Sine-Gordon Field Theory for the Calculation of Universal Finite Size Corrections in the Free Energy of Coulomb Systems at the Debye-Hückel Regime

by

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Dedicated to my parents Lucila and Rodolfo.

Contents

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Chapter 1

Introduction

Some of the most fascinating and difficult questions explored in the present-day research concern the equilibrium properties of systems composed by many interacting particles. In principle, the thermodynamic i.e. macroscopic properties of such a system requires only the calculation of the partition function. In this sense the methods of statistical mechanics make the problem very well defined [1],[2], but as we will see in this work, it can become both complex and subtle, revealing aspects that would be unexpected from mere thermodynamical considerations.

The kind of systems we are interested in are commonly known as classical Coulomb systems. They are systems composed of a great number of charged particles, that will be considered point-like in that follows, interacting by pairs through the Coulomb force. In some context is necessary the introduction of a short distance repulsive potential. Coulomb systems are relevant because they are commonly encountered in nature. For example, at molecular scales Coulomb interaction is dominant, being nuclear forces too short ranged to operate at this scale and gravitational forces completely negligible in magnitude compared with Coulomb force. On the other side, aggregates of atoms and molecules always constitute a Coulomb system at a certain high temperature regime.

The statistical mechanics of Coulomb systems is much harder than for ordinary gases. The reason for this is that the interaction between two charged particles decreases typically as $1/r$ with increasing distance r between the particles. It represents therefore a long range interaction force. As a consequence, in Coulomb systems each particle always interacts with all other particles of the system, in contrast to the case of ordinary gases, where the interactions are supposed to be due to collisions, and usually is assumed that the duration of such collisions is much shorter than the average free time between them. This heuristic model simplifies the calculations but is inapplicable to the case of Coulomb systems.

From the theoretical point of view, Coulomb systems have several characteristics particularly interesting for us. It is known that, in two dimensions, they are exactly solvable (thermodynamics and correlations) at a certain temperature [3]-[8]. Also Coulomb systems can be considered critical systems, in the sense that the electric potential and field correlations are long-ranged. In some sense the electric potential becomes analog to the order parameter of a critical system [9],[10],[11]. This will be broadly discussed later in this work. As a consequence of this criticality, some quantum theories of critical fields are applicable to their study [12],[13],[14]. For example, for models defined in the continuum there is an analogy between statistical mechanics and quantum field theory: the partition function of a d-dimensional statistical model is entirely analogous to the generating functional of a quantum field in d space time dimension in the Euclidean formalism.

The formal equivalence between classical Coulomb systems and quantum theories of critical fields can be used with a twofold propose [15]: to study the field theory based on the physical behavior of the Coulomb system, providing physical insight to quantities that usually don't have from the field theoretical point of view, or on the other hand it may be employed to study the Coulomb system by analyzing the associated quantum field theory. In this thesis we make use of the later perspective to study universal properties of Coulomb systems confined in a finite size region.

Another interesting property of Coulomb systems is its finite size behavior. The importance of studying models over a finite-size region is manifold. For instance, with the recent advance of computers, much information on statistical models or quantum models has been derived from computer simulations, which are necessarily limited to systems of finite-size. In the case of statistical mechanical models, the properties in the thermodynamic limit must be inferred taking the thermodynamic limit of an analytic solution when possible. On the other side, experimental systems are of course finite.

The finite scaling hypothesis allows the study of some response functions for such finite-size models [1],[16]. It is based in the statement that if a given quantity diverges in the infinite limit like ξ^{d-2x}, where ξ is the correlation length, then in a finite system of characteristic size R, the corresponding response function will be given by the scaling law $R^{d-2x}\Phi(R/\xi)$, where Φ is some universal scaling function. At the critical point where $\xi^{-1} = 0$ the response function is proportional to R^{d-2x}.

The scaling of the free energy at criticality is less well understood [22]. It has been argued that for a finite two-dimensional system of characteristic size R as $R \to \infty$ at criticality, the total free energy has a large R expansion of the form

$$\beta F = AR^2 + BR - \frac{c\chi}{6} \ln R + O(R^0) \tag{1.1}$$

The first two terms represent respectively the bulk free energy and the surface free energy. In general, the coefficients A and B are non universal but the dimensionless coefficient of $\ln R$ is universal depending on c, the conformal anomaly number ($c = 1$ for Coulomb systems), 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), and possibly on the nature of the boundary conditions.

In the case of Coulomb systems confined in some simple geometries, this expansion for the free energy has been shown to be valid with a change in the sign of the last term, and it has been calculated explicitly by the use of exactly solvable models for a fixed temperature when $\beta q^2 = 2$ where $\beta^{-1} = k_B T$ and $\pm q$ are the charges of the particles [10].

In this work we develop a method to obtain the free energy expansion for Coulomb systems in the Debye-Hückel regime, that is in the regime in which the average potential coulombic energy is much smaller than the thermal energy [31],[32]. It is based on the mapping of the statistical model to the sine-Gordon field theory. This transform, known as sine-Gordon transformation allows the calculation of the grand canonical partition function to a Coulomb system by functional integrating the gas of particles without two body interaction over imaginary external effective potentials. The usual formulation of the sine-

Gordon transformation assume point like particles, however the transformation has been recently extended to systems in which the particles can be considered as hard spheres of a certain finite-size [18]-[20].

In the Debye-Hückel regime [31],[32],[37] particles can be considered point like and the sine-Gordon transformation, makes possible to express the grand potential function as the logarithm of an infinite product of factors that are functions of the eigenvalues of the Laplace operator. In this work we extend the sine-Gordon transformation to the study of confined systems. In this case one has to state boundary conditions. We find that they can be naturally included in the spectrum of the Laplace operator which depend on the shape of the domain in which the Coulomb system lies. As we will show, it constitute a natural way to introduce the information on the domain to calculate the corresponding finite-size expansion of the grand potential. We show also that the proper treatment of the self-energy terms leads to a well-defined, otherwise divergent expression, for the grand potential in the Debye–Hückel regime.

By this method we have been capable to calculate explicitly the expansion of the grand potential, and by a usual Legendre transform, the free energy expansion (1.1), for Coulomb systems confined in several geometries. We have found that our method gives the correct thermodynamical functions according with results that appear in the literature calculated by other means. In some cases we haven't found previous results to compare, however the mutual consistency of the results guarantees that they are correct in the Debye–Hückel regime.

From a more general point of view, the validity of our method rest in some general results known by mathematician since the middle of the XX century [39],[48]. More precisely, it is known that in some extend, the spectrum of the Laplace operator calculated on a given manifold endowed with a metric, contain information about the geometry of the manifold itself. By the use of these general mathematical results we have proved that our method gives the correct expansion for the free energy in arbitrary geometries. With this proof we extend our results from systems confined in specific domains to a wider class of geometries. Of course if one wants the explicit form of the free energy, a complete calculation similar to the presented in the solved examples is required. Nevertheless the general treatment gives rigorous support to the method, and offers another perspective to the problem.

This work is organized as follows. Chapters 2 and 3 are reference chapters. In chapter 2 we present the general mathematical description of Coulomb systems and introduce some notation. The critical-like behavior is discussed in detail, also, finite-size effects are discussed for two dimensions in the context of conformal field theory. In chapter 3 the usual Debye-Hückel theory in three dimensions is presented. We have also included detailed calculations for the thermodynamical functions and the two dimensional formulation, rarely discussed in textbooks. The other chapters contain the main results. In chapter 4 we present the sine-Gordon theory for the calculation of finite size corrections in the Debye-Hückel regime. In chapter 5 we present an article that will be published in J. Phys. A. There, some of the results obtained until that point of this thesis are presented. Additionally, in this article we include three examples of application of the method. The detailed calculations are not included but they can be found in appendices B and C of this document. The article also includes an appendix with the discussion of the relation of our formulation with the usual Debye-Hückel theory. In chapter 6 we present additional detailed examples for several geometries in two and three dimensions. Finally, in the first sections of chapter 7 we present as reference some known mathematical properties of the spectrum of the Laplace operator on Riemannian manifolds [39],[48], leaving the last sections to the general mathematical considerations on our method.

In order to facilitate the lecture, we have included several appendices which gather detailed but long calculations to which the reader may refer when needed. We have also included a list of symbols and a detailed index at the end.

Chapter 2

Coulomb Systems as Critical Systems

2.1 The Classical Coulomb Systems

The denomination Coulomb system is used in a very wide sense. In general it refers to many particle systems in which Coulomb interaction is dominant. For our proposes a classical (non quantum) Coulomb system will be considered as a fluid in which a large number of charged particles, interacting by pairs via the Coulomb potential, are present to affect the macroscopic properties of the system materially. An example of a physical system which may be described by a classical Coulomb fluid is the case of electrolytes. On the other hand, any gas will be a Coulomb system when it is sufficiently hot, the higher the degree of ionization, the more pronounced the Coulomb system properties. In what follows we suppose that the Coulomb system is completely ionized, in consequence no neutral particles need to be taken into account, and sufficiently hot for being in its conducting phase.

Let a non-confined Coulomb system composed of s species of charged particles $\alpha = 1, ..., s$ each of which have N_α charges q_α with $i = 1, ..., N_\alpha$. Such a system can be represented by the Hamiltonian

$$H = \frac{1}{2} \sum\nolimits'_{\alpha,\gamma} \sum\nolimits'_{i,j} q_\alpha q_\gamma V_d^0(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\gamma,j}) \tag{2.1}$$

where

$$V_d^0(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\gamma.j}) = \begin{cases} |\mathbf{r}_{\alpha,i} - \mathbf{r}_{\gamma.j}|^{-1} & \text{if } \ d = 3 \\ -\ln \left| \frac{\mathbf{r}_{\alpha,i} - \mathbf{r}_{\gamma.j}}{L} \right| & \text{if } \ d = 2 \end{cases} \tag{2.2}$$

is the Coulomb potential in d dimensions, and L is an arbitrary constant that defines the zero value for the potential. The primes in the summations mean that the case when $\alpha = \gamma$ *and* $i = j$ must be omitted. This means that in writing (2.1) *we do not include* the self energy of the particles, that is the energy of the particles own to the field produced by themselves. In both cases $d = 3$ and $d = 2$ the Coulomb potential satisfy the Poisson equation. However, in the latter case it do not represent the interaction of real charges confined on a surface which would still be of the form $|\mathbf{r}_{\alpha,i} - \mathbf{r}_{\gamma.j}|^{-1}$. It is just a two dimensional model that mimic some properties of the three dimensional case. Probably this requires an additional explanation.

If we consider real charges, for instance electrons on a surface, the coulomb potential still is $|\mathbf{r}_{\alpha,i} - \mathbf{r}_{\gamma.j}|^{-1}$, since the charges are surrounded by three dimensional space through which the field lines can penetrate. The properties of such a system *differ* from the properties of a three dimensional system in several ways. Two-dimensional systems with a logarithmic potential must be understood as toy models that mimic some properties of real three-dimensional systems. Nevertheless, the logarithmic models have been proved to have many interesting features, for example, some of them are exactly solvable [3]-[8]. We will see in this work another interesting properties in the Debye-Hückel regime. Finally, the logarithmic potential is chosen in order to satisfy the Poisson equation, which is essential if one hope to mimic properties of the three dimensional case.

In general, for the case we are interested in, that is, confined Coulomb systems, the explicit expression of the Coulomb potential changes, because it must satisfy certain imposed boundary conditions. Suppose that the system is confined in a region Λ whose volume will be denoted by the same symbol. Suppose also that the system is subject to Dirichlet conditions on the boundary $\partial\Lambda$ of Λ. Let V_d denote this new potential. It satisfy the Poisson equation

$$\mathbf{\Delta} V_d(\mathbf{r},\mathbf{r}') \ = -s_d \delta(\mathbf{r}-\mathbf{r}') \tag{2.3}$$

with $s_2 = 2\pi,\ s_3 = 4\pi$. In general $s_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$ where $\Gamma(x)$ is de usual Gamma function, note that s_d corresponds to the area of a sphere in d dimensions. We stress that the Coulomb potential V_d is the potential for a confined system. This is an important point since we will be considering finite size systems, and in general the explicit form for the potentials will change to assure that they take the correct value at the boundaries while $V_d^0(\mathbf{r},\mathbf{r}')$ always conserve its form given in (2.2).

If we include the self energies of the particles, the Hamiltonian of a Coulomb system may be written in a useful way. To do this we introduce the microscopic charge density operator defined by

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^{r} \sum_{i=1}^{N_\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}) \tag{2.4}$$

then we have

$$H' = \frac{1}{2} \sum\nolimits_{\alpha,\gamma} \sum\nolimits_{i,j} q_\alpha q_\gamma V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\gamma,j}) \tag{2.5}$$

$$= \frac{1}{2} \int_\Lambda d\mathbf{r} \int_\Lambda d\mathbf{r}' \sum_{\alpha=1}^{r} \sum_{i=1}^{N_\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}) V_d(\mathbf{r}, \mathbf{r}') \sum_{\gamma=1}^{r} \sum_{j=1}^{N_\gamma} q_\alpha \delta(\mathbf{r}' - \mathbf{r}_{\gamma,j}) \tag{2.6}$$

$$= \frac{1}{2} \int_\Lambda d\mathbf{r} \int_\Lambda d\mathbf{r}' \rho(\mathbf{r}) V_d(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') \tag{2.7}$$

note that the primes were avoided from the beginning, in other words, this expression includes the self energies of the particles, but also, it is written for the confined Coulomb potential V_d. Because of these two reasons H' is not the same Hamiltonian given in (2.1).

We can also introduce for future uses the grand canonical partition function of the Coulomb system, given by

$$\Xi_\Lambda(T, \varsigma) = \sum_{N_1=0}^{\infty} \cdots \sum_{N_r=0}^{\infty} \frac{\varsigma_1^{N_1} ... \varsigma_s^{N_s}}{N_1! ... N_r!} \int \cdots \int e^{-\beta H} \prod_{\alpha=1}^{s} \prod_{i=1}^{N_\alpha} d\mathbf{r}_{\alpha,i} \tag{2.8}$$

where ς denotes collectively the set $\{\varsigma_1 ... \varsigma_\alpha\}$ of the fugacities of each chemical specie. As the reader may be noted, we didn't introduce explicitly the kinetic contribution to the energy in (2.1). The reason is because these terms can be easily integrated in evaluating (2.8) and its contributions are equivalent to multiply by a constant the usual fugacities $z_\alpha = e^{\beta\mu_\alpha}$ involved in the standard definition of Ξ see e.g. [2]. For example, in three dimensions integrating the momenta gives

$$\varsigma_\alpha = \frac{z_\alpha}{\lambda_{\text{TH}}^3} = \frac{e^{\beta\mu_\alpha}}{\lambda_{\text{TH}}^3} \tag{2.9}$$

here μ_α is the chemical potential of specie α and $\lambda_{\rm TH}$ is the de-Broglie thermal wave length $\lambda_{\rm TH} = \frac{h}{(2\pi m k_B T)^{1/2}}$, where h is the Plank constant, k_B is the Boltzmann constant and T is the absolute temperature of the system. Then, the interaction term is the only important to our proposes and is also the most difficult to treat statistically, because the long range character of the Coulomb interaction.

2.2 Critical-Like Behavior

There is a formal relation between the Gaussian model of field theory, which is critical at all temperatures, and Coulomb systems [9],[10]. To see this let us consider the partition function of the Gaussian model $Z_G = \int \mathcal{D}\phi(\mathbf{r}) e^{-\beta S_G}$ defined in terms of a scalar field $\phi(\mathbf{r})$ and the action

$$S_G = \frac{1}{2s_d} \int \left[\nabla\phi(\mathbf{r})\right]^2 d\mathbf{r} \tag{2.10}$$

If we associate $\phi(\mathbf{r})$ with the microscopic electrostatic potential of the Coulomb system, equation (2.10) is just the energy $\frac{1}{2}\int_\Lambda \phi(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ of the system; since, if we consider a system confined in a volume Λ with boundary $\partial\Lambda$

$$\begin{aligned} \frac{1}{2s_d} \int \left[\nabla\phi(\mathbf{r})\right]^2 d\mathbf{r} &= \frac{1}{2s_d} \int_\Lambda \nabla\phi(\mathbf{r})\nabla\phi(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{2s_d} \int_\Lambda \left\{\nabla\left[\phi(\mathbf{r})\nabla\phi(\mathbf{r})\right] - \phi(\mathbf{r})\Delta\phi(\mathbf{r})\right\} d\mathbf{r} \\ &= -\frac{1}{2s_d} \int_\Lambda \phi(\mathbf{r})\Delta\phi(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{2} \int_\Lambda \phi(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \end{aligned} \tag{2.11}$$

where we have used Poisson equation $\Delta\phi = -s_d\rho$ and the fact that $\phi(\mathbf{r}) = 0$ on $\partial\Lambda$. Furthermore, it can be shown that the $n-$point correlations functions for the electrostatic potential and field for a Coulomb system have the same long range behavior that for the Gaussian model [17].

For Coulomb systems spatial correlations between the particles are short-ranged. It is not amazing since Debye screening takes place between the ions as will be discussed in detail in the next chapter, in this sense critical-like behavior of the free energy is unexpected. However an interesting fact occurs with the spatial two point correlation functions of the electrical potential and the electrical field, which exhibit long-range correlation functions. To see this consider a (neutral) Coulomb system in three dimensions described by a Hamiltonian H_0. Suppose that we introduce into the system an infinitesimal test charge q located at $\mathbf{r}$. Then, an additional energy $H_1 = q\phi(\mathbf{r})$ due to the interaction between the test charge and the system appears. The Hamiltonian of the system changes to

$$H = H_0 + H_1 \tag{2.12}$$

we are interested in the change of any observable of the system, say A, due to the introduction of the perturbation. Let us call

$$\langle A \rangle_0 = \frac{1}{Z_0} \int A e^{-\beta H_0} d\Gamma \quad \text{with} \quad Z_0 = \int e^{-\beta H_0} d\Gamma \tag{2.13}$$

the average of the observable computed with the non-perturbed Hamiltonian H_0, and

$$\langle A \rangle = \frac{1}{Z} \int A e^{-\beta H} d\Gamma \quad \text{with} \quad Z = \int e^{-\beta H} d\Gamma \tag{2.14}$$

the average of the observable computed with the perturbed Hamiltonian H. Consider the variation

$$\begin{aligned}\delta A &= \langle A\rangle - \langle A\rangle_0 \qquad (2.15)\\ &= \frac{1}{Z}\int Ae^{-\beta H}d\Gamma - \frac{1}{Z_0}\int Ae^{-\beta H_0}d\Gamma\\ &= \frac{1}{Z}\int Ae^{-\beta H_0}e^{-\beta H_1}d\Gamma - \frac{1}{Z_0}\int Ae^{-\beta H_0}d\Gamma\end{aligned}$$

in the static linear response formalism we can write $e^{-\beta H_1} \simeq 1 - \beta H_1$, and

$$\begin{aligned}\delta A &= \frac{\int Ae^{-\beta H_0}\left(1-\beta H_1\right)d\Gamma}{\int e^{-\beta H_0}\left(1-\beta H_1\right)d\Gamma} - \langle A\rangle_0 \qquad (2.16)\\ &= \frac{Z_0\langle A\rangle_0 - Z_0\langle \beta A H_1\rangle_0}{Z_0 - Z_0\langle \beta H_1\rangle_0} - \langle A\rangle_0\\ &= \frac{\langle A\rangle_0 - \beta\langle AH_1\rangle_0}{1-\beta\langle H_1\rangle_0} - \langle A\rangle_0\end{aligned}$$

now, using the approximation $1 + x \simeq \frac{1}{1-x}$ valid also in the static linear response approximation we can write

$$\begin{aligned}\delta A &= \left(\langle A\rangle_0 - \beta\langle AH_1\rangle_0\right)\left(1+\beta\langle H_1\rangle_0\right) - \langle A\rangle_0\\ &\simeq \langle A\rangle_0\,\beta\langle H_1\rangle_0 - \beta\langle AH_1\rangle_0\\ &= -\beta\langle AH_1\rangle^T \qquad (2.17)\end{aligned}$$

where $\langle AH_1\rangle^T = \langle AH_1\rangle_0 - \langle A\rangle_0\langle H_1\rangle_0$ is the truncated average computed with the original non-perturbed Hamiltonian H_0.

Returning to the two point space correlations of the electrostatic potential $\phi(\mathbf{r})$ using (2.17) with $A = \phi(\mathbf{r}')$ and $H_1 = q\phi(\mathbf{r})$ we can write

$$\delta\phi(\mathbf{r}') = -\beta q\left\langle \phi(\mathbf{r})\phi(\mathbf{r}')\right\rangle^T \qquad (2.18)$$

On the other hand consider the electrostatic field within the system. Let us call $\langle \mathbf{E}(\mathbf{r}')\rangle_0$ the electrostatic field at the point $\mathbf{r}'$ before the inclusion of the test charge q. When we put into the system the test charge at the point $\mathbf{r}$, the mean electrostatic field at $\mathbf{r}'$ changes to $\langle \mathbf{E}(\mathbf{r}') \rangle$ which for large $|\mathbf{r}-\mathbf{r}'|$ is the field produced by q plus $\langle \mathbf{E}(\mathbf{r}') \rangle_0$, that is

$$\left\langle \mathbf{E}(\mathbf{r}') \right\rangle = q \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3} + \left\langle \mathbf{E}(\mathbf{r}') \right\rangle_0 \tag{2.19}$$

then, from the point of view of the potentials we have

$$\left\langle \phi(\mathbf{r}') \right\rangle - \left\langle \phi(\mathbf{r}') \right\rangle_0 = -\frac{q}{|\mathbf{r}-\mathbf{r}'|} + const \tag{2.20}$$

since from definition for $q = 0$, $\langle \phi(\mathbf{r}') \rangle = \langle \phi(\mathbf{r}') \rangle_0$ the integration constant equals zero and using (2.18) we have

$$\beta q \left\langle \phi(\mathbf{r})\phi(\mathbf{r}') \right\rangle^T \sim \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{2.21}$$

the symbol $\sim$ remind us that this is valid in the static linear response approximation and also for $|\mathbf{r}-\mathbf{r}'|$ large compared to the microscopic scale of the system, which in our case is the Debye length, as will be shown in the next chapter.

