Contact value theorem for electric double layers with modulated surface charge density

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Abstract. The contact value theorem was originally derived for Coulomb fluids of mobile charged particles in thermal equilibrium, in the presence of interfaces carrying a uniform surface charge density and in the absence of dielectric discontinuities. It relates the pressure (the effective force) between two parallel electric double layers to the particle number density and the surface charge density at the interface, separately for each of the two electric double layers. In this paper, we generalise the contact value theorem to electric double layers with interfaces carrying a modulated surface charge density. The derivation is based on balance of forces exerted on interfaces. The relevance of particular terms of the contact value theorem is tested on an exactly solvable two-dimensional Coulomb system with counterions only at the coupling constant $\Gamma = 2$.

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1. Introduction

The study of the thermal equilibrium of classical (i.e., non-quantum) fluids of charged particles interacting pairwisely via Coulomb potential is important in soft and condensed matter physics [1].

The Coulomb potential can be defined in any Euclidean space of points \( \mathbf{r} = (x_1, x_2, \ldots, x_\nu) \) (spatial dimensions \( \nu = 1, 2, 3, \ldots \)). In Gauss units and in vacuum with dielectric constant \( \varepsilon = 1 \), it corresponds to the solution of the \( \nu \)-dimensional Poisson equation:

\[
\Delta v(\mathbf{r}) = -s_\nu \delta(\mathbf{r}),
\]

(1.1)

where \( \Delta = \sum_{j=1}^\nu \partial^2 / \partial x_j^2 \) is the \( \nu \)-dimensional Laplacian, \( \delta \) is Dirac’s delta function and \( s_\nu = 2\pi^{\nu/2}/\Gamma(\nu/2) \) the surface area of the \( \nu \)-dimensional unit sphere. In particular,

\[
v(\mathbf{r}) = \begin{cases} 
-r & \text{for } \nu = 1, \\
\ln(r/L) & \text{for } \nu = 2, \\
r^{2-\nu}/(\nu - 2) & \text{for } \nu \geq 3,
\end{cases}
\]

(1.2)

where \( r \) is the modulus of \( \mathbf{r} \) and \( L \) is the free length scale. In a three-dimensional (3D) space, the Coulomb potential has the standard \( 1/r \) form known from electrostatics. The two-dimensional (2D) logarithmic potential can be interpreted in real 3D space as the effective potential between parallel infinite charged lines perpendicular to a plane, mimicking 3D polyelectrolytes. Because the Fourier component of (1.2) exhibits singular behavior of type \( \hat{v}(\mathbf{k}) \propto 1/k^2 \), many generic properties of Coulomb fluids in thermal equilibrium like perfect screening are preserved in any dimension \( \nu \) [2], leading to the well known zeroth-moment and second-moment Stillinger-Lovett conditions for the pair charge-charge densities [3, 4] in the bulk regime and to many other sum rules for the semi-infinite geometries. In dynamical systems of charged colloids exhibiting diffusiophoresis in flow [5, 6] or dielectrophoresis in time-varying electric fields [7], the induced charge clouds carry multipoles and therefore only a limited number of sum rules persists, see section IV of Ref. [2]. In this paper, we restrict ourselves to charged particle systems in thermal equilibrium. It should be emphasized that the fluid sum rules do not apply to large Coulomb couplings characterized by a crystalline phase.

In biological experiments with macromolecules (colloids) immersed in water or similar polar solvents, the colloidal surface acquires a fixed surface charge density through the dissociation of microions (counterions) into the solvent [8]. The solvent contains ions generically of both signs, the corresponding more-component systems are referred to as “with salt added.” One can reach experimentally the deionized (salt-free) solvent [9, 10, 11], the corresponding one-component models are referred to as “with counterions only” (or salt-free limit). Mobile counterions are usually taken as electrons with the negative elementary charge \(-e\) while colloids are large balls whose surfaces contain thousands of positive charges \( e \) fixed at their positions. To simplify the theoretical treatment of models, the curved surface of the colloid is substituted by a planar one and the modulated charge density on the surface by a uniform one. The
finite size of colloids is often ignored by taking the interior of colloids as a semi-infinite walls, with no dielectric jump between the medium the charges are immersed in and the colloid. The charged surface in thermal equilibrium with surrounding mobile charges form a neutral entity which is known as the electric double layer (EDL) \[12, 13, 14, 15\]. The effective interaction of two EDLs, mediated by mobile microions, is the topic of particular interest in soft matter \[16\].

We shall concentrate on two basic versions of Coulomb fluids which are of special experimental and theoretical interest:

- The jellium is a one-component plasma (OCP) of pointlike mobile particles with the same (say elementary) charge \(-e\), immersed in a fixed neutralizing background charge distributed uniformly in space. The definition of the pressure is not unique for the jellium because of the presence of the rigid volume background charge \[17\]. There exists a version of one-component plasmas with the neutralizing charge distributed not in the bulk, but at the surfaces of the walls of the domain the mobile charges are confined to. This is just the model for colloids with counterions only discussed above. In what follows, we shall restrict ourselves to this kind of systems for which, in contrast to jellium models, the pressure is defined uniquely. The only relevant thermodynamic parameter in 2D one-component models, which are in thermal equilibrium at the inverse temperature \(\beta = 1/(k_B T)\), is the coupling constant

\[ \Gamma \equiv \beta e^2. \]  

- The symmetric two-component plasma (TCP), or Coulomb gas, is the overall neutral system of \(\pm e\) charges with a hard core which prevents from a thermodynamic collapse of opposite charges. The hard core is not necessary in the 2D Coulomb gas when the Boltzmann factor corresponding to the interaction of opposite \(\pm e\) charges, \(r^{-\Gamma}\), is integrable at small 2D distances, i.e. for \(\Gamma < 2\). The TCP in the presence of charged walls corresponds to colloids with salt added in solvent discussed above.

