. \quad (23)$$

Using this the excess surface tension is given by

$$\sigma_e(\rho) = -\frac{1}{\beta A} \left[h[E_0^{(B)}(\rho) - E_0^{(B)}(0)] + \ln \left(\frac{\langle \Psi_0^{(E)} | \exp(-hH_S) | \Psi_0^{(B)}(\rho) \rangle}{\langle \Psi_0^{(E)} | \exp(-hH_S) | \Psi_0^{(B)}(0) \rangle} \right) \right]. \quad (24)$$

Using the relations (20) and (21) we thus obtain

$$\sigma_e(\rho) = h\Delta P(\rho) - \frac{1}{\beta A} \ln \left(\frac{\langle \Psi_0^{(E)} | \exp(-hH_S) | \Psi_0^{(B)}(\rho) \rangle}{\langle \Psi_0^{(E)} | \exp(-hH_S) | \Psi_0^{(B)}(0) \rangle} \right), \quad (25)$$

where

$$\Delta P(\rho) = P_B(\rho) - P_B(0) \quad (26)$$

is the bulk pressure due to the presence of the electrolyte. The expression (25) is difficult to evaluate, although an approach using standard quantum-mechanical perturbation theory might be investigated. However, if the original field theory is free or Gaussian, Eq. (25) is relatively straightforward to compute. We shall use Eq. (25) to evaluate the contribution to the surface tension coming from the free Debye-Hückel theory.

III. CUMULANT EXPANSION OF THE EXCESS SURFACE TENSION

Perturbation theory about the Debye-Hückel theory [13] is carried out by decomposing the action S in the following manner:

$$S = S_0 + \Delta S. \quad (27)$$

The first term S_0 is a Gaussian or free term given by

$$S_0 = -\frac{\beta\epsilon_0}{2} \int_{[-L'-h, -h] \times A} d\mathbf{x} (\nabla\phi)^2 - \frac{\beta\epsilon}{2} \int_{[-h, 0] \times A} d\mathbf{x} (\nabla\phi)^2 - \frac{\beta\epsilon}{2} \int_{[0, L-h] \times A} d\mathbf{x} [(\nabla\phi)^2 + m^2\phi^2] + 2\mu(L-h)A, \quad (28)$$

where m is the Debye mass given by $m^2 = 2\rho e^2\beta/\epsilon$. The correction to the Gaussian action ΔS is given by

$$\Delta S = \int_{[0, L-h] \times A} d\mathbf{x} \left[2\mu[\cos(e\beta\phi) - 1] + \frac{\beta\epsilon m^2}{2} \phi^2 \right]. \quad (29)$$

The term ΔS is of the order of the dimensionless coupling constant $g = l_B/l_D$, where $l_D = 1/m$ is the Debye length and

$l_B = e^2\beta/4\pi\epsilon$ is the Bjerrum length. A cumulant expansion in ΔS generates a resummed expansion in g in the sense that the term of order n in the cumulant expansion has the form $C_n = g^n f_n(g)$. In the bulk the function $f_n(g)$ then has the form $f_n(g) = \sum_{m=1}^{\infty} a_{n,m} g^m$. However, in the presence of the interface we will see that $f_n(g)$ has an extra term containing logarithmic terms in g of type $\sum_{m=1}^{\infty} a'_{n,m} g^m \ln(g)$. This can be shown by considering the form of the bulk action S_B written in terms of the dimensionless field $\phi' = e\beta\phi/\sqrt{g}$ and by measuring length in units of the Debye length ($y = mx$). In the new field and length variables one has the bulk action

$$S_B = -\frac{1}{2} \int d\mathbf{y} \frac{1}{4\pi} (\nabla\phi')^2 + \frac{Z(g)}{4\pi g} \int d\mathbf{y} \cos(\sqrt{g}\phi'), \quad (30)$$

where $Z(g)$ defined in Eq. (6) is given by $Z(g) = 1/\langle \cos(\sqrt{g}\phi') \rangle$. It is easy to check that $Z(g) = 1 + z_1 g + z_2 g^2 + \dots$. Using the same decomposition in the bulk as above we obtain

$$S_B = S_0 + \Delta S, \quad (31)$$

where

$$S_0 = -\frac{1}{2} \int d\mathbf{y} \frac{1}{4\pi} [(\nabla\phi')^2 + \phi'^2] + \frac{Z(g)}{4\pi g} \int d\mathbf{y} \quad (32)$$

is the Gaussian or free action and

$$\Delta S = \frac{1}{4\pi g} \int d\mathbf{y} \left[Z(g) \cos(\sqrt{g}\phi') + \frac{g}{2} \phi'^2 - Z(g) \right]. \quad (33)$$

Using the series form for $Z(g)$ we see that ΔS can be expressed as a power series in g with first term $O(g)$. It can also be shown that $\langle \Delta S \rangle = 0$ at $O(g)$ for the homogeneous bulk system; the corollary is that $\langle \Delta S \rangle \neq 0$ at $O(g)$ only for systems which are not translationally invariant such as the system with an interface under discussion here. The outcome is that when calculating to leading order in g we just need to keep the first term in the cumulant expansion of the free-field theory with ΔS treated as a perturbation and the $O(g)$ contributions to $J^{(B)}(L)$ and $J^{(E)}(L')$ in Eq. (12) are zero. We write

$$\Xi = \int d[\phi] \exp(S_0 + \Delta S) \approx \exp(\langle \Delta S \rangle_0) \int d[\phi] \exp(S_0) \quad (34)$$

with

$$\langle \Delta S \rangle_0 = \frac{\int d[\phi] \Delta S \exp(S_0)}{\int d[\phi] \exp(S_0)}. \quad (35)$$

The first term in the cumulant expansion can also be shown to begin with the two-loop term of the standard loop expansion, and hence we shall also refer the calculation that follows as the two-loop, or more correctly, the resummed two-loop calculation.