Equation (2.21) says that the correlation function of the potential is long ranged. In this sense a Coulomb system can be considered a critical system, in correspondence with the behavior of the correlation functions for a statistical model which exhibit a phase transitions, in the neighborhood of a critical point. The previous argument is also valid for systems in two dimensions. In this case the analog to equation (2.21) is

$$\beta q \left\langle \phi(\mathbf{r})\phi(\mathbf{r}') \right\rangle^T \sim -\ln \frac{|\mathbf{r}-\mathbf{r}'|}{L} \tag{2.22}$$

The long range character of the correlation functions of the electrostatic potential is inherited by the correlations of the electrical fields as can be seen from (2.19), of more precisely by considering (in the case of three dimensions)

$$\begin{aligned}
\beta \left\langle E_\mu(\mathbf{r}) E_\nu(\mathbf{r}')\right\rangle^T &= \frac{\partial^2}{\partial r^\mu \partial r'^\nu} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\
&= -\frac{\partial}{\partial r^\mu} \frac{r'_\nu - r_\nu}{|\mathbf{r}-\mathbf{r}'|^3} \\
&= \frac{\delta_{\mu\nu} \left(\mathbf{r}-\mathbf{r}'\right)^2 - 3\left(\mathbf{r}-\mathbf{r}'\right)_\mu \left(\mathbf{r}-\mathbf{r}'\right)_\nu}{|\mathbf{r}-\mathbf{r}'|^5}
\end{aligned} \tag{2.23}$$

Similarly, in the case of a system in two dimensions

$$\begin{aligned}
\beta \left\langle E_\mu(\mathbf{r}) E_\nu(\mathbf{r}')\right\rangle^T &= -\frac{\partial^2}{\partial r^\mu \partial r'^\nu} \ln \frac{|\mathbf{r}-\mathbf{r}'|}{L} \\
&= -\frac{\partial}{\partial r^\mu} \frac{r'_\nu - r_\nu}{|\mathbf{r}-\mathbf{r}'|^2} \\
&= \frac{\delta_{\mu\nu} \left|\mathbf{r}-\mathbf{r}'\right|^2 - 2\left(\mathbf{r}-\mathbf{r}'\right)_\mu \left(\mathbf{r}-\mathbf{r}'\right)_\nu}{|\mathbf{r}-\mathbf{r}'|^4}
\end{aligned} \tag{2.24}$$

we stress that (2.23) and (2.24) are valid for large $|\mathbf{r}-\mathbf{r}'|$ in the sense that distances under consideration should be large compared to the screening length.

2.3 Stress Tensors

There is also a close relation between stress tensor as viewed in conformal field theory of critical systems and the Maxwell stress tensor as appear in the study of classical Coulomb systems. From the former point of view stress tensor may be considered as the generator of deformations of the system which can be described by scale and conformal transformations. From the point of view of Coulomb systems stress tensor allow the calculation of the electrostatic force that the system makes on each of its parts. The explicit form of the tensors differ only by sign as will be shown next.

Let us first introduce the stress tensor from the field theoretical point of view.

Consider a statistical mechanics model to which we make a general infinitesimal coordinate transformation $x^\mu \to x'^\mu = x^\mu + \delta x^\mu$. Under such transformation the action of the system will change in a way that depends locally on the derivatives of δx^μ. At first order in δx^μ we can write that the change of the action is given by

$$\delta S = -\frac{1}{s_d} \int dx T_{\mu\nu}(\mathbf{r}) \partial^\nu \left(\delta x^\mu\right) \tag{2.25}$$

where $T_{\mu\nu}(\mathbf{r})$ is the stress tensor. We can think on equation (2.25) as the definition of $T_{\mu\nu}(\mathbf{r})$, and it can be interpreted as follows. The interactions of statistical system give rise to an effective elasticity of the medium; this elasticity opposes to the deformation that we made with the change of coordinates $x^\mu \to x'^\mu$. The contribution of this additional energy to the Hamiltonian of the system is the integral of the stress tensor contracted with the strain tensor $\partial^\nu \left(\delta x^\mu\right)$ [12],[14].

We can find the explicit form for $T_{\mu\nu}$ for the Gaussian model from a variational principle as follows. Let us consider the original action S defined by a Lagrangian density as

$$S = \frac{1}{s_d} \int d^{d-1}x \int dt \mathcal{L}(\phi, \partial_\mu \phi) = \frac{1}{s_d} \int d^d x \mathcal{L}(\phi(x), \partial_\mu \phi(x)) \tag{2.26}$$

where x is a vector of d components which include the time variable. The variations of this action can be easily evaluated using integration by parts. As usual we can find the equation of motion demanding $\delta S = 0$, which leads to

$$\frac{\partial \mathcal{L}}{\partial \phi} = \partial_\mu \frac{\partial \mathcal{L}}{\partial \left(\partial_\mu \phi\right)} \tag{2.27}$$

On the other hand, under the infinitesimal coordinate transformation $x^\mu \to x'^\mu = x^\mu + \delta x^\mu$, the volume element changes as

$$\begin{aligned} d^d x' &= \left\| \frac{\partial x'}{\partial x} \right\| d^d x = \det \left(\frac{\partial x^\mu}{\partial x^\nu} + \partial^\nu \left(\delta x^\mu \right) \right) d^d x \\ &\simeq \left(1 + \partial_\nu \left(\delta x^\nu \right) \right) d^d x \end{aligned} \tag{2.28}$$

and the Lagrangian density changes as

$$\mathcal{L}'(\phi(x'), \partial_\mu \phi(x')) = \mathcal{L}(\phi(x), \partial_\mu \phi(x)) + \frac{\partial \mathcal{L}}{\partial x^\mu} \delta x^\mu \tag{2.29}$$

noting that

$$\frac{\partial \mathcal{L}}{\partial x^\mu} = \frac{\partial \mathcal{L}}{\partial \phi} \partial_\mu \phi + \frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} \partial_\mu \partial_\nu \phi$$

and using (2.27) we have

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial x^\mu} &= \partial_\mu \frac{\partial \mathcal{L}}{\partial \left(\partial_\mu \phi \right)} \cdot \partial_\mu \phi + \frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} \partial_\mu \partial_\nu \phi \\ &= \partial_\mu \left[\frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} \partial_\mu \phi \right] \end{aligned} \tag{2.30}$$

then the variation in the action becomes

$$\begin{aligned} \delta S &= S - S' \\ &= -\frac{1}{s_d} \int d^d x \left[\partial_\nu \left(\delta x^\nu \right) \mathcal{L} + \left(\delta x^\mu \right) \partial_\nu \left(\frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} \partial_\mu \phi \right) \right] \\ &= -\frac{1}{s_d} \int d^d x \left[\delta^\mu_\nu \mathcal{L} - \left(\frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} \partial_\mu \phi \right) \right] \partial_\nu \left(\delta x^\mu \right) \end{aligned} \tag{2.31}$$

finally, using the Lagrangian density for the Gaussian model (2.10) we have

$$\frac{\partial \mathcal{L}}{\partial \left(\partial_\nu \phi \right)} = \frac{1}{2 s_d} \frac{\partial}{\partial \left(\partial_\nu \phi \right)} \left(\partial_\nu \phi \partial^\nu \phi \right) = \frac{\left(\partial_\nu \phi \right)}{s_d} \tag{2.32}$$

and the variation on the action becomes

$$\begin{aligned} \delta S &= -\frac{1}{s_d} \int d^d x \left[\left(\frac{1}{2 s_d} g_{\mu\nu} \left| \nabla \phi \right|^2 - \frac{1}{s_d} \partial_\nu \phi \partial_\mu \phi \right) \partial^\nu \left(\delta x^\mu \right) \right] \\ &= -\frac{1}{s_d} \int d^d x T_{\mu\nu}(\mathbf{r}) \partial^\nu \left(\delta x^\mu \right) \end{aligned} \tag{2.33}$$

where

$$T_{\mu\nu}(\mathbf{r}) = \frac{1}{s_d}\left(\frac{1}{2}g_{\nu\mu}\left|\nabla\phi\right|^2 - \partial_\nu\phi\partial_\mu\phi\right) \tag{2.34}$$

which gives the explicit form for the stress tensor in the Gaussian model.

From the point of view of electrodynamics the stress tensor appears when we consider the force density that the electromagnetic field makes on a distribution of charge and current ρ and $\mathbf{J}$ respectively, which is given by the Lorenz force $\mathbf{f} = \rho\mathbf{E}+\frac{1}{c}\mathbf{J}\times\mathbf{B}$. Let us consider a system in three dimensions. Using Maxwell equations $s_d\rho = \nabla\cdot\mathbf{E}$ and $\mathbf{J} = \frac{c}{s_d}\left(\nabla\times\mathbf{B}-\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}\right)$ we have

$$\begin{aligned} \mathbf{f} &= \frac{1}{s_d}\left[\mathbf{E}\left(\nabla\cdot\mathbf{E}\right) + \left(\nabla\times\mathbf{B}\right)\times\mathbf{B} - \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}\times\mathbf{B}\right] \\ &= \frac{1}{s_d}\left[\mathbf{E}\left(\nabla\cdot\mathbf{E}\right) - \mathbf{B}\times\left(\nabla\times\mathbf{B}\right) - \frac{1}{c}\frac{\partial}{\partial t}\left(\mathbf{E}\times\mathbf{B}\right) + \frac{1}{c}\mathbf{E}\times\frac{\partial\mathbf{B}}{\partial t}\right] \\ &= \frac{1}{s_d}\left[\mathbf{E}\left(\nabla\cdot\mathbf{E}\right) - \mathbf{B}\times\left(\nabla\times\mathbf{B}\right) - \frac{1}{c}\frac{\partial}{\partial t}\left(\mathbf{E}\times\mathbf{B}\right) - \mathbf{E}\times\left(\nabla\times\mathbf{E}\right)\right] \end{aligned} \tag{2.35}$$

using the identities [36]

$$\mathbf{a}\times\left(\nabla\times\mathbf{a}\right) = \frac{1}{2}\nabla\left(\mathbf{a}\cdot\mathbf{a}\right) - \left(\mathbf{a}\cdot\nabla\right)\mathbf{a} \tag{2.36}$$

$$\left(\mathbf{a}\cdot\nabla\right)\mathbf{a} + \mathbf{a}\left(\nabla\cdot\mathbf{a}\right) - \frac{1}{2}\nabla\left(\mathbf{a}\cdot\mathbf{a}\right) = \nabla\cdot\left(\mathbf{a}\mathbf{a} - \frac{1}{2}\mathbf{1}\left(\mathbf{a}\cdot\mathbf{a}\right)\right) \tag{2.37}$$

where $\mathbf{1} = \sum_{i=1}^{3}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_i$ is the identity diadic we have

$$\begin{aligned} \mathbf{f} &= \frac{1}{s_d}\left[\mathbf{E}\left(\nabla\cdot\mathbf{E}\right) - \frac{1}{2}\nabla\left(\mathbf{B}\cdot\mathbf{B}\right) + \left(\mathbf{B}\cdot\nabla\right)\mathbf{B} - \frac{1}{2}\nabla\left(\mathbf{E}\cdot\mathbf{E}\right) + \left(\mathbf{E}\cdot\nabla\right)\mathbf{E}\right] \\ &\quad - \frac{1}{s_d c}\frac{\partial}{\partial t}\left(\mathbf{E}\times\mathbf{B}\right) \\ &= \frac{1}{s_d}\left[\nabla\cdot\left(\mathbf{E}\mathbf{E} + \mathbf{B}\mathbf{B} - \frac{1}{2}\left(E^2 + B^2\right)\mathbf{1}\right) - \frac{1}{c}\frac{\partial}{\partial t}\left(\mathbf{E}\times\mathbf{B}\right)\right] \end{aligned} \tag{2.38}$$

In our case, we consider particles with velocities low enough for the magnetic field $\mathbf{B}$ to be negligible (this is why only the electrostatic interaction has been kept). Then we have

$$f_\nu = \frac{1}{s_d}\left[\nabla \cdot \left(\mathbf{EE} - \frac{1}{2}\left(E^2\right)\mathbf{1}\right)\right]_{\mu\nu} = \partial^\mu T_{\mu\nu}(\mathbf{r}) \tag{2.39}$$

where

$$T_{\mu\nu}(\mathbf{r}) = \frac{1}{s_d}\left[\mathbf{EE} - \frac{1}{2}\left(E^2\right)\mathbf{1}\right] = -\frac{1}{s_d}\left(\frac{1}{2}g_{\nu\mu}\left|\nabla\phi\right|^2 - \partial_\nu\phi\partial_\mu\phi\right) \tag{2.40}$$

which, with a global change in the sign, is the same stress tensor (2.34) that appears in the field theoretical approach. In consequence, if we want to calculate the force that an arbitrary distribution of charge makes on other charges or on is own parts we integrate the stress tensor over a volume that contain the charges on which we want to evaluate the force:

$$\mathbf{F} = \int_\Lambda \nabla \cdot T_{\mu\nu}(\mathbf{r})dV = \int_S T_{\mu\nu}(\mathbf{r}) \cdot dA \tag{2.41}$$

where S is a surface that wraps the changes.

2.4 Conformal Group and the Conformal Anomaly Number

Conformal field theory has constituted an important tool in theoretical physics. It has shown to be useful in many branches from string theory to statistical mechanics. It is concerned with system that have conformal symmetry, that is, systems invariant under conformal transformations which include translations, dilatations and local rotations of the coordinates. Since the finite size effects for critical systems that we will study from the point of view of the statistical mechanics are consequence of conformal field theory. Because of that, in this section we gather some definitions concerned with this powerful tool. In particular we introduce the conformal anomaly number c that appears in the finite size expansion of the free energy for critical systems in two dimensions.

Following ref. [12] we define a conformal transformation of the coordinates as an invertible mapping $\mathbf{x} \to \mathbf{x}'$ such that

$$g'_{\mu\nu}(\mathbf{x}') = \Lambda(\mathbf{x}) g_{\mu\nu}(\mathbf{x}) \tag{2.42}$$

this means that the metric tensor remain invariant up to a scale factor $\Lambda(\mathbf{x})$ (not to be confused with the volume of the Coulomb system which is denoted without an argument). Conformal transformations leave the angles unchanged, for example, two crossing lines will form the same angle between them before and after a conformal transformation of the coordinates.

Let us consider the consequences of conformal invariance on the variation of the action for a field theory. Let us perform an infinitesimal transformation $x^\nu \to x'^\nu = x^\nu + \varepsilon^\nu(\mathbf{x})$, then at first order in ε the metric tensor changes as

$$g^{\mu\nu} \to g'^{\mu\nu} = g^{\mu\nu} - (\partial^\mu \varepsilon^\nu + \partial^\nu \varepsilon^\mu) \tag{2.43}$$

the requirement (2.42) implies that

$$\partial^\mu \varepsilon^\nu + \partial^\nu \varepsilon^\mu = f(\mathbf{x}) g^{\mu\nu}. \tag{2.44}$$

taking the trace at both sides, the factor $f(\mathbf{x})$ turn to be

$$f(\mathbf{x}) = \frac{2}{d} \partial_\rho \varepsilon^\rho \tag{2.45}$$

where d is the spatial dimension. On the other hand from (2.25) we have

$$\begin{aligned}\delta S &= -\frac{1}{s_d}\int dx T_{\mu\nu}(\mathbf{r})\partial^{\mu}\left(\varepsilon^{\nu}\right)\\ &= -\frac{1}{2s_d}\int dx T_{\mu\nu}(\mathbf{r})\left(\partial^{\mu}\varepsilon^{\nu}+\partial^{\nu}\varepsilon^{\mu}\right)\\ &= -\frac{1}{2s_d}\int dx T_{\mu\nu}(\mathbf{r})\frac{2}{d}\partial_{\rho}\varepsilon^{\rho}g^{\mu\nu}\\ &= -\frac{1}{s_d d}\int dx T_{\mu}{}^{\mu}(\mathbf{r})\partial_{\rho}\varepsilon^{\rho} \end{aligned} \tag{2.46}$$

then if the trace of the stress tensor equals zero, the action is invariant under conformal transformations. This is only true for plane geometry without boundary, the case of confined systems will be treated in the next section.

Another interesting fact related to the stress tensor is its behavior in two dimensions. In this case, the stress tensor can be expressed as a function of the complex coordinate z defining $T(z) = T_{11} - T_{22} + 2iT_{12}$. Its two point correlation function result to be fixed by its definition and is given by [13]

$$\langle T(z)T(0)\rangle = \frac{c/2}{z^4} \tag{2.47}$$

The number c is a universal quantity known as the conformal anomaly number or central charge. As a consequence of this universality in the correlation function, it can be shown that the stress tensor transforms under infinitesimal coordinate transformation $z \to z' = f(z)$ in a given way depending only on the derivatives of $f(z)$ and on the conformal anomaly number

$$T(z) \to (f'(z))^2 T(z') + \frac{c}{12}\frac{f'''f' - \frac{3}{2}f''^2}{f'^2} \tag{2.48}$$

In particular, it can be shown that the last term of the right hand side of (2.48) in the case of the stress tensor of the Gaussian model (2.34) expressed in complex coordinates equals

[22]

$$\frac{1}{12}\frac{f'''f' - \frac{3}{2}f''^2}{f'^2} \tag{2.49}$$

then we conclude that $c = 1$ for the Gaussian model.

2.5 Finite-Size Effects for the Free Energy

As mentioned in the introduction of this work, the finite scaling hypothesis allows the study of some response functions for finite-size models [1],[16]. The scaling of the free energy at criticality for finite-size models is less understood. Initially it had been argued that for a finite two-dimensional system of characteristic size R as $R \to \infty$ at criticality, the total free energy has a large R expansion of the form

$$\beta F = AR^2 + BR + \cdots \tag{2.50}$$

the first two terms represent respectively the bulk free energy and the surface free energy. In general, the coefficients A and B are non universal. The corrections to (2.50) were originally supposed to be $O(R^0)$ but it was recently shown that a correction of $O(\ln R)$ appears [16][22]. The coefficient of this finite size correction is highly universal depending only on c, the conformal anomaly number ($c = 1$ for Coulomb systems), 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), and possibly on the nature of the boundary conditions. In the case of Coulomb systems, this expansion for the free energy has been shown to be valid with a change in the sign of the last term, which is due to the change of the sign in the stress tensor as explained in the previous section. Following reference [22] we study the origin of this logarithmic correction to the free energy.

Consider a statistical mechanical model defined on some manifold $\mathcal{M}_m$ with boundary $\partial\mathcal{M}_m$ and with a given metric m. Suppose that the system has characteristic size R with respect to this metric. The metric may be curved and $\partial\mathcal{M}_m$ may have curvature also. As explained in a previous section, under a conformal transformation of coordinates $r^\mu \to r'^\mu$ an additional term appears in the action of the system, given in terms of the stress tensor by equation (2.46). Let us consider a global dilatation $r^\mu \to r'^\mu = (1+\alpha)r^\mu$, then the response of the system is given by

$$dS = -\frac{\alpha}{2\pi} \int\limits_{\mathcal{M}_m+\partial\mathcal{M}_m} \theta\sqrt{g}d^2r \tag{2.51}$$

where θ is the trace of the stress tensor and g is the determinant of the metric tensor associated with m, $g = \det g_{ij}$. The total partition function of the system must be invariant under such transformation, in consequence at first order in α, $e^{-F(R)} = e^{-F(R+dR)-\langle dS\rangle}$ or

$$\langle dS\rangle = F(R) - F(R+dR) = -R\frac{\partial F}{\partial R} \tag{2.52}$$

equating (2.52) and (2.51) we have

$$R\frac{\partial F}{\partial R} = \frac{1}{2\pi} \int\limits_{\mathcal{M}_m+\partial\mathcal{M}_m} \langle\theta\rangle\sqrt{g}d^2r \tag{2.53}$$

In a plane geometry without boundary θ (and of course $\langle\theta\rangle$) vanish, in consequence $\delta S = 0$ under such global transformation. If the geometry is curved or if it is plane but it has boundaries, $\langle\theta\rangle$ is no longer zero. The reason is that the curvature in the first case or the boundary in the second, provides a scale that spoils the conformal invariance. In fact $\langle\theta\rangle$ can only depend on the local geometry and it can be shown that [22]

$$\langle\theta\rangle = \varrho K \tag{2.54}$$

here K is the scalar curvature and ϱ is a constant that result to be proportional to the conformal anomaly number c. Conformal field theory shows that in the case of a curved geometry without boundaries $\varrho = -c/12$.

In the case of a plane geometry with boundary

$$\langle\theta\rangle = \varrho' J\delta(x_\perp) \tag{2.55}$$

where J is the extrinsic curvature of the boundary and $x_\perp$ is a vector perpendicular to the boundary in everyone of its points. In this case conformal field theory gives $\varrho' = -c/6$.

In consequence, for a system in curved geometry with boundaries we can write

$$\begin{aligned}\frac{\partial F}{\partial R} &= \frac{1}{2\pi}\left[\int\limits_{\mathcal{M}_m+\partial\mathcal{M}_m} \langle\Theta\rangle\sqrt{g}d^2r\right]\frac{1}{R} \qquad (2.56)\\ &= -\frac{1}{2\pi}\left[\frac{c}{12}\int\limits_{\mathcal{M}_m} K\sqrt{g}d^2r + \frac{c}{6}\int\limits_{\partial\mathcal{M}_m} JdS\right]\frac{1}{R}\\ &= -\frac{c}{24\pi}\left[\int\limits_{\mathcal{M}_m} K\sqrt{g}d^2r + 2\int\limits_{\partial\mathcal{M}_m} JdS\right]\frac{1}{R}\\ &= -\frac{c}{24\pi}4\pi\chi\frac{1}{R}\end{aligned}$$

where we have used the Gauss-Bonnet theorem [23]. Integrating we find that the finite size correction to the free energy is $F = -\frac{1}{6}c\ln R$. The same argument apply in the case of Coulomb systems, with the mentioned change in the sign of $\langle\Theta\rangle$, in consequence we have that the free energy of a Coulomb system scales as

$$\beta F = AR^2 + BR + \frac{\chi}{6}\ln R \tag{2.57}$$

Chapter 3

Debye Hückel Theory

3.1 Introduction

The interaction between two charged particles decreases typically as $1/r$ with increasing distance r between particles. It represents therefore a long range interaction force. Because of this any particle in the Coulomb system experiences the effect of the others making the statistical mechanical treatment harder. However the difficulty due to the long range interactions can be partially circumvented in Coulomb systems at the regime in which the electrostatic energy is much less than the thermal energy of the system. In this case there exists an approximate theory due to P. Debye and E. Hückel that allows the calculation of thermodynamic functions of a gas of charged particles, interacting with each other by mean of the Coulomb force [2],[21]. In this chapter we present an introduction to the theory paying special attention to the conditions required for its validity.

