

# Field theoretic derivation of the contact value theorem in planar geometries and its modification by the Casimir effect

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The contact value theorem for Coulomb gases in planar or filmlike geometries is derived using a Hamiltonian field theoretic representation of the system. The case where the film is enclosed by a material of different dielectric constant to that of the film is shown to contain an additional Casimir-like term which is generated by fluctuations of the electric potential about its mean-field value.

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## I. INTRODUCTION

Coulomb gases arise in a huge variety of physical contexts from plasmas to soft condensed matter systems [1,2]. Ideal Coulomb gases, where only pointlike charges are considered, present a number of useful sum rules [3,4]. These sum rules are exact identities between certain statistical mechanical observables. Sum rules are useful for checking the validity of approximation schemes, which must almost always be applied in the case of strongly interacting systems. They also provide potentially useful experimental and numerical methods of indirectly measuring local observables in terms of macroscopically measurable quantities such as the pressure and vice versa. Finally sum rules may also be used to verify the accuracy of numerical simulations where, thanks to the sum rule, the same quantity can be measured in two independent ways.

An example of such a sum rule is the contact value theorem which relates the surface charge and density at the surface of the system to the system's pressure [3,4]. In this paper we use a field theoretic approach to show how the basic contact value theorem can be derived in the case of layered geometries, such as soap films, and show how the contact value theorem is modified when the dielectric constant  $\epsilon$  within the film is different from that outside the film  $\epsilon_0$ . The film geometry is of particular importance as it corresponds to the experimental set up used to study soap films [5]. We exploit the planar geometry to develop a Hamiltonian formulation of the Sine-Gordon field theory which arises for Coulomb gases [6]. In this formulation the perpendicular direction, denoted here by  $z$ , acts as a temporal coordinate in which a field  $\phi(\mathbf{r})$  on the plane perpendicular to  $z$ , and whose coordinates are denoted by the vector  $\mathbf{r}$ , propagates. The case where global electroneutrality holds is treated within this formulation. The condition of electroneutrality can be related to the choice of ground-state wave functional for the dynamical field  $\phi(\mathbf{r})$ .

In the canonical ensemble, the partition function for a system of fixed particle number on a three-dimensional space  $\mathcal{V}$  is given by [6]

$$Z = \text{Tr} \int d[\phi] \exp \left( - \frac{\beta}{2} \int_{\mathcal{V}} d\mathbf{x} \epsilon(\mathbf{x}) (\nabla \phi(\mathbf{x}))^2 + i\beta \int_{\mathcal{V}} d\mathbf{x} \rho_e(\mathbf{x}) \phi(\mathbf{x}) \right), \quad (1)$$

where Tr denotes the classical trace over the particle positions  $1/N! \int_{\mathcal{V}} \prod_{i=1}^N d\mathbf{x}_i$  and  $d[\phi]$  denotes the functional integral over the field  $\phi$ . The field  $\phi$  is the Wick rotated electrostatic field  $\psi$  and is thus related to  $\psi$  via  $\psi = -i\phi$ . The term  $\rho_e(\mathbf{x}) = \sum_{i=1}^N q_i \delta(\mathbf{x} - \mathbf{x}_i) + \rho_q(\mathbf{x})$  is the charge density of the system. The first term is the dynamical charge density which can vary in the system,  $\mathbf{x}_i$  being the position of particle  $i$ , and  $q_i$  its charge. The second term  $\rho_q$  is a quenched background charge which is not dynamical and represents, for example, a fixed surface charge. The integration volume in the action  $\mathcal{V}$  is all space. We note that the above treatment of a two component Coulomb gas needs to be modified where the basic physical description of point charges interacting via a Coulomb potential is thermodynamically unstable. For instance the system can become unstable and have a tendency to collapse at low temperatures if some short range, for example hard core, repulsion is not included. The Sine-Gordon theory can always be regularized by introducing a high momentum or short distance cutoff in the Fourier modes of the field  $\phi$ . We note that the above formulation contains self interactions between the particles, *i.e.*, the terms  $q_i q_j v(\mathbf{r}_i - \mathbf{r}_j)/2$  for  $i=j$  where  $v$  is the effective pairwise interaction are included. The interaction of a particle with its image charges is part of this contribution and should be included, but the self-energy in the bulk medium should not contribute to the physical pressure and so must be subtracted. For a monovalent system in dimension  $d$ , if one removes the bulk self-energy term, the Sine-Gordon free energy is corrected by a term

$$\Delta F = -N \frac{e^2 v(0)}{2} = -\frac{Ne^2}{2\epsilon} \frac{S_d}{(2\pi)^d} \int_0^\Lambda dk k^{d-3}, \quad (2)$$

where  $N$  is the number of particles,  $S_d$  denotes the surface of the unit sphere in  $d$  dimensions and  $\Lambda$  is an ultraviolet or short distance cutoff. Note that for  $d > 2$   $\Delta F$  is a regular function of  $\Lambda$  and so can be absorbed into the fugacity. How-