To this order of approximation the grand potential is given by

$$J = J_0 + \Delta J \quad (36)$$

with

$$-\beta J_0 = \ln \left(\int d[\phi] \exp(S_0) \right), \quad (37)$$

$$-\beta \Delta J = \langle \Delta S \rangle_0. \quad (38)$$

The action S_0 is Gaussian and we define the correlation function of the field ϕ at the same point and a distance z from the surface-exclusion layer by

$$\langle \phi(\mathbf{r}, z) \phi(\mathbf{r}, z) \rangle_0 = G(0, z), \quad (39)$$

where we have used the fact that the system is isotropic in the plane A ($\mathbf{r} \in A$) but is not isotropic in the direction z . As the action S_0 is purely quadratic we also have that

$$\langle \phi(\mathbf{r}, z) \rangle_0 = 0. \quad (40)$$

For the bulk system (i.e., without an interface) we note that the same-point field correlator at this level of approximation is given by

$$\langle \phi(\mathbf{r}, z) \phi(\mathbf{r}, z) \rangle_0 = G_B(0) = G(0, \infty) \quad (41)$$

since the physics as $z \rightarrow \infty$ for the system with an interface at $z=0$ is the same as that of the bulk system. Using this result, we find that for the system with interface

$$\langle \Delta S \rangle_0 = A \int_0^\infty dz \left\{ 2\mu \left[\exp\left(-\frac{e^2 \beta^2 G(0, z)}{2}\right) - 1 \right] + \frac{\beta \epsilon m^2}{2} G(0, z) \right\}. \quad (42)$$

Using Eq. (7) to relate ρ and μ , we find that to $O(g)$ the fugacity μ is determined by

$$\rho = \mu \exp\left(-\frac{\beta^2 e^2}{2} G(0, \infty)\right). \quad (43)$$

Using the results above, we find

$$\langle \Delta S \rangle_0 = A \int dz \left\{ 2\rho \left[\exp\left(-\frac{e^2 \beta^2 G_R(0, z)}{2}\right) - \exp\left(-\frac{e^2 \beta^2 G(0, \infty)}{2}\right) \right] + \frac{\beta \epsilon m^2}{2} G(0, z) \right\}, \quad (44)$$

where we have defined

$$G_R(0, z) = G(0, z) - G(0, \infty). \quad (45)$$

Since we seek a result accurate to $O(g)$ we may expand the second exponential in the integral in Eq. (44) to first order and neglect higher $O(g^2)$ terms. Using the definition of the Debye mass m this yields

$$\frac{\langle \Delta S \rangle_0}{A} = \int dz \left\{ 2\rho \left[\exp\left(-\frac{e^2 \beta^2 G_R(0, z)}{2}\right) - 1 \right] + \frac{\beta \epsilon m^2}{2} G_R(0, z) \right\}. \quad (46)$$

The first term in Eq. (46) is finite even in the limit $h \rightarrow 0$ whereas the second term

$$\Gamma = \frac{\beta \epsilon m^2}{2} \int dz G_R(0, z) \quad (47)$$

is ultraviolet divergent as $h \rightarrow 0$. This divergence is due to the integral over the potential due to the image charge. We might naively resolve this potential difficulty by observing that if we also expand the first exponential in Eq. (46) this term is exactly canceled $\langle \Delta S \rangle_0 = 0$ to $O(g)$, so resolving the difficulty. However, this expansion is incorrect since this divergence is, in fact, canceled by another arising in J_0 . The expansion of the first exponential gives rise to an erroneous divergence which then survives wrongly in the final result; there is no such divergence. The form of Eq. (46) is familiar since the first exponential is the Boltzmann factor for the repulsive image-charge potential that we should expect to appear and is reminiscent of terms in the Mayer expansion.

To calculate $G(0, z)$ it is convenient to use the path integral representation of the problem. Using

$$\phi(\mathbf{r}, z) = \frac{1}{\sqrt{A}} \sum_{\mathbf{p}} \tilde{\phi}(\mathbf{p}, z) \exp(i\mathbf{p} \cdot \mathbf{r}), \quad (48)$$

we find that the Gaussian action S_0 simply becomes sum of independent Harmonic oscillators

$$S_0 = 2\mu AL + \sum_{\mathbf{p}} S_{\mathbf{p}}, \quad (49)$$

where

$$S_{\mathbf{p}} = -\frac{1}{2} \int dz \left[M(z) \frac{\partial \tilde{\phi}(\mathbf{p})}{\partial z} \frac{\partial \tilde{\phi}(-\mathbf{p})}{\partial z} + M(z) \omega^2(\mathbf{p}, z) \tilde{\phi}(\mathbf{p}) \tilde{\phi}(-\mathbf{p}) \right], \quad (50)$$

where $M(z) = \beta \epsilon(z)$, $\omega(\mathbf{p}, z) = |\mathbf{p}| = p$ for $z \in [-L', h]$ and $\omega(\mathbf{p}, z) = \sqrt{p^2 + m^2}$ for $z \in [h, L]$. By expanding in terms of the Fourier modes we find that

$$G(0, z) = \frac{1}{A} \sum_{\mathbf{p}} \langle \tilde{\phi}(\mathbf{p}, z) \tilde{\phi}(-\mathbf{p}, z) \rangle_0. \quad (51)$$