The essence of Debye-Hückel theory rest in the assumption that each ion in the system creates around itself a cloud of charged particles[1]. The effect of such a cloud is that the Coulomb potential is screened. In consequence, the effective interaction has a shorter range than $1/r$. The proof of the previous assertion is slightly different in two or three dimensions. In what follows we consider these two cases separately.

3.2 Debye-Hückel Theory in Three Dimensions

Consider a charge q_α located at $\mathbf{r} = 0$. As mentioned before, we suppose that q_α creates around itself a cloud of charged particles interacting with each other and also with q_α. Let $\{q_\gamma\}$ be the ensemble of charged particles in the cloud and $\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0)$ its charge density in the point $\mathbf{r}$ knowing that q_α is located at $\mathbf{r} = 0$. The potential in a point $\mathbf{r} \neq 0$ will be the potential ϕ_{cloud} created by the cloud plus the potential $q_\alpha/\mathbf{r}$ created by q_α. If we designate by $\Psi_\alpha^{(3D)}(\mathbf{r})$ the potential at the point $\mathbf{r}$ created by q_α *and* its polarization cloud. This potential must satisfy the Poisson equation

$$\Delta\Psi_\alpha^{(3D)}(\mathbf{r}) = -4\pi\left(\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0) + q_0\delta(\mathbf{r})\right) \tag{3.1}$$

The first approximation of Debye-Hückel theory is to suppose that the gas reacts to the combined potential $\Psi_\alpha^{(3D)}(\mathbf{r})$ as an ideal gas in the sense that the charge density distribution function $\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0)$ is given by the Boltzmann distribution

$$\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0) \simeq \langle\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0)\rangle_{ideal} = \sum_\gamma q_\gamma \bar{n}_\gamma e^{-\beta q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})} \tag{3.2}$$

where $\bar{n}_\gamma$ is the mean density of the charges $\{q_\gamma\}$. This simply means that the charge density distribution function in the space, satisfies the Boltzmann distribution law. Equations (3.1)

[1]In the particular case of a system without boundaries the screening cloud is in fact spherical.

and (3.2) give a closed system for the determination of $\Psi_\alpha^{(3D)}(\mathbf{r})$. However the resulting equation is a non linear differential equation. In order to obtain further simplification P. Debye and E. Hückel introduced a second approximation [2]. It consist in the linearization of the resulting differential equation by expanding the exponential in (3.2) to obtain

$$\rho_{cloud}(\mathbf{r}\,|q_\alpha,0) \simeq \sum_\gamma q_\gamma \bar{n}_\gamma - \beta \sum_\gamma q_\gamma^2 \bar{n}_\gamma \Psi_\alpha^{(3D)}(\mathbf{r}) \tag{3.3}$$

Because of the neutrality of the system we have $\sum_\gamma q_\gamma \bar{n}_\gamma = 0$. Replacing (3.3) in (3.1) we obtain

$$\left(\Delta - \kappa_{\mathrm{3DH}}^2\right) \Psi_\alpha^{(3D)}(\mathbf{r}) = -4\pi q_\alpha \delta(\mathbf{r}) \tag{3.4}$$

where $\kappa_{\mathrm{3DH}}^2 = 4\pi\beta \sum_\gamma \bar{n}_\gamma q_\gamma^2$. In what follows we refer κ_{3DH} as the Debye constant. Equation (3.4) is a linear differential equation for $\Psi_\alpha^{(3D)}(\mathbf{r})$ which solution could be difficult to find in the case of a confined system, in fact most of this work is devoted to the solution of this problem. In the case of a system without boundaries its solution is easy to find for example using the Fourier transformation. In solving it, we need to make use of the assumption that $\Psi_\alpha^{(3D)}(\mathbf{r})$ vanish for $\mathbf{r} \to \infty$ as will be shown next.

Fourier transforming both sides of (3.4) we find

$$\frac{1}{(2\pi)^3} \int_{\mathcal{R}^3} \left(\Delta - \kappa_{\mathrm{3DH}}^2\right) e^{-i\mathbf{k}\cdot\mathbf{r}} \Psi_\alpha^{(3D)}(\mathbf{r}) d\mathbf{r} = -\frac{4\pi q_\alpha}{(2\pi)^3} \int_{\mathcal{R}^3} \delta(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \tag{3.5}$$

integration by parts allow us to calculate the first summand of the left side to give

$$\int_{\mathcal{R}^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\partial^2 \Psi_\alpha^{(3D)}(\mathbf{r})}{\partial \mathbf{r}^2} d\mathbf{r} = -k^2 \int_{\mathcal{R}^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \Psi_\alpha^{(3D)}(\mathbf{r}) d\mathbf{r} \tag{3.6}$$

here we assume that $\Psi_\alpha^{(3D)}(\mathbf{r})$ and its gradient are integrable and $\Psi_\alpha^{(3D)}(\mathbf{r})$ is null at infinity.

Replacing (3.6) in (3.5) we obtain

$$\frac{1}{(2\pi)^3}\int_{\mathcal{R}^3} e^{-i\mathbf{k}\cdot\mathbf{r}}\left(k^2+\kappa_{3\mathrm{DH}}^2\right)\Psi_\alpha^{(3D)}(\mathbf{r})d\mathbf{r}=\frac{4\pi q_\alpha}{(2\pi)^3} \tag{3.7}$$

taking the inverse Fourier transform we have

$$\Psi_\alpha^{(3D)}(\mathbf{r})=\frac{4\pi q_\alpha}{(2\pi)^3}\int_{\mathcal{R}^3}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\left(k^2+\kappa_{3\mathrm{DH}}^2\right)}d\mathbf{k} \tag{3.8}$$

the integration is easily done. Using spherical coordinates we have

$$\Psi_\alpha^{(3D)}(\mathbf{r})=\frac{4\pi q_\alpha}{(2\pi)^3}\int_0^\infty\int_0^\pi\int_0^{2\pi}\frac{e^{ikr\cos\theta}}{\left(k^2+\kappa_{3\mathrm{DH}}^2\right)}k^2\sin\theta dk d\theta d\varphi \tag{3.9}$$

with the change of variable $u=\cos\theta$ this can be expressed as

$$\begin{aligned}\Psi_\alpha^{(3D)}(\mathbf{r}) &= \frac{4\pi q_\alpha}{(2\pi)^2}\int_0^\infty\int_{-1}^1\frac{e^{ikru}}{\left(k^2+\kappa_{3\mathrm{DH}}^2\right)}du k^2 dk\\ &= \frac{4\pi q_\alpha}{(2\pi)^2}\frac{1}{ir}\int_0^\infty\frac{1}{k}\frac{e^{ikr}-e^{-ikr}}{\left(k^2+\kappa_{3\mathrm{DH}}^2\right)}k^2dk\\ &= \frac{q_\alpha}{i\pi r}\int_0^\infty\frac{e^{ikr}-e^{-ikr}}{\left(k^2+\kappa_{3\mathrm{DH}}^2\right)}kdk\\ &= \frac{q_\alpha}{2\pi ir}\int_{-\infty}^\infty\frac{e^{ikr}}{(k-i\kappa_{3\mathrm{DH}})(k+i\kappa_{3\mathrm{DH}})}kdk\\ &= \frac{q_\alpha}{2\pi ir}2\pi ie^{-\kappa_{3\mathrm{DH}}r}=\frac{q_\alpha e^{-\kappa_{3\mathrm{DH}}r}}{r}\end{aligned} \tag{3.10}$$

where the residue theorem have been used. The later result can be expressed as $\Psi_\alpha^{(3D)}(\mathbf{r})=\frac{q_\alpha e^{-\frac{r}{l_{3\mathrm{HD}}}}}{r}$. The quantity

$$l_{3\mathrm{HD}}=\kappa_{3\mathrm{DH}}^{-1}=\frac{1}{\sqrt{4\pi\beta\sum_\gamma\bar{n}_\gamma q_\gamma^2}} \tag{3.11}$$

have dimensions of length and is called Debye length. $l_{3\mathrm{HD}}$ can be regarded as determining the dimension of the charged cloud that each ion q_α creates around itself.

From (3.3) we see that the Debye-Hückel argument is valid only in the limit in which $e^{-\beta q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})} \simeq 1 - \beta q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})$, that is if $\frac{q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})}{k_B T} \ll 1$ or

$$\frac{q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})}{k_B T} \sim \frac{q_\alpha q_\gamma / a}{k_B T} = \frac{q_\alpha q_\gamma \bar{n}^{1/3}}{k_B T} \ll 1 \tag{3.12}$$

where a is the mean distance between particles and $\bar{n}$ its mean density. This is equivalent to say that the thermal energy of the particles is greater than their electrostatic energy.

Debye-Hückel theory also allows the calculation of the thermodynamic functions of the system. To see how this is possible note that the charge density $\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0)$ is related with the two point density function $n_\gamma^{(2)}(\mathbf{r}\,|q_\alpha, 0)$

$$\rho_{cloud}(\mathbf{r}\,|q_\alpha, 0) = \sum_\gamma q_\gamma \frac{n_{\gamma\alpha}^{(2)}(\mathbf{r},0)}{n_\alpha(\mathbf{r})} \tag{3.13}$$

then $n_{\gamma\alpha}^{(2)}(\mathbf{r}\,|0)$ gives the probability of finding a charge q_γ of the system in the point $\mathbf{r}$ given that there's another charge q_α in $\mathbf{r} = 0$. In other words $n_{\gamma\alpha}^{(2)}(\mathbf{r}\,|0)$ is the two point density correlation function for charges of the system. Using (3.3) we find

$$\begin{aligned} n_{\gamma\alpha}^{(2)}(\mathbf{r}\,|0) &= \bar{n}_\alpha \bar{n}_\gamma e^{-\beta q_\gamma \Psi_\alpha^{(3D)}(\mathbf{r})} \simeq \bar{n}_\alpha \bar{n}_\gamma \left(1 - \beta q_\gamma \Psi_\alpha^{(3D)}(r)\right) \\ &= \bar{n}_\alpha \bar{n}_\gamma \left(1 - \beta q_\gamma q_\alpha \frac{e^{-\kappa_{3\mathrm{DH}} r}}{r}\right) \end{aligned} \tag{3.14}$$

where (3.10) is used. We have recognized $g_{\alpha\gamma}(r) = 1 - \beta q_\gamma q_\alpha \frac{e^{-\kappa_{3\mathrm{DH}} r}}{r}$ as the correlation function of the system.

Now we can use the well known formulas of the statistical mechanics that relate correlation functions and thermodynamic functions. In the case of the interaction energy we know that

$$U_{int} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \sum_{\alpha,\gamma} n_{\alpha\gamma}^{(2)}(\mathbf{r}, \mathbf{r}') q_\alpha q_\gamma V_3^0(\mathbf{r}, \mathbf{r}') \tag{3.15}$$

using (3.14) we have

$$\begin{aligned} U_{int} &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\sum_{\alpha,\gamma}\bar{n}_\alpha\bar{n}_\gamma\left(1-\beta q_\gamma q_\alpha\frac{e^{-\kappa_{3\mathrm{DH}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right)\frac{q_\alpha q_\gamma}{|\mathbf{r}-\mathbf{r}'|} \\ &= -\frac{4\pi\Lambda}{2}\sum_{\alpha,\gamma}\beta\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\int_0^\infty e^{-\kappa_{3\mathrm{DH}}r}dr \\ &= -2\pi\Lambda\sum_{\alpha,\gamma}\beta\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\kappa_{3\mathrm{DH}}^{-1} \end{aligned} \tag{3.16}$$

where $r = |\mathbf{r}-\mathbf{r}'|$ and we have used the neutrality of the system: $\sum_{\alpha,\gamma}\bar{n}_\alpha\bar{n}_\gamma q_\alpha q_\gamma = 0$. By using (3.11) expression (3.16) may be written in the form

$$U_{int} = -\frac{1}{2}\kappa_{3\mathrm{DH}}\Lambda\sum_\alpha \bar{n}_\alpha q_\alpha^2 \tag{3.17}$$

The excess pressure in the system due to the electrostatic interaction between particles may also be easily evaluated using the well known virial formula [2]

$$\beta p_{exc} = \frac{1}{6\Lambda k_B T}\int d\mathbf{r}_1\int d\mathbf{r}_2 r_{12}\frac{dV_3^0(r_{12})}{dr_{12}}n_{\alpha\gamma}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \tag{3.18}$$

using (3.14) we find

$$\begin{aligned} \beta p_{exc} &= \frac{1}{6\Lambda k_B T}\int d\mathbf{r}_1\int d\mathbf{r}_2 r_{12}\frac{dV_3^0(r_{12})}{dr_{12}}\sum_{\alpha,\gamma}\bar{n}_\alpha\bar{n}_\gamma\left(1-\beta q_\gamma q_\alpha\frac{e^{-\kappa_{3\mathrm{DH}}r_{12}}}{r_{12}}\right) \\ &= -\frac{4\pi}{6\Lambda k_B T}\sum_{\alpha,\gamma}\beta\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\int_0^\infty e^{-\kappa_{3\mathrm{DH}}r}dr \\ &= -\frac{\kappa_{3\mathrm{DH}}^3}{24\pi} \end{aligned} \tag{3.19}$$

Results of Debye-Hückel theory in two dimensions are slightly different as will be seen in the next section.

3.3 Debye-Hückel Theory in Two Dimensions

In the case of a system in two dimension the equivalent of equation (3.1) is

$$\Delta\Psi_{\alpha}^{(2D)}(\mathbf{r}) = -2\pi\left(\rho_{cloud}(\mathbf{r}\,|q_{\alpha},0) + q_0\delta(\mathbf{r})\right) \tag{3.20}$$

proceeding in a similar fashion as in the three dimensional case we obtain

$$\Psi_{\alpha}^{(2D)}(\mathbf{r}) = \frac{2\pi q_{\alpha}}{(2\pi)^2}\int_{\mathcal{R}^2}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\left(k^2+\kappa_{2\mathrm{DH}}^2\right)}d\mathbf{k} \tag{3.21}$$

Now $\kappa_{2\mathrm{DH}}^2 = 2\pi\beta\sum_{\gamma}\bar{n}_{\gamma}q_{\gamma}^2$ and the integration is restricted to an infinite plane ($d = 2$). To perform this integration we can use the integral formula [44]

$$\frac{1}{(2\pi)^d}\int_{\mathcal{R}^d}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(k^2+\xi^{-2})}d\mathbf{k} = \frac{1}{(2\pi)^{d/2}}\frac{\left(\xi^{-2}r\right)^{d/2-1}}{r^{d-2}}K_{d/2-1}\left(\xi^{-1}r\right) \tag{3.22}$$

where $K_{d/2-1}$ is the modified Bessel function of order $l = d/2-1$. Then we have

$$\Psi_{\alpha}^{(2D)}(\mathbf{r}) = \frac{2\pi q_{\alpha}}{(2\pi)}K_0\left(\kappa_{2\mathrm{DH}}r\right) = q_{\alpha}K_0\left(\kappa_{2\mathrm{DH}}r\right) \tag{3.23}$$

and the Debye length is given by

$$l_{2\mathrm{HD}} = \kappa_{2\mathrm{DH}}^{-1} = \frac{1}{\sqrt{2\pi\beta\sum_{\gamma}\bar{n}_{\gamma}q_{\gamma}^2}} \tag{3.24}$$

then, we have found that in this case there's screening for the Coulomb potential also. This can be seen easily for large values of r, for which the modified Bessel function admits the approximation

$$K_0\left(\kappa_{2\mathrm{DH}}r\right) \sim \sqrt{\frac{\pi}{2r\kappa_{2\mathrm{DH}}}}e^{-\kappa_{2\mathrm{DH}}r} \tag{3.25}$$

note that again $l_{2\mathrm{DH}} = \kappa_{2\mathrm{DH}}^{-1}$ can be interpreted as the mean size of the screening cloud.

For the calculation of the thermodynamic functions we can use similar formulas as those we used in the three dimensional case noting that now

$$n^{(2)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}') = \bar{n}_\alpha \bar{n}_\gamma \left(1 - \beta q_\alpha q_\gamma K_0(\kappa^2 \left|\mathbf{r}-\mathbf{r}'\right|)\right) \tag{3.26}$$

using the expression corresponding to (3.15) in the case of two dimensions, that is replacing V_3^0 by V_2^0 we have

$$\begin{aligned}
U_{int} &= -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \sum_{\alpha,\gamma} \bar{n}_\alpha \bar{n}_\gamma \left(1 - \beta q_\gamma q_\alpha K_0(\kappa_{\mathrm{2DH}}\left|\mathbf{r}-\mathbf{r}'\right|)\right) q_\gamma q_\alpha \ln \frac{|\mathbf{r}-\mathbf{r}'|}{L} \\
&= \frac{\Lambda}{2}\sum_{\alpha,\gamma} \beta \left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\int_0^\infty K_0(\kappa_{\mathrm{2DH}} r)\ln\left(\frac{r}{L}\right) r dr \\
&= \pi\Lambda\beta \sum_{\alpha,\gamma}\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\left[-\frac{C + \ln\kappa_{\mathrm{2DH}} - \ln\left(\frac{2}{L}\right)}{\kappa_{\mathrm{2DH}}^2}\right] \\
&= -\frac{\Lambda}{4\pi\beta}\kappa_{\mathrm{2DH}}^2\left[C + \ln\frac{L\kappa_{\mathrm{2DH}}}{2}\right]
\end{aligned} \tag{3.27}$$

where C is the Euler gamma constant defined as $-\left.\frac{d\ln\Gamma(x)}{dx}\right|_{x=1}$. The pressure is also easily evaluated using the two dimensional version of equation (3.18)

$$\begin{aligned}
\beta p_{exc} &= -\frac{1}{\Lambda k_B T}\int d\mathbf{r}_1 \int d\mathbf{r}_2 r_{12}\frac{d\ln(r_{12}/L)}{dr_{12}}\sum_{\alpha,\gamma}\bar{n}_\alpha\bar{n}_\gamma\left(1 - \beta q_\alpha q_\gamma K_0(\kappa_{\mathrm{2DH}} r_{12})\right) \\
&= \frac{2\pi}{k_B T}\sum_{\alpha,\gamma}\beta\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\int_0^\infty K_0(\kappa_{\mathrm{2DH}} r) r dr \\
&= \frac{2\pi}{k_B T}\sum_{\alpha,\gamma}\beta\left(\bar{n}_\alpha q_\alpha^2\right)\left(\bar{n}_\gamma q_\gamma^2\right)\frac{1}{4\kappa_{\mathrm{2DH}}^2} \\
&= -\frac{\kappa_{\mathrm{2DH}}^2}{8\pi} \\
&= -\frac{1}{4}\beta\sum_\alpha n_\alpha q_\alpha^2
\end{aligned} \tag{3.28}$$

it is interesting to note that this expression equals the exact result which is valid even out of the Debye-Hückel regime.

Chapter 4

Sine-Gordon Theory for Coulomb Systems at the Debye-Hückel Regime

In this chapter we present the sine-Gordon transformation, this formalism allows the expression the grand canonical partition function of a Coulomb system in an exact fashion, in terms of certain functional integral over auxiliary imaginary fields. In the case of systems in the Debye-Hückel regime, the calculations can be carried further, to obtain an expression for the grand potential function as the logarithm of an infinite product of factors that are functions of the eigenvalues of the Laplace operator. We begin with the general formulation.

4.1 The general formulation of the Sine-Gordon Transformation.

In the development of the Debye-Hückel theory we considered the effect of an internal charge q_α on the other charges of a Coulomb system. We found that the charge q_α create around itself a polarization cloud that screens the Coulomb potential. Debye-Hückel theory express the interactions in this heuristic way in terms of effective screened potentials. The sine-Gordon transformation allows the development of a more rigorous version of this idea in terms of auxiliary external potentials.

The Grand Partition Function of a Coulomb system may be represented by a field theory by mean of a technique known as Gaussian representation. From the point of view of quantum field theory, this is useful since it provide physical insight to quantities that usually don't have [15]. From the point of view we are interested in, that is finite Coulomb systems, it is a powerful tool since it allows to establish a relation between thermodynamic functions and the geometry in which the system is confined.

To see how this is possible consider the Poisson equation written in the form $\mathbf{\Delta} V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j}) = -s_d \delta(\mathbf{r}_{\alpha,i} - \mathbf{r}_{\beta,j})$. Then, we can think on $\mathbf{\Delta}$ as the operator inverse of the operator whose kernel is V_d, that is

$$V_d = -s_d \mathbf{\Delta}^{-1} \tag{4.1}$$

We can also find the eigenvalue problem for V_d : $V_d \left|\psi_k\right\rangle = -\frac{s_d}{\lambda_k} \left|\psi_k\right\rangle$ where $\left|\psi_k\right\rangle$ are the eigenfunctions of $-s_d \mathbf{\Delta}^{-1}$ which obviously are the same eigenfunctions of $-s_d \mathbf{\Delta}$ and λ_k are the eigenvalues of the Laplace operator $\mathbf{\Delta}$ evaluated with some boundary condition that by now we suppose is of the Dirichlet type. It is well known in analysis that $\{|\psi_k\rangle\}$ is a complete set, then if we consider two particles say i and j of species α and β located at $\mathbf{r}_{\alpha,i}$ and $\mathbf{r}_{\beta,j}$ we can express $V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j})$, the potential that gives the interparticle energy as

$$\begin{aligned} V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j}) &= \sum_{k=1} \sum_{l=1} \langle \mathbf{r}_{\alpha,i} | \, \psi_k \rangle \, \langle \psi_k | \, V_d \, |\psi_l \rangle \, \langle \psi_l | \, \mathbf{r}_{\beta,j} \rangle \\ &= \sum_{k=1} \sum_{l=1} -\frac{s_d}{\lambda_k} \langle \mathbf{r}_{\alpha,i} | \, \psi_k \rangle \, \langle \psi_k | \, |\psi_l \rangle \, \langle \psi_l | \, \mathbf{r}_{\beta,j} \rangle \\ &= \sum_{k=1} -\frac{s_d}{\lambda_k} \langle \mathbf{r}_{\alpha,i} | \, \psi_k \rangle \, \langle \psi_k | \, \mathbf{r}_{\beta,j} \rangle \end{aligned} \tag{4.2}$$

where we suppose that the eigenfunctions of V_d have been normalized. We can use (4.2) to find the self energy $V_{S-E}(\mathbf{r}_{\alpha,i})$ of the i-th particle of specie α located at $\mathbf{r}_{\alpha,i}$, that is, the energy of the particle in the field produced by itself:

$$\begin{aligned} V_{S-E}(\mathbf{r}_{\alpha,i}) &= V_d^0(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\alpha,i}) \\ &= \sum_{k=1} -\frac{s_d}{\lambda_k^0} \langle \mathbf{r}_{\alpha,i} | \, \psi_k^0 \rangle \, \langle \psi_k^0 | \, \mathbf{r}_{\alpha,i} \rangle \\ &= \sum_{k=1} -\frac{s_d}{\lambda_k^0} \left| \psi_k^0(\mathbf{r}_{\alpha,i}) \right|^2 \end{aligned} \tag{4.3}$$

the zero superscript remind us that contrary to equation (4.2), these eigenvalues are evaluated for each particle in free space, that is, without boundary.