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ever, for  $d=2$  the integral in Eq. (2) has an infrared divergence at  $k=0$ , which must be cut off at the inverse system size  $1/L$  giving

$$\Delta F = -\frac{Ne^2}{4\pi\epsilon}[\ln(\Lambda) - \ln(1/L)]. \quad (3)$$

Thus, in two dimensions there is a correction to the sine-Gordon pressure of

$$\Delta P = -\frac{\rho e^2}{4\pi\epsilon}, \quad (4)$$

where  $2\rho = N/L^2$  is twice the density of electrolyte.

Normally the particles  $i$  are restricted to a subvolume  $V$ , for instance in the interior of a soap film for electrolyte solutions. In the case where  $\epsilon$  is constant, the functional integral over  $\phi$  is easily done and we recover a system of  $N$  particles interacting via the Coulomb potential. For a varying dielectric constant  $\epsilon$  the resulting interaction depends on the spatial variation of  $\epsilon$  and the resulting integration gives rise to a more complicated interaction which can be interpreted in terms of image charges. The partition function  $Z$  in Eq. (1) thus contains a term which is due to the pairwise interparticle interaction, plus a functional determinant coming from the integration over  $\phi$ . Both of these terms are present in the physics of the problem and should be taken into account. The form of Eq. (1) comes directly from a static approximation to quantum electrodynamics (QED) where the nonzero frequency, Matsubara frequencies, and electric currents (and thus the magnetic field) are neglected in the action of QED [6–8]. This approximation is justified when the charge distribution is very weakly coupled to nonzero Matsubara frequencies [9], that is to say the response time of the charge to the nonzero frequencies is large. The nonzero Matsubara frequencies, when decoupled from the charge distribution, yield a van der Waals interaction between the surfaces in the problem and can be calculated independently in this approximation [9].

## II. HAMILTONIAN FIELD THEORETIC FORMALISM

For simplicity in what follows we consider a film system that is to say an inner region having two interfaces separating it from an outer region. The surface of the film has area  $A$  in the  $(x,y)=\mathbf{r}$  plane, the direction  $z$  is perpendicular to the film surface. For a system consisting of a film of thickness  $L$ , the film is in the region  $z \in [0,L]$  and the exterior of the film is in  $[-T',0]$  (the left exterior) and  $[L,T-L]$  (right exterior). The total length of the physical system in the  $z$  direction  $T+T'$  is taken to be constant and we consider the limit of  $T$  and  $T'$  as large. In the simplest case, which we study here, the electrolyte is monovalent and the fugacity of cations and anions is the same and denoted by  $\mu$  within the film region and is zero outside. This can be encoded in a spatially varying fugacity  $\mu(\mathbf{x}) = \mu(\mathbf{r},z) = \mu(z)$ , with  $\mu(z) = \mu$  for  $z \in [0,L]$  and  $\mu(z) = 0$  for  $z \notin [0,L]$ . The dielectric constant within the film is denoted by  $\epsilon$  and the external dielectric constant is denoted by  $\epsilon_0$ . For a soap film, for example,  $\epsilon_0$

could be the dielectric constant of air and  $\epsilon$  the dielectric constant of water. We may also consider systems where the regions  $z \in [-\delta,0]$  and  $z \in [L,L+\delta]$  have a dielectric constant determined by the dielectric constant of a surfactant and its concentration at the surface.

