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Finite-size corrections for Coulomb systems in the Debye–Hückel regime

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Abstract

It has been argued that for a finite two-dimensional classical Coulomb system of characteristic size R , in its conducting phase, as $R \rightarrow \infty$ the total free energy (times the inverse temperature β) admits an expansion of the form: $\beta F = AR^2 + BR + \frac{1}{6}\chi \ln R$, where χ is the Euler characteristic of the manifold where the system exists. The first two terms represent the bulk free energy and the surface free energy, respectively. The coefficients A and B are non-universal but the coefficient of $\ln R$ is universal: it does not depend on the detail of the microscopic constitution of the system (particle densities, temperature, etc). By doing the usual Legendre transform this universal finite-size correction is also present in the grand potential. The explicit form of the expansion has been checked for some exactly solvable models for a special value of the coulombic coupling. In this paper we present a method for obtaining these finite-size corrections in the Debye–Hückel regime. It is based on the sine-Gordon field theory to find an expression for the grand canonical partition function in terms of the spectrum of the Laplace operator. As an example we find explicitly the grand potential expansion for a Coulomb system confined in a disc and in an annulus with ideal conductor walls.

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1. Introduction

There are several reasons to study models over a finite-size region. For instance, with the recent advance of computers, much information on statistical models has been derived from computer simulations, which are necessarily limited to systems of finite size [1]. Also experimental systems are finite (although very large). The finite scaling hypothesis allows the study of some response functions for such finite-size models. For a d -dimensional system, this finite scaling hypothesis states that if a given response function (for example, the susceptibility in a magnetic

system) diverges in the bulk such as ξ^{d-2x} , where ξ is the correlation length and x is called the scaling dimension of the corresponding studied quantity (the magnetization in the above example), then in a finite system of characteristic size R , the response function should obey the scaling law $R^{d-2x}\Phi(R/\xi)$, where Φ is some universal scaling function [2, 3]. At the critical point where the correlation length diverges, the response function is then proportional to R^{d-2x} . However, the scaling of the free energy at criticality is less well understood at least for arbitrary dimension. In two dimensions, using methods from conformal field theory, it has been shown that for a finite system with smooth boundary, of characteristic size R as $R \rightarrow \infty$, at criticality, the total free energy F has a large- R expansion of the form [3, 4]

$$\beta F = AR^2 + BR - \frac{c\chi}{6} \ln R + \mathcal{O}(1). \quad (1)$$

with $\beta = (k_B T)^{-1}$ the inverse reduced temperature. The first two terms represent, respectively, the bulk free energy and the ‘surface’ (perimeter in two dimensions) contribution to the free energy. In general, the coefficients A and B are non-universal but the dimensionless coefficient of $\ln R$ is universal depending only on c , the conformal anomaly number, and on χ , the Euler characteristic of the manifold ($\chi = 2 - 2h - b$, where h is the number of handles and b is the number of boundaries). Surprisingly enough, for classical Coulomb systems in their conducting phase—not at criticality—this expansion for the free energy seems to hold with $c = 1$ and a change of sign in the last term. This is surprising initially because in the conducting phase (when the Coulomb system can screen any infinitesimal external charge) the particle correlations are short range as opposed to the case when the system is at a critical point (for instance at the liquid–gas second-order transition point) when the particle correlation becomes long range. The argument put forward by Cardy [3] using conformal field theory relies on the fact that the system under study is at a critical point. However, the finite-size expansion of the free energy has been explicitly checked for Coulomb systems lying on some simple geometries for some exactly solvable models for the fixed temperature defined by $\beta q^2 = 2$ where $\beta^{-1} = k_B T$ and $\pm q$ are the charges of the particles [5–8] and also it has been verified numerically for the one-component plasma confined in a disc [9] for other values of the coulombic coupling. The existence of the universal finite-size correction has also been proved for the two-component plasma confined in a disc with hard walls in the whole regime where the system of point particles is stable ($\beta q^2 < 2$) [10]. For the one-component plasma [11], for the symmetric two-component plasma [12] and for the asymmetric two-component plasma [13] confined in a sphere the existence of the finite-size correction has been proved for any temperature (provided that the system is stable) by the application of the stereographic projection and some non-trivial sum rules concerning the density–density correlation function in the plane geometry [14, 15].

Although the particle and charge correlations in Coulomb systems in their conducting phase are short range because of the screening, the electric potential correlations are long range [16, 17]. It has been argued [5, 6] that in this sense the system is comparable to a critical system and therefore the expansion of the free energy (1) should hold.

In this paper we present a method for obtaining the grand potential finite-size expansion for a confined Coulomb system in the Debye–Hückel regime and confirm the existence of the logarithmic universal finite-size correction. The Debye–Hückel regime is defined by the requirement that the average coulombic energy is much smaller than the thermal energy [18, 19]. By the usual Legendre transform between the free energy and the grand potential it can be inferred that the free energy will have the same logarithmic finite-size corrections as the grand potential. Our method is based on the sine-Gordon field theory [20] to calculate the grand canonical partition function.

2. Sine-Gordon theory in the Debye–Hückel regime

There is a well-known analogy between statistical mechanics and quantum field theory: often the partition function of a d -dimensional statistical model is formally analogous to the generating functional of a quantum field in d spacetime dimensions in the Euclidean formalism [21]. The simplest example of a quantum field theory which has relevance in statistical mechanics is the free boson or Gaussian model. In this section we show that the grand canonical partition function of a Coulomb system in the Debye–Hückel regime may be represented as the generating functional of a massive free boson theory and therefore it can be obtained exactly from a Gaussian integration as an infinite product of functions of the eigenvalues of the Laplace operator calculated on the manifold where the system exists.

Let a classical (i.e. non-quantum) Coulomb system be composed of $\alpha = 1, \dots, r$ species of particles each of which have N_α charges q_α confined in a d -dimensional Riemannian manifold of volume V . Suppose that the system is confined by grounded ideal conductor walls, thus imposing vanishing Dirichlet boundary conditions on the electric potential. We shall describe the system in the grand canonical ensemble with fugacities $\zeta_\alpha = e^{\beta\mu_\alpha} / \Lambda_\alpha^d$ for the species α , where μ_α is the chemical potential and Λ_α is the de Broglie thermal wavelength which appears when the Gaussian integration over the kinetic part of the Hamiltonian is carried out. For a finite but macroscopically large system, the interior of the system will be at an almost constant electric potential ψ_0 . The value of ψ_0 is controlled by the choice of the fugacities. We will suppose in the following that the fugacities satisfy the relation

$$\sum_{\alpha} q_{\alpha} \zeta_{\alpha} = 0 \quad (2)$$

which is often referred to in the literature [26] as the pseudo-neutrality condition. In appendix B we consider the general case when the fugacities do not satisfy the condition (2).

Let us introduce the Coulomb potential for a non-confined system for unit charges

$$v_d^0(\mathbf{r}, \mathbf{r}') = \begin{cases} \frac{1}{|\mathbf{r} - \mathbf{r}'|} & \text{if } d = 3 \\ -\ln \frac{|\mathbf{r} - \mathbf{r}'|}{L} & \text{if } d = 2. \end{cases} \quad (3)$$

In two dimensions, a solution of Poisson's equation that vanishes at large distances does not exist, therefore it is necessary to introduce an arbitrary length L that fixes the zero of the electric potential. However, as we will see later, in the formulation of the Debye–Hückel theory proposed here it will be necessary to suppose that $L \rightarrow \infty$, thus receding the zero of the electric potential to infinity. The necessity to choose $L \rightarrow \infty$ also appears in the formulation of the Debye–Hückel theory from the Ornstein–Zernicke equation and the approximation of the direct correlation function by the Coulomb potential [22].