The weak-coupling (high-temperature) region of Coulomb systems is described by the Poisson-Boltzmann (PB) mean-field theory or its linearized version – the Debye-Hückel theory \[14, 18\]. Like-charged colloids always effectively repel one another in the weak-coupling limit \[19, 20, 21, 22\]. Two-dimensional Coulomb models are exactly solvable, besides the high-temperature limit, also at a specific value \(\Gamma = 2\) of the coupling constant \[13\]. The OCP is mappable onto a system of free fermions \[23, 24\] while the TCP onto the so-called Thirring field model \[25, 26\]. The thermodynamics and many-body densities of these 2D Coulomb fluids were obtained in the bulk as well as semi-infinite and fully finite geometries, see reviews \[27, 28\]. The complete thermodynamics and the asymptotic behavior of the charge and density particle correlation functions are available for the 2D Coulomb gas even in the whole stability region of the coupling constant \(0 < \Gamma < 2\) via an equivalence with the integrable 2D sine-Gordon field theory \[29, 30, 31\]. The strong-coupling (low-temperature) regime, studied mainly for charged
colloid surfaces with counterions only, is controversial. The leading term of functional approaches based on a virial fugacity expansion \[32, 33, 34\], corresponding to a single-particle theory, agrees with Monte-Carlo simulations \[32, 33, 35, 36\], but higher-order terms fail. Other approaches based on the creation of classical Wigner crystals on charged walls by Coulomb particles at zero temperatures \[37, 38, 39, 40\] or the idea of the correlation hole \[41, 42, 43\] reproduce the leading single-particle theory and imply correction terms which are in good agreement with Monte-Carlo data. These strong-coupling theories explain a counter-intuitive effective attraction of likely-charged plates observed at low enough temperatures, experimentally \[44, 45, 46, 47, 48\] as well as by computer simulations \[12, 49, 50\].

There exists an exact relation known as the contact value theorem which holds in any spatial dimension. It was originally derived for planar interfaces carrying a uniform surface charge density, with no dielectric jump between the medium the particles are immersed in and the material of the plates/walls \[4, 51, 52, 53, 54\]. In the geometry of one EDL with planar interface, the contact value theorem relates the bulk pressure to the particle number density at the interface and the surface charge density. In the geometry of two parallel EDLs at a certain distance, it relates the pressure (the effective force) between EDLs to the particle number density at the interface and the surface charge density. In the 3D case of one EDL with the surface charge modulated along one direction only, exact PB solutions were constructed in an inverse way by exploring the general result for the 2D Liouville equation (models with counterions only) and the two-soliton solutions of the 2D sinh-Gordon equation.
Contact value theorem for interfaces with modulated surface charge density

The partition function and many-particle densities of 2D one-component systems with the coupling constant $\Gamma = 2\gamma$ ($\gamma$ is a positive integer) can be expressed in terms of an anticommuting-field theory defined on a one-dimensional chain of sites \cite{75, 76}. This mapping was used recently \cite{77} to derive, under certain conditions on the matrix of interaction strengths among anticommuting variables, exact formulas for the density profile and the pressure for special interfaces with modulated line charge densities at the free-fermion coupling $\Gamma = 2$. As a by-product of special transformations of anticommuting field variables leaving the composite form of their action invariant, the contact value theorem was generalised to interfaces with modulated line charge densities for any coupling constant $\Gamma = 2\gamma$ with $\gamma$ a positive integer (and therefore by analytic continuation to all real $\Gamma$s in the fluid region), see equations (4.5) and (5.7), (5.8) of Ref. \cite{77} for the geometries of one EDL and two parallel EDLs, respectively. The generalisation of the contact value theorem to 2D one-component systems with modulated line charge densities seemed to be related to special techniques available only in 2D. However, being motivated by the exact 2D result, we show in this article that the generalisation can be derived alternatively based on balance of forces exerted on interface(s) by mobile charges. This enables us to extend the contact value theorem for modulated surface charge densities from the special case of the 2D one-component plasma to multi-component Coulomb fluids in any spatial dimension.

The paper is organised as follows. The case of one EDL with modulated surface charge density is the subject of section 2. Basic formalism, the notation and the main 2D result of reference \cite{77} are presented in section 2.1. The derivation of the contact value theorem for multi-component Coulomb fluids in any spatial dimensions, based on balance of forces exerted on interface by mobile charges, is given in section 2.2. The case of two parallel EDLs with modulated surface charge densities is discussed in section 3. As before, basic formalism and the derivation of the contact value theorem are presented in sections 3.1 and 3.2, respectively. Section 4 deals with the analysis of relevance of particular terms in the contact value relation within the framework of a 2D exactly solvable model. A brief recapitulation and concluding remarks are given in section 5.

2. Geometry of one EDL

2.1. Basic formalism and notation

The geometry of one EDL with modulated surface charge density is presented in figure 1. We consider an infinite $\nu$-dimensional Euclidean space of points $\mathbf{r} = (x, \mathbf{y})$ where Cartesian coordinates $x \in \mathbb{R}$ and $\mathbf{y} = (y_1, \ldots, y_{\nu-1}) \in \mathbb{R}^{\nu-1}$. The dielectric wall in the half-space $x < 0$ mimics the interior of a colloid, pointlike particles move in the complementary half-space $\Lambda = \{x > 0, \mathbf{y}\}$. The $\pm e$ charges of particles means that the pictured system is the symmetric TCP, the OCP contains particles of the same charge (say $-e$). The $(\nu - 1)$-dimensional interface of points $\partial\Lambda = \{\mathbf{r} = (x = 0, \mathbf{y})\}$ carries a
modulated surface charge density $\sigma(y)e$. In real experiments, $\sigma(y)$ is a periodic function of $y$ and it is finite at every point $y \in \partial \Lambda$. The surface of the interface is taken infinite, $|\partial \Lambda| \to \infty$. Dielectric constants of the wall $\varepsilon_w$ and of the medium the particles are immersed in $\varepsilon$ are taken to be the same, $\varepsilon_w = \varepsilon = 1$, so that there are no dielectric image charges.