The Euclidean Feynman propagator for a simple harmonic oscillator, with Hamiltonian denoted by $H_o(\omega, M)$, over a time t given by [22]

$$\begin{aligned} &\langle X|\exp[-tH_o(\omega,M)]|Y\rangle \\ &= \left(\frac{M\omega}{2\pi\sinh(\omega t)}\right)^{1/2} \exp\left(-\frac{1}{2}M\omega\coth(\omega t)[X^2+Y^2\right. \\ &\quad \left.-2XY\operatorname{sech}(\omega t)]\right) \end{aligned} \quad (52)$$

and the ground-state wave function is given by

$$\langle\psi_0(\omega,M)|X\rangle = \left(\frac{M\omega}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}M\omega X^2\right) \quad (53)$$

with energy $E_0(\omega,M)=\omega/2$. In the free-field theory we thus find

$$\langle\tilde{\phi}(\mathbf{p},z)\tilde{\phi}(-\mathbf{p},z)\rangle_0 = \frac{\langle\psi_0(\omega_E(\mathbf{p}),M_E)|\exp[-hH_o(\omega_S(\mathbf{p}),M_S)]\exp[-zH_o(\omega_B(\mathbf{p}),M_B)]X^2|\psi_0(\omega_B(\mathbf{p}),M_B)\rangle}{\langle\psi_0(\omega_E(\mathbf{p}),M_E)|\exp[-hH_o(\omega_S(\mathbf{p}),M_S)]\exp[-zH_o(\omega_B(\mathbf{p}),M_B)]|\psi_0(\omega_B(\mathbf{p}),M_B)\rangle}, \quad (54)$$

where the subscripts B , E , and S refer to the bulk exterior and surface-exclusion layer values of the various simple harmonic oscillator Hamiltonians H_o and the corresponding masses M and frequencies ω in these regions.

Carrying out the Gaussian integrations we thus obtain that

$$\langle\tilde{\phi}(\mathbf{p},z)\tilde{\phi}(-\mathbf{p},z)\rangle_0 = D_{33}^{-1}, \quad (55)$$

where D is the matrix

$$D = \begin{pmatrix} a & -b & 0 \\ -b & c & -d \\ 0 & -d & e \end{pmatrix}. \quad (56)$$

The elements of D are given by

$$a = \beta\epsilon_0 p + \beta\epsilon p \coth(ph),$$

$$b = \beta\epsilon p \operatorname{cosech}(ph),$$

$$c = \beta\epsilon p \coth(ph) + \beta\epsilon\sqrt{p^2+m^2}\coth(\sqrt{p^2+m^2}z),$$

$$d = \beta\epsilon\sqrt{p^2+m^2}\operatorname{cosech}(\sqrt{p^2+m^2}z),$$

$$e = \beta\epsilon\sqrt{p^2+m^2}[1 + \coth(\sqrt{p^2+m^2}z)]. \quad (57)$$

A long but straightforward calculation now gives the result

$$G(0,z) = \frac{m}{2\pi\beta\epsilon} \int dk k \frac{K \coth(Kmz) + kB}{K(kB+K)[1 + \coth(Kmz)]}, \quad (58)$$

where the integral over k is between 0 and Λ/m where Λ is an ultraviolet cutoff in the Fourier modes of the field ϕ in the plane A . In the present calculation we will see there are no ultraviolet divergences and we may take the limit $\Lambda \rightarrow \infty$. In Eq. (58) and throughout the rest of this paper we use the following definitions:

$$K = \sqrt{k^2 + 1} \quad (59)$$

and

$$B = \frac{1 - \Delta \exp(-2kmh)}{1 + \Delta \exp(-2kmh)}, \quad (60)$$

where

$$\Delta = \frac{\epsilon - \epsilon_0}{\epsilon_0 + \epsilon}. \quad (61)$$

Using Eq. (58) we find that

$$G(0,\infty) = \frac{m}{4\pi\beta\epsilon} \int dk \frac{k}{K}, \quad (62)$$

and using Eqs. (58) and (62) we obtain

$$G_R(0,z) = \frac{m}{4\pi\beta\epsilon} \int dk \frac{k(K-kB)}{K(kB+K)} \exp(-2K mz) = \frac{g}{e^2\beta^2} A(zm). \quad (63)$$

In the case $\Delta=1$, Levin and Flores-Mena in Eq. (8) of Ref. [12] quote a similar formula for $W(z)$ in their notation. Comparing our result at $\Delta=1$ with theirs, we note a misprint where the exponential $\exp[-2k(z-d)]$ in the integrand of their equation should read $\exp(-2pz)$. With this correction we identify

$$W(z) = \frac{g}{2} A(mz) \Big|_{\Delta=1}, \quad \text{with } d \equiv h. \quad (64)$$

Our result, however, applies for all Δ , $0 \leq \Delta \leq 1$, and all $h \geq 0$.

Using Eqs. (63) and (47) we find

$$\Gamma = \frac{\rho g}{2m} \int dk k \frac{K - kB}{K^2(kB + K)}. \quad (65)$$

Repeating the above calculation for a pure bulk system, we see that in the absence of an interface that $G_R(z,0)=0$ and consequently that the corresponding term $\langle\Delta S\rangle_0$ is zero, and so for the pure bulk without interface we have to one loop that $J^{(B)}=J_0^{(B)}$. For a pure exterior system the action is purely Gaussian and $\Delta S^{(E)}=0$ identically, and so to one loop Eq. (12) becomes

$$\sigma = \frac{1}{A}(\Delta J + J_0 - J_0^B - J_0^E). \tag{66}$$

$$\sigma_e^*(\rho) = \frac{\Delta J}{A} \tag{68}$$

The excess surface tension is thus given by

$$\sigma_e(\rho) = \sigma_e^*(\rho) + \sigma_e^{(0)}(\rho), \tag{67}$$

where

and $\sigma_e^{(0)}(\rho)$ is the excess surface tension for a system with just the action S_0 which can be calculated exactly in the quantum mechanical formulation as all the simple harmonic oscillators are decoupled. We have from Eq. (25),