With this definition we can write the Hamiltonian of a system *confined* with Dirichlet boundary conditions as

$$H_{conf} = \frac{1}{2} \sum\nolimits'_{\alpha,\gamma} \sum\nolimits'_{i,j} q_\alpha q_\gamma V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\gamma,j}) + \frac{1}{2} \sum_{\alpha=1}^{r} \sum_{i=1}^{N_\alpha} q_\alpha^2 \left[V_d(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\alpha,i}) - V_{S-E}(\mathbf{r}_{\alpha,i}) \right] \tag{4.4}$$

As before, the prime in the first summation mean 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 applicable to compute the Coulomb potential $\hat{V}_d$, this energy can also be seen as the energy between each particle and its image. Equation (4.4) can be written as

$$H_{conf} = \frac{1}{2}\int_\Lambda d\mathbf{r}\int_\Lambda d\mathbf{r}\rho(\mathbf{r})V_d(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') - \frac{1}{2}\sum_{\alpha=1}^{r}\sum_{i=1}^{N_\alpha} q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,i}) \tag{4.5}$$

where $\hat{\rho}(\mathbf{r})$ is the microscopic charge density operator defined in (2.4). Notice that with this notation, the terms $q_\alpha^2 V_d(\mathbf{r}_{\alpha,i},\mathbf{r}_{\alpha,i})/2$ that appear in the right hand side of (4.4) have been included in the first term of the right hand side of (4.5). Let us write equation (4.5) as

$$-\beta H_{conf} = \frac{1}{2}\int_\Lambda d\mathbf{r}\int_\Lambda d\mathbf{r}\left(-i\beta\rho(\mathbf{r})\right)\frac{V_d(\mathbf{r},\mathbf{r}')}{\beta}\left(-i\beta\rho(\mathbf{r}')\right) + \frac{1}{2}\beta\sum_{\alpha=1}^{r}\sum_{i=1}^{N_\alpha} q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,i}) \tag{4.6}$$

observe that the first term in the integrand can be written as $B\cdot A^{-1}\cdot B$ with the substitutions

$$A^{-1} = \frac{V_d}{\beta}\ ;\quad B = -i\beta\rho(\mathbf{r}) \tag{4.7}$$

This allow us to use the before mentioned Gaussian representation to write the Boltzmann factor involved in the calculation of $\Xi_\Lambda(\beta,\varsigma)$.

The sine-Gordon transformation is based on the integral identity

$$e^{\frac{1}{2}\mathbf{B}\cdot\mathbf{A}^{-1}\cdot\mathbf{B}} = \frac{\int\mathcal{D}\mathbf{X}e^{-\frac{1}{2}\mathbf{X}\cdot\mathbf{A}\cdot\mathbf{X}+\mathbf{B}\cdot\mathbf{X}}}{\int\mathcal{D}\mathbf{X}e^{-\frac{1}{2}\mathbf{X}\cdot\mathbf{A}\cdot\mathbf{X}}} \tag{4.8}$$

Since $A^{-1} = \frac{V}{\beta}$ using (4.1) we find $A = -\frac{\beta\mathbf{\Delta}}{s_d}$, and using the value for B given in (4.7) we can express the Boltzmann factor as

$$e^{-\beta H_{conf}} = \frac{\int\mathcal{D}\phi e^{\frac{\beta}{2s_d}\int\phi(\mathbf{r})\mathbf{\Delta}\phi(\mathbf{r})d\mathbf{r}-\beta\int i\rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}+\frac{1}{2}\beta\sum_{\alpha=1}^{r}\sum_{i=1}^{N_\alpha}q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,i})}}{\int\mathcal{D}\phi e^{\frac{\beta}{2s_d}\int\phi(\mathbf{r})\mathbf{\Delta}\phi(\mathbf{r})d\mathbf{r}}} \tag{4.9}$$

here $\mathbf{X} = \phi(\mathbf{r})$ is an auxiliary *external* field with units of charge and charge per distance in two and three dimensions respectively, which are also in each case, the dimensions of the electrostatic potential. Defining the average of any operator o as

$$\langle o\rangle = \frac{\int \mathcal{D}\phi o e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}}}{\int \mathcal{D}\phi e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}}} = \frac{1}{Z_0}\int \mathcal{D}\phi o e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}} \tag{4.10}$$

where $Z_0 = \int \mathcal{D}\phi e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}}$, equation (4.9) may be written as

$$e^{-\beta H_{conf}} = \left\langle \exp\left[-\beta\int i\rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} + \frac{1}{2}\beta\sum_{\alpha=1}^{r}\sum_{i=1}^{N_\alpha} q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,i})\right]\right\rangle \tag{4.11}$$

with the Boltzmann factor expressed in this form, the explicit form for the grand partition function

$$\Xi_\Lambda(\beta,\varsigma) = \sum_{N_1=0}^{\infty}\cdots\sum_{N_r=0}^{\infty}\frac{\varsigma_1^{N_1}...\varsigma_r^{N_r}}{N_1!...N_r!}\int\cdots\int e^{-\beta H_{conf}}\prod_{\alpha=1}^{r}\prod_{i=1}^{N_\alpha} d\mathbf{r}_{\alpha,i} \tag{4.12}$$

is

$$\sum_{N_1=0}^{\infty}\cdots\sum_{N_s=0}^{\infty}\frac{\varsigma_1^{N_1}...\varsigma_s^{N_s}}{N_1!...N_s!}\int\cdots\int\left\langle \exp\left[-\beta\int i\rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} + \frac{1}{2}\beta\sum_{\alpha=1}^{s}\sum_{j=1}^{N_\alpha} q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,j})\right]\right\rangle\prod_{\alpha=1}^{s}\prod_{j=1}^{N_\alpha} d\mathbf{r}_{\alpha,j}$$

since the only quantities affected by the average are the ones depending on $\phi(\mathbf{r})$ we can write

$$\left\langle\sum_{N_1=0}^{\infty}\cdots\sum_{N_s=0}^{\infty}\frac{\varsigma_1^{N_1}...\varsigma_s^{N_s}}{N_1!...N_s!}\int\cdots\int \exp\left[-\beta\int i\rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} + \frac{1}{2}\beta\sum_{\alpha=1}^{s}\sum_{j=1}^{N_\alpha} q_\alpha^2 V_{S-E}(\mathbf{r}_{\alpha,j})\right]\prod_{\alpha=1}^{s}\prod_{j=1}^{N_\alpha} d\mathbf{r}_{\alpha,j}\right\rangle$$

collecting terms and using the definition of the microscopic charge density (2.4) we have

$$\Big\langle \textstyle\sum_{N_1=0}^{\infty}\frac{\varsigma_1^{N_1}}{N_1!}\int e^{\beta\sum_j^{N_1}\left[-q_1 i\phi(\mathbf{r}_{1,j})+\frac{1}{2}q_1^2 V_{S-E}(\mathbf{r}_{1,j})\right]}\prod_{j=1}^{N_1} d\mathbf{r}_{1,j}\cdots \sum_{N_s=0}^{\infty}\frac{\varsigma_s^{N_s}}{N_s!}\int e^{\beta\sum_j^{N_s}\left[-q_s i\phi(\mathbf{r}_{\alpha,j})+\frac{1}{2}q_s^2 V_{S-E}(\mathbf{r}_{\alpha,j})\right]}\prod_{j=1}^{N_j} d\mathbf{r}_{s,j}\Big\rangle \tag{4.13}$$

using the properties of the exponential function we have

$$\left\langle\sum_{N_1=0}^{\infty}\frac{1}{N_1!}\left[\varsigma_1\int e^{\beta\left[-q_1 i\phi(\mathbf{r})+\frac{1}{2}q_1^2 V_{S-E}(\mathbf{r})\right]}d\mathbf{r}\right]^{N_1}\cdots\sum_{N_s=0}^{\infty}\frac{1}{N_s!}\left[\varsigma_s\int e^{\beta\left[-q_s i\phi(\mathbf{r})+\frac{1}{2}q_s^2 V_{S-E}(\mathbf{r})\right]}d\mathbf{r}\right]^{N_s}\right\rangle \tag{4.14}$$

we recognize in each of these sums the series expansion of the exponential function, then

$$\left\langle \exp\left[\varsigma_1 \int e^{\beta\left[-q_1 i\phi(\mathbf{r})+\frac{1}{2}q_1^2 V_{S-E}(\mathbf{r})\right]} d\mathbf{r}\right] \cdots \exp\left[\varsigma_r \int e^{\beta\left[-q_r i\phi(\mathbf{r})+\frac{1}{2}q_r^2 V_{S-E}(\mathbf{r})\right]} d\mathbf{r}\right]\right\rangle \tag{4.15}$$

which is the same that

$$\Xi_\Lambda(\beta,\varsigma) = \left\langle \exp\left[\sum_\alpha^s \varsigma_\alpha \int e^{\beta\left[-q_\alpha i\phi(\mathbf{r})+\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})\right]} d\mathbf{r}\right]\right\rangle \tag{4.16}$$

note that the terms $iq_\alpha\phi(\mathbf{r})+\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})$ are just the energy of the charge q_α due to the presence of the external field $i\phi(\mathbf{r})$ plus it self energy $\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})$. Remembering that we defined the average in terms of the functional integration in equation (4.10) we can correctly say that the grand partition function of the interacting system, exactly equals a functional integral of a non interacting system over external fields $i\phi(\mathbf{r})$ [15],[37].

It is interesting to notice that in the case of a system composed of two species of particles of charges $\pm q$ and fugacities $\varsigma_1 = \varsigma_2 = \varsigma$ we can write

$$\begin{aligned}
\sum_\alpha^r \varsigma_\alpha \int e^{\beta\left[q_\alpha i\phi(\mathbf{r})+\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})\right]} d\mathbf{r} &= \varsigma e^{\beta\left[qi\phi(\mathbf{r})+\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})\right]} + \varsigma e^{\beta\left[-qi\phi(\mathbf{r})+\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})\right]} \\
&= \left(e^{[\beta qi\phi(\mathbf{r})]} + e^{-[\beta qi\phi(\mathbf{r})]}\right)\varsigma e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \\
&= 2\varsigma e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \cos\left(\beta q\phi(\mathbf{r})\right)
\end{aligned} \tag{4.17}$$

then we can write the grand canonical partition function as

$$\begin{aligned}
\Xi_\Lambda(\beta,\varsigma) &= \left\langle \exp\left[2\varsigma e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \cos\left(\beta q\phi(\mathbf{r})\right)\right]\right\rangle \\
&= \frac{\int \mathcal{D}\phi \exp \int \left[2\varsigma e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \cos\left(\beta q\phi(\mathbf{r})\right) + \frac{\beta}{2s_d}\phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})\right] d\mathbf{r}}{\int \mathcal{D}\phi e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}}}
\end{aligned} \tag{4.18}$$

where we have used (4.10). The term in square brackets in (4.18) is quite similar to the Lagrangian density of the sine-Gordon field theory. If we write

$$\Xi_\Lambda = \frac{\int \mathcal{D}\phi e^{-S[\phi]}}{\int \mathcal{D}\phi} \tag{4.19}$$

where $S[\phi] = \int \mathcal{L} d\mathbf{r}$ and

$$\mathcal{L} = -2\varsigma e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \cos\left(\beta q \phi(\mathbf{r})\right) - \frac{\beta}{2s_d} \phi(\mathbf{r}) \boldsymbol{\Delta} \phi(\mathbf{r}) \tag{4.20}$$

using this we can find the classical equation of motion for the fields $\phi(\mathbf{r})$ demanding that the variation of the action functional equals zero:

$$\frac{\delta \mathcal{L}}{\delta \phi(\mathbf{r})} = -2\varsigma \beta q e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})} \sin \beta q \phi(\mathbf{r}) - \frac{\beta}{2s_d} 2 \boldsymbol{\Delta} \phi(\mathbf{r}) = 0 \tag{4.21}$$

and simplifying we have

$$\boldsymbol{\Delta} \phi(\mathbf{r}) - m^2 \sin \beta q \phi(\mathbf{r}) = 0 \tag{4.22}$$

where $m^2 = 2s_d \varsigma q e^{\frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})}$. (4.22) is the equation of motion for the fields $\phi(\mathbf{r})$ it is known as the sine Gordon equation, so is the name of the transformation.

4.2 Sine-Gordon Theory in the Debye-Hückel Regime

Although (4.5) is a general, exact expression, for the Grand Partition Function, it cannot be evaluated analytically because the complicated nature of the functional integral involved. However, for the regime we are interested in, that is the Debye-Hückel high temperature low density regime, the integrals involved are Gaussian, and can be easily evaluated.

To see this first note that in the Debye-Hückel regime we can write

$$e^{\beta\left[-q_\alpha i\phi(\mathbf{r}) + \frac{1}{2}q_\alpha^2 V_{S-E}(\mathbf{r})\right]} \simeq 1 - \beta q_\alpha i \phi(\mathbf{r}) + \frac{1}{2}\beta q_\alpha^2 V_{S-E}(\mathbf{r}) - \frac{\left(\beta q_\alpha \phi(\mathbf{r})\right)^2}{2} \tag{4.23}$$

where we neglect terms of order $\left(\beta q_\alpha^2\right)^2$ and $\left(\beta q_\alpha^2 \varsigma_\alpha^{1/3}\right)^2$ for the two and three dimensional cases respectively. Introducing this in (4.16) we have

$$\Xi_\Lambda(\beta,\varsigma) = \left\langle \exp\left[\sum_\alpha \varsigma_\alpha \int \left(1-\beta q_\alpha i\phi(\mathbf{r}) + \frac{1}{2}\beta q_\alpha^2 V_{S-E}(\mathbf{r}) - \frac{(\beta q_\alpha \phi(\mathbf{r}))^2}{2}\right) d\mathbf{r}\right]\right\rangle \tag{4.24}$$

let us assume for simplicity that the pseudo-neutrality property of Coulomb systems holds[1]: $\sum_\alpha \varsigma_\alpha q_\alpha$=0. Then, the term that is lineal in $\phi(\mathbf{r})$ in the above expression equals zero

$$\sum_\alpha \varsigma_\alpha \beta q_\alpha \phi(\mathbf{r}) = 0 \tag{4.25}$$

then we have that $\Xi_\Lambda(\beta,\varsigma)$ in the Debye-Hückel regime may be given as

$$\begin{aligned} &\left\langle \exp\left[\sum_\alpha \varsigma_\alpha \int \left(-\frac{(\beta q_\alpha \phi(\mathbf{r}))^2}{2} + \frac{1}{2}\beta q_\alpha^2 V_{S-E}(\mathbf{r})\right) d\mathbf{r}\right]\right\rangle e^{\sum_\alpha \Lambda\varsigma_\alpha} \\ =& \left\langle \exp\left[\sum_\alpha \varsigma_\alpha \int \left(-\frac{(\beta q_\alpha \phi(\mathbf{r}))^2}{2} - \frac{1}{2}\sum_{k=1} \frac{\beta q_\alpha^2 s_d}{\lambda_k^0} \left|\psi_k^0(\mathbf{r})\right|^2\right) d\mathbf{r}\right]\right\rangle e^{\sum_\alpha \Lambda\varsigma_\alpha} \end{aligned} \tag{4.26}$$

where we have used the explicit form of the self energy operator (4.3). Using the normalization condition$\int \left|\psi_k^0(\mathbf{r}_\alpha)\right|^2 d\mathbf{r} = 1$ for the eigenfunctions of $V_{S-E}(\mathbf{r}_\alpha)$ we have for $\Xi_\Lambda(\beta,\varsigma)$

$$\begin{aligned} &\left\langle \exp\left[\int \left(\sum_\alpha -\frac{\varsigma_\alpha (\beta q_\alpha \phi(\mathbf{r}))^2}{2}\right) d\mathbf{r} - \frac{1}{2}\sum_{\alpha=1}^{r}\sum_{k=1} \frac{s_d \varsigma_\alpha \beta q_\alpha^2}{\lambda_k^0}\right]\right\rangle e^{\sum_\alpha \Lambda\varsigma_\alpha} \\ =& \left\langle \exp\left[\int \left(\sum_\alpha -\frac{\varsigma_\alpha (\beta q_\alpha \phi(\mathbf{r}))^2}{2}\right) d\mathbf{r}\right]\right\rangle e^{\sum_{\alpha=1}^{r}\sum_{k=1} -\frac{1}{2}\frac{\beta\varsigma_\alpha q_\alpha^2 s_d}{\lambda_k^0}} e^{\sum_\alpha \Lambda\varsigma_\alpha} \end{aligned} \tag{4.27}$$

where we putted outside the average brackets the term that has to do with the self energies, since it now doesn't depend on $\phi(\mathbf{r})$. Using the definition (4.10), the averaged quantity is equal to

$$\frac{1}{Z_0}\int \mathcal{D}\phi \exp\left[\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r} - \int \left(\sum_\alpha \frac{\varsigma_\alpha (\beta q_\alpha \phi(\mathbf{r}))^2}{2}\right) d\mathbf{r}\right] \tag{4.28}$$

which can be written as

$$\frac{1}{Z_0}\int \mathcal{D}\phi \exp\left[\frac{1}{2}\int \phi(\mathbf{r})\left(\frac{\beta\boldsymbol{\Delta}}{s_d} - \sum_\alpha \varsigma_\alpha (\beta q_\alpha)^2\right)\phi(\mathbf{r})d\mathbf{r}\right] \tag{4.29}$$

[1]A a more detailed discussion see on this point is presented in chapter 5.

now we note that this is simply a Gaussian integration on ϕ. It can be easily evaluated using the well know formula [12]

$$\int d\mathbf{X} e^{-\frac{1}{2}\mathbf{X}\cdot\mathbf{A}\cdot\mathbf{X}+\mathbf{B}\cdot\mathbf{X}} = \left[\det \frac{\mathbf{A}}{2\pi}\right]^{-1/2} e^{\frac{1}{2}\mathbf{B}\cdot\mathbf{A}^{-1}\cdot\mathbf{B}} \tag{4.30}$$

with $\mathbf{A} = \left(\sum_\alpha \varsigma_\alpha (\beta q_\alpha)^2 - \frac{\beta\boldsymbol{\Delta}}{s_d}\right)$ and $\phi(\mathbf{r}) = \mathbf{X}$ as before. Replacing this we have for the averaged quantity

$$\frac{1}{Z_0}\left(\det\left[-\frac{1}{2\pi}\left(\frac{\beta\boldsymbol{\Delta}}{s_d} - \sum_\alpha \varsigma_\alpha (\beta q_\alpha)^2\right)\right]\right)^{-1/2} \tag{4.31}$$

$Z_0 = \int \mathcal{D}\phi e^{\frac{\beta}{2s_d}\int \phi(\mathbf{r})\boldsymbol{\Delta}\phi(\mathbf{r})d\mathbf{r}}$ has the same structure with $\mathbf{A} = -\frac{\beta\boldsymbol{\Delta}}{\mathbf{s_d}}$. Integrating to find Z_0 and putting all together we have that the averaged quantity equals

$$\left(\frac{\det\left[-\frac{1}{2\pi}\left(\frac{\beta\boldsymbol{\Delta}}{s_d} - \sum_\alpha \varsigma_\alpha (\beta q_\alpha)^2\right)\right]}{\det\left[-\frac{1}{2\pi}\left(\frac{\beta\boldsymbol{\Delta}}{s_d}\right)\right]}\right)^{-1/2} \tag{4.32}$$

simplifying

$$\left(\det\left[1 - \frac{\sum_\alpha s_d\varsigma_\alpha\beta q_\alpha^2}{\boldsymbol{\Delta}}\right]\right)^{-1/2} \tag{4.33}$$

let $\kappa^2 = \sum_\alpha s_d\varsigma_\alpha\beta q_\alpha^2$. Replacing this value for the averaged quantity in (4.27) we finally have

$$\Xi_\Lambda(\beta,\varsigma) = \left(\det\left(1 - \frac{\kappa^2}{\boldsymbol{\Delta}}\right) e^{\sum_k \frac{\kappa^2}{\lambda_k^0}}\right)^{-1/2} e^{\sum_\alpha \Lambda\varsigma_\alpha} \tag{4.34}$$

since the determinant of any matrix, in particular the matrix $[\mathbf{M}] =: \left(1 - \frac{\kappa^2}{\boldsymbol{\Delta}}\right)$ representing the operator involved in equation (4.34) is an invariant, it will not change if we represent $[\mathbf{M}]$ in the base in which it is diagonal. Then $\det[\mathbf{M}]$ is just the product of the elements of its diagonal, that is, its eigenvalues. After doing this we finally obtain

$$\Xi_\Lambda(\beta,\varsigma) = \left(\prod_k \left[\left(1 - \frac{\kappa^2}{\lambda_k}\right) e^{\frac{\kappa^2}{\lambda_k^0}}\right]\right)^{-1/2} e^{\sum_\alpha \Lambda\varsigma_\alpha} \tag{4.35}$$

where λ_k are the eigenvalues of the Laplace operator calculated using the boundary conditions. Note that (4.35) is a product of factors that are a function of the eigenvalues λ_i of $\mathbf{\Delta}$. The $\lambda_i s$ depend on the shape of the domain in which the Coulomb system lies. They constitute the natural way to introduce the geometric information on the domain to calculate the corresponding finite size corrections to the thermodynamic functions.