2.1.1. OCP For the OCP with counterions of charge $-e$, there are $N$ particles moving in the half-space domain $\Lambda$. The condition of the overall electroneutrality reads as

$$N(-e) + \int_{\partial \Lambda} dy \, \sigma(y)e = 0. \quad (2.1)$$

For a given configuration of $N$ charges $\{r_1, r_2, \ldots, r_N\}$, the microscopic density of particles at point $r \in \Lambda$ is defined by $\hat{n}(r) = \sum_{j=1}^{N} \delta(r - r_j)$. The averaged particle number density at point $r \in \Lambda$ is given by

$$n(r) = \langle \hat{n}(r) \rangle, \quad (2.2)$$

where $\langle \cdots \rangle$ denotes the statistical average over the canonical ensemble at the inverse temperature $\beta$. The total number of particles is equal to

$$N = \int_{\Lambda} d\mathbf{r} \, n(\mathbf{r}). \quad (2.3)$$
As there is a finite number of particles per unit surface of the interface, the density must vanish at large distances from the interface,
\[ \lim_{x \to \infty} n(r) = 0. \] (2.4)
This automatically means that the bulk pressure (the derivative of the free energy with respect to the volume) \( P \) vanishes as well.

The microscopic charge density is defined by \( \hat{\rho}(r) = \sum_{j=1}^{N} (-e) \delta(r - r_j) \) and the corresponding averaged charge density \( \rho(r) = \langle \hat{\rho}(r) \rangle \). Its relation to the averaged particle density is trivial for the OCP:
\[ \rho(r) = -en(r). \] (2.5)
The electroneutrality condition (2.1) together with equation (2.3) imply that
\[ \int_{\Lambda} \mathrm{d}r \rho(r) + \int_{\partial\Lambda} \mathrm{d}y \sigma(y)e = 0. \] (2.6)
The theory simplifies itself substantially when the surface charge density is uniform, \( \sigma(y) = \sigma \). The averaged particle and charge densities then depend only on the coordinate \( x \) perpendicular to the interface, i.e., \( n(r) = n(x) \) and \( \rho(r) = \rho(x) \). The electroneutrality condition (2.6) and the asymptotic relation (2.4) then become
\[ \int_{0}^{\infty} \mathrm{d}x n(x) = \sigma, \quad \lim_{x \to \infty} n(x) = 0. \] (2.7)
The contact value theorem \([4, 51, 52, 53, 54]\) fixes the density of counterions at the interface as follows
\[ n(0) = \frac{1}{2} \frac{s_{\nu} \beta e^2 \sigma^2}{}, \] (2.8)
keeping in mind that the bulk pressure \( P = 0 \) for the considered OCP. This contact value relation was checked on the exact solutions of the OCP in the weak-coupling PB limit in any dimension \([18]\) and at the free fermion coupling \( \Gamma = 2 \) in 2D \([78, 79]\).

2.1.2. TCP Let the TCP be composed of \( N_+ \) particles with charge \(+e\) and \( N_- \) particles with charge \(-e\), the total number of particles \( N = N_+ + N_- \). The electroneutrality condition reads as
\[ N_+ - N_- = \int_{\partial\Lambda} \mathrm{d}y \sigma(y). \] (2.9)
For a configuration of \( N_+ \) particles with charge \(+e\), \( \{r_1^+, r_2^+, \ldots, r_{N_+}^+\} \), the microscopic density of \(+e\) particles at point \( r \in \Lambda \) is \( n_+(r) = \sum_{j=1}^{N_+} \delta(r - r_j^+) \) and the averaged number density of \(+e\) particles at point \( r \in \Lambda \) is \( n_+(r) = \langle \hat{n}_+(r) \rangle \). Analogously, for a configuration of \( N_- \) particles with charge \(-e\), \( \{r_1^-, r_2^-, \ldots, r_{N_-}^-\} \), the microscopic density of \(-e\) particles at point \( r \in \Lambda \) is \( n_-(r) = \sum_{j=1}^{N_-} \delta(r - r_j^-) \) and the averaged number density of \(-e\) particles at point \( r \in \Lambda \) is \( n_-(r) = \langle \hat{n}_-(r) \rangle \). The total averaged number density of particles \( n(r) \) and charge density \( \rho(r) \) are given by
\[ n(r) = n_+(r) + n_-(r), \quad \rho(r) = e \left[ n_+(r) - n_-(r) \right]. \] (2.10)
Contact value theorem for interfaces with modulated surface charge density

As there is a finite charge per unit surface of the interface, the charge density induced by particles must vanish at asymptotically large distances from the interface,

$$\lim_{x \to \infty} \rho(r) = 0.$$  \hspace{1cm} (2.11)

On the other hand, the particle number density is, in general, nonzero and constant (due to the charge screening, not touched by the surface charge density) at asymptotically large distances from the interface,

$$\lim_{x \to \infty} n(r) = n,$$  \hspace{1cm} (2.12)

where the bulk density $n$ is controlled by the chemical potential. The electroneutrality condition (2.9) can be written as the previous one (2.10).

If the surface charge density is uniform, $\sigma(y) = \sigma$, the averaged particle and charge densities depend only on the $x$-coordinate. The asymptotic relations (2.11) and (2.12) then become

$$\lim_{x \to \infty} \rho(x) = 0, \quad \lim_{x \to \infty} n(x) = n.$$  \hspace{1cm} (2.13)

The contact value theorem \cite{4, 51, 52, 53, 54} takes the form

$$\beta P = n(0) - \frac{1}{2} s_{\nu} \beta e^2 \sigma^2,$$  \hspace{1cm} (2.14)

where the bulk pressure $P$, corresponding to the particle density $n$, includes electrostatic as well as non-electrostatic interactions like the Lennard-Jones interaction, the excluded volume effects \cite{80}, etc. Notice that the contact theorem for the OCP (2.8), characterized by $P = 0$, is in fact identical to the one for the TCP (2.14). The relation (2.14) was checked by using the exact solutions of the TCP in the weak-coupling PB limit in any dimension \cite{18} and at the coupling $\Gamma = 2$ in 2D \cite{25, 26}.

2.2. Balance of forces

The contact value theorem for one interface with modulated surface charge density can be obtained from the balance of the forces exerted to the wall surface. The total force along the $x$-direction (perpendicular to the interface) consists of three components.

The particles with the density $n(0, y)$ at the interface $\partial \Lambda$ push on the wall by the force

$$F_{1}^x = -\frac{1}{\beta} \int_{\partial \Lambda} dy \, n(0, y),$$  \hspace{1cm} (2.15)

oriented to the left along the $x$-axis in figure II.