$$\begin{aligned} \sigma_e^{(0)}(\rho) = & 2\mu h - \frac{1}{\beta A} \sum_{\mathbf{p}} \left[h[E_0(\omega_B(\mathbf{p}, \rho), M_B) - E_0(\omega_B(\mathbf{p}, 0), M_B)] \right. \\ & \left. + \ln \left(\frac{\langle \psi_0(\omega_E(\mathbf{p}), M_E) | \exp[-hH_o(\omega_S(\mathbf{p}), M_S)] | \psi_0(\omega_B(\mathbf{p}, \rho), M_B) \rangle}{\langle \psi_0(\omega_E(\mathbf{p}), M_E) | \exp[-hH_o(\omega_S(\mathbf{p}), M_S)] | \psi_0(\omega_B(\mathbf{p}, 0), M_B) \rangle} \right) \right], \end{aligned} \tag{69}$$

where we have made explicit the dependence of the bulk frequencies ω_B on ρ , $\omega_B(\mathbf{p}; \rho) = \sqrt{p^2 + m^2(\rho)}$. Note that the first term in the right-hand side of the above comes from the constant, or ideal, term in the action S_0 .

Using Eqs. (52) and (53) we obtain

$$\begin{aligned} \sigma_e^{(0)}(\rho) = & P_{Debye} h + \frac{\rho g}{m\beta} \int k dk \left\{ 2 \ln \left[1 + \frac{K-k}{2k} (1 + \Delta \right. \right. \\ & \left. \left. \times \exp(-2kmh)) \right] - \ln \left(\frac{K}{k} \right) \right\} \end{aligned} \tag{70}$$

with P_{Debye} the Debye pressure, that is, to say the bulk pressure to $O(g)$, given by

$$\beta P_{Debye} = 2\mu - \frac{1}{4\pi} \int k dk (K - k) = 2\rho - \frac{m^3}{24\pi} = 2\rho \left(1 - \frac{g}{6} \right), \tag{71}$$

where the rightmost expression in Eq. (71) is obtained after calculating μ in terms of ρ [16].

Collecting all these contributions we arrive at our final result for the excess surface tension

$$\begin{aligned} \beta \sigma_e = & 2\rho h \left(1 - \frac{g}{6} \right) + \frac{2\rho}{m} \int mdz \left\{ 1 - \exp \left[-\frac{g}{2} A(mz) \right] \right\} \\ & + g \frac{\rho}{2m} \int dk k \left\{ 4 \ln \left[1 + \frac{K-k}{2k} [1 + \Delta \exp(-2kmh)] \right] \right. \\ & \left. - 2 \ln \left(\frac{K}{k} \right) + \frac{(kB - K)}{K^2(kB + K)} \right\}, \end{aligned} \tag{72}$$

where the function $A(mz)$ as defined by Eq. (63), and we have arranged the terms to explicitly show the dependence on the dimensionless coupling g . We denote the first term to be the exclusion term, the second to be the depletion term, and the third to be the Casimir term. This last designation is made because this term represents the contribution from the quadratic thermal fluctuations of the electrostatic field in the presence of a dielectric discontinuity in the Debye-Hückel approximation. This term gives rise to the Casimir attraction between two parallel interfaces but also generalizes to other case including the one discussed here of a single interface.

To evaluate this expression it is convenient to decompose $A(mz)$ into a component which is singular as $z \rightarrow 0$, which gives the direct interaction with the image charge, and a component finite in this limit:

$$\begin{aligned} A(mz) = & \frac{\Delta \exp[-2m(z+h)]}{2m(z+h)} + \int_0^\infty d\theta \sinh \theta \left[\left(\frac{\exp(-2mz \cosh \theta - 2\theta) [1 - \Delta^2 \exp(-4mh \sinh \theta)]}{1 + \Delta \exp(-2mh \sinh \theta - 2\theta)} \right) + \Delta \exp(-2mz \cosh \theta) \right. \\ & \left. \times [\exp(-2mh \sinh \theta) - \exp(-2mh \cosh \theta)] \right], \end{aligned} \tag{73}$$

where the change of variable $k = \sinh \theta$ has been used.

The result for σ_e is correct in perturbation theory to $O(g)$ and holds for $0 \leq \Delta \leq 1$ and $h \geq 0$. In the depletion term, the

function $A(mz)$ is the potential due to the interaction of a charge with its image and, as is seen above, not only includes the screened Coulomb (Yukawa) potential, which is singular

as $z \rightarrow 0$ when $h=0$, but also contains nonsingular correction terms which, in particular, are important when $h > 0$. We have derived Eq. (72) directly from the perturbation expansion for the free energy but the same result would be obtained from the Gibbs adsorption isotherm or the Güntelberg charging process; in both cases a perturbation expansion can be obtained for the appropriate quantity which is then appropriately integrated. Levin and collaborators [11] have derived a similar result to Eq. (72) at $O(g)$ for the case $\Delta=1, h=0$ but they assume the phenomenological form for $A(mz)$ given by the screened Coulomb potential at $h=0$: the first term in Eq. (73). As we shall see in the following section, the result by Levin [11] for σ_e is numerically similar to ours when evaluated at $\Delta=1, h=0$ but for general values of Δ, h the full result for $A(mz)$ in Eq. (73) is needed for an accurate calculation of the depletion term. The Casimir term is generated automatically in the Güntelberg charging process used by Levin but again to obtain the general result correct to $O(g)$ presented here, the process must be derived from the perturbation expansion for the energy density considered as a function of the electric charge e . In addition, in our approach, whatever the method for deriving σ_e , the perturbation series for σ_e can systematically be calculated to higher orders in g by including terms of higher order using the cumulant expansion in ΔS , Eq. (33).

In the next two sections we discuss the consequences of this result.