Chapter 5

Finite-Size Corrections for Coulomb Systems in the Debye-Hückel Regime

In this chapter we present an article that will be published in J. Phys. A. It gathers some of the results presented in detail up to now. Additionally it contains specific examples of application of our method to the calculation of finite size corrections to the free energy. The detailed calculations of these three examples are included in appendix B and C. Another interesting aspect included is a discussion on the relation of our results with the usual Debye-Hückel theory for a confined Coulomb system with Dirichlet boundary conditions for the electric potential. A detailed appendix concerning the pseudo-neutrality property of Coulomb systems is included. Some notation differ slightly from the rest of the thesis, since the article is self contained, it certainly won't be a problem to the reader.

Chapter 6

Calculation of the Finite Size Corrections for the Free Energy: Additional Examples

In this chapter we develop further examples on the calculation of finite size corrections for several geometries in two and three dimensions. They are interesting because some of this finite size corrections have been found by other methods before [9],[10], [46], what allows us to compare our results, like in the case of a Coulomb system confined between two infinite planes or on a spherical surface. Some problems considered in this chapter, especially those related with three dimensions are less known, which also makes them interesting. In the case of Coulomb systems confined in domains of two dimensions, there are predictions from conformal field theory that allow the evaluation of the finite size corrections in the free energy [22],[16]. We have tried to include the details of the calculations in each case. Some long but essential are relegated to the appendices.

6.1 Spherical Surface

To continue with the study of examples in two dimensions let us consider the notable case of a Coulomb system lying on a spherical surface. In this particular example is necessary to modify slightly the formulation of the eigenvalue problem, because rigorously, the Coulomb potential for a system on a sphere do not exist, since in this case the Poisson equation has no solution; and the sine-Gordon transformation is not strictly applicable [30] and we can't even write (4.2) for this case. Nevertheless, it is possible define a logarithmic potential that has shown to be useful in doing calculations, it is defined in terms of the angle α, the angle formed by the vectors which determine the positions of the particles on the surface

$$V(\alpha) = -\ln\left[\frac{2R\sin\frac{\alpha}{2}}{L}\right] = -\ln\left[\sin\frac{\alpha}{2}\right] - \ln\frac{2R}{L} \tag{6.1}$$

note that (6.1) tend to the usual logarithmic potential for small α. This potential is the solution of the Poisson equation for a point-like particle and a neutralizing uniform background [11]:

$$\Delta V = -2\pi\left[\delta - \frac{1}{4\pi R^2}\right] \tag{6.2}$$

We can use the spectral representation for this potential using the formula [50]

$$-\ln\left[\sin\frac{\alpha}{2}\right] = \sum_{l=1}^{\infty}\frac{2l+1}{2l(l+1)}P_l(\cos\alpha) + \frac{1}{2}P_0(\cos\alpha) \tag{6.3}$$

where the P_l are the Legendre functions of order l. Then

$$V(\alpha) = \sum_{l=1}^{\infty}\frac{2l+1}{2l(l+1)}P_l(\cos\alpha) + \left[\frac{1}{2} - \ln\frac{2R}{L}\right]P_0(\cos\alpha) \tag{6.4}$$

note that we have used $P_0(\cos\alpha) = 1$. Then, the eigenvalues of the operator inverse of the operator V, which are the eigenvalues that appear in the sine-Gordon transformation, are the eigenvalues corresponding to the inverse operator of (6.4), which are easily found using the identity

$$P_l(\cos\alpha) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y^*_{lm}(\theta',\varphi')Y_{lm}(\theta,\varphi) \tag{6.5}$$

where α is again the angle between the vectors that determine the positions of the particles on the surface. Then we can write

$$\begin{aligned} V(\alpha) &= \sum_{l=1}^{\infty}\frac{4\pi}{2l(l+1)}\sum_{m=-l\ (l\neq 0)}^{l} Y^*_{lm}(\theta',\varphi')Y_{lm}(\theta,\varphi) \\ &\quad + \left[\frac{1}{2} - \ln\frac{2R}{L}\right] 4\pi Y^*_{00}(\theta',\varphi')Y_{00}(\theta,\varphi) \end{aligned} \tag{6.6}$$

then the spectral decomposition for the operator inverse to (6.6) is given by

$$\begin{aligned} \left(\frac{V(\alpha)}{2\pi}\right)^{-1} &= \sum_{l.m\ (l\neq 0)}^{\infty} l(l+1)Y^*_{lm}(\theta',\varphi')Y_{lm}(\theta,\varphi) \\ &\quad + \frac{1}{2}\left[\frac{1}{2} - \ln\frac{2R}{L}\right]^{-1} Y^*_{00}(\theta',\varphi')Y_{00}(\theta,\varphi). \end{aligned} \tag{6.7}$$

summarizing, the eigenvalues involved in the sine-Gordon transformation for a sphere surface of radius 1 are

$$\lambda_l = -l(l+1) \qquad \text{for} \qquad l = 1, 2, ... \tag{6.8}$$

$$\lambda_0 = -\frac{1}{2}\left[\frac{1}{2} - \ln\frac{2R}{L}\right]^{-1} \quad \text{for} \quad l = 0 \tag{6.9}$$

each of these eigenvalues is degenerated with degeneration $2l+1$. In what follows we consider apart the eigenvalue λ_0 (not to be confused with the spectrum of the non-confined case λ_k^0). Using (4.35) we see that in the case of a spherical surface of radius R, the grand potential is given by

$$\beta\Omega = \frac{1}{2}\ln\left[\prod_{l=1}^{\infty}\left(1-\frac{R^2\kappa^2}{\lambda_l}\right)^{2l+1}\left(1-\frac{R^2\kappa^2}{\lambda_0}\right)\right]+\frac{1}{2}\sum_k\frac{\kappa^2}{\lambda_k^0}-\sum_\alpha\Lambda\varsigma_\alpha \tag{6.10}$$

the infinite product can be written as an infinite sum using the properties of the logarithm function

$$\ln\left[\prod_{l=1}^{\infty}\left(1+\frac{R^2\kappa^2}{l(l+1)}\right)^{2l+1}\right]=\sum_{l=1}^{\infty}(2l+1)\ln\left(1+\frac{R^2\kappa^2}{l(l+1)}\right) \tag{6.11}$$

let us introduce the non dimensional parameter $\alpha = R\kappa$ which characterize the size of the system. Then we can write for the logarithm in the first term of the right side of (6.10)

$$\ln\left(1-\frac{R^2\kappa^2}{\lambda_0}\right)+\sum_{l=1}^{\infty}(2l+1)\ln\left(1+\frac{\alpha^2}{l(l+1)}\right) \tag{6.12}$$

after regularizing the infinite sum with an upper cutoff N we can use the Euler-McLaurin summation formula[1] to evaluate the second term in the right side of (6.12). Once this is done, we take the limit $N\to\infty$, and we find that (6.12) equals

$$\begin{aligned}
&\ln\left(1-\frac{\alpha^2}{\lambda_0}\right)+\alpha^2\left(1+2\ln\frac{N}{\alpha}\right)-\frac{4}{3}\ln\alpha+O(\alpha^0)\\
=\;&\ln\left(\frac{1}{\alpha^2}-\frac{1}{\lambda_0}\right)+\alpha^2\left(1+2\ln\frac{N}{\alpha}\right)-\frac{4}{3}\ln\alpha+\ln\alpha^2+O(R^0)\\
=\;&\alpha^2\left(1+2\ln\frac{N}{\alpha}\right)+\frac{2}{3}\ln\alpha+o(\ln\alpha)
\end{aligned} \tag{6.13}$$

where using (6.9) we note that the first term in (6.13) gives terms of order $o(\ln\alpha)$, that is, smaller than $\ln\alpha$. Then, from (6.11) we find

$$\ln\left[\prod_{l=1}^{\infty}\left(1+\frac{R^2\kappa^2}{l(l+1)}\right)^{2l+1}\left(1-\frac{R^2\kappa^2}{\lambda_0}\right)\right]=\alpha^2\left(1+2\ln\frac{N}{\alpha}\right)+\frac{2}{3}\ln\alpha+o(\ln\alpha) \tag{6.14}$$

[1] In this case the Euler-McLaurin formula is enough to obtain the logarithmic corrections we are looking for, however, in one looks for terms of smaller order this formula fails, and an expansion similar to one the used in ref. [11] is required.

using (6.10) we have

$$\begin{aligned}
\beta\Omega &= \alpha^2\left(\frac{1}{2}+\ln\frac{N}{\alpha}\right)+\frac{1}{3}\ln\alpha+\frac{1}{2}\sum_k\frac{\kappa^2}{\lambda_k^0}-\sum_\alpha\Lambda\varsigma_\alpha+o(\ln\alpha)\\
&= 4\pi R^2\left(\frac{\kappa^2}{4\pi}\left(\frac{1}{2}+\ln\frac{N}{\alpha}\right)\right)+\left(-\frac{1}{2}\frac{2\pi}{(2\pi)^2}\kappa^2\ln\frac{k_{\max}}{k_{\min}}-\sum_\alpha\varsigma_\alpha\right)\Lambda+\frac{1}{3}\ln\alpha+o(\ln\alpha)\\
&= \left(\frac{\kappa^2}{4\pi}\left(\frac{1}{2}+\ln\frac{N}{\alpha}\right)-\frac{\kappa^2}{4\pi}\ln\frac{k_{\max}}{k_{\min}}-\sum_\alpha\varsigma_\alpha\right)\Lambda+\frac{1}{3}\ln a+o(\ln\alpha) \qquad (6.15)
\end{aligned}$$

where $\Lambda = 4\pi R^2$ is the "volume" (surface) of the system. Equating the first term of the right side with the bulk grand potential for the case of two dimensions and remembering that $k_{\min} = \frac{2e^{-\gamma}}{L}$

$$\begin{aligned}
\frac{\kappa^2}{4\pi}\left(\frac{1}{2}+\ln\frac{N}{\alpha}-\ln\frac{k_{\max}}{k_{\min}}\right)-\sum_\alpha\varsigma_\alpha &= \frac{\kappa^2}{4\pi}\left[-\ln\frac{\kappa L}{2}-\gamma+\frac{1}{2}\right]-\sum_\alpha\varsigma_\alpha \qquad (6.16)\\
\left(\frac{1}{2}+\ln\frac{N}{\alpha}-\ln\frac{k_{\max}}{k_{\min}}\right) &= \left[\ln k_{\min}-\ln\kappa+\frac{1}{2}\right]\\
-\ln k_{\max} &= -\ln\kappa-\ln\frac{N}{\alpha}
\end{aligned}$$

then we have

$$k_{\max}=\frac{\kappa N}{\alpha}=\frac{N}{R} \qquad (6.17)$$

finally the grand potential is

$$\beta\Omega=\left(\frac{\kappa^2}{4\pi}\left[-\ln\frac{\kappa L}{2}-\gamma+\frac{1}{2}\right]-\sum_\alpha\varsigma_\alpha\right)4\pi R^2+\frac{1}{3}\ln\alpha+o(\ln\alpha) \qquad (6.18)$$

this expression gives the expected finite size logarithmic correction and the correct value for the coefficient depending on the Euler characteristic, which in the case of a spherical surface equals $\frac{1}{3}$.

6.2 Space Between Two Infinite Planes: The Slab in 3D

We begin the study of three dimensional finite size corrections considering the corrections for a system confined in the space between two infinite planes separated by a distance w. In the direction normal to the planes, the eigenvalues appear quantized because of the imposition of Dirichlet boundary conditions. Let us take the $x-$axis of our coordinate system along in this direction. In any direction parallel to the planes, that is orthogonal to the $x-$axis, there is no confinement. Then we can write the eigenfunctions as

$$\Psi(\mathbf{r}) \propto e^{i(\mathbf{k}_\perp \cdot \mathbf{r}_\perp)} \sin x k_x \tag{6.19}$$

where $\mathbf{k}_\perp \cdot \mathbf{r}_\perp = y k_y + z k_z$, and satisfying the boundary conditions $\Psi(0, y, z) = 0$ and $\Psi(w, y, z) = 0$. Which means that we must have $\sin w k_x = 0$ that is $k_x = \frac{n\pi}{w}$. Then in this case, using the eigenvalue equation for the Laplace operator $\Delta\Psi(\mathbf{r}) = \lambda\Psi(\mathbf{r})$ we have

$$\lambda_{n,\mathbf{k}_\perp} = -\left(\frac{n\pi}{w}\right)^2 - \mathbf{k}_\perp^2,\ n = 1, 2...;\ \mathbf{k}_\perp \in \mathcal{R}^2 \tag{6.20}$$

Using (4.35) and (6.20) we have

$$\begin{aligned} \beta\Omega &= \frac{1}{2} \ln \prod_k \left(1 - \frac{\kappa^2}{\lambda_k}\right) + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda \varsigma_\alpha \\ &= \frac{1}{2} \frac{A}{(2\pi)^2} \int \ln \prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2 + \mathbf{k}_\perp^2}\right) d\mathbf{k}_\perp + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda \varsigma_\alpha \end{aligned} \tag{6.21}$$

where we integrate over the continuous part of the spectrum. A represent the area of the planes. Note that the infinite product over the quantized index n starts in 1, since $\Psi(\mathbf{r})$ is not an eigenfunction of Δ when $k_x = 0$.

To calculate the infinite product in first term of (6.21) consider the identity [50]

$$\prod_{n=1}^{\infty}\left(1-\frac{x}{n-a}\right)\left(1+\frac{x}{n+a}\right)=\frac{a}{x+a}\frac{\sin\pi(x+a)}{\sin\pi a} \tag{6.22}$$

expanding the factors in the right side product symbol we have

$$\begin{aligned}\left(1-\frac{x}{n-a}\right)\left(1+\frac{x}{n+a}\right) &= 1-\frac{x^2}{n^2-a^2}+\frac{x\,(n-a)-(n+a)\,x}{n^2-a^2} \\ &= 1-\frac{x^2}{n^2-a^2}-\frac{2ax}{n^2-a^2} \\ &= 1-\frac{x^2+2ax}{n^2-a^2}\end{aligned} \tag{6.23}$$

then we can write

$$\prod_{n=1}^{\infty}\left(1-\frac{x^2+2ax}{n^2-a^2}\right)=\frac{a}{x+a}\frac{\sin\pi(x+a)}{\sin\pi a} \tag{6.24}$$

with the change of variables $u=ia$ and $z=ix$ we find

$$\begin{aligned}\prod_{n=1}^{\infty}\left(1+\frac{z^2+2uz}{n^2+u^2}\right) &= \frac{u}{z+u}\frac{\sin\pi i(z+u)}{\sin\pi iu}=\frac{u}{z+u}\frac{e^{-\pi(z+u)}-e^{\pi(z+u)}}{e^{-\pi u}-e^{\pi u}} \\ &= \frac{u}{z+u}\frac{\sinh(\pi(z+u))}{\sinh\pi u}\end{aligned} \tag{6.25}$$

finally the infinite product in (6.21) can be written as

$$\prod_{n=1}^{\infty}\left(1+\frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2+\mathbf{k}_\perp^2}\right)=\prod_{n=1}^{\infty}\left(1+\frac{\frac{w^2\kappa^2}{\pi^2}}{\left(n^2+\frac{w^2\mathbf{k}_\perp^2}{\pi^2}\right)}\right) \tag{6.26}$$

and can be evaluated using (6.25) identifying

$$u^2 = \frac{w^2\mathbf{k}_\perp^2}{\pi^2} \tag{6.27}$$

$$z^2+2uz = \frac{w^2\kappa^2}{\pi^2} \tag{6.28}$$

from (6.27) and (6.28) we can find the value of $z+u$

$$z+u=\pm\sqrt{\frac{w^2\kappa^2}{\pi^2}+u^2}=\pm\sqrt{\frac{w^2\kappa^2}{\pi^2}+\frac{w^2\mathbf{k}_\perp^2}{\pi^2}} \tag{6.29}$$

and using (6.25) we have

$$\prod_{n=1}^{\infty}\left(1+\frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2+\mathbf{k}_\perp^2}\right)=\frac{\mathbf{k}_\perp}{\sqrt{\kappa^2+\mathbf{k}_\perp^2}}\frac{\sinh\left(w\sqrt{\kappa^2+\mathbf{k}_\perp^2}\right)}{\sinh w\mathbf{k}_\perp} \tag{6.30}$$

note that in order to obtain this identity we can use any sign for $z+u$ in (6.29) since sinh is an odd function.

Returning to (6.21) and keeping in mind (6.30) we note that the integrals on $\mathbf{k}_\perp$ diverge. We regularize them introducing the upper cutoff $k_{\max}$. In polar coordinates we can write $\mathbf{k}_\perp=\sqrt{k_y^2+k_z^2}=k$ and we have for the integral of the infinite product in (6.21)

$$\begin{aligned}
&\int \ln\prod_{n=1}^{\infty}\left(1+\frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2+\mathbf{k}_\perp^2}\right)d\mathbf{k}_\perp^2 \qquad (6.31)\\
=&\int_0^{2\pi}\int_0^{k_{\max}}\ln\left[\frac{k}{\sqrt{\kappa^2+k^2}}\frac{\sinh\left(w\sqrt{\kappa^2+k^2}\right)}{\sinh wk}\right]kdkd\varphi\\
=&\ 2\pi\int_0^{k_{\max}}\ln\left[\frac{k}{\sqrt{\kappa^2+k^2}}\right]kdk+2\pi\int_0^{k_{\max}}\ln\left[\sinh\left(w\sqrt{\kappa^2+k^2}\right)\right]kdk\\
&-2\pi\int_0^{k_{\max}}\ln\left[\sinh wk\right]kdk
\end{aligned}$$

performing these integrations we have

$$\begin{aligned}
&\int_0^{k_{\max}}\ln\left[\frac{k}{\sqrt{\kappa^2+k^2}}\right]kdk= \qquad (6.32)\\
&\frac{1}{2}\left[k_{\max}^2\ln k_{\max}+\kappa^2\ln\kappa-\frac{1}{2}\left(\kappa^2+k_{\max}^2\right)\ln\left(\kappa^2+k_{\max}^2\right)\right]
\end{aligned}$$

$$\begin{aligned}
\int_0^{k_{\max}}\ln\left(e^{w\sqrt{\kappa^2+k^2}}-e^{-w\sqrt{\kappa^2+k^2}}\right)kdk &\simeq \int_0^{k_{\max}}\ln\left(e^{w\sqrt{\kappa^2+k^2}}\right)kdk \qquad (6.33)\\
&= w\int_0^{k_{\max}}\sqrt{\kappa^2+k^2}kdk\\
&= w\left[\frac{1}{3}\left(\kappa^2+k_{\max}^2\right)^{3/2}-\frac{1}{3}\kappa^3\right]\\
&\simeq \frac{w}{3}\left[k_{\max}^3+\frac{3}{2}\kappa^2k_{\max}-\kappa^3\right]
\end{aligned}$$

$$\begin{aligned}\int_0^{k_{\text{max}}} \ln\left[e^{wk} - e^{-wk}\right] kdk &= \int_0^{k_{\text{max}}} \ln\left[e^{wk}\left(1 - e^{-2wk}\right)\right] kdk \\ &= \int_0^{k_{\text{max}}} \left[wk + \ln\left(1 - e^{-2wk}\right)\right] kdk \\ &= \frac{wk_{\text{max}}^3}{3} + \frac{1}{4w^2}\int_0^{2wk_{\text{max}}} u \ln\left(1 - e^{-u}\right) du\end{aligned} \tag{6.34}$$

where we have made the change of variables $u = 2wk$. The last integration can be done using integration by parts

$$\begin{aligned}&\int_0^{2wk_{\text{max}}} u \ln\left(1 - e^{-u}\right) du \\ =& \left[\frac{u^2}{2}\ln\left(1 - e^{-u}\right)\Big|_0^{2wk_{\text{max}}} - \frac{1}{2}\int_0^{2wk_{\text{max}}} \frac{u}{1 - e^{-u}} du\right] \\ =& \left[2\left(wk_{\text{max}}\right)^2 \ln\left(1 - e^{-2wk_{\text{max}}}\right) - \frac{1}{2}\Gamma(3)\varsigma(3)\right] \\ \simeq& -\varsigma(3)\end{aligned} \tag{6.35}$$

which is valid for $k_{\text{max}} \to \infty$. Note that we have used a well known integral representation of the Riemann zeta function $\varsigma(z)$ [47]

$$\varsigma(z) = \frac{1}{\Gamma(z)}\int_0^{\infty} \frac{x^{z-1}}{e^x - 1} dx \tag{6.36}$$

and the fact that for $k_{\text{max}} \to \infty$, $k_{\text{max}}^2 \ln\left(1 - e^{-2wk_{\text{max}}}\right) = 0$. Finally

$$\int_0^{k_{\text{max}}} \ln\left(1 - e^{-2wk}\right) kdk = \frac{wk_{\text{max}}^3}{3} - \frac{\varsigma(3)}{4w^2} \tag{6.37}$$

putting all together we have

$$\begin{aligned}&\frac{1}{2}\frac{A}{(2\pi)^2}\int \ln \prod_{n=1}^{\infty}\left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2 + \mathbf{k}_{\perp}^2}\right) d\mathbf{k}_{\perp}^2 \\ =& \frac{A}{8\pi}\left[k_{\text{max}}^2 \ln k_{\text{max}} + \kappa^2 \ln \kappa - \frac{1}{2}\left(\kappa^2 + k_{\text{max}}^2\right)\ln\left(\kappa^2 + k_{\text{max}}^2\right)\right] \\ &+ \frac{1}{12\pi}\Lambda\left[\frac{3}{2}\kappa^2 k_{\text{max}} - \kappa^3\right] + A\frac{\varsigma(3)}{16\pi w^2}\end{aligned} \tag{6.38}$$

where we have written $\Lambda = Aw$ for the volume of the system.