The charged particles inside the domain $\Lambda$ induce at the point $(0, y') \in \partial \Lambda$ the electric field

$$E_{2}^x(0, y') = -\int_{\Lambda} d\mathbf{r} \, \rho(\mathbf{r}) \frac{\partial}{\partial(-x)} v(x, |y - y'|).$$  \hspace{1cm} (2.16)
The corresponding force exerted on the surface charge density reads as

\[ F_x^2 = \int_{\partial \Lambda} d y' \sigma(y') e E_x^y(0, y') \]

\[ = e \int_{\partial \Lambda} d y' \sigma(y') \int_{\Lambda} d r \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|). \quad (2.17) \]

There is another wall at \( x \to \infty \) with no surface charge density and of the same surface as the one at \( x = 0 \), see the dashed line in figure I. The particles of bulk density \( n \) (controlled by the chemical potential) push on this wall by the force

\[ F_x^3 = P |\partial \Lambda|, \quad (2.18) \]

where \( P \) is the bulk pressure corresponding to the particle density \( n \).

The total force acting on the interface \( \partial \Lambda \) and the one at infinity must be zero in thermal equilibrium, i.e.,

\[ F_1^x + F_2^x + F_3^x = 0. \quad (2.19) \]

Introducing the mean particle density at the interface

\[ \bar{n}(0) \equiv 1 \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda} d y \ n(0, y), \quad (2.20) \]

the balance of forces \((2.19)\) implies the relation

\[ \beta P = \bar{n}(0) - \frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} d y' \sigma(y') \int_{\Lambda} d r \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|). \quad (2.21) \]

This relation can be adapted further by considering the point-dependent deviations of the surface charge density from its mean value \( \bar{\sigma} \),

\[ \sigma(y) = \bar{\sigma} + \delta \sigma(y), \quad \bar{\sigma} \equiv 1 \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda} d y \sigma(y). \quad (2.22) \]

The mean value \( \bar{\sigma} \) is mathematically well defined since the surface charge density \( \sigma(y) \) is assumed to be finite at every point \( y \in \partial \Lambda \). The surface integral over deviations must vanish by definition,

\[ \int_{\partial \Lambda} d y \delta \sigma(y) = 0. \quad (2.23) \]

Inserting the decomposition \((2.22)\) into \((2.21)\), one gets

\[ \beta P = \bar{n}(0) - \frac{\beta e \bar{\sigma}}{|\partial \Lambda|} \int_{\partial \Lambda} d y' \int_{\Lambda} d r \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|) \]

\[ - \frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} d y' \delta \sigma(y') \int_{\Lambda} d r \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|). \quad (2.24) \]

According to Fubini’s theorem, the order of integration of an absolutely integrable function can be exchanged \([81]\). Since

\[ \frac{\partial}{\partial x} v(x, |y - y'|) = -x \frac{x}{(x^2 + |y - y'|^2)^{3/2}} \quad (2.25) \]
and the charge density $\rho(\mathbf{r})$ is finite at every point $\mathbf{r} \in \Lambda$, one can interchange the order of integrations over $\mathbf{y}'$ and $\mathbf{r}$ in the first integral on the rhs of equation (2.24) and concentrate on the integral

$$\int_{\partial \Lambda} \frac{d\mathbf{y}'}{\partial x} v(x, |\mathbf{y} - \mathbf{y}'|) = \int_{\partial \Lambda} \frac{d\mathbf{y}'}{\partial x} v(x, |\mathbf{y}'|),$$

(2.26)

where the substitution $\mathbf{y}' - \mathbf{y} \rightarrow \mathbf{y}'$ was made within an infinite domain’s boundary $\partial \Lambda$. Using the radial coordinate system on the $(\nu - 1)$-dimensional interface $\partial \Lambda$, the integral (2.26) can be expressed as

$$-\int_0^\infty dy' s_{\nu-1} y'^{\nu-2} \frac{x}{(x^2 + y'^2)^{\nu/2}} = -s_{\nu-1} \frac{\sqrt{\pi} \Gamma\left(\frac{\nu-1}{2}\right)}{2 \Gamma\left(\frac{\nu}{2}\right)} = -\frac{1}{2} s_{\nu}. \quad (2.27)$$

The first integral on the rhs of equation (2.24) can be thus written as

$$\int_{\partial \Lambda} d\mathbf{y}' \int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial x} v(x, |\mathbf{y} - \mathbf{y}'|) = -\frac{1}{2} s_{\nu} \int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}). \quad (2.28)$$

Finally, since the electroneutrality condition (2.6) implies that

$$\int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}) = -\int_{\partial \Lambda} d\mathbf{y} \sigma(\mathbf{y}) e = -\bar{\sigma} e |\partial \Lambda|,$$

(2.29)

equation (2.24) simplifies itself to

$$\beta P = \bar{n}(0) - \frac{1}{2} s_{\nu} \beta e^2 \sigma^2$$

$$-\frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} d\mathbf{y}' \delta \sigma(\mathbf{y}') \int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial y_j} v(x, |\mathbf{y} - \mathbf{y}'|). \quad (2.30)$$

We see that the modulation of the surface charge density induces into the contact value theorem the charge density of particles inside the whole domain $\Lambda$. In the uniform case $\delta \sigma(\mathbf{y}) = 0$ with $\bar{n}(0) = n(x = 0)$, the previous contact value relation (2.14) is reproduced. Note that the derivation of the contact value theorem (2.30) was based on the consideration of balance of electrostatic forces, the non-electrostatic forces contribute only to the bulk pressure $P$.