A. The Onsager-Samaras limiting law

In this section we shall consider the case where $h=0$ and the case $\epsilon > \epsilon_0$. We show how the Onsager-Samaras limiting law [4] for σ_e at $\Delta=1$ follows from our result and we derive the generalization to cases where $\Delta < 1$.

When $h=0$ Eq. (72) becomes

$$\beta\sigma_e = \frac{2\rho}{m} \int du \left[1 - \exp\left(-\frac{g}{2}A(u)\right) \right] + \frac{\rho g}{4m} \Delta. \quad (74)$$

We thus see that the calculation of $\sigma_e(\rho)$ to the first order in the cumulant expansion about the Debye-Hückel approximation is divergence free. We now discuss the physical origins of these terms. The first term gives a contribution to the surface tension $\sigma_e^{(D)}$ which can be interpreted as being proportional to the depletion of solute with respect to the bulk at the interface within the Debye-Hückel approximation. This term appears in the original Onsager-Samaras calculation where it is then integrated with respect to the fugacity via the Gibbs adsorption equation to obtain the excess surface tension. In the Debye-Hückel approximation it is easy to see that

$$\beta\sigma_e^{(D)} = - \int_0^\infty dz [\rho_+(z) + \rho_-(z) - 2\rho], \quad (75)$$

where $\rho_\pm(z)$ indicates the average cation/anion density at a distance z from the surface. The origin of the second term is less clear but it can be thought of as the modification of the thermal fluctuations of the electrostatic field because of the presence of the electrolyte.

When $h=0$ we have

$$A(u) = \frac{\Delta \exp(-2u)}{2u} + (1 - \Delta^2) \int_0^\infty d\theta \sinh \theta \exp(-2u \cosh \theta) \times \left(\frac{\exp(-2\theta)}{1 + \Delta \exp(-2\theta)} \right). \quad (76)$$

We find the asymptotic expansion of σ_e in the limit of small g to be

$$\beta\sigma_e = - \frac{\rho g \Delta}{2m} \left[\ln\left(\frac{g\Delta}{2}\right) + 2\gamma - \frac{3}{2} - \frac{1}{2\Delta^2}(1 + \Delta)[2\Delta \ln(2) - (1 + \Delta)\ln(1 + \Delta)] \right] + O(g^2 \ln(g)). \quad (77)$$

When $\Delta=1$ Eq. (77) is in agreement with the result of Onsager and Samaras [4], thus showing that the limiting law is exact up to the order of the correction indicated in Eq. (77). We note that from our earlier discussion higher-order corrections coming from the cumulant expansion will also be $O(g^2)$.

B. The general case

Our results for σ_e and $A(mz)$ in Eqs. (72) and (73) apply generally for all $0 \leq \Delta \leq 1, h \geq 0$. When h is nonzero the addition of another length scale in the problem renders the derivation of analytical results considerably more complicated. The first term of Eq. (72) has a simple physical interpretation, it gives a contribution $P_{Debye}h$ to σ_e which can be interpreted as the work done to expel the ions from the surface-exclusion layer into the bulk. In the limit where $hm \ll 1$, i.e., $h \ll l_D$ in the second two terms of Eq. (72) we can set $h \approx 0$ and recover Eq. (77) for these two terms. We now present some numerical results based on the highly accurate VEGAS [23] integration package.

To carry out the integration over z in Eq. (72) we need to accurately determine the function $A(mz)$ given in Eq. (63) and this itself requires an integration over k . The decomposition for $A(mz)$ given in Eq. (73) is vital for good convergence of this latter integral since it is converted to a well behaved integral over θ with the singular nature of the potential $A(mz)$ expressed explicitly. To attempt the integration over k in Eq. (63) numerically would not accurately produce this singular behavior especially in the region where it is most important, namely as $z \rightarrow 0$. We use VEGAS to carry out the $d\theta$ integration in Eq. (73) and so accurately determine $A(mz)$ on a discrete set of closely spaced points for z in the range $0 \leq mz \leq 4$ and use interpolation to evaluate this function at intermediate points. To calculate σ_e we carry out the separate integrations in Eq. (72) again using VEGAS. Accurate convergence of the numerical integration in all cases is rapid and errors are negligible. In Fig. 2 we show the separate contributions to σ_e of the exclusion term, the depletion term, and the Casimir term [the first, second and third terms in Eq. (72), respectively] and the total value, as a function of solute molarity $0 < x \leq 1.0$ for $h=0.0, 0.1, 0.2, 0.3$ nm and a temperature of 20°C and $\Delta=0.975$, appropriate for water where $\epsilon/\epsilon_0 \approx 80$.