We still have to evaluate the last two terms in (6.21). Since the λ_k^0 refers to the eigenvalues of Δ for a non-confined system, we can change the summation by an integral over all space. In spherical coordinates we have

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha = -\frac{1}{2}\frac{\Lambda m^2}{(2\pi)^3}\int d\Omega \int_0^\infty \frac{k^2 dk}{k^2} - \sum_\alpha \Lambda\varsigma_\alpha \tag{6.39}$$

as expected, the integration in the variable k diverges for $k \to \infty$. This divergence is the one that cancels the divergence of the first term in the right side of (6.21). To see how this works we introduce the upper limit $K_{\max}$ Then,

$$-\frac{1}{2}\frac{\Lambda m^2}{(2\pi)^3}\int d\Omega \int_0^{K_{\max}} \frac{k^2 dk}{k^2} - \sum_\alpha \Lambda\varsigma_\alpha = \left(-\frac{\kappa^2}{4\pi^2}K_{\max} - \sum_\alpha \varsigma_\alpha\right)\Lambda \tag{6.40}$$

and using (6.38) the bulk grand potential per volume is

$$\begin{aligned} \frac{\beta\Omega_{bulk}}{\Lambda} &= \frac{1}{12\pi}\left[\frac{3}{2}\kappa^2 k_{\max} - \kappa^3\right] - \frac{\kappa^2}{4\pi^2}K_{\max} - \sum_\alpha \varsigma_\alpha \\ &= -\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha + \frac{1}{8\pi}\kappa^2 k_{\max} - \frac{\kappa^2}{4\pi^2}K_{\max} \end{aligned} \tag{6.41}$$

equating with the bulk potential for non-confined systems in three dimensions (A.1) we find

$$\frac{1}{8\pi}\kappa^2 k_{\max} - \frac{\kappa^2}{4\pi^2}K_{\max} = 0 \tag{6.42}$$

or

$$k_{\max} = \frac{2}{\pi}K_{\max} \tag{6.43}$$

then, the two upper limits are proportional as expected in order to cancel the divergence of Ω and

$$\frac{\beta\Omega_{bulk}}{\Lambda} = \left[-\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha\right] \tag{6.44}$$

as expected.

Now, we can find also the surface tension, from (6.38) we have

$$\frac{\beta\Omega_{surface}}{A} = \frac{1}{8\pi}\left[\kappa^2 \ln\frac{\kappa}{k_{\max}} - \frac{\kappa^2}{2}\right] \tag{6.45}$$

Two interesting aspects of this expression are worthy of being mentioned. First note that taking the limit $k_{\max} \to \infty$ in (6.45) (which is equivalent to take $K_{\max} \to \infty$ since they are proportional) we see that the surface tension diverges as

$$\beta\Omega_{surface} \to -\frac{A\kappa^2}{8\pi}\ln\frac{k_{\max}}{\kappa} = -\frac{\mathcal{A}\kappa^2}{16\pi}\ln\frac{k_{\max}}{\kappa} \tag{6.46}$$

where $\mathcal{A} = 2A$ is the total area of the boundary of the system. This divergence in the surface tension can be understood if we note that the particles tend to move to the frontier because of the ideal conductor character of the boundaries. This is easy to see from a physical argument: maintain the zero potential condition on the boundaries is equivalent to introduce an image charge at the other side of the boundary for each particle in the system. Particles near the boundary “feel” an attraction to the boundary own to their proximity with its corresponding images. This effect makes the surface grand potential diverge in a way that depends on the number of particles near to the wall, since

$$A\kappa^2 = \sum_\alpha A\varsigma_\alpha s_d \beta q_\alpha^2 \tag{6.47}$$

where $A\varsigma_\alpha = A\bar{n}_\alpha$ in the Debye-Hückel approximation, gives the number of particles of specie α near the boundary. This explain the divergence of the surface tension. Similar effects will be found when we study other cases in three dimensions however this divergence in the surface tension is not presented for systems confined in two dimensions. That is because in this case the interaction of the particle and its image is proportional to the logarithm of its separation, and this function is integrable for small separation distances, that is, for particles near to the boundary. On the contrary, in the case of three dimensions, the interaction is proportional to the inverse of the separation distance between the charge and its image, and the integral in this case diverges for small separation distances.

The second interesting aspect is related to the finite-size corrections. In this case we don't have logarithmic finite size corrections. One could expect that the next important order of finite size corrections would depend on w^{-1}. Instead we found a finite size correction depending on w^{-2}

$$\frac{\varsigma(3)}{16\pi w^2} \tag{6.48}$$

This agree with the results by Jancovici and Téllez for systems with ideal conductor boundaries [9]. These authors predict that the universal finite-size correction for a slab in d dimensions must be

$$\Gamma(d/2)\frac{\varsigma(d)}{2^d \pi^{d/2} w^{d-1}} \tag{6.49}$$

which in our case $d = 3$ gives

$$\Gamma(3/2)\frac{\varsigma(3)}{2^3 \pi^{3/2} w^2} = \frac{\sqrt{\pi}}{2}\frac{\varsigma(3)}{8\pi^{3/2} w^2} = \frac{\varsigma(3)}{16\pi w^2} \tag{6.50}$$

that it is exactly the finite size correction that we found. Summarizing, the expansion for the grand potential per area takes the form

$$\frac{\beta\Omega}{A} = \left[-\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha\right] w + \frac{1}{8\pi}\left[\kappa^2 \ln\frac{\kappa}{k_{\max}} - \frac{\kappa^2}{2}\right] + \frac{\varsigma(3)}{16\pi w^2} \tag{6.51}$$

6.3 Space Between Two Infinite Lines: The Slab in 2D

An interesting extension of the results of the last section is the case of a two dimensional Coulomb system confined between two infinite parallel lines spaced by a distance w. Let us assume that the confining lines are in the direction of the $y-$axis. In consequence, the eigenvalues take discrete values in the k_x direction, and the eigenfunctions in this case can be written as

$$\Psi(\mathbf{r}) \propto e^{i(k_\perp y)} \sin x k_x \tag{6.52}$$

satisfying the boundary conditions $\Psi(0, y) = 0$ and $\Psi(w, y) = 0$. Which means that we must have $\sin w k_x = 0$ that is $k_x = \frac{n\pi}{w}$. Since there is no confinement in the direction of the $y-$axis, any real number is an eigenvalue in this direction. Then in this case, using the eigenvalues equation for the Laplace operator $\Delta\Psi(\mathbf{r}) = \lambda\Psi(\mathbf{r})$ we have

$$\lambda_{n,k_\perp} = -\left(\frac{n\pi}{w}\right)^2 - k_\perp^2, \; n = 1, 2...; \; k_\perp \in \mathcal{R} \tag{6.53}$$

Using (4.35) and (6.53) we have

$$\begin{aligned} \beta\Omega &= \frac{1}{2} \ln \prod_k \left(1 - \frac{\kappa^2}{\lambda_k}\right) + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \\ &= \frac{1}{2} \frac{l}{(2\pi)} \int_{-\infty}^{\infty} \ln \prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2 + k_\perp^2}\right) dk_\perp + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \end{aligned} \tag{6.54}$$

where l is a line segment in the $y-$direction. As in the previous section, the infinite product is convergent and we can write

$$\prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2 + k_\perp^2}\right) = \frac{k_\perp}{\sqrt{\kappa^2 + k_\perp^2}} \frac{\sinh\left(w\sqrt{\kappa^2 + k_\perp^2}\right)}{\sinh w k_\perp} \tag{6.55}$$

since sinh is an odd function the whole expression is even and we can write

$$\begin{aligned}
&\int_{-\infty}^{\infty} \ln \prod_{n=1}^{\infty}\left(1+\frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2+k_\perp^2}\right) dk_\perp \\
&= 2\int_{0}^{\infty} \ln \prod_{n=1}^{\infty}\left(1+\frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2+k_\perp^2}\right) dk_\perp \\
&= 2\int_{0}^{\infty} \ln \left[\frac{k_\perp}{\sqrt{\kappa^2+k_\perp^2}} \frac{\sinh\left(w\sqrt{\kappa^2+k_\perp^2}\right)}{\sinh w k_\perp}\right] dk_\perp
\end{aligned} \tag{6.56}$$

As before, the integral in (6.56) diverges at infinity. This divergence will be cancelled with the divergence of the second term of the right hand side of (6.54). To see this let us introduce the upper limit $k_{\max}$. We can expand the logarithm in (6.56) to write the integral as

$$\int_0^{k_{\max}} \ln\left[\frac{k_\perp}{\sqrt{\kappa^2+k_\perp^2}}\right] dk_\perp + \int_0^{k_{\max}} \ln\left[\sinh\left(w\sqrt{\kappa^2+k_\perp^2}\right)\right] dk_\perp - \int_0^{k_{\max}} \ln\left[\sinh w k_\perp\right] dk_\perp \tag{6.57}$$

performing the first integration we find

$$\begin{aligned}
\int_0^{k_{\max}} \ln\left[\frac{k_\perp}{\sqrt{\kappa^2+k_\perp^2}}\right] dk_\perp &= k_{\max}\ln k_{\max} - \frac{1}{2}k_{\max}\ln\left(\kappa^2+k_{\max}^2\right) - \kappa \arctan\frac{k_{\max}}{\kappa} \\
&= -\frac{1}{2}\pi\kappa + O\left(\frac{1}{k_{\max}}\right)
\end{aligned} \tag{6.58}$$

the second integral in (6.57) can be done writing

$$\begin{aligned}
&\int_0^{k_{\max}} \ln\left(e^{w\sqrt{m^2+k_\perp^2}} - e^{-w\sqrt{m^2+k_\perp^2}}\right) dk_\perp \\
\simeq\ & \int_0^{k_{\max}} \ln\left(e^{w\sqrt{m^2+k^2}}\right) dk + O(e^{-mw}) \\
=\ & w\int_0^{k_{\max}} \sqrt{m^2+k^2}dk \\
=\ & w\left[\frac{1}{2}k_{\max}\sqrt{(\kappa^2+k_{\max}^2)} + \frac{1}{2}\kappa^2\ln\left(k_{\max}+\sqrt{(\kappa^2+k_{\max}^2)}\right) - \frac{1}{2}\kappa^2\ln\kappa\right] \\
=\ & w\left[\frac{1}{2}k_{\max}^2 + \frac{1}{2}\kappa^2\ln 2k_{\max} - \frac{1}{2}\kappa^2\ln\kappa + \frac{1}{4}\kappa^2\right] + O\left(\frac{1}{k_{\max}^2}\right)
\end{aligned} \tag{6.59}$$

where to obtain the last line we have taken the limit $k_{\max} \to \infty$. Finally the last integration in (6.57) can be easily performed writing

$$\begin{aligned}\int_0^{k_{\max}} \ln\left[e^{wk} - e^{-wk}\right] dk &= \int_0^{k_{\max}} \ln\left[e^{wk}\left(1 - e^{-2wk}\right)\right] dk \\ &= \int_0^{k_{\max}} \left[wk + \ln\left(1 - e^{-2wk}\right)\right] dk \\ &= \frac{w}{2}k_{\max}^2 + \frac{1}{2w}\int_0^{2wk_{\max}} \ln\left(1 - e^{-u}\right) du \qquad (6.60)\end{aligned}$$

where we have made the change of variables $u = 2wk$. The last integral in (6.60) converges even if we put $k_{\max} = \infty$, in fact, with a difference in the sign, it converges to the well known value for the zeta Riemann function $\varsigma(2)$

$$\int_0^{\infty} \ln\left(1 - e^{-u}\right) du = -\frac{\pi^2}{6} = -\varsigma(2) \qquad (6.61)$$

Then, putting all this together we can write

$$\begin{aligned}&\int_{-\infty}^{\infty} \ln \prod_{n=1}^{\infty}\left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{w}\right)^2 + k_\perp^2}\right) dk_\perp \qquad (6.62)\\ &= -\pi\kappa + w\left[\kappa^2 \ln 2k_{\max} - \kappa^2 \ln\kappa + \frac{1}{2}\kappa^2\right] + \frac{1}{w}\varsigma(2)\end{aligned}$$

Now, the last two terms in the right side of (6.54) can be written as

$$\begin{aligned}&\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \\ &= -\frac{\Lambda\kappa^2}{4\pi}\int_{k_{\min}}^{K_{\max}} \frac{dk}{k} - \sum_\alpha \Lambda\varsigma_\alpha \\ &= -\frac{\kappa^2}{4\pi}\left(\ln K_{\max} - \ln k_{\min}\right)\Lambda - \sum_\alpha \Lambda\varsigma_\alpha \qquad (6.63)\end{aligned}$$

where $\Lambda = lw$ is the extension (area) of the system between a portion of length l of the confining lines. Similarly to the case of the slab in 3D, we introduced the limits $K_{\max}$ and $k_{\min}$ to avoid the otherwise divergent integral $\int_0^\infty \frac{dk}{k}$. Replacing the above results in (6.54) the grand potential gives

$$\begin{aligned} \beta\Omega &= \frac{l}{4\pi}\left(w\left[\kappa^2 \ln 2k_{\max} - \kappa^2 \ln\kappa + \frac{1}{2}\kappa^2\right] + \frac{1}{w}\varsigma(2) - \pi\kappa\right) \\ &\quad -\frac{\kappa^2}{4\pi}\left(\ln K_{\max} - \ln k_{\min}\right)\Lambda - \sum_\alpha \Lambda\varsigma_\alpha \end{aligned} \tag{6.64}$$

from (6.64) we can find the bulk grand potential per area Λ

$$\frac{\beta\Omega_{Bulk}}{\Lambda} = \frac{1}{4\pi}\left[\kappa^2 \ln 2k_{\max} - \kappa^2 \ln\kappa + \frac{1}{2}\kappa^2\right] - \frac{\kappa^2}{4\pi}\left(\ln K_{\max} - \ln k_{\min}\right) - \sum_\alpha \varsigma_\alpha \tag{6.65}$$

equating with the bulk grand potential that we found for a non confined system in two dimensions: $\frac{\Lambda\kappa^2}{4\pi}\left[\ln\frac{k_{\min}}{\kappa} + \frac{1}{2}\right] - \sum_\alpha \Lambda\varsigma_\alpha$ we can write

$$\frac{\kappa^2}{4\pi}\left[\ln 2k_{\max} - \ln\kappa + \frac{1}{2}\right] - \frac{\kappa^2}{4\pi}\left(\ln K_{\max} - \ln k_{\min}\right) = \frac{\kappa^2}{4\pi}\left[\ln\frac{k_{\min}}{\kappa} + \frac{1}{2}\right] \tag{6.66}$$

$$\ln 2k_{\max} - \ln\kappa - \left(\ln K_{\max} - \ln k_{\min}\right) = \ln\frac{k_{\min}}{\kappa} \tag{6.67}$$

$$\ln 2k_{\max} = \ln K_{\max} \tag{6.68}$$

that is to say

$$K_{\max} = 2k_{\max} \tag{6.69}$$

then, once again the two upper limits $K_{\max}$ and $k_{\max}$ turn to be proportional and the divergence of the corresponding integrals effectively cancel each other.

From (6.64) we can also find the surface tension per total length of the boundary which obviously equals $2l$, then

$$\frac{\beta\Omega_{Surface}}{2l} = -\frac{\kappa}{8} \tag{6.70}$$

which is the same surface tension per length that we found in the case of the disk and the annulus as expected. Finally, from (6.64) we can find also the finite size correction per length for the case of the slab in two dimensions which gives

$$\frac{1}{4\pi w}\varsigma(2) \tag{6.71}$$

which accords with the general prediction (6.49)

$$\Gamma(d/2)\frac{\varsigma(d)}{2^d\pi^{d/2}w^{d-1}} = \Gamma(1)\frac{\varsigma(2)}{2^2\pi w} = \frac{1}{4\pi w}\varsigma(2) \tag{6.72}$$

as expected.

Summarizing, the grand potential per length is given by

$$\frac{\beta\Omega}{l} = \left[\frac{1}{4\pi}\kappa^2 \ln\left(\frac{2e^{-\gamma+\frac{1}{2}}}{L\kappa}\right) - \sum_{\alpha}\varsigma_\alpha\right] w - \frac{\kappa}{4} + \frac{\pi}{24w} \tag{6.73}$$

It is interesting to note that contrary to the case of the slab in three dimensions, and as will be seen in all examples in three dimensions, the surface tension in this case doesn't diverge. We also found non-divergent surface tensions in the example of the disk and the annulus before. It suggest that in two dimensions the effect that we explained in the previous section, which makes the particles near the boundary "feel" an attraction to the boundary own to their proximity with its corresponding images, is not enough for systems confined in two dimensions to produce a divergence in the surface tension.

6.4 Coulomb System Inside a Sphere

We continue the study of finite size corrections calculating the grand potential for a Coulomb system in three dimensions confined in a spherical domain. We have to solve the eigenvalue problem $\mathbf{\Delta}\Psi(r,\theta,\varphi) = \lambda\Psi(r,\theta,\varphi)$ where

$$\mathbf{\Delta} \equiv \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.74}$$

is the Laplace operator expressed in spherical coordinates. We look for a solution of the form $\Psi(r,\theta,\varphi) = f(r)Y_l^m(\theta,\varphi)$, replacing in the eigenvalue equation we have

$$\frac{1}{f(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{Y_l^m}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_l^m}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_l^m}{\partial\varphi^2}\right] = r^2\lambda \tag{6.75}$$

again, we recognize in (6.75) the presence of the square of the angular momentum operator

$$\hat{L}^2 \equiv -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.76}$$

which satisfy the eigenvalue equation $\hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)Y_l^m(\theta,\varphi)$ for $l = 0, 1, 2...$ Then the eigenvalue equation (6.75) takes the form

$$\frac{1}{f(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) - r^2\lambda = l(l+1) \tag{6.77}$$

which is an equation for the radial part of the eigenfunctions. It can be written in the form

$$r^2 f''(r) + 2rf'(r) - \left[r^2\lambda + l(l+1)\right] f(r) = 0 \tag{6.78}$$

which is the modified spherical Bessel equation. The solutions of this equation that are regular at $r = 0$ are the functions $\sqrt{\frac{\pi}{2r\lambda^{1/2}}} I_{l+1/2}(\sqrt{\lambda}r)$ where $I_{l+1/2}(x)$ are the modified Bessel functions of half integer order and the eigenvalues λ are determined from the Dirichlet boundary condition. The eigenvalues are thus the roots of the equation

$$I_{l+1/2}(\sqrt{\lambda}R) = 0 \tag{6.79}$$

where R is the radius of the sphere. Then we have that for each value of n, the eigenvalues are given by

$$\lambda_k = \frac{\upsilon_{l+1/2,n}}{R}, \quad \upsilon_{l+1/2,n} \text{ is the n-th root of } (6.79) \text{ for } l = 0, 1, 2... \tag{6.80}$$

Contrary to the two-dimensional case of the disk, the spectrum is degenerate and we have $2l+1$ factors for a given value of l. Then, our expression for the grand potential (4.35) takes the form

$$\beta\Omega = \frac{1}{2}\ln\left[\prod_{l=0}^{\infty}\left(\prod_{n=1}^{\infty}\left(1 - \frac{R^2\kappa^2}{\nu_{l+1/2,n}^2}\right)\right)^{2l+1}\right] + \frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \tag{6.81}$$

where the indexes n and $l+1/2$ denote the root and the order of the modified Bessel function $I_{l+1/2}(x)$ respectively. To evaluate the double product in (6.81) we introduce the non dimensional parameter $\alpha = R\kappa$, then we can write

$$\frac{1}{2}\ln\left[\prod_{l=0}^{\infty}\left(\prod_{n=1}^{\infty}\left(1 - \frac{\alpha^2}{\nu_{l+1/2,n}^2}\right)\right)^{2l+1}\right] = \frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\ln\prod_{n=1}^{\infty}\left(1 - \frac{\alpha^2}{\nu_{l+1/2,n}^2}\right) \tag{6.82}$$

the infinite product in the index n converges. In fact, in a very similar way to the case of the disk studied before, it is nothing but the infinite product representation of the modified Bessel function of half integer order

$$\begin{aligned}\prod_{n=1}^{\infty}\left(1 - \frac{\alpha^2}{\nu_{l+1/2,n}^2}\right) &= (l+1/2)!\left(\frac{2}{\alpha}\right)^{l+1/2} I_{l+1/2}(\alpha) \\ &= \Gamma\left(l+\frac{3}{2}\right)\left(\frac{2}{\alpha}\right)^{l+1/2} I_{l+1/2}(\alpha)\end{aligned} \tag{6.83}$$

note that it is multiplied by a factor depending on l that assures that for $\alpha \to 0$ both sides of this equation tend to 1. Then using (6.82) we can write

$$\begin{aligned}
& \frac{1}{2}\sum_{l=0}^{\infty}(1+2l)\ln\prod_{n=1}^{\infty}\left(1-\frac{\alpha^2}{\nu_{l+1/2,n}^2}\right) \\
= & \frac{1}{2}\sum_{l=0}^{\infty}(1+2l)\ln\left[\Gamma\left(l+\frac{3}{2}\right)\left(\frac{2}{\alpha}\right)^{l+1/2} I_{l+1/2}(\alpha)\right] \\
= & \frac{1}{2}\sum_{l=0}^{\infty}(1+2l)\ln\left[I_{l+1/2}(\alpha)\right]+\frac{1}{2}\sum_{l=0}^{\infty}(1+2l)\ln\left[\Gamma\left(l+\frac{3}{2}\right)\left(\frac{2}{\alpha}\right)^{l+1/2}\right] \qquad (6.84)
\end{aligned}$$

As usual, these summations diverge and we regularize them introducing an upper cutoff N on l and apply Euler-McLaurin summation formula to evaluate each sum. The detailed calculation for the first term of (6.84) is developed in appendix D. To evaluate these terms we use the Debye approximation formula for $I_{l+1/2}(x)$ valid for large values of the argument, and apply Euler-McLaurin to each of the resulting terms. The second term is worked in appendix E using the asymptotic expansion for the Gamma function.