The Coulomb potential in d dimensions for the system confined with Dirichlet boundary conditions will be referred to as v_d . This potential satisfies the Poisson equation

$$\Delta v_d(\mathbf{r}, \mathbf{r}') = -s_d \delta(\mathbf{r} - \mathbf{r}') \quad (4)$$

with $s_2 = 2\pi$ and $s_3 = 4\pi$, and the Dirichlet boundary condition. If one considers $v_d(\mathbf{r}, \mathbf{r}')$ as the kernel of an integral operator which we will also call v_d , we have $v_d = -s_d \Delta^{-1}$. Let $\Psi_n(\mathbf{r})$ be the normalized eigenfunctions of the Laplacian with Dirichlet boundary conditions, that is $\Delta \Psi_n(\mathbf{r}) = \lambda_n \Psi_n(\mathbf{r})$, where $\lambda_n \leq 0$ are the corresponding eigenvalues. These functions are also eigenfunctions of v_d with the corresponding eigenvalues $-s_d / \lambda_n \geq 0$. Consider two particles located at $\mathbf{r}_{\alpha,i}$ and $\mathbf{r}_{\beta,j}$. A standard operator spectral decomposition gives for the

interparticle potential

$$v_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j}) = - \sum_n \frac{S_d}{\lambda_n} \overline{\Psi_n(\mathbf{r}_{\alpha,i})} \Psi_n(\mathbf{r}_{\beta,j}). \quad (5)$$

The bar over Ψ indicates complex conjugation. In addition to the interparticle energy we consider the energy of each particle located at $\mathbf{r}_{\alpha,i}$ in the presence of the field produced by itself $v_d^0(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\alpha,i}) = v_{S-E}(\mathbf{r}_{\alpha,i})$. This term is (twice) the self-energy of a unit charge. Proceeding as in (5) it may be given by

$$v_{S-E}(\mathbf{r}_{\alpha,i}) = - \sum_k \frac{S_d}{\lambda_k^0} |\Psi_k^0(\mathbf{r}_{\alpha,i})|^2 \quad (6)$$

where the λ_k^0 refer to eigenvalues calculated for the system without boundaries. Of course, because of the form of the Coulomb potential the self-energy is in fact infinite. This divergence may be avoided by the introduction of a short-distance potential [19] to cut off the singularity of the Coulomb potential at the origin. To simplify the notation, we will not write down this short-distance potential explicitly in what follows. It should be noted however that the introduction of this short-distance potential is mandatory in classical statistical mechanics of Coulomb systems in order to have a well-defined partition function in three dimensions (in two dimensions at low coulombic couplings a system of point particles is stable). On the other hand it turns out that the Debye–Hückel approximation is well defined for a system of point particles: as we shall see later the short-distance potential does not appear in the final results. Let us remark that for systems governed by quantum mechanics if all particles of the same sign are fermions then the system is stable [23]. This is the case in nature where quantum mechanics is responsible for the creation of stable-bound states. Therefore our classical analysis will apply only to fully ionized systems.

The potential energy of the system is given by

$$H = \frac{1}{2} \sum_{\alpha,\beta} \sum'_{i,j} q_\alpha q_\beta v_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j}) + \frac{1}{2} \sum_\alpha \sum_i q_\alpha^2 [v_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\alpha,i}) - v_{S-E}(\mathbf{r}_{\alpha,i})]. \quad (7)$$

The prime in the first summation means that the case when $\alpha = \beta$ and $i = j$ must be omitted. The first term is the usual interparticle energy between pairs. The second term is the Coulomb energy of a particle and the polarization surface charge density that the particle has induced in the boundaries of the system. When the method of images is applied to compute the Coulomb potential v_d , this energy can also be seen as the energy between each particle and its image.

Using the microscopic charge density defined as

$$\hat{\rho}(\mathbf{r}) = \sum_{\alpha=1}^r \sum_{i=1}^{N_\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}) \quad (8)$$

we can write the potential part of the Hamiltonian of the system as

$$H = \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \hat{\rho}(\mathbf{r}) v_d(\mathbf{r}, \mathbf{r}') \hat{\rho}(\mathbf{r}') - \frac{1}{2} \sum_{\alpha=1}^r \sum_{i=1}^{N_\alpha} q_\alpha^2 v_{S-E}(\mathbf{r}_{\alpha,i}). \quad (9)$$

Note that with this notation, in the first term, the terms $q_\alpha^2 v_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\alpha,i})/2$ have been included. Often in the sine-Gordon transformation [20, 24] the second term is omitted in the Hamiltonian in equation (9), which implies that the self-energy (infinite for point particles) is included in the Hamiltonian when it should not be. This problem can be cured with a proper renormalization of the fugacity [25]; however, this method is not convenient to use for the Debye–Hückel approximation, therefore, we will proceed to subtract the self-energy from the start as shown in equation (9).

Now, using the well-known Gaussian integral

$$\exp\left(\frac{1}{2}\mathbf{B}\cdot\mathbf{A}^{-1}\cdot\mathbf{B}\right)=\frac{\int d\mathbf{X}\exp\left(-\frac{1}{2}\mathbf{X}\cdot\mathbf{A}\cdot\mathbf{X}+\mathbf{B}\cdot\mathbf{X}\right)}{\int d\mathbf{X}\exp\left(-\frac{1}{2}\mathbf{X}\cdot\mathbf{A}\cdot\mathbf{X}\right)} \quad (10)$$

we can represent the Boltzmann factor as¹

$$e^{-\beta H}=\left\langle\exp\left[-\beta\int i\hat{\rho}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}+\frac{\beta}{2}\sum_{\alpha=1}^r\sum_{i=1}^{N_\alpha}q_\alpha^2v_{S-E}(\mathbf{r}_{\alpha,i})\right]\right\rangle \quad (11)$$

where we have defined the average of any operator \hat{o} as $\langle\hat{o}\rangle=\frac{1}{Z}\int\mathcal{D}\phi\hat{o}\times\exp\left(\frac{\beta}{2s_d}\int\phi(\mathbf{r})\Delta\phi(\mathbf{r})d\mathbf{r}\right)$, with $Z=\int\mathcal{D}\phi\exp\left(\frac{\beta}{2s_d}\int\phi(\mathbf{r})\Delta\phi(\mathbf{r})d\mathbf{r}\right)$. On the other hand, using (8) and (11) after some calculations the grand partition function is given by [20]

$$\begin{aligned} \Xi(\beta,\zeta_1,\dots,\zeta_r,V) &= \sum_{N_1=0}^{\infty}\dots\sum_{N_r=0}^{\infty}\frac{\zeta_1^{N_1}\dots\zeta_r^{N_r}}{N_1!\dots N_r!}\int\dots\int e^{-\beta H}\prod_{\alpha=1}^r\prod_{i=1}^{N_\alpha}d\mathbf{r}_{\alpha,i} \\ &= \left\langle\exp\left[\sum_{\alpha}^r\zeta_\alpha\int\exp\left(\beta\left(-iq_\alpha\phi(\mathbf{r})+\frac{q_\alpha^2}{2}v_{S-E}(\mathbf{r})\right)\right)d\mathbf{r}\right]\right\rangle \end{aligned} \quad (12)$$

with V the volume of the manifold containing the system. We see from equation (12) that the partition function for a gas of particles with two-body interactions may be obtained as the average of the partition function of an ideal gas in an external fluctuating potential $i\phi(\mathbf{r})$. In general the integration involving the calculation of (12) cannot be performed analytically—with the notable exception of the two-dimensional two-component plasma (charge symmetric 1 : 1 and charge asymmetric +2 : -1) which has been exactly solved in the bulk and in some semi-infinite geometries [25, 28–30].