In the grand canonical ensemble, the grand partition function is written as

$$\Xi = \int d[\phi] \exp(-S[\phi,L]). \quad (5)$$

The film the pressure is therefore given by

$$\beta P = \frac{1}{A} \frac{\partial \ln(\Xi)}{\partial L}. \quad (6)$$

In the case considered here,  $S$  is the action of a generalized Sine-Gordon field theory [6]

$$S[\phi,L] = \frac{\beta}{2} \int_V d\mathbf{x} \epsilon(z) (\nabla \phi)^2 - 2 \int_V d\mathbf{x} \mu(z) \cos(e\beta\phi(\mathbf{x})) - i\beta \int_{z=0} d\mathbf{r} \sigma \phi(\mathbf{x}) + i\beta \int_{z=L} d\mathbf{r} \sigma \phi(\mathbf{x}), \quad (7)$$

where the integrations over three space, denoted by  $d\mathbf{x} = d\mathbf{r}dz$ , are over the  $(x,y)=\mathbf{r}$  plane of area  $A$  and over the coordinate  $z$ . The last terms are the (constant uniform) surface charge contributions from the transverse planes of area  $A$  at  $z=0$  and  $z=L$ .

We now rewrite the action using the 2+1 decomposition in terms of the field  $\phi(\mathbf{r})$ , which evolves with a temporal coordinate  $z$

$$\Xi = \int \mathcal{D}[\phi] \exp\left(-\int dz \mathcal{S}[\phi,z]\right), \quad (8)$$

where the path integral action  $\mathcal{S}$  is given by

$$\begin{aligned} \mathcal{S}[\phi,z] = & \frac{\beta\epsilon(z)}{2} \int_A \left(\frac{\partial\phi}{\partial z}\right)^2 d\mathbf{r} + \frac{\beta\epsilon(z)}{2} \int_A d\mathbf{r} (\nabla_{\mathbf{r}}\phi)^2 \\ & - 2\mu(z) \int_A d\mathbf{r} \cos(e\beta\phi) - i\beta\sigma[\delta(z) \\ & + \delta(z-L)] \int_A d\mathbf{r} \phi. \end{aligned} \quad (9)$$

The functional Schrödinger Hamiltonian for the path integral outside the film is given by

$$H_E = \int_A d\mathbf{r} \left[ -\frac{1}{2\beta\epsilon_0} \frac{\delta^2}{\delta\phi(\mathbf{r})^2} + \frac{\beta\epsilon_0}{2} (\nabla_{\mathbf{r}}\phi)^2 \right]. \quad (10)$$

Inside the film the Hamiltonian is

$$H_F = \int_A d\mathbf{r} \left[ -\frac{1}{2\beta\epsilon} \frac{\delta^2}{\delta\phi(\mathbf{r})^2} + \frac{\beta\epsilon}{2} (\nabla_{\mathbf{r}}\phi)^2 - 2\mu \cos(e\beta\phi) \right]. \quad (11)$$

The terms containing the surface charge and other more general surface interactions may be included as source terms. We note here that in the case of the 1d Coulomb gas the field  $\phi$  is interpreted as the position of a single particle and the quantum mechanical formalism then leads to an exact solution [10]. In this formulation we postulate that

$$\Xi = \text{Tr} \exp(-TH_E) \mathcal{O} \exp(-LH_F) \mathcal{O} \exp(-(T'-L)H_E), \quad (12)$$

where Tr denotes the trace over a complete set of states. The source term  $\mathcal{O}$  for a constant surface charge is clearly given by

$$\mathcal{O} = \exp\left(i\beta\sigma \int_A d\mathbf{r} \phi(\mathbf{r})\right). \quad (13)$$

The reason we say that Eq. (12) is postulated, is that the boundary conditions for the above path integral are not straightforward to determine. We shall see later that the above choice assures the electroneutrality of the film since in the limit  $T, T' \rightarrow \infty$  it only involves the ground-state wave functional  $|\Psi_0\rangle$  of the Hamiltonian  $H_E$ . In general, instead of taking the trace, we could specify any linear combination of wave functionals of  $H_E$  as the initial (and final) state for the field  $\phi$ , however, as long as it has a nonzero component of the wave function  $|\Psi_0\rangle$ , in the limit where  $T$  and  $T'$  are large the result will be the same. So, in the limit of large  $T$  and  $T'$  the grand partition function may thus be written as

$$\Xi = \langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp(-LH_F) \mathcal{O} \times \exp(-(T'-L)H_E) | \Psi_0 \rangle. \quad (14)$$