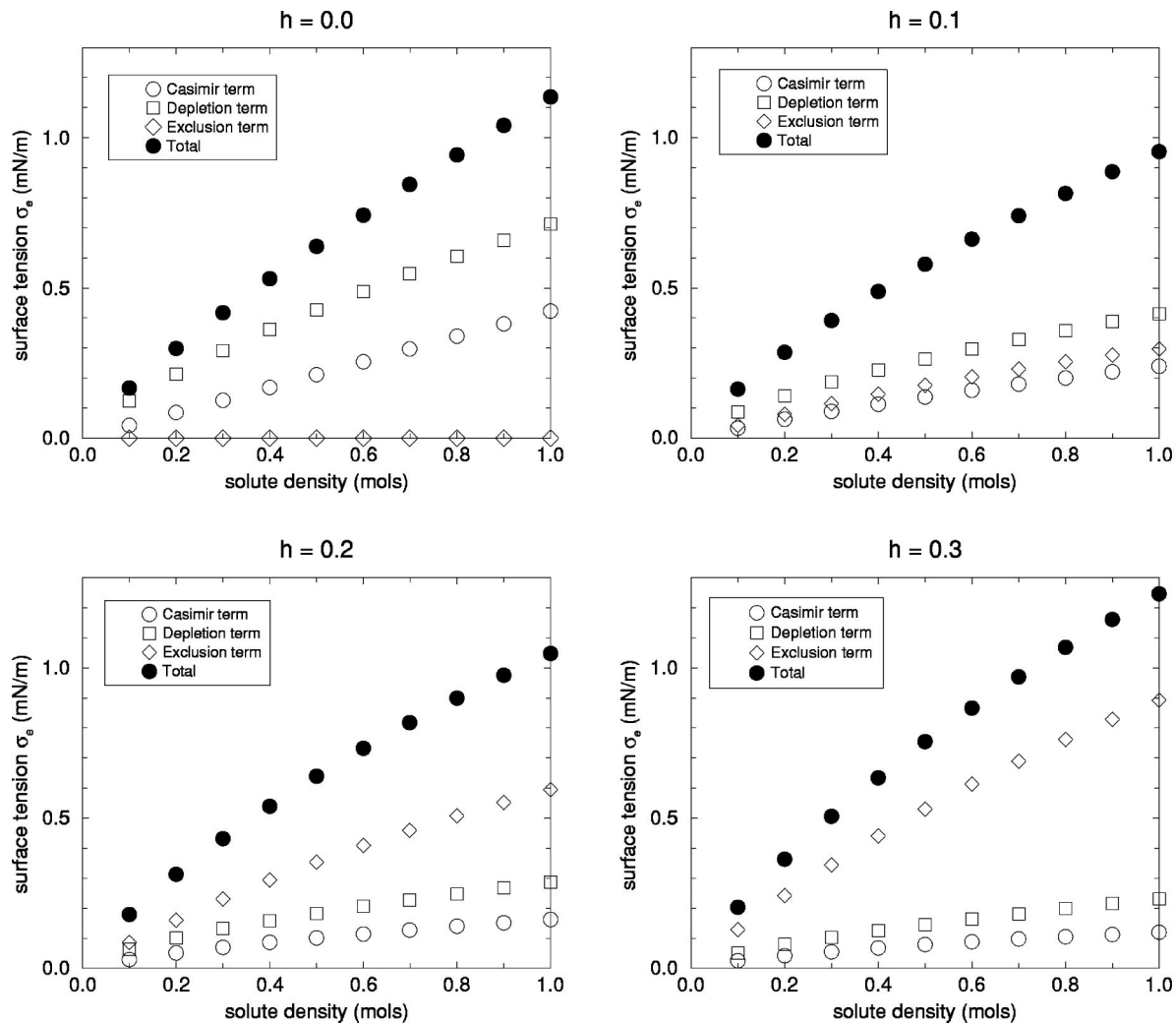


FIG. 2. The component contributions to the surface tension in mN/m vs the molar density for surface exclusion layer thickness $h = 0.0, 0.1, 0.2, 0.3$ nm, $\Delta = 0.975$, and $T = 20$ °C.

From Fig. 2 we note that for $0 < h < 0.3$ nm the dependence of σ_e on h is rather mild especially at low solute density, for example, 0.2 mol; σ_e initially decreases with increasing h but then increases as the exclusion contribution begins to dominate and the effect of the depletion and Casimir terms is reduced. Obviously, for larger h the domination of the exclusion term is complete and σ_e will rise linearly with h , Eq. (72), for fixed solute density. However, the range of h considered here is typical of physical films and should be compared with the Debye length at solute density of 1 mol and $T = 20$ °C of $l_D = 0.305$ nm.

It is interesting to compare the result for the depletion term calculated from the full expression for $A(mz)$ given in Eq. (73) with that for $A(mz)$ approximated by the first term: the Yukawa potential. This is relevant because the Yukawa contribution has an obvious physical significance as the potential for the image-charge repulsion and is the extension to nonzero h of the potential used by Levin [11]. We can then examine the importance of the nonsingular correction term in Eq. (73), whose origin is not so phenomenologically obvious. For solute density of 1 mol we show in Table I the respective contributions of these two calculations as h in-

creases for two values of $\Delta = 0.975, 0.6$ at $T = 20$ °C. The first value corresponds to the water-air interface with $\epsilon_{H_2O}/\epsilon_0 = 80$, $\epsilon_{exterior}/\epsilon_0 = 1$, and the second value is for an interface between water and an exterior medium with $\epsilon_{exterior}/\epsilon_0 = 20$. In each case, the first column gives the contribution when $A(mz)$ is approximated by the Yukawa term and the second column tabulates the contribution when the full expression is used for $A(mz)$. For the water/air interface there is negligible difference for $h = 0$ nm but while both contributions decrease with h the full result is over five times larger than the phenomenological Yukawa approximation suggests. The difference is much more marked in the case with $\Delta = 0.6$ even at $h = 0$ nm with the full result an order of magnitude larger than the Yukawa approximation when $h = 0.3$ nm. Note that the Debye length is $l_D = 0.305$ nm, comparable with the largest value of h here. These results show that in a realistic film, which will generally have a surface layer of thickness in the range discussed here, the corrections to the Yukawa approximation to the image-charge interaction, Eq. (73) are overwhelmingly important, especially when the thickness $h \geq l_D$. For higher solute densities this inequality is likely to be easily satisfied. A similar effect occurs for the Casimir term, and