The coulombic coupling Γ is defined as the average Coulomb energy divided by the thermal energy. We can actually define a coupling for each species of particles as follows. In two dimensions these are defined as $\Gamma_{2,\alpha}=\beta q_\alpha^2$. On the other hand, in three dimensions $\Gamma_{3,\alpha}=\beta q_\alpha^2\zeta_\alpha^{1/3}$. In the Debye–Hückel regime we have $\Gamma_{d,\alpha}\ll 1$ and we can expand

$$\begin{aligned} \exp\left[\beta\left[-iq_\alpha\phi(\mathbf{r})+\frac{q_\alpha^2}{2}v_{S-E}(\mathbf{r})\right]\right] \\ = 1 - i\beta q_\alpha\phi(\mathbf{r}) + \frac{\beta q_\alpha^2}{2}v_{S-E}(\mathbf{r}) - \frac{(\beta q_\alpha\phi(\mathbf{r}))^2}{2} + o(\Gamma_{d,\alpha}^2). \end{aligned} \quad (13)$$

In two dimensions the field $\phi(\mathbf{r})$ has dimensions of charge q_α , therefore, the above approximation is an expansion to the order $(\Gamma_{2,\alpha})^2$ in the coulombic couplings $\Gamma_{2,\alpha}$. In three dimensions the field $\phi(\mathbf{r})$ has dimensions of charge/distance. One can change a variable in the functional integral to have a dimensionless field $\tilde{\phi}=\zeta^{-1/3}\phi/q$, then it is clear that the approximation (13) is again an expansion to the second order in the coulombic couplings $\Gamma_{3,\alpha}$. Note that the self-energy term $\beta q_\alpha^2 v_{S-E}(\mathbf{r})/2$ is already of order $(\Gamma_{d,\alpha})^2$. This can be seen by noting that the covariance of the Gaussian measure $\frac{1}{Z}\mathcal{D}\phi\exp\left(\frac{\beta}{2s_d}\int\phi\Delta\phi\right)$ is $\langle\phi(\mathbf{r})\phi(\mathbf{r}')\rangle=\beta^{-1}v_d(\mathbf{r},\mathbf{r}')$. Then it is clear that the self-energy term $\beta q_\alpha^2 v_{S-E}(\mathbf{r})/2$ is of the same order as $(\beta q_\alpha\phi(\mathbf{r}))^2$. Therefore we do not include any terms of order $(\beta q_\alpha^2 v_{S-E}(\mathbf{r})/2)^2$ or $\beta^2 q_\alpha^3\phi(\mathbf{r})v_{S-E}(\mathbf{r})$ which are of higher order in the expansion (13).

¹ Rigorously speaking this Gaussian transformation cannot be formulated with the Coulomb potential $v_d(\mathbf{r},\mathbf{r}')$ because this potential diverges when $\mathbf{r}=\mathbf{r}'$. This problem can be solved as in [27] using instead a potential such as $(1-\exp(-\kappa r/\epsilon))/r$ which is regularized at short distances and taking the limit $\epsilon\rightarrow 0$ at the end of the calculations. Again, for simplicity, we will omit explicitly this detail in what follows.

Using equation (13) and the pseudo-neutrality condition (2) we have

$$\begin{aligned} \Xi(\beta, \zeta_1 \dots \zeta_\alpha, V) = & \left\langle \exp \left[- \int \sum_{\alpha} \frac{\zeta_{\alpha} (\beta q_{\alpha} \phi(\mathbf{r}))^2}{2} \mathbf{d}\mathbf{r} \right] \right\rangle \\ & \times \exp \left(- \sum_{\alpha=1}^r \sum_n \frac{\beta \zeta_{\alpha} q_{\alpha}^2 s_d}{2 \lambda_n^0} \right) \exp \left(\sum_{\alpha} V \zeta_{\alpha} \right) \end{aligned} \quad (14)$$

where the spectral decomposition (6) of the self-energy and the normalization condition $\int |\Psi_n^0(\mathbf{r}_{\alpha})|^2 \mathbf{d}\mathbf{r} = 1$ have been used to write the contribution of the self-energy terms as a sum over the eigenvalues λ_n^0 of the Laplacian without boundaries. Now performing the Gaussian integration the averaged quantity equals

$$\frac{1}{Z} \int \mathcal{D}\phi \exp \left(\frac{1}{2} \int \phi(\mathbf{r}) \left(\frac{\beta \Delta}{s_d} - \sum_{\alpha} \zeta_{\alpha} (\beta q_{\alpha})^2 \right) \phi(\mathbf{r}) \mathbf{d}\mathbf{r} \right) = \left(\det \left[1 - \frac{\sum_{\alpha} s_d \zeta_{\alpha} \beta q_{\alpha}^2}{\Delta} \right] \right)^{-1/2}. \quad (15)$$

Note that the averaged quantity we had just computed is the generating functional of a free boson theory with mass proportional to the inverse Debye length defined by $\kappa = \sqrt{\sum_{\alpha} s_d \zeta_{\alpha} \beta q_{\alpha}^2}$. Using the invariance of the determinant we obtain for the grand canonical partition function

$$\Xi(\beta, \zeta_1, \dots, \zeta_{\alpha}, V) = \left(\prod_m \left(1 - \frac{\kappa^2}{\lambda_m} \right) \prod_n \exp \left(\frac{\kappa^2}{\lambda_n^0} \right) \right)^{-1/2} \exp \left(\sum_{\alpha} V \zeta_{\alpha} \right). \quad (16)$$

This is simply a product of factors that are a function of the eigenvalues λ_i of Δ . The λ_i depend on the shape of the domain in which the Coulomb system lies. As we see, they constitute a natural way of introducing the information on the domain to calculate the corresponding finite-size expansion of the grand potential Ω . It is interesting to point out here that in the case of a non-confined system $\lambda_n = \lambda_n^0$ and the infinite products in (16) become a regularized Weierstrass product $\prod_n [(1 - \kappa^2/\lambda_n^0) \exp(\kappa^2/\lambda_n^0)]$. The $\prod \exp(\kappa^2/\lambda_n^0)$ term cancels out the ultraviolet divergence coming from the $\prod (1 - \kappa^2/\lambda_n)$ term. This product converges for systems in three dimensions [31]. However, as will be seen in the next section, in two dimensions some infrared divergences appear and the product must be regularized by introducing a lower cutoff. The sine-Gordon transformation has been known for some time [19, 20, 24]. For three-dimensional non-confined systems the sine-Gordon transformation has been used to go beyond the Debye–Hückel approximation and to perform low fugacity [35], high temperature [36] or loopwise [37] expansions. The main point of this section was to show that the proper subtraction of the self-energy terms (which have to be added initially to perform the sine-Gordon transformation) leads to a well-defined expression for the grand potential in the Debye–Hückel approximation which could be eventually evaluated for confined systems. In appendix A we show how this formulation of the Debye–Hückel theory is related to the usual one. In the following section we apply this method for the calculation of the grand potential $\Omega = -k_B T \ln \Xi$ of a Coulomb system confined in some simple geometries.

3. Finite-size corrections to the grand potential for a confined Coulomb system

3.1. Non-confined systems: the bulk

Before applying our method to confined systems let us illustrate some points of the calculation of the grand potential from equation (16) for a bulk system. For a d -dimensional non-confined

system the eigenfunctions corresponding to the λ_k^0 are given by $\Psi_{\mathbf{k}}^0(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{V}$ and $\Delta\Psi_{\mathbf{k}}^0(\mathbf{r}) = \lambda_k^0\Psi_{\mathbf{k}}^0(\mathbf{r}) = -\mathbf{k}^2\Psi_{\mathbf{k}}^0(\mathbf{r})$. Then substituting into equation (16) the grand potential is given by

$$\beta\Omega = \frac{V}{2} \int \frac{d^d\mathbf{k}}{(2\pi)^d} \left[\ln \left(1 + \frac{\kappa^2}{k^2} \right) - \frac{\kappa^2}{k^2} \right] - \sum_{\alpha} V\zeta_{\alpha}. \quad (17)$$

In three dimensions $d = 3$ the above integral is convergent giving the result for the bulk grand potential per unit volume [27]

$$\frac{\beta\Omega}{V} = -\frac{\kappa^3}{12\pi} - \sum_{\alpha} \zeta_{\alpha}. \quad (18)$$

The density n_{α} of the particles can be obtained by using the usual thermodynamic relation

$$n_{\alpha} = -\zeta_{\alpha} \frac{\partial(\beta\Omega/V)}{\partial\zeta_{\alpha}} = \zeta_{\alpha} + \frac{\kappa}{2}\beta q_{\alpha}^2 \zeta_{\alpha} \quad (19)$$

which can be replaced back into equation (18) to give the well-known equation of state from the Debye–Hückel theory [27, 32]

$$\beta p = -\frac{\beta\Omega}{V} = \sum_{\alpha} n_{\alpha} - \frac{\kappa_{\text{DH}}^3}{24\pi}. \quad (20)$$

Note that in the last equation the Debye length that we have defined by $\kappa^{-1} = [\sum_{\alpha} s_{\alpha} \zeta_{\alpha} \beta q_{\alpha}^2]^{-1/2}$ has been replaced by the usual Debye length in terms of the density $\kappa_{\text{DH}}^{-1} = [\sum_{\alpha} s_{\alpha} n_{\alpha} \beta q_{\alpha}^2]^{-1/2}$. This is correct at the order of approximation we are working on since $\kappa = \kappa_{\text{DH}}[1 + \mathcal{O}(\Gamma_{3,\alpha}^{3/2})]$.