In this formulation, the derivative with respect to  $L$  is taken easily and unambiguously, we find that

$$\begin{aligned} \frac{\partial \Xi}{\partial L} &= -\langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp(-LH_F) H_F \mathcal{O} \\ &\times \exp(-(T'-L)H_E) | \Psi_0 \rangle + \langle \Psi_0 | \exp(-TH_E) \mathcal{O} \\ &\times \exp(-LH_F) \mathcal{O} H_E \exp(-(T'-L)H_E) | \Psi_0 \rangle. \end{aligned} \quad (15)$$

We now define the momentum operator for the field  $\phi$  at the point  $\mathbf{r}$  by

$$P_{\phi(\mathbf{r})} = -i \frac{\delta}{\delta \phi(\mathbf{r})}. \quad (16)$$

This leads to the commutation relation

$$[P_{\phi(\mathbf{r})}, \phi(\mathbf{r}')] = -i \delta(\mathbf{r} - \mathbf{r}'). \quad (17)$$

The kinetic operator  $K$  is then defined by

$$K = \int_A d\mathbf{r} P_{\phi(\mathbf{r})}^2 = - \int_A d\mathbf{r} \frac{\delta^2}{\delta \phi(\mathbf{r})^2}. \quad (18)$$

In this notation the exterior and interior Hamiltonians read

$$H_E = \frac{K}{2\beta\epsilon_0} + V_E, \quad (19)$$

$$H_F = \frac{K}{2\beta\epsilon} + V_F, \quad (20)$$

where the functional potentials of the Hamiltonians are given by

$$V_E = \frac{\beta\epsilon_0}{2} \int_A d\mathbf{r} (\nabla_{\mathbf{r}} \phi)^2, \quad (21)$$

$$V_F = \frac{\beta\epsilon}{2} \int_A d\mathbf{r} (\nabla_{\mathbf{r}} \phi)^2 - 2\mu \int_A d\mathbf{r} \cos(e\beta\phi(\mathbf{r})). \quad (22)$$

We note that these functional potentials are pure functionals and involve no functional derivative operators, thus they commute with other functionals, notably  $\mathcal{O}$ . The Eq. (15) is now written as

$$\begin{aligned} \frac{\partial \Xi}{\partial L} &= -\langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp(-LH_F) ([H_F, \mathcal{O}] \\ &- \mathcal{O}(H_E - H_F)) \exp(-(T'-L)H_E) | \Psi_0 \rangle. \end{aligned} \quad (23)$$

Using the result

$$[P_{\phi(\mathbf{r})}^2, \mathcal{O}] = 2\beta\sigma \mathcal{O} P_{\phi(\mathbf{r})} + \beta^2 \sigma^2 \mathcal{O}, \quad (24)$$

we obtain

$$\begin{aligned} \frac{\partial \Xi}{\partial L} &= -A \frac{\beta\sigma^2}{2\epsilon} \Xi - \frac{\sigma}{\epsilon} \left\langle \Psi_0 \left| \exp(-TH_E) \mathcal{O} \exp(-LH_F) \right. \right. \\ &\times \mathcal{O} \left( \int_A d\mathbf{r} P_{\phi(\mathbf{r})} \right) \exp(-(T'-L)H_E) \left. \left| \Psi_0 \right. \right\rangle \\ &+ \langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp(-LH_F) \mathcal{O} (H_E - H_F) \\ &\times \exp(-(T'-L)H_E) | \Psi_0 \rangle. \end{aligned} \quad (25)$$

The final result for the pressure is thus

$$\beta P = -\frac{\beta\sigma^2}{2\epsilon} + \frac{1}{A} \langle (H_E - H_F) |_{s^+} \rangle - \frac{1}{A} \frac{\sigma}{\epsilon} \left\langle \int_A d\mathbf{r} P_{\phi(\mathbf{r})} \right|_{s^+} \rangle, \quad (26)$$

where the above notation indicates the normalized expectation values of the operators shown, evaluated at the rightmost outer surface of the film  $s^+$ , *i.e.*, at  $z=L^+$ . The third term above can be shown to be zero in the case of systems which are globally electroneutral; we will demonstrate this more technical point later. We note the relation

$$H_F = \frac{\epsilon_0}{\epsilon} H_E - \int_A d\mathbf{r} \left[ 2\mu \cos(e\beta\phi) - \frac{\beta\epsilon}{2} \left( 1 - \frac{\epsilon_0^2}{\epsilon^2} \right) (\nabla_{\mathbf{r}} \phi)^2 \right]. \quad (27)$$