As for the force components along directions $\mathbf{y}$ parallel to the interface, it is first necessary to specify boundary conditions at $\pm$ infinity. In analogy with the previous work [77], let us consider the periodic boundary conditions for which only the component of type (2.17) survives:

$$F_2^y = \int_{\partial \Lambda} d\mathbf{y}' \sigma(\mathbf{y}') e E_2^y(0, \mathbf{y}')$$

$$= e \int_{\partial \Lambda} d\mathbf{y}' \sigma(\mathbf{y}') \int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial y_j} v(x, |\mathbf{y} - \mathbf{y}'|) \quad (2.31)$$

($j = 1, 2, \ldots, \nu - 1$). Using here the decomposition (2.22), changing the order of integrations attached to the term $\sigma$ and setting the force in equilibrium equal to zero, one obtains the equality

$$\int_{\partial \Lambda} d\mathbf{y}' \delta \sigma(\mathbf{y}') \int_{\Lambda} d\mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial y_j} v(x, |\mathbf{y} - \mathbf{y}'|) = 0, \quad j = 1, 2, \ldots, \nu - 1. \quad (2.32)$$

In 2D, this relation was derived by using symmetry transformations of anticommuting variables, see equation (4.8) in Ref. [77].
3. Geometry of two parallel EDLs

3.1. Basic formalism and notation

The geometry of two parallel interfaces at distance \( d \) is pictured in figure 2. The “left” wall in the half-space \( x < 0 \) with interface \( \partial \Lambda_L \) at \( x = 0 \) carries a modulated surface charge density \( \sigma_L(y)e \). The wall in the half-space \( x > d \), with interface \( \partial \Lambda_R \) at \( x = d \), carries \( \sigma_R(y)e \). Pointlike particles of the symmetric TCP with \( \pm e \) charges move inside the domain \( \Lambda = \{ \mathbf{r} = (x, y), 0 < x < d, y \in \mathbb{R}^{\nu-1} \} \).

When the surface charge densities are uniform, i.e., \( \sigma_L(y) = \sigma_L \) and \( \sigma_R(y) = \sigma_R \), the averaged particle number and charge densities depend only on the \( x \)-coordinate, \( n(\mathbf{r}; d) = n(x; d) \) and \( \rho(\mathbf{r}; d) = \rho(x; d) \). The contact value theorem \[4, 51, 52, 53, 54\] relates the pressure of the Coulomb fluid between EDLs \( P \) and the contact particle...
number densities on both interfaces as follows

\[
\beta P(d) = n(0; d) - \frac{1}{2} s_v \beta e^2 \sigma_L^2
\]

\[
= n(d; d) - \frac{1}{2} s_v \beta e^2 \sigma_R^2. \tag{3.3}
\]

In the limit of infinite distance between the two EDLs \(d \to \infty\), the system decomposes itself onto two separate (noninteracting) EDLs with the bulk pressure

\[
\lim_{d \to \infty} P(d) = P; \tag{3.4}
\]

the relations (3.3) then correspond to two independent contact value theorems for one EDL of type (2.14). Taking the left and right walls as plates of a finite thickness (as it is in the case of two big colloids), the effective force per unit surface between the plates mediated by the Coulomb fluid in between is equal to \(P(d) - P\). In view of relation (3.4), this force goes to 0 at \(d \to \infty\) as it should be. The positive (negative) value of the pressure \(P(d) - P > 0\) \((P(d) - P < 0)\) means the repulsion (attraction) of the interfaces.

3.2. Balance of forces

The force acting on the left interface is balanced completely by the opposite force acting on the right interface, so that the total force on the Coulomb system in thermal equilibrium vanishes as it should be. Note that all considered forces act along the \(x\)-axis.

Let us first consider the left wall with the interface \(\partial \Lambda_L\). In analogy with section 2.2, the particles with the density \(n(0, y)\) push on \(\partial \Lambda_L\) by the force

\[
F_1^x = -\frac{1}{\beta} \int_{\partial \Lambda} \, dy \ n(0, y). \tag{3.5}
\]

The force induced by the charged particles inside the domain \(\Lambda\) reads as

\[
F_2^x = e \int_{\partial \Lambda} \, dy' \sigma_L(y') \int_{\Lambda} \, dr \ \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|). \tag{3.6}
\]

The particles push on the opposite wall with interface \(\partial \Lambda_R\) by the force

\[
F_3^x = P(d) |\partial \Lambda|. \tag{3.7}
\]

Finally, the force exerted by the charged interface \(\partial \Lambda_R\) on the one \(\partial \Lambda_L\) is given by

\[
F_4^x = e^2 \int_{\partial \Lambda_L} \, dy \int_{\partial \Lambda_R} \, dy' \sigma_L(y) \frac{\partial}{\partial d} v(d, |y - y'|) \sigma_R(y'). \tag{3.8}
\]

The total force acting on the two interfaces must be zero,

\[
F_1^x + F_2^x + F_3^x + F_4^x = 0. \tag{3.9}
\]

In terms of the mean particle density at the interface \(\partial \Lambda_L\)

\[
\bar{n}(0) = \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda_L} \, dy \ n(0, y), \tag{3.10}
\]
the balance of forces (3.9) leads to the relation

\[
\beta P(d) = \tilde{n}(0) - \frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} dy' \sigma_L(y') \int_{\Lambda} dr \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|) \\
- \frac{\beta e^2}{|\partial \Lambda|} \int_{\partial \Lambda} dy \int_{\partial \Lambda_R} \frac{\partial}{\partial d} v(d, |y - y'|) \delta \sigma_L(y').
\]  

(3.11)

For each of the interfaces, we introduce point-dependent deviations of the surface charge density from its mean value,

\[
\sigma_L(y) = \bar{\sigma}_L + \delta \sigma_L(y), \quad \bar{\sigma}_L = \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda} dy \sigma_L(y),
\]  

(3.12)

\[
\sigma_R(y) = \bar{\sigma}_R + \delta \sigma_R(y), \quad \bar{\sigma}_R = \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda} dy \sigma_R(y).
\]  

(3.13)

The surface integral over deviations must vanish for each of the interfaces,

\[
\int_{\partial \Lambda} \delta \sigma_L(y) = 0, \quad \int_{\partial \Lambda} \delta \sigma_R(y) = 0.
\]  

(3.14)

Inserting the decompositions (3.12) and (3.13) into (3.11), we do again the procedure between equations (2.26) and (2.29) of section 2.2. With the aid of the electroneutrality condition (3.2), the total pressure \( P \) is obtained as the sum of two contributions,

\[
\beta P(d) = \beta P_{\text{part}}(d) + \beta P_{\text{dev}}(d),
\]  

(3.15)

where

\[
\beta P_{\text{part}}(d) = \tilde{n}(0) - \frac{1}{2} s \nu \beta e^2 \bar{\sigma}_L^2
- \frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} dy' \delta \sigma_L(y') \int_{\Lambda} dr \rho(r) \frac{\partial}{\partial x} v(x, |y - y'|)
\]  

(3.16)

is the “particle” part which depends on the mean particle number density in contact \( \tilde{n}(0) \) defined in (3.10) and the profile of the particle charge density \( \rho(r) \) inside the whole domain \( \Lambda \), and

\[
\beta P_{\text{dev}}(d) = - \frac{\beta e^2}{|\partial \Lambda|} \int_{\partial \Lambda} dy \int_{\partial \Lambda_R} \frac{\partial}{\partial d} v(d, |y - y'|) \delta \sigma_R(y').
\]  

(3.17)

is the “deviation” part corresponding to the pure Coulomb interaction of the surface charge deviations on the two interfaces.