Let us point out that the proper subtraction of the self-energy terms makes the integral (17) convergent and avoids the need to use some other arbitrary regularization scheme, such as for instance dimensional regularization used in [24] which, by the way, yields the incorrect result $\sum_{\alpha} \zeta_{\alpha} - \kappa^3/(24\pi)$ for the pressure when it is expressed in terms of the *fugacities*. Our regularization scheme is actually equivalent to the normal ordering for the product : $\phi(\mathbf{r})^2$: used in [27].

As was pointed out in the preceding section the infinite product (16) for a non-confined system is a regularized Weierstrass product. The order of the sequence of the Laplacian eigenvalues is $\mu = d/2$ [31], therefore for $d = 3$, $\mu = 3/2 > 1$ with integer part equal to 1, and the terms $\exp(\kappa^2/\lambda_k^0)$ in the product (16) are enough to regularize the infinite product.

The situation in two dimensions $d = 2$ is more delicate since $\mu = 1$ is a limiting case. If we blindly try to compute (17) we will note that the integral is not well defined for $k \rightarrow 0$. Trying to cure an ultraviolet divergence, we introduced an infrared one. The problem can be traced back to the spectral decomposition (5) of the Coulomb potential. Evaluating the interparticle energy explicitly using expression (5) gives

$$v_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\infty} \frac{k \exp(ik|\mathbf{r} - \mathbf{r}'|\cos\theta)}{k^2} dk d\theta = \int_0^{\infty} \frac{dk}{k} J_0(k|\mathbf{r} - \mathbf{r}'|) \quad (21)$$

with J_0 the Bessel function of order 0. This integral diverges at $k = 0$. To avoid this, we introduce a cutoff k_{min} at $k \rightarrow 0$

$$v_2(\mathbf{r}, \mathbf{r}') = \int_{k_{\text{min}}}^{\infty} \frac{dk}{k} J_0(k|\mathbf{r} - \mathbf{r}'|) \quad (22)$$

$$= -C + \ln \frac{2}{|\mathbf{r} - \mathbf{r}'| k_{\text{min}}} + o(1) \quad (23)$$

where $k_{\min} \rightarrow 0$ and C is the Euler constant. Since we know that $v_2(\mathbf{r}, \mathbf{r}') = -\ln(|\mathbf{r} - \mathbf{r}'|/L)$ we can find the expression for k_{\min} by comparison: $v_2(|\mathbf{r} - \mathbf{r}'|) = -\ln(|\mathbf{r} - \mathbf{r}'|k_{\min}/2 e^{-C}) = -\ln(|\mathbf{r} - \mathbf{r}'|/L)$; then

$$k_{\min} = \frac{2 e^{-C}}{L}. \quad (24)$$

We note that for the above calculation to be consistent it is necessary to choose $L \rightarrow \infty$, as has been discussed earlier in the preceding section. The necessity of this choice for the arbitrary constant L is also discussed in appendix B of [22].

Returning to the calculation of the grand potential in two dimensions, we impose the infrared cutoff $k_{\min} = 2 e^{-C}/L$ on the integral (17) to obtain the result for the grand potential

$$\frac{\beta\Omega}{V} = \frac{\kappa^2}{4\pi} \left[-\ln \frac{\kappa L}{2} - C + \frac{1}{2} \right] - \sum_{\alpha} \zeta_{\alpha}. \quad (25)$$

In the above expression all terms that vanish when $L \rightarrow \infty$ have been omitted. The density–fugacity relation is now

$$n_{\alpha} = -\zeta_{\alpha} \frac{\partial(\beta\Omega/V)}{\partial\zeta_{\alpha}} = \zeta_{\alpha} - \zeta_{\alpha} \frac{\beta q_{\alpha}^2}{2} \left[\ln \frac{\kappa L}{2} + C \right]. \quad (26)$$

For a two-component plasma it can be checked that this result is reproduced from the small- βq^2 expansion of the exact relation between the density and the fugacity [25]. Note again that κ can be replaced by κ_{DH} at the order of approximation we are working on, since $\kappa = \kappa_{\text{DH}}[1 + \mathcal{O}(\Gamma_{2,\alpha} \ln \Gamma_{2,\alpha})]$. Applying equation (26) back into equation (25) one obtains the equation of state, which turns out to be exact at the level of the Debye–Hückel approximation,

$$\beta p = \sum_{\alpha} n_{\alpha} \left(1 - \frac{\beta q_{\alpha}^2}{4} \right). \quad (27)$$

Doing the usual Legendre transform $F = \Omega + \sum_{\alpha} \mu_{\alpha} N_{\alpha}$, one can recover the known expression for the excess free energy in the Debye–Hückel approximation [33, 34]

$$\frac{\beta F_{\text{exc}}}{V} = \frac{\kappa_{\text{DH}}^2}{4\pi} \left[\frac{1}{2} - \ln \frac{\kappa_{\text{DH}} L}{2} - C \right]. \quad (28)$$

To conclude with the results for a two-dimensional system let us clarify a point regarding the limit $L \rightarrow \infty$. Actually in equation (23) and below we require that L be large compared to the average distance between particles which is of order $n^{-1/2}$ with n the density. In the Debye–Hückel approximation the density n is of the same order as the fugacity ζ . Therefore we require that $L\zeta^{1/2} \gg 1$. In the results for the grand potential (25), the densities (26) and the free energy (28), the quantity κL appears, which is proportional to $(\beta q^2)^{1/2} L\zeta^{1/2} = \Gamma^{1/2}(L\zeta^{1/2})$. Note that in the above expression $L\zeta^{1/2} \gg 1$ but the coulombic coupling $\Gamma \ll 1$. Therefore we require that in two dimensions the Debye–Hückel limit should be taken with $\Gamma \rightarrow 0$, $L\zeta^{1/2} \rightarrow \infty$ but $\Gamma^{1/2}(L\zeta^{1/2})$ should remain of order 1.

3.2. The disc

We now consider a two-dimensional Coulomb fluid confined in a disc of radius R . To apply the method outlined in section 2, we first need to compute the eigenvalues of the Laplace operator for this geometry. Let $\Psi(r, \varphi) = R(r)\Phi(\varphi)$, we look for the solution of the equation $\Delta\Psi(r, \varphi) = \lambda\Psi(r, \varphi)$. Using the explicit form of the Laplace operator in polar coordinates we find $\Psi(r, \varphi) = R(r)\Phi(\varphi) \propto e^{\pm i l \varphi} I_l(\sqrt{\lambda} r)$, where $I_l(x)$ is the modified Bessel function of order l . Using the boundary conditions $\Psi(R, \varphi) = 0$; $\Psi(r, 0) = \Psi(r, 2\pi)$, we find $l \in \mathbb{Z}$ and

$I_l(\sqrt{\lambda_k}R) = 0$, that is $\sqrt{\lambda_k}R = v_{l,n}$ is the n th zero of I_l .² Then replacing these eigenvalues into equation (16) gives for the grand potential the expression

$$\beta\Omega = \frac{1}{2} \sum_{l=-\infty}^{\infty} \ln \prod_{n=1}^{\infty} \left(1 - \frac{R^2\kappa^2}{v_{l,n}^2}\right) - \frac{V\kappa^2}{2(2\pi)} \int_{k_{\min}}^{\infty} \frac{dk}{k} - \sum_{\alpha} V\zeta_{\alpha}. \tag{29}$$

The second term, written as an integral over k , comes from the terms involving the Laplacian eigenvalues for a non-confined system: $\exp(\kappa^2/\lambda_k^0)$, with the same infrared cutoff k_{\min} discussed previously and given by equation (24). Both the sum and the integral diverge separately for large values of l and k but when we put together both terms the ultraviolet divergences should cancel. It is however more convenient to compute each term separately. Therefore we will impose an upper cutoff N for l and k_{\max} for k . Both cutoffs are of course proportional; the exact relation between N and k_{\max} can be obtained at the end of the calculations by imposing that for the bulk grand potential we should recover the result (25) from the last section.