Also it is straightforward to see that

$$\langle \mu \exp(\pm i e \beta \phi(\mathbf{r}))|_z \rangle = \langle \rho^\pm(\mathbf{r}, z) \rangle \quad (28)$$

is the mean value of the cation/anion density at the point  $(\mathbf{r}, z)$ . Putting these results together we obtain

$$\begin{aligned} \beta P = & \langle \rho^+|_s + \rho^-|_s \rangle - \frac{\beta \sigma^2}{2\epsilon} - \frac{\beta \epsilon}{2} \left( 1 - \frac{\epsilon_0^2}{\epsilon^2} \right) \langle (\nabla_{\mathbf{r}} \phi)^2|_s \rangle \\ & + \frac{1}{A} \left( 1 - \frac{\epsilon_0}{\epsilon} \right) \langle H_E|_{s^+} \rangle, \end{aligned} \quad (29)$$

where all but the last term are evaluated on the surface  $s$  ( $z = L$ ) at any given point (by homogeneity in the plane  $A$ ). Here there is no ambiguity with regards to the interior or exterior of the surface as the terms are pure functionals of the field  $\phi$  and commute with  $\mathcal{O}$  as it is, itself, a pure functional of the field  $\phi$ . The last term is evaluated at the outer surface  $s^+$  (at  $z = L^+$ ). We thus obtain

$$\begin{aligned} \beta P = & \langle \rho^+|_s + \rho^-|_s \rangle - \frac{\beta \sigma^2}{2\epsilon} - \frac{\beta \epsilon}{2} \left( 1 - \frac{\epsilon_0^2}{\epsilon^2} \right) \langle (\nabla_{\mathbf{r}} \phi)^2|_s \rangle \\ & + \frac{E_0}{A} \left( 1 - \frac{\epsilon_0}{\epsilon} \right), \end{aligned} \quad (30)$$

where  $E_0$  is the energy of the ground-state wave functional  $|\Psi_0\rangle$ . In the case where  $\epsilon_0 = \epsilon$ , Eq. (30) immediately yields the classic contact value theorem [3] as the third and fourth terms are identically zero.

While the functional terms appearing in the expectation values of the Hamiltonians are easy to interpret in terms of observables, the kinetic term  $K$  requires more work. The key result here is

$$\left\langle \frac{1}{2\beta\epsilon(z)} P_{\phi(\mathbf{r})}^2 \Big|_z \right\rangle = - \left\langle \frac{\beta\epsilon(z)}{2} \left( \frac{\partial \phi(\mathbf{r}, z)}{\partial z} \right)^2 \right\rangle. \quad (31)$$

This can be seen in the Heisenberg formalism which gives

$$\left\langle \left( \frac{\partial \phi(\mathbf{r}, z)}{\partial z} \right)^2 \right\rangle = \langle [H, \phi(\mathbf{r})]^2|_z \rangle. \quad (32)$$

We therefore can see that for a point  $z$  inside the film

$$\begin{aligned} \langle H_F|_z \rangle = & \left\langle \int_A d\mathbf{r} \left[ -\frac{\beta\epsilon}{2} \left( \frac{\partial \phi(\mathbf{r}, z)}{\partial z} \right)^2 + \frac{\beta\epsilon}{2} (\nabla_{\mathbf{r}} \phi)^2 \right. \right. \\ & \left. \left. - 2\mu \cos(e\beta\phi) \right] \Big|_z \right\rangle, \end{aligned} \quad (33)$$

and outside the film

$$\langle H_E|_z \rangle = \left\langle \int_A d\mathbf{r} \left[ -\frac{\beta\epsilon_0}{2} \left( \frac{\partial \phi(\mathbf{r}, z)}{\partial z} \right)^2 + \frac{\beta\epsilon_0}{2} (\nabla_{\mathbf{r}} \phi)^2 \right] \Big|_z \right\rangle. \quad (34)$$

Using Eq. (34) in Eq. (29) we find the alternative expression

$$\begin{aligned} \beta P = & \langle \rho^+|_s + \rho^-|_s \rangle - \frac{\beta \sigma^2}{2\epsilon} - \frac{\beta}{2} (\epsilon - \epsilon_0) \langle (\nabla_{\mathbf{r}} \phi)^2|_s \rangle \\ & - \frac{\beta \epsilon_0}{2} \left( 1 - \frac{\epsilon_0}{\epsilon} \right) \left\langle \left( \frac{\partial \phi}{\partial z} \right)^2 \Big|_{s^+} \right\rangle. \end{aligned} \quad (35)$$