TABLE I. The contribution to σ_e of the second (depletion) term in Eq. (72) for solute density of 1 mol as a function of the exclusion layer thickness h in nm. The second column gives the contribution when $A(mz)$ defined in Eq. (73) is approximated by the first (Yukawa) term and the third column tabulates the contribution when the full expression is used for $A(mz)$. The results shown are for two values of $\Delta=0.975, 0.6$, and $T=20^\circ\text{C}$. The first value corresponds to the water-air interface with $\epsilon_{H_2O}/\epsilon_0=80, \epsilon_{exterior}/\epsilon_0=1$, and the second value is for an interface between water and an exterior medium with $\epsilon_{exterior}/\epsilon_0=20$. For the water/air interface there is negligible difference for $h=0$ nm but while both contributions decrease with h the full result is over five times larger than the phenomenological Yukawa approximation suggests. The difference is much more marked in the case with $\Delta=0.6$ with the full result being an order of magnitude larger than the Yukawa approximation when $h=0.3$ nm. Note that the Debye length is $l_D=0.305$ nm, comparable with the largest value of h here.

h (nm)	$\Delta=0.975$		$\Delta=0.6$	
	Yukawa (mN/m)	Full (mN/m)	Yukawa (mN/m)	Full (mN/m)
0.0	0.710	0.712	0.561	0.598
0.1	0.286	0.414	0.188	0.331
0.2	0.106	0.287	0.067	0.241
0.3	0.042	0.231	0.026	0.205

it is the slower decrease of both these terms with h compared with the phenomenological prediction that almost exactly balances the increase of the exclusion term with h so that the h dependence of σ_e is relatively weak in the range shown in Fig. 2 (for $\Delta=0.975$ here). An outcome is that the result of Levin [11] for σ_e , which applies only to the case $h=0$ nm, $\Delta=1$, is numerically similar to ours for $\Delta=0.975$ but here we have extended the results accurately to general Δ and h to $O(g)$.

It should be noted that in the exclusion term in Eq. (72) the Debye-Hückel formula for the pressure has been used and for solute density of 1 mol and $T=20^\circ\text{C}$ the dimensionless coupling constant is $g=2.33913$, and so the Debye-Hückel correction to the free gas law pressure is nearly 40%. This indicates that corrections to the bulk pressure at $O(g^2)$ and higher will make a significant contribution at this and higher solute densities and, by inference, the higher-order corrections to both the depletion and Casimir terms in Eq. (72) should be calculated. This is the aim of work in hand.

In Fig. 3 we show the temperature dependence $10^\circ\text{C} \leq T \leq 30^\circ\text{C}$ for different values of h and solute density of 1 mol. It is clear from the $h=0$ nm results that the temperature dependence of the depletion and Casimir terms is very weak, and that the dominant contribution for $h>0$ nm is from the exclusion term and simply comes from the T dependence of the free gas pressure $\propto T$ plus the dependence of the Debye-Hückel correction $\propto T^{-1/2}$.

IV. CONCLUSIONS

We have shown that the calculation of σ_e for a simple model of an electrolyte can be formulated in terms of a per-

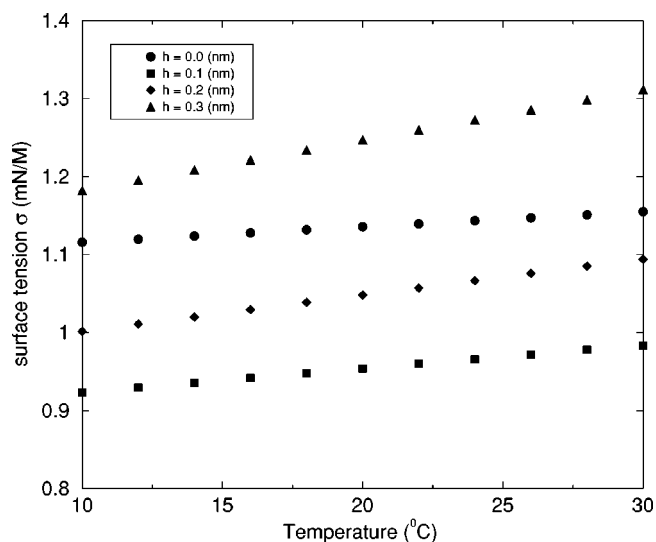


FIG. 3. The temperature dependence of σ for solution of density 1 mol for T in range $10\text{--}30^\circ\text{C}$ and for surface-exclusion layer thicknesses $h=0.0, 0.1, 0.2, 0.3$ nm. The dependence on T becomes more marked as h increases, being about 10% over this range for $h=0.3$ nm. This effect is almost entirely due to the exclusion contribution whose T dependence comes from the formula for the free-gas pressure $\propto T$ plus the dependence of the Debye-Hückel correction $\propto T^{-1/2}$. Here $\Delta=0.975$.

turbation expansion in the dimensionless coupling constant $g=l_B/l_D$, where l_B and l_D are the Bjerrum and Debye lengths, respectively. We derive the full general expressions for σ_e to $O(g)$ for general values of $\Delta=(\epsilon-\epsilon_0)/(\epsilon+\epsilon_0)$, $0<\Delta\leq 1$, and $h\geq 0$ nm. The calculational method is based on a direct calculation of the grand potential difference between a system with bulk/exterior interface and a bulk and exterior system with no interface (both with periodic boundary conditions). In this simple model an exclusion layer for the hydrated ions at the surface was included, both cations and anions are implicitly taken to be of the same size and thus had the same range of exclusion h . Due to the symmetry between cations and anions in the model here, no mean field or average electrostatic potential or effective surface was generated. The Onsager-Samaras limiting law is shown to be the limiting form of the first term in this expansion for small g and we have derived its generalization in Eq. (77) to the case where $\Delta<1, h=0$ nm. The calculation presented above is at two-loop order and gives a finite result. It would be interesting to extend the calculation to higher loop orders but the results at three loops and higher are singular and need to be regulated with a short-distance or hard core cutoff because of the inherent instability in the pointlike description of charged particles in three dimensions. However, it should be noted that there are no such singular contributions from two-loop terms. Indeed, it can be shown that the two-loop contribution to the pressure in the bulk system is absent.