Using the infinite product representation of the modified Bessel function $\prod_{n=1}^{\infty} (1 - \kappa^2 R^2/v_{l,n}^2) = l!(2/\kappa R)^l I_l(\kappa R)$ [38] and the property $I_l(x) = I_{-l}(x)$ we have

$$\begin{aligned} \beta\Omega &= \sum_{l=0}^N \ln l! + \ln\left(\frac{2}{\kappa R}\right) \sum_{l=0}^N l + \sum_{l=0}^N \ln I_l(\kappa R) \\ &\quad - \frac{1}{2} \ln [I_0(\kappa R)] - \frac{\kappa^2 V}{4\pi} \int_{k_{\min}}^{k_{\max}} \frac{dk}{k} - \sum_{\alpha} V\zeta_{\alpha}. \end{aligned} \tag{30}$$

Using the Stirling approximation: $\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N) + \dots$, the Euler–McLaurin summation formula: $\sum_{l=0}^N f(l) = \int_0^N f(l) dl + \frac{1}{2} [f(0) + f(N)] + \frac{1}{12} [f'(N) - f'(0)] + \dots$ and the uniform Debye expansion [38] for $\ln I_l(z)$, valid for large z :

$$\ln I_l(z) = -\frac{1}{2} \ln(2\pi) - \frac{1}{4} \ln(z^2 + l^2) + \eta(l, z) + \frac{3u - 5u^3}{24l} + o\left(\frac{1}{z^2 + l^2}\right) \tag{31}$$

$$\eta(l, z) = (z^2 + l^2)^{1/2} - l \sinh^{-1}\left(\frac{l}{z}\right) \quad u = \frac{l}{(z^2 + l^2)^{1/2}} \tag{32}$$

after some calculations we finally obtain the large- R expansion

$$\beta\Omega = \frac{\kappa^2 R^2}{4} \left(1 + \ln \frac{2e^{-C}}{\kappa L} \frac{2N}{k_{\max} R} - \frac{4\pi \sum_{\alpha} \zeta_{\alpha}}{\kappa^2}\right) - R \left(\frac{\kappa\pi}{4}\right) + \frac{1}{6} \ln R + \mathcal{O}(R^0). \tag{33}$$

In the above expression all terms that vanish when $N \rightarrow \infty$ and $k_{\max} \rightarrow \infty$ have been omitted. The bulk term (proportional to πR^2) of the above equation (33) should be the same as in equation (25), therefore the cutoffs N and k_{\max} should be related by $k_{\max} = \frac{2N}{R} e^{1/2}$. Finally

$$\beta\Omega = \beta\omega_b \pi R^2 + 2\pi R\beta\gamma + \frac{1}{6} \ln(\kappa R) + \mathcal{O}(R^0) \tag{34}$$

with the bulk grand potential per unit volume ω_b (equal to minus the bulk pressure p_b) given by

$$\beta\omega_b = -\beta p_b = \frac{\kappa^2}{4\pi} \left[-\ln \frac{\kappa L}{2} - C + \frac{1}{2}\right] - \sum_{\alpha} \zeta_{\alpha} \tag{35}$$

² Note that since the zeros of I_l are imaginary then $\sqrt{\lambda_k}$ is imaginary; this is expected since the Laplacian eigenvalues λ_k are negative.

and the surface tension γ is given by

$$\beta\gamma = -\frac{\kappa}{8}. \tag{36}$$

The two-dimensional two-component plasma near a plane ideal conductor electrode has been solved exactly [28]. For a two-component plasma our result (36) for the surface tension agrees with the lower-order expansion in βq^2 of the exact result of [28]. In equation (34) we note the existence of the universal logarithmic finite-size correction $\frac{1}{6} \ln R$ with $\chi = 1$ for the disc.

3.3. The annulus

We now consider a Coulomb fluid confined in an annulus of inner radius R_1 and outer radius R_2 . As before we need to calculate the eigenvalues of the Laplace operator for this geometry. The eigenfunction of the Laplacian with eigenvalue λ , in this geometry, is $\Psi(r, \varphi) = [AI_l(\sqrt{\lambda}r) + BK_l(\sqrt{\lambda}r)]e^{i\ell\varphi}$. Imposing the Dirichlet boundary conditions yields the linear system of equations $\Psi(R_1, \varphi) = 0$ and $\Psi(R_2, \varphi) = 0$. To have a non-vanishing solution for the eigenproblem we require that the determinant of this system vanishes. This gives the equation that defines the eigenvalues for this problem

$$I_l(\sqrt{\lambda}R_1)K_l(\sqrt{\lambda}R_2) - K_l(\sqrt{\lambda}R_1)I_l(\sqrt{\lambda}R_2) = 0 \tag{37}$$

which means that $\lambda_k = z_{l,n}^2$ where $z_{l,n}$ is the n th root of the equation

$$I_l(zR_1)K_l(zR_2) - K_l(zR_1)I_l(zR_2) = 0. \tag{38}$$

Note that the roots of this equation are the same for l and $-l$, therefore we will concentrate on the case $l > 0$. To compute the grand partition function from equation (16) we need to evaluate the infinite product $\prod_l \prod_n (1 - \kappa^2/z_{l,n}^2)$. For a given l , the product over the index n of the roots of equation (38) can be performed using a generalization of the infinite product representation of the Bessel functions used in the last section [6, 8, 39]. For $l > 0$, let us introduce the entire function

$$f_l(z) = \frac{2l}{\left(\frac{R_1}{R_2}\right)^l - \left(\frac{R_2}{R_1}\right)^l} [I_l(zR_1)K_l(zR_2) - K_l(zR_1)I_l(zR_2)]. \tag{39}$$

By construction the zeros of the function f_l are $z_{l,n}$ and it has the following properties: $f_l(0) = 1$, $f'_l(0) = 0$ and $f_l(z) = f_l(-z)$. Therefore f_l admits a Weierstrass infinite product representation of the form [40]

$$f_l(z) = \prod_n \left(1 - \frac{z^2}{z_{l,n}^2}\right). \tag{40}$$

Then the infinite product we wish to evaluate is simply $\prod_n (1 - \kappa^2/z_{l,n}^2) = f_l(\kappa)$. For $l = 0$ the function f_0 should read

$$f_0(z) = \frac{1}{\ln(R_1/R_2)} [I_0(zR_1)K_0(zR_2) - K_0(zR_1)I_0(zR_2)]. \tag{41}$$

The grand potential is then given by

$$\beta\Omega = \sum_{l=1}^N \ln f_l(\kappa) + \frac{1}{2} \ln f_0(\kappa) - \frac{\kappa^2 V}{4\pi} \int_{k_{\min}}^{k_{\max}} \frac{dk}{k} - \sum_{\alpha} V \zeta_{\alpha}. \tag{42}$$

As in the case of the disc we regularize the summation on l by introducing an upper cutoff N and the integral with an ultraviolet cutoff k_{\max} . These cutoffs are proportional in order to cancel the divergences. However, their exact relationship is *a priori* different from that in the

disc case and can be found at the end of the calculations by requiring that we recover the same bulk value of the grand potential as in the previous examples. On the other hand, the infrared cutoff $k_{\min} = 2e^{-C}/L$ is the same as before.