In the mean-field theory, when the field  $\phi$  is replaced by its mean field electrostatic field  $-i\psi_c$ , the electroneutrality of the system implies that  $\partial\psi_c/\partial z = 0$  outside the film and the homogeneous nature of the mean-field solution in the plane of the film yields  $\nabla_{\mathbf{r}}\psi_c = 0$ . Thus the third and fourth terms of Eq. (35) are zero and hence the contact value theorem as classically stated is always verified at the mean-field level. If we expand about the mean field solution, we see that the correction term due to the variation of the dielectric constants comes from fluctuations about the mean-field solution. The value of this term can be calculated in the case of weak electrolyte strength in the Debye-Hückel approximation [9,6,11].

We now return to the question of the global electroneutrality of the system. Using the correspondence between the field  $\phi$  and  $\psi$  we have

$$\left\langle \frac{\partial \psi(\mathbf{r}, z)}{\partial z} \right\rangle = -i \left\langle \frac{\partial \phi(\mathbf{r}, z)}{\partial z} \right\rangle. \quad (36)$$

If the film is electroneutral then, by symmetry about the film's midplane, the integral of the electric field over every plane perpendicular to the  $z$  direction outside the film must vanish, and thus

$$\left\langle \int_A d\mathbf{r} \frac{\partial \psi(\mathbf{r})}{\partial z} \Big|_z \right\rangle = 0, \quad (37)$$

for  $z > L$  (and also for  $z < 0$ ). Using the Heisenberg formalism we find

$$\begin{aligned} -i \left\langle \int_A d\mathbf{r} \frac{\partial \phi(\mathbf{r})}{\partial z} \Big|_z \right\rangle & = i \left\langle \int_A d\mathbf{r} [H_E, \phi(\mathbf{r})] \Big|_z \right\rangle \\ & = \frac{1}{\epsilon_0 \beta} \left\langle \int_A d\mathbf{r} P(\mathbf{r}) \Big|_z \right\rangle, \end{aligned} \quad (38)$$

and using the fact that

$$\exp(-(T' - L)H_E)|\Psi_0\rangle = \exp(-(T' - L)E_0)|\Psi_0\rangle, \quad (39)$$

we may write

$$\begin{aligned} & \int_A d\mathbf{r} P_{\phi(\mathbf{r})} \exp(-(T' - L)H_E)|\Psi_0\rangle \\ & = \exp(-(T' - L)H_E) \int_A d\mathbf{r} P_{\phi(\mathbf{r})} |\Psi_0\rangle. \end{aligned} \quad (40)$$

The final step in the proof of our result is to show that

$$\int_A d\mathbf{r} P_{\phi(\mathbf{r})} |\Psi_0\rangle = 0. \quad (41)$$

Outside the film we consider the Fourier representation of the field

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{A}} \sum_{\mathbf{p}} \tilde{\phi}(\mathbf{p}) \exp(i\mathbf{p} \cdot \mathbf{r}). \quad (42)$$

On this basis the exterior Hamiltonian becomes

$$H_E = \sum_{\mathbf{p}} \left[ -\frac{1}{2\beta\epsilon_0} \frac{\delta^2}{\delta\tilde{\phi}(\mathbf{p})\delta\tilde{\phi}(-\mathbf{p})} + \frac{\beta\epsilon_0\mathbf{p}^2}{2} \tilde{\phi}(\mathbf{p})\tilde{\phi}(-\mathbf{p}) \right]. \quad (43)$$

Thus outside the film, each Fourier mode of  $\phi$  is the coordinate of an independent harmonic oscillator and the ground-state wave functional is given by

$$\langle \tilde{\phi} | \Psi_0 \rangle \propto \prod_{\mathbf{p}} \exp\left(-\frac{1}{2} M \omega(\mathbf{p}) \tilde{\phi}(\mathbf{p}) \tilde{\phi}(-\mathbf{p})\right), \quad (44)$$

where  $M = \beta\epsilon_0$  and  $\omega(\mathbf{p}) = |\mathbf{p}|$ . We now note that

$$\int_A d\mathbf{r} P_{\phi(\mathbf{r})} = -i\sqrt{A} \frac{\delta}{\delta\tilde{\phi}(\mathbf{0})}. \quad (45)$$

However from Eq. (44)  $|\Psi_0\rangle$  is clearly independent of  $\tilde{\phi}(\mathbf{0})$  and so the desired result Eq. (41) follows directly.