Applying the same procedure to the the right interface \( \partial \Lambda_R \) results in the split formula (3.15) with the particle part

\[
\beta P_{\text{part}}(d) = \tilde{n}(d) - \frac{1}{2} s \nu \beta e^2 \bar{\sigma}_R^2
+ \frac{\beta e}{|\partial \Lambda|} \int_{\partial \Lambda} dy' \delta \sigma_R(y') \int_{\Lambda} dr \rho(r) \frac{\partial}{\partial x} v(d - x, |y - y'|)
\]  

(3.18)

and the deviation part \( \beta P_{\text{dev}}(d) \) given by the previous formula (3.17). Here,

\[
\tilde{n}(d) = \frac{1}{|\partial \Lambda|} \int_{\partial \Lambda_R} dy \tilde{n}(d, y)
\]  

(3.19)
is the mean particle density in contact with the right interface $\partial \Lambda_R$. Note that in the large-$d$ limit the deviation part $\beta P_{\text{dev}}$ \[3.17\] vanishes and one is left with the pair of independent one-EDL counterparts of type \[2.30\].

4. Analysis of an exactly solvable 2D model

As was mentioned in the Introduction, many types of 2D Coulomb fluid are exactly solvable at the coupling constant $\Gamma = 2$.

For the geometry of two parallel lines at distance $d$, carrying the uniform line charge densities $\sigma_L e$ and $\sigma_R e$ with counterions of charge $-e$ only, the exact formula for the pressure $P$ at $\Gamma = 2$ was derived in \[82, 83\]:

$$\beta P_0(d; \sigma_L, \sigma_R) = \beta P_0(d; \sigma_L) + \beta P_0(d; \sigma_R), \quad (4.1)$$

where

$$\beta P_0(d; \sigma) = \frac{1}{2\pi d^2} \int_0^{2\pi \sigma d} \frac{dt}{\sinh t} e^{-t}$$

and the subscript “0” in $P_0$ means that the line charge densities are uniform. In the case of like-charged lines $0 < \sigma_L \leq \sigma_R$, the pressure is always positive, $P_0(d) > 0$, i.e., the charged lines repeal each other for any distance $d$. The pressure diverges at small distances $d$,

$$\beta P_0(d; \sigma_L, \sigma_R) \sim \frac{\sigma_L + \sigma_R}{d}, \quad (4.3)$$

and decays monotonously to 0 from above at asymptotically large $d$,

$$\beta P_0(d; \sigma_L, \sigma_R) \sim \frac{1}{\pi d^2} \int_0^\infty \frac{dt}{\sinh t} e^{-t} = \frac{\pi}{12} \frac{1}{d^2}. \quad (4.4)$$

Note that this asymptotic decay is universal, independent of the line charge densities $\sigma_L$ and $\sigma_R$.

The necessary conditions under which a 2D system with modulated line charge densities is exactly solvable at $\Gamma = 2$ were established in \[77\]. A version of integrable model is given by the mean line charge densities $\sigma_L e$ and $\sigma_R e$ and the periodic deviations

$$\delta \sigma_L(y) = A_L \cos \left(\frac{2\pi y}{\lambda}\right), \quad \delta \sigma_R(y) = A_R \cos \left(\frac{2\pi y}{\lambda}\right), \quad (4.5)$$

with $\lambda$ being the period and the amplitudes are constrained by $|A_L| \leq \sigma_L$ and $|A_R| \leq \sigma_R$. This model is exactly solvable provided that

$$\lambda (\sigma_L + \sigma_R) \leq 1. \quad (4.6)$$

In terms of the dimensionless pressure

$$\bar{P}(d) \equiv \lambda^2 \beta P(d), \quad (4.7)$$

the exact solution can be written as the decomposition of type \[3.15\]

$$\bar{P}(d) = \bar{P}_{\text{part}}(d) + \bar{P}_{\text{dev}}(d), \quad (4.8)$$
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with

\[ \tilde{P}_{\text{part}}(d) = \frac{\partial}{\partial(d/\lambda)} g \left( d/\lambda, \lambda\sigma_L; \{\lambda A_L, \lambda A_R\} \right) + \frac{\partial}{\partial(d/\lambda)} g \left( d/\lambda, \lambda\sigma_R; \{\lambda A_R, \lambda A_L\} \right) \]  

and

\[ \tilde{P}_{\text{dev}}(d) = \pi (\lambda A_L)(\lambda A_R)e^{-2\pi d/\lambda}. \]  

Here,

\[ g \left( d/\lambda, \lambda\sigma; \{\lambda A, \lambda A'\} \right) = \frac{1}{4\pi} \int_0^{4\pi\lambda\sigma} \text{dr} \ln \left\{ \int_0^{d/\lambda} \text{dx} e^{-rx} \right. \]  

\[ \times I_0 \left( \lambda A e^{-2\pi x} + \lambda A' e^{-2\pi d/\lambda+2\pi x} \right) \} \],

where \( I_0 \) denotes the modified Bessel function of the first kind [84].