We now proceed to find the finite-size expansion of the grand potential. We consider a very large annulus with $R_1 \rightarrow \infty$, $R_2 \rightarrow \infty$, $R_2 - R_1 \rightarrow \infty$ and $x = R_1/R_2 < 1$ finite and fixed. The calculations are similar to those of the disc; we now use the uniform Debye expansion of $\ln K_l(z)$ valid for large arguments [38]

$$\ln K_l(z) = \ln \left[\frac{\sqrt{\pi}}{\sqrt{2}} \right] - \frac{1}{4} \ln(l^2 + z^2) - \eta(l, z) + \ln \left[1 - \frac{3u - 5u^3}{24l} \right] + o \left(\frac{1}{l^2 + z^2} \right) \quad (43)$$

with $\eta(l, z)$ and u defined in equation (32). Note that in the functions $f_l(\kappa)$, the contribution of $K_l(\kappa R_2)I_l(\kappa R_1)$ is exponentially smaller than that from the term $I_l(\kappa R_2)K_l(\kappa R_1)$. Using again the Euler–McLaurin summation formula to transform the sum over l into an integral, after some calculations we find in the limit $N \rightarrow \infty$,

$$\beta\Omega = \frac{1}{4} \left(R_2^2 \ln \frac{2N}{k_{\max} R_2} - R_1^2 \ln \frac{2N}{k_{\max} R_1} \right) + \frac{\kappa^2(R_2^2 - R_1^2)}{4} \left(\frac{1}{2} + \ln \frac{2e^{-C}}{\kappa L} \right) - \frac{\pi}{4} \kappa(R_2 + R_1) + \mathcal{O}(1). \quad (44)$$

All terms that vanish when $N \rightarrow \infty$ have been omitted. To recover the proper bulk value of the grand potential and ensure extensivity, the first term in equation (44) should vanish. This imposes the relationship between the ultraviolet cutoffs N and k_{\max} :

$$\frac{2N e^{1/2}}{k_{\max}} = R_2 x \frac{x^2}{x^2 - 1}. \quad (45)$$

This relation is similar to that found in the disc replacing R by $R_2 x^{x^2/(x^2-1)}$.

Returning to the grand potential we conclude that its large annulus expansion is

$$\Omega = \pi(R_2^2 - R_1^2)\omega_b + 2\pi(R_1 + R_2)\gamma + \mathcal{O}(1) \quad (46)$$

with the ω_b and γ given by equations (35) and (36), respectively. In the $\mathcal{O}(1)$ neglected terms there are terms of the form $\ln(R_1/R_2)$ and more generally functions of $x = R_1/R_2$ which are indeed of order 1. There are no logarithmic finite-size corrections, such as $\ln(\kappa\sqrt{R_1 R_2})$, according to the fact that $\chi = 0$ for an annulus.

4. Summary and conclusion

The method presented here gives a practical prescription for the calculation of finite-size corrections of the grand potential of a Coulomb system in the Debye–Hückel regime, which can be easily applied to more complicated geometries in two and three dimensions. The proper subtraction of the self-energies avoids the divergence of the infinite products involved in the calculations. In the disc and annulus geometry that we used to illustrate our method, we recovered the bulk pressure and the surface tension of the system in the Debye–Hückel regime. For the disc we obtained a universal finite-size correction $\frac{1}{6} \ln R$, with the expected value $\chi = 1$, for the Euler characteristic of the disc. For the annulus since $\chi = 0$ no finite-size correction is expected and we confirmed this result by direct calculation of the finite-size expansion. In the case of a system in a domain of arbitrary shape, the logarithmic universal correction to the grand potential may be obtained from the asymptotic properties of the spectrum of the Laplace operator and its relation with the geometry of the manifold for which this spectrum is calculated [41, 42]. Work in this direction is in progress.

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Appendix A. Relationship with the usual formulation of the Debye–Hückel theory

The usual formulation of the Debye–Hückel theory [32], for a confined Coulomb system with Dirichlet boundary conditions for the electric potential, starts by computing the electric potential $\Phi_\alpha(\mathbf{r}, \mathbf{r}')$ created at \mathbf{r}' by a particle of charge q_α located at \mathbf{r} and its polarization cloud. We have $\Phi_\alpha(\mathbf{r}, \mathbf{r}') = q_\alpha K(\mathbf{r}, \mathbf{r}')$ with the Debye–Hückel kernel K that satisfies

$$(\Delta - \kappa_{\text{DH}}^2) K(\mathbf{r}, \mathbf{r}') = -s_d \delta(\mathbf{r} - \mathbf{r}') \quad (\text{A.1})$$

with $\kappa_{\text{DH}}^2 = \sum_\alpha \beta q_\alpha^2 n_\alpha s_d$. Formally K can be written as

$$K(\mathbf{r}, \mathbf{r}') = \left\langle \mathbf{r} \left| \frac{-s_d}{\Delta - \kappa_{\text{DH}}^2} \right| \mathbf{r}' \right\rangle \quad (\text{A.2})$$

where the Laplacian is considered to satisfy Dirichlet boundary conditions. Then, one computes the internal potential energy U of the system as

$$U = \frac{1}{2} \int d\mathbf{r} \sum_\alpha q_\alpha^2 n_\alpha \lim_{\mathbf{r}' \rightarrow \mathbf{r}} (K(\mathbf{r}, \mathbf{r}') - v_d^0(\mathbf{r}, \mathbf{r}')) \quad (\text{A.3})$$

which can formally be written as

$$U = -\frac{1}{2} \sum_\alpha q_\alpha^2 n_\alpha s_d \int d\mathbf{r} \left\langle \mathbf{r} \left| \frac{1}{\Delta - \kappa_{\text{DH}}^2} - \frac{1}{\Delta^0} \right| \mathbf{r} \right\rangle \quad (\text{A.4})$$

$$= -\frac{\kappa_{\text{DH}}^2}{2\beta} \text{Tr} \left[\frac{1}{\Delta - \kappa_{\text{DH}}^2} - \frac{1}{\Delta^0} \right] \quad (\text{A.5})$$

$$= -\frac{\kappa_{\text{DH}}^2}{2\beta} \sum_n \left[\frac{1}{\lambda_n - \kappa_{\text{DH}}^2} - \frac{1}{\lambda_n^0} \right]. \quad (\text{A.6})$$

The notation Δ^0 denotes the Laplacian operator with free boundary conditions.

On the other hand, the internal excess energy U can be computed from the thermodynamic relation $U = -(\partial \ln \Xi / \partial \beta)_{\zeta, V}$. Using the sine-Gordon formulation, we can obtain an independent expression for the internal excess energy and compare it to equation (A.6). Using equation (16) gives

$$\begin{aligned} -\left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\zeta, V} &= \frac{1}{2} \frac{\partial}{\partial \beta} \sum_n \left[\ln \left(1 - \frac{\kappa^2}{\lambda_n} \right) + \frac{\kappa^2}{\lambda_n} \right] \\ &= -\frac{\kappa^2}{2\beta} \sum_n \left[\frac{1}{\lambda_n - \kappa^2} - \frac{1}{\lambda_n^0} \right]. \end{aligned} \quad (\text{A.7})$$

At the Debye–Hückel level of approximation κ_{DH} (expressed in terms of the densities) can be replaced by κ (expressed in term of the fugacities) with corrections of higher order. Therefore with equation (16) for the grand potential and equation (A.7), one recovers the expression (A.6) for the internal excess energy obtained from the usual formulation of the Debye–Hückel theory.