Using the fact that the Hamiltonian  $H_F$  commutes with itself we may also rewrite Eq. (15) as

$$\begin{aligned} \frac{\partial \Xi}{\partial L} &= -\langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp\left(-\frac{1}{2} LH_F\right) H_F \\ &\quad \times \exp\left(-\frac{1}{2} LH_F\right) \mathcal{O} \exp(-(T'-L)H_E) | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | \exp(-TH_E) \mathcal{O} \exp(-LH_F) \mathcal{O} H_E \\ &\quad \times \exp(-(T'-L)H_E) | \Psi_0 \rangle. \end{aligned} \quad (46)$$

Applying the results derived above and using Eq. (11) lead to

$$\begin{aligned} \beta P &= \langle \rho_+ |_m + \rho_- |_m \rangle - \frac{\beta\epsilon}{2} \langle (\nabla_{\mathbf{r}}\phi)^2 |_m \rangle + \frac{\beta\epsilon}{2} \left\langle \left( \frac{\partial\phi}{\partial z} \right)^2 \Big|_m \right\rangle \\ &\quad + \frac{\beta\epsilon_0}{2} \langle (\nabla_{\mathbf{r}}\phi)^2 |_s \rangle - \frac{\beta\epsilon_0}{2} \left\langle \left( \frac{\partial\phi}{\partial z} \right)^2 \Big|_{s,+} \right\rangle, \end{aligned} \quad (47)$$

where  $m$  in the above indicates the value taken at the midplane of the film  $z=L/2$ . At the mean-field level for an electroneutral film the last term again vanishes and, in addition, by symmetry the mean-field solution  $\psi_c$  obeys  $\partial\psi_c/\partial z=0$  at  $z=L/2$ . Hence if we neglect the corrections to mean field in the second two terms, the so-called midplane formula for the mean-field approximation [1,2] is immediately recovered. It is also worth noting that Eq. (47) is valid for any surface

charge operator  $\mathcal{O}$ , thus explaining why various charge regulated models obey the classic midplane formula at the mean-field level [12,6].

The Hamiltonian formalism is also illuminating in the case of a bulk calculation. Here the grand partition function is given by

$$\Xi_B = \text{Tr} \exp(-LH_F) \quad (48)$$

which gives the pressure bulk pressure as

$$\beta P_B = -\frac{1}{A} \langle H_F \rangle \quad (49)$$

where the expectation above is taken at any value of  $z$ . Now using the relation Eq. (33) and the homogeneity in the transverse plane  $A$  we find

$$\beta P_B = 2\rho - \frac{\beta\epsilon}{2} \langle (\nabla_{\mathbf{r}}\phi)^2 \rangle + \frac{\beta\epsilon}{2} \left\langle \left( \frac{\partial\phi}{\partial z} \right)^2 \right\rangle, \quad (50)$$

where  $\rho$  is the bulk electrolyte density. Using the isotropy of the bulk system we finally obtain

$$\beta P_B = 2\rho - \frac{\beta\epsilon}{6} \langle (\nabla\phi)^2 \rangle, \quad (51)$$

where the gradient above is the full three-dimensional gradient. The first term above can be interpreted as an osmotic term and the second term has its origin in the Maxwell stress tensor for the electrostatic field [13].

In  $d$  dimensions, using exactly the same decomposition in terms of a temporal coordinate  $z$  and  $d-1$  dimensional hypersurface, the above expression becomes

$$\beta P_B = 2\rho - \frac{\beta\epsilon}{2d} (d-2) \langle (\nabla\phi)^2 \rangle. \quad (52)$$

Note that the above expression recovers [14] the physical pressure for a two-dimensional neutral Coulomb gas which is given by the simple formula

$$P_p = 2\rho k_B T \left( 1 - \frac{e^2}{8\pi\epsilon k_B T} \right) \quad (53)$$

where the Sine-Gordon pressure has been corrected by the two-dimensional self-energy term of Eq. (4). This result can be simply understood from the logarithmic nature of the Coulomb potential in two dimensions and is valid in the region of the thermodynamic stability of a purely Coulomb system in two dimensions [14].