For simplicity, we shall restrict ourselves to the symmetrically charged lines with the equivalent mean values of the line charge densities

\[ \sigma_L = \sigma_R = \sigma \]  

and the equivalent (positive) amplitudes

\[ A_L = A_R = A, \quad 0 < A \leq \sigma. \]  

For this symmetric case

\[ \sigma_L(y) = \sigma_R(y) = \sigma + A \cos \left( \frac{2\pi}{\lambda} y \right), \]  

the condition of exact solvability (4.6) takes the form

\[ \lambda\sigma \leq \frac{1}{2}. \]  

Let us consider the extreme value \( \lambda\sigma = \frac{1}{2} \) for which

\[ \lambda A \leq \lambda\sigma = \frac{1}{2}. \]  

The dimensionless pressure is again given by (4.8) where

\[ \tilde{P}_{\text{part}}(d/\lambda, \lambda A) = 2 \frac{\partial}{\partial(d/\lambda)} g \left( d/\lambda; \lambda A \right) \]  

and

\[ \tilde{P}_{\text{dev}}(d/\lambda, \lambda A) = \pi (\lambda A)^2 e^{-2\pi d/\lambda}. \]  

The \( g \)-function reads as

\[ g \left( d/\lambda; \lambda A \right) = \frac{1}{4\pi} \int_0^{2\pi} \text{dr} \ln \left\{ \int_0^{d/\lambda} \text{dx} e^{-rx} \right. \]  

\[ \times I_0 \left( \lambda A e^{-2\pi x} + e^{-2\pi d/\lambda+2\pi x} \right) \} \].
The above exact formulas for \( \tilde{P}_{\text{part}}(d/\lambda, \lambda A) \) in terms of \( g(d/\lambda; \lambda A) \) are rather complicated and they can be treated for the given values of the dimensionless amplitudes \( \lambda A \) and distances \( d/\lambda \) only numerically. The analytic treatment is possible in special limits, like for instance in the limit of small amplitudes \( \lambda A \) when the Bessel function in (4.19) can be expanded as \[84\]

\[ I_0 \left( \lambda A [e^{-2\pi x} + e^{-2\pi d/\lambda + 2\pi x}] \right) = 1 + \frac{(\lambda A)^2}{4} \left( e^{-4\pi x} + 2e^{-2\pi d/\lambda} + e^{-4\pi d/\lambda + 4\pi x} \right) + O \left( (\lambda A)^4 \right). \quad (4.20) \]

Performing then the integration over the \( x \)-variable in (4.19), the logarithm takes the following argument

\[ \ln \left\{ \frac{1 - e^{-rd/\lambda}}{r} + \frac{(\lambda A)^2}{4} \left( \frac{1 - e^{-4\pi d/\lambda}}{4\pi + r} + 2e^{-2\pi d/\lambda} \right) + O \left( (\lambda A)^4 \right) \right\}. \quad (4.21) \]

Expanding the logarithm in \( \lambda A \) results in

\[ g \left( d/\lambda; \lambda A \right) = \frac{1}{4\pi} \int_0^{2\pi} dr \ln \left( \frac{1 - e^{-rd/\lambda}}{r} \right) + \frac{(\lambda A)^2}{4} \frac{1}{4\pi} \int_0^{2\pi} dr \left[ \frac{1 - e^{-4\pi d/\lambda}}{4\pi + r} + 2e^{-2\pi d/\lambda} + \frac{e^{-rd/\lambda} - e^{-4\pi d/\lambda}}{1 - e^{-rd/\lambda}} \right] + O \left( (\lambda A)^4 \right). \quad (4.22) \]

The first term on the rhs of this equation is related to the dimensionless pressure \( \tilde{P}_0(d; \sigma, \sigma) \equiv \lambda^2 \beta P_0(d, \sigma, \sigma) \) with uniform line charge densities \( \sigma_L = \sigma_R = 1/(2\lambda) \), see formulas (4.1) and (4.2), as follows

\[ \tilde{P}_0 \left( d; \sigma_L = \frac{1}{2\lambda}, \sigma_R = \frac{1}{2\lambda} \right) = 2\frac{\partial}{\partial (d/\lambda)} \frac{1}{4\pi} \int_0^{2\pi} dr \ln \left( \frac{1 - e^{-rd/\lambda}}{r} \right). \quad (4.23) \]

The second term on the rhs of equation (4.22), proportional to \( (\lambda A)^2 \), can be treated analytically in two limits \( d/\lambda \to 0 \) and \( d/\lambda \to \infty \).

- In the limit \( d/\lambda \to 0 \), one simply Taylor expands the function under integration over \( r \) in powers of \( (d/\lambda) \) and then integrate over \( r \), with the result

\[ (\lambda A)^2 \left[ \frac{1}{2} - \frac{\pi d}{\lambda} + \frac{7}{6} \left( \frac{\pi d}{\lambda} \right)^2 - \left( \frac{\pi d}{\lambda} \right)^3 \right] + O \left( (\pi d/\lambda)^4 \right). \quad (4.24) \]

With regard to the relation (4.17), one can write

\[ \tilde{P}_{\text{part}}(d/\lambda, \lambda A) = \tilde{P}_0 \left( d; \sigma_L = \frac{1}{2\lambda}, \sigma_R = \frac{1}{2\lambda} \right) + (\lambda A)^2 \left[ - 2\pi \frac{14\pi \pi d}{\lambda} - 6\pi \left( \frac{\pi d}{\lambda} \right)^2 + O \left( (\pi d/\lambda)^3 \right) \right]. \quad (4.25) \]

Comparing the leading term \( -2\pi (\lambda A)^2 \) to the one \( \pi (\lambda A)^2 \) of the line charge interaction pressure \( \tilde{P}_{\text{dev}}(d/\lambda, \lambda A) \) in (4.18) we see that it is twice larger by
the amplitude and has a minus sign, in agreement with the hypothesis that the modulation of the line charge densities diminish the pressure between the two lines.