Appendix B. On the pseudo-neutrality condition and the potential difference between the system and the walls

Coulomb systems have the interesting property that any excess charge in the system is expelled to the boundaries [23]. Therefore any infinite system is neutral. When the system is described in the grand canonical ensemble with fugacities ζ_α^* the electroneutrality has the consequence that the fugacities are not independent. Several choices of the fugacities can describe the same system. More precisely, the grand potential does not depend on the combination $\sum_\alpha q_\alpha \zeta_\alpha^*$ [23, 26, 43]. Therefore one can impose the so-called pseudo-neutrality condition

$$\sum_\alpha q_\alpha \zeta_\alpha^* = 0. \quad (\text{B.1})$$

For a confined Coulomb system the situation is more involved. Suppose that the confined system, described in the grand canonical ensemble with fugacities ζ_α , is in equilibrium with an infinite neutral reservoir at zero electric potential with fugacities ζ_α^* that satisfy the pseudo-neutrality condition (B.1). Let us consider that the confined system is large and that, far from the boundaries, the average electric potential of the system is a constant ψ_0 . Writing down the equilibrium condition that the electrochemical potentials of the system and the reservoir should be equal yields $\zeta_\alpha^* = \zeta_\alpha \exp(-\beta q_\alpha \psi_0)$. Therefore the confined system can be described with the fugacities ζ_α which *a priori* do not satisfy the pseudo-neutrality condition or with the fugacities ζ_α^* which satisfy the pseudo-neutrality condition plus the parameter ψ_0 which is the potential difference between the system and the reservoir. In this paper we have supposed so far that the fugacities ζ_α satisfy the pseudo-neutrality conditions. In the following we will consider the general case when the fugacities do not satisfy the pseudo-neutrality condition and we will explore how they are related to the potential $\psi_0 \neq 0$ in an approximate mean field picture. If $\psi_0 \neq 0$ this potential difference will create a surface charge density near the boundaries and we would expect that this effect will add to the grand potential and the free energy a *surface* term. We will show that this contribution turns out to be $-\frac{1}{2}Q\psi_0$, where Q is the excess charge of the system which is spread over the surface of the boundaries [23].

Actually we can justify this argument within our formalism of the sine-Gordon transformation by adapting some arguments put forward in [26] for the case of free boundary conditions. In the case of two-dimensional systems, we will also show that if the potential difference ψ_0 is not too high, the contributed surface term is of higher order in the coulombic coupling constant than the surface tension already computed in section 3.2 and given by equation (36), and therefore it can be neglected in the Debye–Hückel approximation.

Let us rewrite equation (12) for the grand canonical partition function as

$$\Xi(\beta, \zeta_\alpha, V) = \frac{1}{Z} \int \mathcal{D}\phi \exp[-S] \quad (\text{B.2})$$

with the action S given by

$$-S = \int \left[\frac{\beta}{2s_d} \phi \Delta \phi + \sum_\alpha \zeta_\alpha \exp(-i\beta q_\alpha \phi) \right]. \quad (\text{B.3})$$

To lighten the notation, in this appendix we will often omit the variable \mathbf{r} in the integrals: $\int \phi = \int \phi(\mathbf{r}) \mathbf{d}\mathbf{r}$. For simplicity we have omitted the self-energy term which is irrelevant in the present discussion (one could eventually consider that the fugacities ζ_α are renormalized by multiplying by $\exp(\beta q_\alpha^2 v_{S-E}/2)$).

If the fugacities do not satisfy the pseudo-neutrality condition, the stationary point of the action S is not $\phi = 0$ as before. Let $\psi(\mathbf{r})$ be i times the solution of $\delta S/\delta\phi = 0$. This field satisfies

$$\Delta\psi(\mathbf{r}) + s_d \sum_{\alpha} \zeta_{\alpha} q_{\alpha} \exp(-\beta q_{\alpha} \psi(\mathbf{r})) = 0. \quad (\text{B.4})$$

with Dirichlet boundary conditions: $\psi(\mathbf{r})$ vanishes on the boundary. This is the Poisson–Boltzmann equation and the field $\psi(\mathbf{r})$ is the average electrostatic potential in the mean field approximation [44]. Note that if the fugacities ζ_{α} satisfy the pseudo-neutrality condition then $\psi(\mathbf{r}) = 0$ is a solution of the Poisson–Boltzmann equation (B.4). In this case, and in the mean field approximation, the potential difference between the boundaries and the system is zero. If the fugacities ζ_{α} do not satisfy the pseudo-neutrality condition then $\psi(\mathbf{r})$ is not zero, and contrary to what has been done before, the expansion to the quadratic order of the action S should now be done around $\phi = -i\psi$ instead of $\phi = 0$. To accomplish this let us change the variable in the functional integral $\phi' = \phi + i\psi$. We have $\mathcal{D}\phi = \mathcal{D}\phi'$ and the action is now given by

$$-S = \int \frac{\beta}{2s_d} [\phi' \Delta\phi' - 2i\phi' \Delta\psi - \psi \Delta\psi] + \sum_{\alpha} \zeta_{\alpha} \exp(-\beta q_{\alpha} (\psi + i\phi')). \quad (\text{B.5})$$

The new field ϕ' fluctuates around 0 and now we can expand the exponential to the second order in the coulombic coupling. The linear terms in ϕ' in the action S are cancelled by applying the stationary condition (Poisson–Boltzmann) equation (B.4) and we find $S = S_1 + S_2 + o(\Gamma_{d,\alpha}^{d/2})$ with

$$S_1 = \frac{1}{2} \int \phi'(\mathbf{r}) \left(\frac{-\beta\Delta}{s_d} + \sum_{\alpha} (\beta q_{\alpha})^2 \zeta_{\alpha} \exp(-\beta q_{\alpha} \psi(\mathbf{r})) \right) \phi'(\mathbf{r}) \, d\mathbf{r} \quad (\text{B.6})$$

$$S_2 = \int \left[\frac{\beta}{2s_d} \psi(\mathbf{r}) \Delta\psi(\mathbf{r}) - \sum_{\alpha} \zeta_{\alpha} \exp(-\beta q_{\alpha} \psi(\mathbf{r})) \right] d\mathbf{r}. \quad (\text{B.7})$$

The term S_1 is of order $\Gamma_{d,\alpha}^{d/2}$ in the coupling constants. To verify this, note that in two dimensions the field ϕ' can be written as $qf(\kappa\mathbf{r})$ with f some function of order one and q is the magnitude of the elementary charges in the system, for example $q = \max |q_{\alpha}|$. Rescaling the distances in the integral by the inverse Debye length κ shows that S_1 is of order $\Gamma_{2,\alpha}$. In three dimensions $\phi' = q\kappa f(\kappa\mathbf{r})$ and doing the same scaling in the integral as above shows that S_1 is now of order $\Gamma_{3,\alpha}^{3/2}$. To know the order of magnitude of S_2 we need further assumptions. To proceed, we shall need in principle the solution $\psi(\mathbf{r})$ of the Poisson–Boltzmann equation (B.4). However, the solution of the Poisson–Boltzmann equation is not known explicitly except for a few very simple geometries [45–48]. Nevertheless the qualitative behaviour of the mean field $\psi(\mathbf{r})$ is very simple. It vanishes on the boundary and a few screening lengths away from the boundary it is almost equal to a constant value ψ_0 . This constant average value of the potential ψ_0 is given by the Poisson–Boltzmann equation (B.4) for a constant field:

$$\sum_{\alpha} q_{\alpha} \zeta_{\alpha} \exp(-\beta q_{\alpha} \psi_0) = 0. \quad (\text{B.8})$$

Let us define the renormalized fugacities $\zeta_{\alpha}^* = \zeta_{\alpha} \exp(-\beta q_{\alpha} \psi_0)$. By equation (B.8) these new fugacities satisfy the pseudo-neutrality condition (B.1). The physical interpretation of these new fugacities is of course the one exposed at the beginning of this appendix: they are the fugacities of the infinite neutral grounded reservoir. Let us now write $\psi(\mathbf{r}) = \psi_0 + \delta\psi(\mathbf{r})$.