The expression Eq. (51) may also be used to calculate the physical bulk pressure of a three-dimensional Coulomb gas within the Debye-Hückel approximation. One finds that

$$\beta P_B = 2\rho - \frac{1}{12\pi^2} \int_0^\Lambda dk \frac{k^4}{k^2 + m^2}, \quad (54)$$

where  $\Lambda$  is again an ultraviolet cutoff and  $m = \sqrt{2\rho e^2 \beta/\epsilon}$  is the Debye mass. This gives for large  $\Lambda$

$$\beta P_B = 2\rho - \frac{1}{12\pi^2} \left( \frac{\Lambda^3}{3} - m^2\Lambda + m^3 \frac{\pi}{2} \right) \quad (55)$$

which is clearly divergent. However the physical pressure due to the ions  $P_p$  is given by

$$\beta P_p = \beta P_B - \beta P_B(0) - \beta P_S, \quad (56)$$

where  $\beta P_B(0)$  is the pressure due to an electrostatic field in the absence of ions and  $P_S$  is a contribution coming from the self-interaction of the ions with themselves. To see the origin of  $P_S$  we note that

$$\epsilon \nabla \phi = -i \epsilon \nabla \psi = i \mathbf{E}, \quad (57)$$

where  $\mathbf{E}$  is the electric field. Clearly  $\mathbf{E} = \sum_i \mathbf{E}_i$ , where  $\mathbf{E}_i$  is the field due to the single particle  $i$ . The term in  $\mathbf{E}^2$  which contributes to the interaction between particles is thus  $\mathbf{E}^2 - \sum_i \mathbf{E}_i^2$ . This means that

$$P_S = \frac{1}{6\epsilon} \left\langle \sum_i \mathbf{E}_i^2 \right\rangle = \frac{N}{6\epsilon} \langle \mathbf{E}_i^2 \rangle. \quad (58)$$

Hence if  $\psi'$  is the electrostatic potential generated by a single particle at the position of interest then

$$\beta P_S = \frac{2\rho\epsilon\beta}{6} \int d\mathbf{r} (\nabla \psi')^2 = \frac{\rho e^2 \beta}{6\pi^2 \epsilon} \int_0^\Lambda dk = \frac{1}{12\pi^2} m^2 \Lambda. \quad (59)$$

Putting all this together gives us the well known Debye pressure formula

$$\beta P_p = 2\rho - \frac{m^3}{24\pi}. \quad (60)$$

We state here that the general result Eq. (52) may also be derived by putting the field theory on a lattice and changing the volume of the system by varying the lattice size [15].

### III. CONCLUSION

We have shown in the case of planar geometries that the sine-Gordon type field theory for Coulomb systems can be expressed in terms of a 2+1 path integral for a field  $\phi$  on the 2D surface parallel to the film surface. The expression has the form of an  $S$  matrix and the choice of the ground-state wave functional for the ingoing and outgoing states of the field  $\phi$  imposes the global electroneutrality of the system. In the case of constant dielectric constant throughout the system, the classic contact value theorem is recovered. In the presence of dielectric variations, we see how the contact value theorem is corrected by fluctuations about the mean-field solution. A corresponding version of the midplane formula is also derived, which is also shown to be generically valid at the mean-field level. We again see that the corrections come from fluctuations about the mean-field solution. In both cases these fluctuations about the mean-field solution are known to be of Casimir type and can be calculated within various approximations. The results show clearly that the pressure of the system has two distinct, though inter-related, contributions: an osmotic pressure term plus a term coming from static thermal fluctuations of the field  $\phi$ . The present Hamiltonian technique has the advantage of giving an unambiguous way of taking the derivative of the grand partition function with respect to the film thickness  $L$  in the presence of surface charges and dielectric discontinuities. In the usual field theoretic formulation the taking of this derivative and the interpretation of the resulting terms as thermodynamic averages is far from obvious. In this Hamiltonian approach, the passage between the contact value result and midplane result is also straightforward. We have also shown how the Hamiltonian approach provides an alternative method for representing the pressure of bulk systems, giving results in accordance with those obtained via other methods.

As far as future work is concerned, using the results obtained here, similar results can be obtained for more complicated layer geometries (additional dielectric layers for instance) and also for more complicated surface charges, for instance modulated surface charges and surface charges built up from thermodynamic or chemical surface charging mechanisms (i.e., charge regulated models) [6,12].

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