The method is equivalent to other approaches to calculating σ_e such as the Gibbs adsorption isotherm and the Guntelberg charging process, both of which can be formulated using our techniques as perturbation series in g . The strength of our method is that it gives a systematic expansion which

can be extended to higher orders in g by including the higher-order terms in the cumulant expansion in ΔS in Eq. (33). The explicit terms given here in Eq. (72) to $O(g)$ are, respectively, the exclusion term due to the exclusion of the gas of solute ions from the surface layer, the depletion term which gives the contribution from the image-charge repulsion for ions approaching the surface, and the Casimir term arising from the change in energy of electric field modes due to the presence of the surface. Terms higher order in g will correct the first two of these contributions. Our method also gives the exact form for these terms, and especially gives the full expression for the image-charge potential $G(z, 0) = gA(mz)/e^2\beta$ defined in Eqs. (63) and (73). The expected screened Coulomb (Yukawa) potential used by Levin [11] can be identified from Eq. (73) but the nonsingular correction term is not so easily argued phenomenologically, and from Table I it is seen to be important for $h > 0$. By inference a similar effect occurs for the Casimir term. For the exclusion term in Eq. (72), dominant for large h , higher-order corrections to the Debye-Hückel approximation are necessary for solute densities greater than 1 mol, and by inference

the other terms will also need correction at higher densities. It should be noted that Levin [11] uses the free-gas law to compute the exclusion term omitting the Debye-Hückel correction which is equivalent to setting $g=0$ in this term.

The formalism used here can be extended to deal with cases where an effective surface charge is present due to either a difference in hydrated ionic sizes; the behavior of the surface charge in such a model was recently analyzed in a weak charging approximation by the authors [17]. In addition, one may also apply this formalism to other systems with different energetic or thermodynamic mechanisms leading to surface charging; these are the so-called charge regulated models [24]. In all cases, one can go beyond the first-order expansion used here, although this will require a more sophisticated theory with a short-distance cutoff to regularize the divergences arising at higher orders in perturbation theory; for example, the use of a regularization scheme based on an additional repulsive short range Yukawa interaction will permit the use of the path integral techniques employed in this work.

-
- [1] A. Heydweiller, *Ann. Phys. (Leipzig)* **33**, 145 (1910); *Phys. Z.* **3**, 329 (1902).
- [2] P. K. Weissenborn and R. J. Pugh, *J. Colloid Interface Sci.* **184**, 550 (1996); N. Matsubayasi *et al.*, *ibid.* **209**, 398 (1998).
- [3] C. Wagner, *Phys. Z.* **25**, 474 (1924).
- [4] L. Onsager and N. N. T. Samaras, *J. Chem. Phys.* **2**, 528 (1934).
- [5] G. Jones and W. A. Ray, *J. Am. Chem. Soc.* **59**, 187 (1937); **63**, 288 (1941); M. Dole and J. A. Swartout, *ibid.* **62**, 3039 (1940).
- [6] M. Dole, *J. Am. Chem. Soc.* **60**, 904 (1939).
- [7] B. W. Ninham and V. Yaminsky, *Langmuir* **13**, 2097 (1997).
- [8] M. Bostroöm, D. R. M. Williams, and B. W. Ninham, *Langmuir* **17**, 4475 (2001).
- [9] V. S. Markin and A. G. Volkov, *J. Phys. Chem. B* **106**, 11810 (2002).
- [10] K. A. Karraker and C. J. Radke, *Adv. Colloid Interface Sci.* **96**, 231 (2002).
- [11] Y. Levin, *J. Stat. Phys.* **110**, 825 (2003); *J. Chem. Phys.* **113**, 9722 (2000).
- [12] Y. Levin and J. R. Flores-Mena, *Europhys. Lett.* **56**, 187 (2001).
- [13] R. R. Netz and H. Orland, *Eur. Phys. J. E* **1**, 203 (2003).
- [14] J. E. B. Randles, *Discuss. Faraday Soc.* **24**, 194 (1957).
- [15] R. Podgornik and B. Zeks, *J. Chem. Soc., Faraday Trans. 2* **84**, 611 (1988).
- [16] D. S. Dean and R. R. Horgan, *Phys. Rev. E* **65**, 061603 (2002).
- [17] D. S. Dean and R. R. Horgan, *Phys. Rev. E* **68**, 051104 (2003).
- [18] D. S. Dean and R. R. Horgan, *Phys. Rev. E* **68**, 061106 (2003).
- [19] J. Israelachvili, *Intermolecular and Surface Forces* (Academic, New York, 1992).
- [20] J. Mahanty and B. Ninham, *Dispersion Forces* (Academic, London, 1976).
- [21] S. Edwards and A. Lenard, *J. Math. Phys.* **3**, 778 (1962); D. S. Dean, R. R. Horgan, and D. Sentenac, *J. Stat. Phys.* **90**, 899 (1998).
- [22] R. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- [23] G. P. Lepage, *Vegas: An Adaptive Multidimensional Integration Program CLNS-80/447* (Cornell University, Ithaca, 1980), Vol. 4, pp. 190–195.
- [24] B. W. Ninham and A. Parsegian, *J. Theor. Biol.* **31**, 405 (1971); O. Spalla and L. Belloni, *J. Chem. Phys.* **95**, 7689 (1991); O. Spalla and L. Belloni, *Phys. Rev. Lett.* **74**, 2515 (1995); D. S. Dean and D. Sentenac, *Europhys. Lett.* **38**, 645 (1997); D. Sentenac and D. S. Dean, *J. Colloid Interface Sci.* **196**, 35 (1997); M. N. Tamashoro and P. Pincus, *Phys. Rev. E* **60**, 6549 (1999); P. A. Pincus and S. A. Safran, *Europhys. Lett.* **42**, 103 (1998).