Note that $\delta\psi(\mathbf{r})$ is almost zero in the deep interior of the system and only has significant values near the boundaries. Let us suppose that the variations of $\delta\psi(\mathbf{r})$ are small, more precisely, let us suppose that $\delta\psi(\mathbf{r}) = qg(\kappa\mathbf{r})$ in two dimensions or $\delta\psi(\mathbf{r}) = \kappa qg(\kappa\mathbf{r})$ in three dimensions with g some function of order 1. Then expanding S_1 for small $\delta\psi$ yields

$$S_1 = \frac{1}{2} \int \phi'(\mathbf{r}) \left(\frac{-\beta\Delta}{s_d} + \sum_{\alpha} (\beta q_{\alpha})^2 \zeta_{\alpha}^* \right) \phi'(\mathbf{r}) \, d\mathbf{r} + \mathcal{O}(\Gamma_{d,\alpha}^d). \quad (\text{B.9})$$

For the second part of the action the same expansion yields

$$S_2 = - \sum_{\alpha} \zeta_{\alpha}^* V + \frac{\beta\psi_0}{2s_d} \int \Delta(\delta\psi) + \frac{\beta}{2s_d} \int \delta\psi(\Delta - \kappa^2)\delta\psi + \mathcal{O}(\Gamma_{d,\alpha}^d) \quad (\text{B.10})$$

where we have defined the inverse Debye length κ in terms of the renormalized fugacities ζ_{α}^* as $\kappa = \sqrt{\beta s_d \sum_{\alpha} \zeta_{\alpha}^* q_{\alpha}^2}$. Actually a closer inspection of equation (B.10) shows that the last term of S_2 is actually of higher order than the two other terms. Indeed expanding the Poisson–Boltzmann equation (B.4) for $\delta\psi$ small shows that

$$\Delta(\delta\psi) - \kappa^2\delta\psi = \mathcal{O}(\zeta_{\alpha}^* q_{\alpha} (\beta q_{\alpha} \delta\psi)^2). \quad (\text{B.11})$$

Therefore

$$-\frac{\beta}{2s_d} \int \delta\psi(\Delta - \kappa^2)\delta\psi = \mathcal{O}(\Gamma_{d,\alpha}^d) \quad (\text{B.12})$$

and

$$S_2 = - \sum_{\alpha} \zeta_{\alpha}^* V + \frac{\beta\psi_0}{2s_d} \int_V \Delta(\delta\psi) + \mathcal{O}(\Gamma_{d,\alpha}^d). \quad (\text{B.13})$$

Note now that only S_1 depends on ϕ' and the result of the functional Gaussian integration over the field ϕ' will be the same as in section 2, equation (15), except that the fugacities ζ_{α} have to be replaced by ζ_{α}^* . The term S_2 does not depend on the field ϕ' and will give only an additive contribution to the grand potential. Finally we obtain for the grand potential

$$\Omega = \frac{k_B T}{2} \ln \left(\prod_m \left(1 - \frac{\kappa^2}{\lambda_m} \right) \prod_n \exp \left(\frac{\kappa^2}{\lambda_n^0} \right) \right) - k_B T \sum_{\alpha} V \zeta_{\alpha}^* + \Omega_S. \quad (\text{B.14})$$

That is the same grand potential as before but evaluated for the fugacities ζ_{α}^* instead of ζ_{α} plus a contribution

$$\Omega_S = S_2 + \sum_{\alpha} \zeta_{\alpha}^* V = -\frac{\psi_0}{2} \int_V \rho(\mathbf{r}) \, d\mathbf{r} = -\frac{1}{2} \psi_0 Q. \quad (\text{B.15})$$

We have used Poisson's equation $\Delta\psi = -s_d\rho$ with ρ the average charge density of the system in the mean field approximation. The excess total charge is $Q = \int_V \rho$. Let us remark on a few points about this term. The charge density $\rho(\mathbf{r})$ is different from zero near the boundaries and a few Debye lengths away from the boundaries it vanishes. The charge Q is spread near the surface of the system. Therefore the additional contribution Ω_S to the grand potential is actually a surface contribution. This is even more clear if from equation (B.13) we use the Gauss theorem to write Ω_S as

$$\Omega_S = \frac{\psi_0}{2s_d} \oint_{\partial V} \nabla\psi(\mathbf{r}) \cdot d\mathbf{S} = \frac{\psi_0}{2} \oint_{\partial V} \sigma_w(\mathbf{r}) \, dS \quad (\text{B.16})$$

where $\sigma_w = s_d \partial_n \psi$ is the surface charge density induced in the boundary walls of an ideal conductor. This charge is external to the system. Since the ideal conductor is grounded and

it is in total influence with the Coulomb system we have $\oint_{\partial V} \sigma_w dS = -Q$, thus recovering equation (B.15). This term could further be expressed as

$$\Omega_S = \frac{\psi_0 \kappa^2}{2s_d} \int_V \delta\psi(\mathbf{r}) d\mathbf{r} \quad (\text{B.17})$$

where we have used equation (B.11). Let us point out that this additional contribution Ω_S is not the naive electrostatic energy $U_{\text{elst}} = \frac{1}{2} \int_V \rho(\mathbf{r})\psi(\mathbf{r}) d\mathbf{r}$. This can be checked for the two-dimensional two-component plasma near a planar wall made of ideal conductor. Using the results from [28], for small coulombic coupling, the mean field electric potential is $\psi(x) = \psi_0(1 - e^{-\kappa x})$, with x the distance from the wall. Then in this case $U_{\text{elst}} = -\Omega_S/2$.

In general in two or three dimensions Ω_S is of order $\Gamma_{d,\alpha}$. However, for two-dimensional systems when the pseudo-neutrality condition is satisfied, we have found a surface tension given by equation (36) which is of lower order $\Gamma_{2,\alpha}^{1/2}$. Therefore in two dimensions the surface contribution Ω_S to the grand potential due to the potential difference ψ_0 between the system and the reservoir found in this appendix can be neglected in front of the surface tension given in equation (36). This fact has also been noticed in [28] where the exact expression of the surface tension for a symmetric two-component plasma has been computed and its expansion for small coulombic coupling parameter shows that the potential ψ_0 does not contribute in the dominant order.

For two-dimensional systems, we can conclude that the results of sections 2 and 3 also apply when the fugacities do not satisfy the pseudo-neutrality condition, provided that one replaces the original fugacities ζ_α with the renormalized fugacities $\zeta_\alpha^* = \zeta_\alpha \exp(-\beta q_\alpha \psi_0)$ which do satisfy the pseudo-neutrality condition.

In three dimensions the situation is somehow different. By dimensional analysis one would expect that for a system of characteristic size R and with $\psi_0 = 0$ the surface term of the grand potential will be proportional to $\kappa^2 R^2$, therefore of order $\Gamma_{3,\alpha}$.³ Then for a system with $\psi_0 \neq 0$ the additional surface contribution Ω_S found in this appendix will in principle contribute to the total surface tension (see, however, the footnote).

Let us mention that if the potential difference ψ_0 is large one should go back to equations (B.6) and (B.7) and try to study the whole nonlinear problem. There is an interesting regime where the fluctuations ϕ' around the mean field are small enough to expand the action S to the second order as $S = S_1 + S_2$ but that the mean field ψ_0 could be large and further expansion of S_1 , equation (B.9), and S_2 , equation (B.13), is not possible. It is expected that some very interesting phenomena could occur in this nonlinear regime, for instance renormalization and saturation of the surface charge Q and the potential ψ_0 , as in the studies of highly charged colloids [49–51].

To conclude this discussion we should highlight a delicate point. The analysis done in this appendix is based on a mean field approximation: the function $\psi(\mathbf{r})$ and its constant value ψ_0 inside the system are the solution of the Poisson–Boltzmann equation (B.4). In full generality they are different from the average electric potential inside the system. Only at the first order, in the ideal gas approximation ($n_\alpha = \zeta_\alpha^*$), can we identify both. Nevertheless our goal was to obtain an estimation of the corrections to the grand potential when the pseudo-neutrality condition is not satisfied, and based on this estimate we can conclude that these corrections are of higher order.

³ Applying our method to three-dimensional systems actually gives a surface tension $\gamma = \beta^{-1}(\kappa^2/16\pi) \ln(\kappa/k_{\text{max}})$ with k_{max} an ultraviolet cutoff. This result will be reported in a future work currently under preparation. Therefore it turns out that the dominant term in the surface tension is of order $\Gamma_{3,\alpha} \ln \Gamma_{3,\alpha}$ and the correction Ω_S is again of higher order.

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