After applying the Euler-McLaurin approximation to each factor, we put all this together and take the limits $N \to \infty$ and $\alpha \to \infty$. Finally, the regularized infinite product in (6.81) is found to be

$$\begin{aligned}
& \frac{1}{2}\ln\left[\prod_{l=0}^{N}\left(\prod_{n=1}^{\infty}\left(1-\frac{R^2\kappa^2}{\nu_{l+1/2,n}^2}\right)\right)^{2l+1}\right] \\
= & \left(\frac{N}{4\alpha}-\frac{1}{9}\right)\alpha^3+\frac{1}{8}\left(1+2\ln\frac{\alpha}{N}\right)\alpha^2+\frac{1}{3}\alpha+o(\alpha)+o(N) \qquad (6.85)
\end{aligned}$$

approximating the sum over the bulk eigenvalues in (6.81) by an integral with upper limit $k_{\max}$ we have

$$\frac{1}{2}\sum_{k}\frac{\kappa^2}{\lambda_k^0}=-\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^3}\int\frac{d\mathbf{k}}{\mathbf{k}^2}=-\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^3}\int d\Omega\int_0^{k_{\max}}\frac{k^2dk}{k^2} \qquad (6.86)$$

writing $\Lambda = \frac{4}{3}\pi R^3$ we find

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{\kappa^2}{3\pi} R^3 k_{\max} \tag{6.87}$$

using (6.85) for the grand potential (6.81) and putting all this together we find

$$\begin{aligned}
\beta\Omega &= \frac{1}{2}\ln\left[\prod_{l=0}^{\infty}\left(\prod_{n=1}^{\infty}\left(1-\frac{\alpha^2}{\nu_{l+1/2,n}^2}\right)\right)^{2l+1}\right] + \frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \\
&= \left(\frac{N}{4\alpha}-\frac{1}{9}\right)\alpha^3 + \frac{1}{8}\left(1+2\ln\frac{\alpha}{N}\right)\alpha^2 + \frac{1}{3}\alpha - \frac{\kappa^2}{3\pi}R^3 k_{\max} - \frac{4}{3}\pi R^3 \sum_\alpha \varsigma_\alpha + o(\alpha) + o(N) \\
&= \left[-\frac{\kappa^3}{12\pi} + \frac{3\kappa^2}{16\pi}\frac{N}{R} - \frac{\kappa^2}{4\pi^2}k_{\max} - \sum_\alpha \varsigma_\alpha\right]\frac{4\pi}{3}R^3 + \left(1+2\ln\frac{R\kappa}{N}\right)\frac{\kappa^2 R^2}{8} \\
&\quad + \frac{\kappa R}{3} + O(R^0) + O(N^0)
\end{aligned} \tag{6.88}$$

where we have used $\alpha = R\kappa$. Equating the bulk grand potential with the expression for the grand potential for a non-confined system that we found previously: $\beta\Omega_{bulk} = \left(-\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha\right)\Lambda$ we have

$$-\frac{\kappa^3}{12\pi} + \frac{3\kappa^2}{16\pi}\frac{N}{R} - \frac{\kappa^2}{4\pi^2}k_{\max} - \sum_\alpha \varsigma_\alpha = -\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha \tag{6.89}$$

then we have

$$\frac{\kappa^2}{4\pi^2}k_{\max} = \frac{3\kappa^2}{16\pi}\frac{N}{R} \tag{6.90}$$

$$k_{\max} = \frac{3\pi}{4}\frac{N}{R} \tag{6.91}$$

replacing this value for $k_{\max}$ in the expression for the grand potential we find

$$\beta\Omega = \left[-\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha\right]\frac{4\pi}{3}R^3 + \left(\frac{\kappa^2}{32\pi} + \frac{\kappa^2}{16\pi}\ln\frac{\kappa R}{N}\right)4\pi R^2 + \frac{\kappa}{3}R + o(R) + o(N) \tag{6.92}$$

the first term in the right side of (6.92) is the usual bulk term in three dimensions (A.1) what is not any surprise. The second term is more interesting since it gives the surface tension for the system. We can write it in the form

$$\frac{\beta\Omega_{surface}}{\mathcal{A}} = \kappa^2 \left(\frac{1}{32\pi} + \frac{1}{16\pi} \ln \frac{3\pi\kappa}{4} \right) - \frac{\kappa^2}{16\pi} \ln k_{\max} \tag{6.93}$$

where $\mathcal{A}$ is the total area of the boundary. From (6.93) we see that for $k_{\max} \to \infty$ the surface tension diverges in the same way, and for the same reason, that the surface tension in equation (6.46) for the system confined in the slab in three dimensions.

6.5 Spherical Shell

Another interesting example of the application of our method to the calculation of finite size corrections is the case of a Coulomb system confined in a spherical shell. Let a and b the inner and outer radium of the shell respectively. We separate the wave functions into its radial and angular parts $\Psi(r,\theta,\varphi) = f(r)Y_l^m(\theta,\varphi)$ and proceeding as in the case of a spherical surface, we solve the eigenvalue problem for this domain finding that the most general solution for the radial part of the eigenfunctions satisfy the modified Bessel equation

$$r^2 f''(r) + 2rf'(r) - \left[r^2\lambda + l(l+1)\right] f(r) = 0. \tag{6.94}$$

This equation has two linear independent solutions which are the functions

$$\sqrt{\frac{\pi}{2r\lambda^{1/2}}} I_{l+1/2}(\sqrt{\lambda}r) \tag{6.95}$$

$$\sqrt{\frac{\pi}{2r\lambda^{1/2}}} K_{l+1/2}(\sqrt{\lambda}r) \tag{6.96}$$

where $I_{l+1/2}(x)$ and $K_{l+1/2}(x)$ are the modified Bessel functions of fractional order [44],[47]. Then we can write for the eigenfunction

$$\Psi(r,\theta,\varphi) = \left[A\sqrt{\frac{\pi}{2r\lambda^{1/2}}} I_{l+1/2}(\sqrt{\lambda}r) + B\sqrt{\frac{\pi}{2r\lambda^{1/2}}} K_{l+1/2}(\sqrt{\lambda}r) \right] Y_l^m(\theta,\varphi) \tag{6.97}$$

it must satisfy the Dirichlet boundary conditions $\Psi(a,\theta,\varphi)=\Psi(b,\theta,\varphi)=0$. Then we have

$$AI_{l+1/2}(\sqrt{\lambda}a)+B\ K_{l+1/2}(\sqrt{\lambda}a) = 0 \tag{6.98}$$

$$AI_{l+1/2}(\sqrt{\lambda}b)+B\ K_{l+1/2}(\sqrt{\lambda}b) = 0 \tag{6.99}$$

this two equations can be considered as a linear system of equations for the coefficients A and B. It has a non trivial solution if

$$\det\begin{pmatrix} I_{l+1/2}(\sqrt{\lambda}a) & K_{l+1/2}(\sqrt{\lambda}a) \\ I_{l+1/2}(\sqrt{\lambda}b) & K_{l+1/2}(\sqrt{\lambda}b) \end{pmatrix}=0 \tag{6.100}$$

this condition gives the equation satisfied by the eigenvalues, that is

$$I_{l+1/2}(\sqrt{\lambda}a)K_{l+1/2}(\sqrt{\lambda}b)-I_{l+1/2}(\sqrt{\lambda}a)K_{l+1/2}(\sqrt{\lambda}b)=0 \tag{6.101}$$

then we can write

$$\lambda_k=\upsilon_{l,n}\ \ \text{: n-th root of equation (6.101) for}\ \ l=0,1,2... \tag{6.102}$$

Now we proceed to introduce these eigenvalues in the expression for the grand potential. Then we have

$$\beta\Omega=\frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\ln\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l+1/2,n}^2}\right)+\frac{1}{2}\sum_k\frac{\kappa^2}{\lambda_k^0}-\sum_\alpha\Lambda\varsigma_\alpha \tag{6.103}$$

the infinite product in the index n, which denotes the n-th root of equation (6.101) converges to the expression

$$\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l+1/2,n}^2}\right)=\frac{\left[I_{l+1/2}(\kappa a)K_{l+1/2}(\kappa b)-K_{l+1/2}(\kappa a)I_{l+1/2}(\kappa b)\right]}{\frac{1}{2(l+1/2)}\left(\left(\frac{a}{b}\right)^{l+1/2}-\left(\frac{b}{a}\right)^{l+1/2}\right)}\ \text{for}\ l=0,1,2... \tag{6.104}$$

Again, the denominator in (6.104) assures that both sides of the equation tend to 1 when $\kappa\to\infty$. In a similar way to the case of the disk, the contribution of $K_l(\kappa b)I_l(\kappa a)$ is exponentially smaller than the one from the term $I_l(\kappa b)K_l(\kappa a)$, in consequence we can correctly write

$$\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon^2_{l+1/2,n}}\right)\simeq\frac{-K_{l+1/2}(\kappa a)I_{l+1/2}(\kappa b)}{\frac{1}{2(l+1/2)}\left(\left(\frac{a}{b}\right)^{l+1/2}-\left(\frac{b}{a}\right)^{l+1/2}\right)}\quad\text{for } l=0,1,2... \tag{6.105}$$

and the first term of the right side of (6.103) can be written as

$$\frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\ln\left[\frac{K_{l+1/2}(\kappa a)I_{l+1/2}(\kappa b)}{\frac{1}{2(l+1/2)}\left(\left(\frac{b}{a}\right)^{l+1/2}-\left(\frac{a}{b}\right)^{l+1/2}\right)}\right]+O(e^{-(b-a)\kappa}) \tag{6.106}$$

Now we introduce an upper cutoff N to regularize the divergent sum on l. Expanding the logarithm (6.106) can be written as

$$\begin{aligned}&\frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln I_{l+1/2}(\kappa b)+\frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln K_{l+1/2}(\kappa a)\\&-\frac{1}{2}\sum_{l=0}^{N}(1+2l)\sum_{l=0}^{N}\ln\left[\frac{1}{2\,(l+1/2)}\left(\left(\frac{b}{a}\right)^{l+1/2}-\left(\frac{a}{b}\right)^{l+1/2}\right)\right].\end{aligned} \tag{6.107}$$

The first sums were calculated, using the Euler-McLaurin formula, when we studied the case of a Coulomb system confined in a single sphere. The details of this calculation can be found in appendix D. The calculation of the next term is quite similar and the details are also presented in appendix D. The last two terms in (6.107) corresponding to the asymptotic pre-factor are worked in appendix F.

Putting the results of the appendices together and taking the limits $b-a\to\infty$ with $b-a>0$, we find that the infinite product involved in the calculation of the grand potential can be written as

$$\begin{aligned}&\frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\ln\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon^2_{l+1/2,n}}\right) \qquad (6.108)\\=\;&-\frac{1}{9}\left(b^3-a^3\right)\kappa^3+\frac{1}{4}\left(\frac{N}{b\kappa}\kappa b^3-\frac{N}{a\kappa}\kappa a^3\right)+\frac{1}{8}\left(2\ln\frac{a\kappa}{N}-3\right)a^2\kappa^2\\&+\frac{1}{8}\left(2\ln\frac{b\kappa}{N}+1\right)b^2\kappa^2+\frac{1}{3}\left(b-a\right)\kappa+o(a)+o(b)\end{aligned}$$

approximating the sum over the bulk eigenvalues in (6.103) by an integral with upper limit $k_{\max}$ we have

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^3}\int\frac{d\mathbf{k}}{\mathbf{k}^2} = -\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^3}\int d\Omega\int_0^{k_{\max}}\frac{k^2dk}{k^2} \tag{6.109}$$

writing $\Lambda = \frac{4}{3}\pi\left(b^3 - a^3\right)$ for the total volume of the system we find

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{\kappa^2}{3\pi}\left(b^3 - a^3\right)k_{\max} \tag{6.110}$$

then, we have for the grand potential

$$\begin{aligned}\beta\Omega &= \frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\ln\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l+1/2,n}^2}\right)+\frac{1}{2}\sum_k\frac{\kappa^2}{\lambda_k^0}-\sum_\alpha\Lambda\varsigma_\alpha \qquad (6.111)\\ &= \left(\frac{N\kappa^3}{4b\kappa}-\frac{\kappa}{9}\right)b^3-\left(\frac{N\kappa^3}{4a\kappa}-\frac{\kappa}{9}\right)a^3-\frac{\kappa^2}{3\pi}\left(b^3-a^3\right)k_{\max}-\frac{4}{3}\pi\left(b^3-a^3\right)\sum_\alpha\varsigma_\alpha+\\ &\frac{1}{8}\left(2\ln\frac{a\kappa}{N}-3\right)a^2\kappa^2+\frac{1}{8}\left(2\ln\frac{b\kappa}{N}+1\right)b^2\kappa^2+\frac{1}{3}(b-a)\kappa+o(N^0)+o(a^0)+o(b^0)\end{aligned}$$

also we can identify from (6.111) the bulk grand potential. Equating this value with the grand potential for a non-confined systems in three dimensions given in (A.1) we can find the value for $k_{\max}$ as follows. From (6.111) we note that

$$\beta\Omega_{bulk} = \left(\frac{N\kappa^3}{4b\kappa}-\frac{\kappa}{9}-\frac{\kappa^2k_{\max}}{3\pi}-\frac{4}{3}\pi\sum_\alpha\varsigma_\alpha\right)b^3-\left(\frac{N\kappa^3}{4a\kappa}-\frac{\kappa}{9}-\frac{\kappa^2k_{\max}}{3\pi}-\frac{4}{3}\pi\sum_\alpha\varsigma_\alpha\right)a^3 \tag{6.112}$$

on the other hand, for a non confined system

$$\beta\Omega_{bulk} = \left(-\frac{\kappa^3}{12\pi}-\sum_\alpha\varsigma_\alpha\right)\frac{4}{3}\pi\left(b^3-a^3\right) \tag{6.113}$$

Then equating (6.112) and (6.113) we find

$$-\frac{\kappa}{9}\left(b^3-a^3\right) = \left(\frac{N\kappa_D^3}{4b\kappa_D}-\frac{\kappa}{9}-\frac{\kappa^2k_{\max}}{3\pi}\right)b^3-\left(\frac{N\kappa_D^3}{4a\kappa_D}-\frac{\kappa}{9}-\frac{\kappa^2k_{\max}}{3\pi}\right)a^3 \tag{6.114}$$

which is the same as

$$\left(\frac{N\kappa^2}{4b} - \frac{\kappa^2 k_{\max}}{3\pi}\right) b^3 = \left(\frac{N\kappa^2}{4a} - \frac{\kappa^2 k_{\max}}{3\pi}\right) a^3 \tag{6.115}$$

solving for $k_{\max}$ we find

$$\begin{aligned} \left(b^3 - a^3\right) \frac{1}{3\pi} k_{\max} &= \frac{N}{4}\left(b^2 - a^2\right) \\ k_{\max} &= N\left(\frac{3\pi}{4}\frac{b^2 - a^2}{b^3 - a^3}\right) \end{aligned} \tag{6.116}$$

replacing this value for $k_{\max}$ in (6.103) we find

$$\begin{aligned} \beta\Omega &= \left(-\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha\right) \frac{4\pi}{3}\left(b^3 - a^3\right) + \frac{1}{8}\left(2\ln\frac{a\kappa}{N} - 3\right) a^2\kappa^2 \\ &+ \frac{1}{8}\left(2\ln\frac{b\kappa}{N} + 1\right) b^2\kappa^2 + \frac{1}{3}\left(b - a\right)\kappa + o(N) + o(a) + o(b) \end{aligned} \tag{6.117}$$

which is the expansion for the grand potential. Some additional comments are in order. From (6.116) we note that the value for $k_{\max}$ tends to the value that we found in the case of a system in a single sphere (6.91) when we take the inner radius $a \to 0$. The divergence in the surface tension, familiar to us at this point, is also present. However it don't have the simple form that we found in the case of the sphere since the expression

$$\beta\Omega_{surface} = \frac{1}{8}\left(2\ln\frac{a\kappa}{N} - 3\right) a^2\kappa^2 + \frac{1}{8}\left(2\ln\frac{b\kappa}{N} + 1\right) b^2\kappa^2 \tag{6.118}$$

contain two different arguments for the logarithm. Also, the expression (6.116) that we found for this case is not as simple as equation (6.91) for the case of a single sphere. However, when we take the limit $k_{\max} \to \infty$ we find for the surface tension

$$\beta\Omega_{surface} \to \left(-\frac{\kappa^2}{16\pi}\ln k_{\max}\right) 4\pi\left(b^2 + a^2\right) \tag{6.119}$$

which is the same divergence that we found in other cases in three dimensions as expected.

Chapter 7

Calculation of the Finite Size Expansion for the Free Energy: General Considerations.

Until this point we have seen, how the grand canonical partition function for a Coulomb system confined in a perfect grounded conductor with certain geometry can be expressed, in the Debye-Hückel regime, as an infinite product of functions of the eigenvalues of the Laplace operator. This spectrum and the corresponding infinite products depend on the shape of the conductor, and must be calculated for each particular case. However, from a more general mathematical point of view, it is possible to define functions of the spectrum for certain differential operators that admit asymptotic expansions, that turn out to have properties that are independent of the explicit form of the eigenvalues. These results are known by mathematician since the middle of the XX century [39],[48],[49]. In particular, it is known that in some extend the spectrum of the Laplace operator calculated on a given manifold endowed with a metric, contain information about the geometry of the manifold itself. In this chapter we make use of these to extend our results from systems confined in specific domains to a wider class of geometries. Of course if one wants the explicit form of the free energy, a complete calculation similar to the presented in the solved examples is required. Nevertheless, the general treatment proportionate rigorous support to the method, and offers another perspective to the problem.

7.1 Definitions and General Properties of the Spectrum of Δ for Riemannian Manifolds

Let $\mathcal{M}$ a Riemannian manifold with boundary $\partial\mathcal{M}$ and Δ the Laplace operator defined on $\mathcal{M}$. We define the spectrum of $\mathcal{M}$ as the set $\{0 \geqslant \lambda_0 \geqslant \lambda_1 \geqslant \cdots \downarrow -\infty\}$ of eigenvalues of Δ, that are solutions of

$$\Delta\Psi = \lambda\Psi \tag{7.1}$$

where Ψ are the eigenfunctions of Δ defined in $\mathcal{M}$ that must satisfy certain boundary conditions on $\partial\mathcal{M}$ which we impose to be of the Dirichlet type, that is $\Psi = 0$ on $\partial\mathcal{M}$. We are interested in the following general question: does the spectrum of $\mathcal{M}$ "characterize" the shape of $\mathcal{M}$?. To specify what we mean by "characterize" let us first make some definitions.

Consider two manifolds $\mathcal{M}_m, \mathcal{M}'_{m'}$ endowed with certain metrics m and m' respectively. We say that the spectra of $\mathcal{M}_m$ and $\mathcal{M}'_{m'}$ are equal if they equal in the sense of set theory. On the other hand, we say that the two manifolds are equal: $\mathcal{M}_m = \mathcal{M}'_{m'}$ if we can establish diffeomorphisms $f : \mathcal{M}_m \to \mathcal{M}'_{m'}$ such that $f^*m' = m$. Now we can formulate our question as: does spectral equality imply $\mathcal{M}_m = \mathcal{M}'_{m'}$?. This question was answered in the negative [41]. However there are some geometrical conclusions due to isospectrality. For example, it is known that the spectrum of a manifold characterize its dimension, volume and curvature [49].

To formulate this results in mathematical language let us introduce the heat kernel $\Theta(t)$ that is, the series

$$\Theta(t) = \sum_{k=0}^{\infty} e^{t\lambda_k}. \tag{7.2}$$

where $\{\lambda_k\}$ is a sequence of numbers and t is a complex number. Let us also consider an

open d dimensional Riemannian manifold $\mathcal{M}_m$ with compact $(d-1)-$dimensional boundary $\partial\mathcal{M}_m$. For such a manifold the Laplace operator Δ is substituted by the associated Laplace-Beltrami operator

$$\Delta = \frac{1}{\sqrt{g}} \frac{\partial}{\partial x^i} g^{ij} \sqrt{g} \frac{\partial}{\partial x^j} \tag{7.3}$$

where $g = \sqrt{\det g^{ij}}$. This incorporates the metric by mean of the metric tensor $g^{-1} = (g^{ij})$. Let K be the scalar curvature and J the mean curvature at a point of the boundary $\partial\mathcal{M}_m$. Then it can be shown that

$$(4\pi t)^{d/2}\Theta(t) = A + B + C + D + o(t^{3/2}) \tag{7.4}$$

where

$$
\begin{aligned}
A &= \text{the (Riemannian) volume of } \mathcal{M}_m = A' && (7.5)\\
B &= -\frac{1}{4}\sqrt{4\pi t} \times \text{the (Riemannian) surface area of } \partial\mathcal{M}_m = -\frac{1}{4}\sqrt{4\pi t}B' && (7.6)\\
C &= \frac{t}{3} \times \text{ the curvatura integra: } \int_{\mathcal{M}_m} K = \frac{t}{3}C' && (7.7)\\
D &= \frac{t}{6} \times \text{ the integrated mean curvature: } \int_{\partial\mathcal{M}_m} J = \frac{t}{6}D' && (7.8)
\end{aligned}
$$

where $\Theta(t)$ is calculated for the eigenvalues $\{0 \geqslant \lambda_0 \geqslant \lambda_1 \geqslant \cdots \downarrow -\infty\}$ of the Laplace-Beltrami operator [48],[49][1]. Equation (7.4) is valid not only for Δ but also for any elliptic partial differential operator of degree 2.

7.2 Fredholm Determinant, Generalized Zeta Function and Mellin Transforms

There are several interesting functions that can be associated with numerical sequences such as the spectra of differential operators as the one we are studying. However, in order to do this the spectra must satisfy certain requirements [39]. First of all the heat kernel (7.2) that we introduced in the previous section must be convergent for all $\mathrm{Re}\, t > 0$. It also must admit an asymptotic expansion in all orders of t, for $t \to 0$

$$\Theta(t) \sim \sum_{n=0}^{\infty} c_{i_n} t^{i_n} \tag{7.9}$$

for $t \to 0$. Here $\{i_n\}$ is a certain increasing sequence of real numbers and $i_0 < 0$. The coefficients $\{c_{i_n}\}$ are supposed to be known quantities and $c_{i_0} > 0$. The exponent $-i_0$ is

[1] We warn to the reader that in this paper, Mr. McKean and Mr. Singer take the convention of assuming as positive the direction of a vector penetrating from the outside to the inner side of the manifold. This of course is unimportant for their conclusions but it implies a change in the sign of our eq. (7.8), where we have used the opposite (perhaps more usual) sign convention.

particularly important because it is the divergent leading term in the sequence (7.9). It is called μ, the order of the sequence. It satisfies

$$\mu = -i_0 = \frac{d}{m} \tag{7.10}$$

where m is the order of the differential operator considered and d is the dimension of the manifold.

The Laplace operator satisfy both conditions and the order of its associated sequence is $\frac{d}{2}$. For our purposes we are interested in three spectral functions. The first is known as Fredholm determinant defined as

$$f(\lambda) = \prod_{k=0}^{\infty} \left(1 - \frac{\lambda}{\lambda_k}\right) \tag{7.11}$$

whose form is similar to the infinite product that we found for the grand canonical partition function after performing the sine-Gordon transformation. Strictly speaking, this product converges for sequences with[2] $\mu = \frac{d}{m} < 1$. The second function is the Zeta function

$$Z(s) = \sum_{k=0}^{\infty} (-\lambda_k)^{-s} \tag{7.12}$$

which is convergent for any value s such that $\operatorname{Re} s > \mu$. The third spectral function we are interested in, is the generalized Zeta function

$$Z(s,a) = \sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \tag{7.13}$$

which is convergent for $\operatorname{Re} s > \mu$ and $a \geqslant \lambda_0$. Note that $Z(s,0) = Z(s)$.