- In the limit $d/\lambda \to \infty$, one can neglect certain terms under integration over $r$ vanishing exponentially in this limit, to get

$$
\frac{(\lambda A)^2}{4} \frac{1}{4\pi} \int_0^{2\pi} dr \left\{ \frac{-r}{4\pi - r} + \frac{1}{1 - e^{-rd/\lambda}} \left[ \frac{r}{4\pi + r} + \frac{r}{4\pi - r} \right] \right\}. \tag{4.26}
$$

This expression can be further manipulated as follows

$$
\frac{(\lambda A)^2}{4} \left[ \left( \frac{1}{2} - \ln 2 \right) + \frac{1}{4\pi} \int_0^{2\pi} dr \sum_{n=1}^{\infty} e^{-nrd/\lambda} \frac{8\pi r}{(4\pi)^2 - r^2} \right]. \tag{4.27}
$$

Since it holds

$$
\int_0^{2\pi} dr e^{-nrd/\lambda} \frac{2r}{(4\pi)^2 - r^2} \sim \frac{1}{8\pi^2 n^2(d/\lambda)^2} + O \left( \frac{1}{(d/\lambda)^3} \right), \tag{4.28}
$$

one ends up with

$$
(\lambda A)^2 \left[ \frac{1}{4} \left( \frac{1}{2} - \ln 2 \right) + \frac{\zeta(2)}{32\pi^2(d/\lambda)^2} \right], \tag{4.29}
$$

where $\zeta(2)$ is the Riemann zeta function at point 2 $[84]$,

$$
\zeta(2) = \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}. \tag{4.30}
$$

Finally, using (4.17) one arrives at

$$
P_{\text{part}}(d/\lambda, \lambda A) = \tilde{P}_0 \left( d; \sigma_L = \frac{1}{2\lambda}, \sigma_R = \frac{1}{2\lambda} \right) - (\lambda A)^2 \frac{1}{48} \frac{1}{(d/\lambda)^3} + O \left( \frac{1}{(d/\lambda)^4} \right). \tag{4.31}
$$

Since the deviation part of the pressure (4.18) decays exponentially at large distances $d/\lambda$, the above obtained long-ranged term dominates and its negative sign indicates the diminution of the pressure due to the line charge modulations at large distances as well. Notice that the pressure for uniformly charged lines (4.4) goes down more slowly.

We conclude that within the split of the total pressure onto its particle and deviation parts (3.15), implied by the contact value theorem, both short-distance and large-distance asymptotics due to the surface charge modulations are dominated by the particle term $\beta P_{\text{part}}(d)$. This term effectively diminishes the pressure in the absence of the line charge modulation $\tilde{P}_0(d)$ as was expected.

Keeping in mind that we consider the extreme value of the parameter $\lambda \sigma = \frac{1}{2}$ preserving the exact solvability of our model with the line charge modulation, let us consider also the extreme value of the dimensionless amplitude of the modulated surface charge density $\lambda A = \frac{1}{2}$ constrained by (4.16). This means that the line charge densities

$$
\lambda \sigma_L(y) = \lambda \sigma_R(y) = \frac{1}{2} \left[ 1 + \cos \left( \frac{2\pi}{\lambda} y \right) \right], \tag{4.32}
$$
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Figure 3. The exactly solvable 2D model of two parallel EDLs with counterions only, the symmetric line charge modulations are given by \((4.32)\). The numerical results for various pressure contributions described in the text, see equations \((4.33)\), \((4.34)\), and \((4.35)\), as the functions of the dimensionless interface distance \(d/\lambda\). The difference between the pressures with and without the line charge modulations, \(\delta \tilde{P}(d)\), is always negative as it should be.

are positive, except for the points \(y = \pm \lambda/2, \pm 3\lambda/2, \ldots\) where they vanish. The numerical results for various pressure contributions as the functions of the dimensionless interface distance \(d/\lambda\) are presented in figure 3. In particular,

\[
\delta P_{\text{part}}(d) \equiv \tilde{P}_{\text{part}}(d) - \tilde{P}_0(d) \quad (4.33)
\]

(dashed curve) is the (always negative) difference between the particle part of the pressure and the pressure with the uniform line charge densities \((\lambda A = 0)\),

\[
\tilde{P}_{\text{dev}}(d) = \frac{\pi}{4} e^{-2\pi d/\lambda} \quad (4.34)
\]

(dotted curve) is the (always positive) deviation part of the pressure and

\[
\delta \tilde{P}(d) \equiv \tilde{P}(d) - \tilde{P}_0(d) = \delta \tilde{P}_{\text{part}}(d) + \tilde{P}_{\text{dev}}(d) \quad (4.35)
\]

(solid curve) is the difference between the pressures with and without the line charge modulations. It is seen that \(\delta \tilde{P}\) is negative in the displayed interval of the distances \(d/\lambda\) as was expected.
5. Conclusion

Rigorous or exact results in the thermodynamics of Coulomb fluids, valid for any spatial dimension, are rare. The contact value theorem belongs to such results. In its most general formulation, it relates the pressure to the averaged one- and two-body densities inside the particle domain. In this paper, we generalized the contact value theorem to EDLs with modulated surface charge densities, see equation (2.30) for the geometry of one EDL and equations (3.15)-(3.18) for two parallel EDLs at distance \( d \). These equations involve the particle density at the wall interfaces and the charge density of particles inside the whole domain \( \Lambda \), in formal analogy with the jellium systems characterized by the volume background charge density \([17, 55]\). In the case of two parallel EDLs the total pressure is obtained as the sum of the particle and surface-charge deviation parts, see equations (3.15)-(3.18). We tested these two contributions on a symmetric 2D model with counterions only which was solved exactly in \([77]\). It turns out that the (negative) particle part dominates over the (positive) deviation part which explains the diminution of the total pressure due to the surface charge modulation.

As concerns a potential application of the present contact value theorem in future, it may motivate someone to establish a general proof about the pressure diminution due to the surface charge modulation. A step towards the general proof might be the consideration of small surface charge deviations \( \delta \sigma_L(y) \) and \( \delta \sigma_R(y) \) on the left and right interfaces, respectively. In this limit, the contributions of the surface charge deviations to the particle number and charge densities can be treated perturbatively around the system with the uniform surface charge densities within the linear response theory. A technical problem is that the first nonzero contribution to the pressure, bilinear in the deviations \( \delta \sigma_L(y) \) and \( \delta \sigma_R(y) \), involves three-body densities of the unperturbed system which are difficult to deal with.

Another possible extension of the present work is to consider dielectric discontinuities between the walls and the medium in which charged particles move and Casimir-like forces. This requires the inclusion of the interaction of particles with their image charges (one-wall geometry) or an infinite array of image charges (two-wall geometry) which ultimately leads to the presence of higher-order particle densities in the formalism.

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