[2]A generalization of this determinant will be introduced later to threat the cases $\mu = 1$ and $\mu = 3/2$ which we are interested in.

We can establish a relation between $Z(s,a)$ and $\Theta(t)$ by mean of the so called Mellin transform. Let $f(t)$ be a function defined on $0 < t < \infty$, that satisfies the estimates

$$f(t) = O(t^{i_0}) \quad \text{for } t \to +0 \quad (i_0 \leq \infty) \tag{7.14}$$

$$f(t) = O(t^{j_0}) \quad \text{for } t \to +\infty \quad (-\infty \leq j_0) \tag{7.15}$$

with $j_0 < i_0$. Then $f(t)$ admits a Mellin transform $M[f(t)]$ defined as

$$M[f(t)] = \int_0^\infty f(t) t^{s-1} dt \tag{7.16}$$

in the vertical strip $-i_0 < \operatorname{Re} s < -j_0$. Note that with this definition we can write

$$\begin{aligned} Z(s,a) &= \frac{M\left[\Theta(t)e^{-at}\right]}{\Gamma(s)} \\ &= \frac{1}{\Gamma(s)} \int_0^\infty \Theta(t) e^{-at} t^{s-1} dt \end{aligned} \tag{7.17}$$

where Γ is the usual Gamma function.

7.3 Relation with Finite Size Corrections in the Free Energy

As mentioned before, equation (7.11) is quite similar to the infinite products that we had to work with, when we calculated the finite size correction for given geometries. Our goal in this section is relate this kind of products with the geometrical information on the domain for which the spectrum is calculated. We stress at this point that although equation (7.4) holds for an arbitrary dimension d, in what follows we will restrict our calculations to the case of two dimensions. The idea is to extract this geometrical information from the heat kernel associated with the spectrum by mean of the asymptotic expansion given in equation (7.2). To see how this can be done consider first the case of a system of fixed volume equal to 1. The generalized Zeta function introduced in the previous section for this case is

$$Z_1(s,a) = \sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \tag{7.18}$$

where we use the subscript 1 to remember that the volume of the system is normalized. Formally, differentiating with respect to the variable s we have

$$\begin{aligned} \frac{\partial Z_1(s,a)}{\partial s} &= \frac{\partial}{\partial s} \sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \\ &= -\sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \ln (a - \lambda_k) \\ &= -\sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \left[\ln \left(1 - \frac{a}{\lambda_k} \right) + \ln (-\lambda_k) \right] \end{aligned} \tag{7.19}$$

from (7.19) we can obtain an infinite product similar to the one we are interested in, since

$$\begin{aligned} \left. \frac{\partial Z_1(s,a)}{\partial s} \right|_{s=0,a} &= -\sum_{k=0}^{\infty} \ln \left(1 - \frac{a}{\lambda_k} \right) + \ln \left(\frac{1}{-\lambda_k} \right) \\ &= -\ln \prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k} \right) + \left. \frac{\partial Z_1(s,a)}{\partial s} \right|_{s=0,a=0} \end{aligned} \tag{7.20}$$

it is equivalent to

$$\ln \prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k} \right) = \left. \frac{\partial Z_1(s,a)}{\partial s} \right|_{s=0,a=0} - \left. \frac{\partial Z_1(s,a)}{\partial s} \right|_{s=0,a} . \tag{7.21}$$

To find our product we need to evaluate the derivative of the generalized Zeta function and then calculate the subtraction of the derivatives evaluated in the appropriate values of the variables s and a as given in (7.21). Note that it seem that we are equating a divergent product to a finite quantity. However, it most be clearly understood that relation (7.21) and the following manipulations are merely formal. Relation (7.21) is known as the Zeta regularization for the infinite product. A more rigorous approach will be given in section 7.4, where we generalize the Fredholm determinant for sequences of order bigger that 1.

Now, if we want to evaluate the infinite product for a system of characteristic size R like the ones we have been working with, we have to define the appropriate Zeta function for that system, by obvious reasons we call this function $Z_R(s,a)$. This function also have an associated heat kernel $\Theta_R(t)$ that in principle is different from the one that appears in (7.17), since the eigenvalues of Δ calculated on a manifold of characteristic size R result to be corrected by a factor R^{-2}, that is

$$\lambda_k \to \frac{\lambda_k}{R^2} \tag{7.22}$$

Let us call the heat kernel for normalized volume $\Theta_1(t)$. The relation between $Z_R(s,a)$ and $Z_1(s,a)$ can be easily found since by definition

$$\begin{aligned} Z_R(s,a) &= \frac{1}{\Gamma(s)}\int_0^\infty \Theta_R(t)e^{-at}t^{s-1}dt \\ &= \frac{1}{\Gamma(s)}\int_0^\infty \Theta_1\left(\frac{t}{R^2}\right)e^{-at}t^{s-1}dt \\ &= \frac{1}{\Gamma(s)}\int_0^\infty \Theta_1\left(t'\right)e^{-aR^2t'}\left(R^2t'\right)^{s-1}R^2dt' \\ &= R^{2s}\frac{1}{\Gamma(s)}\int_0^\infty \Theta_1\left(t'\right)e^{-aR^2t'}\left(t'\right)^{s-1}dt' \\ &= R^{2s}Z_1(s,aR^2) \end{aligned} \tag{7.23}$$

where we have used the change of variable $t = R^2t'$.

Finally, to find the infinite product associated with the system of characteristic size R we must evaluate a relation similar to (7.21) involving the function $Z_R(s,a)$:

$$\ln \prod_{k=0}^{\infty}\left(1-\frac{aR^2}{\lambda_k}\right) = \left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} - \left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0} \tag{7.24}$$

$$= \left.\frac{\partial}{\partial s}\left[R^{2s}Z_1(s,aR^2)\right]\right|_{s=0,a=0} - \left.\frac{\partial}{\partial s}\left[R^{2s}Z_1(s,aR^2)\right]\right|_{s=0}$$

$$= 2R^{2s}Z_1(s,aR^2)\ln R\big|_{s=0,a=0} + R^{2s}\left.\frac{\partial}{\partial s}\left[Z_1(s,aR^2)\right]\right|_{s=0,a=0}$$

$$- 2R^{2s}Z_1(s,aR^2)\ln R\big|_{s=0} - R^{2s}\left.\frac{\partial}{\partial s}\left[Z_1(s,aR^2)\right]\right|_{s=0} \tag{7.25}$$

To evaluate the last term in (7.25) we note that, as mentioned before, the Mellin transform allow to express the generalized Zeta function as

$$Z_1(s,a) = \frac{1}{\Gamma(s)}\int_0^{\infty}\Theta(t)e^{-at}t^{s-1}dt \tag{7.26}$$

in two dimensions for $t \to 0$, we can use the asymptotic expansion for the heat kernel given in equation (7.2) and we can write

$$Z_1(s,a) = \frac{1}{\Gamma(s)}\int_0^{\infty}\left[\frac{A'}{4\pi t} - \frac{\sqrt{4\pi}B'}{16\pi t^{1/2}} + \frac{C'}{12\pi} + \frac{D'}{24\pi}\right]e^{-at}t^{s-1}dt \tag{7.27}$$

note that the primed quantities in the last equation are given for a system of volume 1. Now, using the Gauss-Bonnet theorem [23] we note that[3]

$$2C' + D' = 2\int_{\mathcal{M}_g} K + \int_{\partial\mathcal{M}_g} J = 4\pi\chi \tag{7.28}$$

where χ is the Euler characteristic of the manifold. Then we have

$$Z_1(s,a) = \frac{1}{\Gamma(s)}\int_0^{\infty}\left[\frac{A'}{4\pi t} - \frac{B'}{4\sqrt{4\pi}t^{1/2}} + \frac{1}{6}\chi\right]e^{-at}t^{s-1}dt \tag{7.29}$$

[3]Remember that this part our calculations hold in two dimensions exclusively.

expanding the product and performing the integrations we have

$$
\begin{aligned}
Z_1(s,a) &= \frac{1}{\Gamma(s)}\int_0^\infty \frac{A'}{(4\pi t)} e^{-at}t^{s-1}dt - \frac{1}{\Gamma(s)}\int_0^\infty \frac{B'}{4\sqrt{4\pi}t^{1/2}} e^{-at}t^{s-1}dt + \frac{1}{\Gamma(s)}\int_0^\infty \frac{1}{6}\chi e^{-at}t^{s-1}dt \\
&= \frac{A'}{(4\pi)}\frac{1}{\Gamma(s)}\int_0^\infty e^{-at}t^{s-2}dt - \frac{B'}{4\sqrt{4\pi}}\frac{1}{\Gamma(s)}\int_0^\infty e^{-at}t^{s-3/2}dt + \frac{1}{6}\chi\frac{1}{\Gamma(s)}\int_0^\infty e^{-at}t^{s-1}dt \\
&= \frac{A'}{(4\pi)}\frac{\Gamma(s-1)}{a^{s-1}\Gamma(s)} + \frac{B'}{4\sqrt{4\pi}}\frac{\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s)} + \frac{1}{6}\chi a^{-s} \qquad (7.30)
\end{aligned}
$$

where Γ is the usual Gamma function. Simplifying

$$
Z_1(s,a) = \frac{A'}{(4\pi)}\frac{1}{a^{s-1}(s-1)} - \frac{B'}{4\sqrt{4\pi}}\frac{\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s)} + \frac{1}{6}\chi a^{-s} \qquad (7.31)
$$

now we are ready to evaluate the derivative

$$
\frac{\partial Z_1(s,a)}{\partial s} = \frac{A'}{(4\pi)}\frac{\partial}{\partial s}\left[\frac{1}{a^{s-1}(s-1)}\right] + \frac{B'}{4\sqrt{4\pi}}\frac{\partial}{\partial s}\left[\frac{\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s)}\right] + \frac{1}{6}\chi\frac{\partial}{\partial s}\left[a^{-s}\right] \qquad (7.32)
$$

the derivatives in the first and last terms of (7.32) are

$$
\begin{aligned}
\frac{\partial}{\partial s}\left(\frac{1}{a^{s-1}(s-1)}\right) &= -a^{-s+1}\frac{s\ln a - \ln a + 1}{(s-1)^2} \qquad (7.33) \\
\frac{\partial}{\partial s}a^{-s} &= -a^{-s}\ln a \qquad (7.34)
\end{aligned}
$$

using the properties of the Γ function, the middle term inside square brackets can be written as

$$
\frac{\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s)} = \frac{s\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s+1)} \qquad (7.35)
$$

and

$$
\frac{\partial}{\partial s}\left[\frac{s\Gamma(s-1/2)}{a^{s-1/2}\Gamma(s+1)}\right] = -\frac{1}{\Gamma(s+1)}a^{1/2-s}\Gamma(s-1/2)\left(-1 + s\ln a - s\psi(s-1/2) + s\psi(s+1)\right) \qquad (7.36)
$$

where $\psi(x)$ is the Psi function defined as $\frac{d}{dx}\ln\Gamma(x)$. Putting all together and evaluating the resulting expression for $s=0$ we have

$$\begin{aligned}\left.\frac{\partial Z_1(s,a)}{\partial s}\right|_{s=0} &= \frac{A'}{(4\pi)}a\,(\ln a-1)-\frac{B'}{4\sqrt{4\pi}}a^{1/2}\Gamma(-1/2)-\frac{1}{6}\chi\ln a\\ &= \frac{A'}{(4\pi)}a\,(\ln a-1)+\frac{B'}{4}a^{1/2}-\frac{1}{6}\chi\ln a \qquad (7.37)\end{aligned}$$

where we have used $\Gamma(-1/2)=-2\sqrt{\pi}$. Now we can find the desired product (7.24). Using (7.31) we find

$$Z_1(s,a)|_{s=0}=-\frac{aA'}{4\pi}+\frac{1}{6}\chi \qquad (7.38)$$

and replacing together with (7.37) in (7.24) we have

$$\begin{aligned}\ln\prod_{k=0}^{\infty}\left(1-\frac{aR^2}{\lambda_k}\right) &= 2R^{2s}Z_1(s,aR^2)\ln R\big|_{s=0,a=0}+R^{2s}\frac{\partial}{\partial s}\left[Z_1(s,aR^2)\right]\Big|_{s=0,a=0} \qquad (7.39)\\ &- 2R^{2s}Z_1(s,aR^2)\ln R\big|_{s=0}-R^{2s}\frac{\partial}{\partial s}\left[Z_1(s,aR^2)\right]\Big|_{s=0}\\ &= \frac{1}{3}\chi\ln R+\left(\frac{aR^2A'}{4\pi}-\frac{1}{6}\chi\right)2\ln R-\frac{A'}{4\pi}aR^2\left(\ln aR^2-1\right) \qquad (7.40)\\ &-\frac{B'}{4}a^{1/2}R+\frac{1}{6}\chi\ln\left(aR^2\right)+O(R^0) \qquad (7.41)\end{aligned}$$

Note that the term $\frac{\partial}{\partial s}\left[Z_1(s,aR^2)\right]\big|_{s=0,a=0}$ of the right side of (7.39) is a constant of order $O(1)$. Finally, we evaluate at $a=\kappa^2$ to find

$$\begin{aligned}&\ln\prod_{k=0}^{\infty}\left(1-\frac{\kappa^2R^2}{\lambda_k}\right)\\ &= \frac{1}{3}\chi\ln R+\left(\frac{\kappa^2R^2A'}{4\pi}-\frac{1}{6}\chi\right)2\ln R-\frac{A'\kappa^2R^2}{4\pi}\left(\ln\kappa^2R^2-1\right)-\frac{B'}{4}\kappa R+\frac{1}{6}\chi\ln\left(a^2R^2\right)+O(R^0)\\ &= \frac{1}{3}\chi\ln R-\frac{1}{3}\chi\ln R-\frac{A'\kappa^2R^2}{4\pi}\left(2\ln\kappa-1\right)-\frac{B'}{4}\kappa R+\frac{1}{3}\chi\ln\left(R\right)+O(R^0)\\ &= -\frac{A'\kappa^2R^2}{4\pi}\left(2\ln\kappa-1\right)-\frac{B'}{4}\kappa R+\frac{1}{3}\chi\ln R+O(R^0) \qquad (7.42)\end{aligned}$$

which is just the relation between the desired product and the geometry of the manifold. Finally, It must be remembered that in this expression A' and B' are defined for a system of unit volume. We recognize the logaritmic finite size correction with the coefficient $\frac{1}{6}\chi$ that appears in the expansion for the grand potential, (remember that to find the grand potential the infinite product is multiplied by a factor $\frac{1}{2}$). We find also the boundary factor multiplied by the non-universal coefficient $-\frac{B'}{4}\kappa$.

Note that what we have obtained in (7.42), which is consequence of (7.21), is a finite expression for an infinite product. We stress that (7.42) must be understood as the Zeta regularization for the infinite product and is not rigorously true. As explained in the paragraph following (7.21) this is done in order to deal with the manipulations and a more rigorous treatment is given in the following section, where we generalize the Fredholm determinant for sequences of order greater than 1 and the resulting infinite product doesn't diverges, contrary to case of the infinite product involved in (7.21).

When we consider the bulk term, we miss some factors that appeared in the solved examples in two dimensions. Apart from the obvious factor depending on the fugacities, we miss the terms depending on k_{min} and k_{max}. As mentioned before, these terms come from the substraction of the self energies, which contributes with an additional factor to our infinite product. In the next section we include the terms that are lacking and find the general relation between the geometry and the grand potential for a system of characteristic size R.

7.4 Calculation of the Grand Potential Using Functional Determinants

Up to now we have been capable of establish a general asymptotic relation between the infinite product (7.11) and the expansion of the heat kernel (7.4), that is to say a relation between the spectrum of the Laplace operator defined on a given manifold and the geometry of the manifold. However, we are interested in establish a general relationship between the grand potential and the geometry. As mentioned, because of the substraction of the self energies, the expression for the grand partition function (4.35) involves a product slightly different to (7.11):

$$\Xi_\Lambda(\beta,\varsigma) = \left(\prod_k \left[\left(1-\frac{\kappa^2}{\lambda_k}\right) e^{\frac{\kappa^2}{\lambda_k^0}}\right]\right)^{-1/2} e^{\sum_\alpha \Lambda\varsigma_\alpha} \tag{7.43}$$

To establish the connection with this product we consider the generalization for the Fredholm determinant for $\mu > 1$ which is

$$F(\lambda) = \prod_{k=0}^{\infty}\left(1-\frac{\lambda}{\lambda_k}\right)\exp\left[\frac{\lambda}{\lambda_k}+\frac{\lambda^2}{2\lambda_k^2}+...+\frac{\lambda^{[\mu]}}{[\mu]\lambda_k^{[\mu]}}\right] \tag{7.44}$$

where $[\mu]$ is the integer part of μ. The exponential term in expression (7.44) is introduced in order to make the infinite product convergent when the order of the sequence is larger than one. We are interested in two and three dimensional manifolds when μ equals 1 or $\frac{3}{2}$ respectively. In both cases expression (7.44) equals

$$F(\lambda) = \prod_{k=0}^{\infty}\left(1-\frac{\lambda}{\lambda_k}\right) e^{\frac{\lambda}{\lambda_k}} \tag{7.45}$$

As the reader could have noticed, the case $\mu = 1$, that is, the two dimensional case is excluded in this formulation. As we will see, in this case an infrared divergence appears, the same divergence that we control with the cutoff $k_{\min}$ in the particular cases. Of course our final result for the grand potential will depend on this cutoff as does in the solved examples. Finally, remember that $k_{\min}$ depends on the arbitrary constant L which fixes the zero value for the Coulomb potential, and can be chosen as small as we want fixing this zero value at infinity.

Equation (7.45) is not exactly the product involved in the grand canonical partition function. The eigenvalues that appear in the exponential function in equation (7.43), are the eigenvalues calculated for a system without boundaries, and are different to those that appear in the exponential term in (7.45). However we can find a relationship with the grand partition function writing formally

$$\begin{aligned} \mathcal{F}(\lambda) &= \prod_{k=0}^{\infty}\left(1-\frac{\lambda}{\lambda_k}\right)e^{\frac{\lambda}{\lambda_k}} \\ &= \prod_{k=0}^{\infty}\left(1-\frac{\lambda}{\lambda_k}\right)e^{\frac{\lambda}{\lambda_k}+\frac{\lambda}{\lambda_k^0}-\frac{\lambda}{\lambda_k^0}} \\ &= \prod_{k=0}^{\infty}\left(1-\frac{\lambda}{\lambda_k}\right)e^{\frac{\lambda}{\lambda_k^0}+\frac{\lambda}{\lambda_k}-\frac{\lambda}{\lambda_k^0}} \end{aligned} \tag{7.46}$$

since from (7.43) we have

$$\left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2} = \prod_k\left[\left(1-\frac{\kappa^2}{\lambda_k}\right)e^{\frac{\kappa^2}{\lambda_k^0}}\right] \tag{7.47}$$

we can write

$$\begin{aligned} \mathcal{F}(R^2\kappa^2) &= \left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2}\prod_{k=0}^{\infty} e^{\frac{R^2\kappa^2}{\lambda_k}-\frac{R^2\kappa^2}{\lambda_k^0}} \\ &= \left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2}\exp\left(\sum_k\frac{R^2\kappa^2}{\lambda_k}-\sum_k\frac{R^2\kappa^2}{\lambda_k^0}\right) \\ &= \left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2}\exp\left[-R^2\kappa^2 Z_1(1)+R^2\kappa^2 Z^0(1)\right] \end{aligned} \tag{7.48}$$

where we have used the definition (7.12) that is to say that Z_1 and Z^0 are the Zeta functions for the eigenvalues of V_d calculated for a system of volume 1 and for V_d^0 respectively. Note that since Z^0 involves the continuum spectrum for a system without boundaries, it can be written as

$$Z^0(s) = \sum_{k=0}^{\infty} \frac{1}{\left(-\lambda_k^0\right)^s} = \frac{A'}{(2\pi)^2} \int \frac{d\mathbf{k}}{\left(-\lambda_k^0\right)^s}$$

where A' is for a system of volume 1 as before.

In the last section, equation (7.25) we introduced formally an expression of the type $\left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0}$ in order to evaluate the infinite product (7.11). In a more rigorous way one can define the functional determinant

$$D(R^2\kappa^2) = \exp\left[-\frac{\partial Z_R(0, R^2\kappa^2)}{\partial s}\right] \tag{7.49}$$

which is a finite regularization of the product (7.11) since $Z_R(s,a)$ is analytic in $s=0$. We found a formal relation between $\ln D(x)$ and the infinite product (7.11) which is divergent for $\mu > 1$. We saw how this allows the relation with the asymptotic expansion of the heat kernel up to terms $O(R^0)$. Furthermore, it is possible to probe that it exist an exact relationship between the functional determinant D and the infinite product (7.45). In fact they only differ by computable factor [39]:

$$D(R^2\kappa^2) = \exp\left[-\left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} + \mathrm{FP}\left[Z_1(1)\right] R^2\kappa^2\right] F(R^2\kappa^2) \tag{7.50}$$

where Z is again the Zeta function and $FP[f(s)]$ is the finite part of $f(s)$ defined as

$$\mathrm{FP}\left[f(s)\right] = f(s) \qquad \text{if } s \text{ is not a pole} \tag{7.51}$$

$$\mathrm{FP}\left[f(s)\right] = \lim_{\in\to 0} f(s+\in) - \frac{\mathrm{Residue}\left[f(s)\right]}{\in} \qquad \text{if } s \text{ is a simple pole} \tag{7.52}$$

The functional determinant $D(x)$ is known as the Zeta regularization of the Fredholm determinant, since expressed in the form (7.50) it regularize the otherwise divergent infinite product (7.11). From (7.50) we have

$$F(R^2\kappa^2) = D(R^2\kappa^2)\exp\left[\left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} - \mathrm{PF}Z_1(1)R^2\kappa^2\right] \tag{7.53}$$

then, using (7.48) we find

$$\left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2}\exp\left[R^2\kappa^2 R^2 Z^0(1) - \kappa^2 R^2 Z_1(1)\right] = D(\kappa^2)\exp\left[\left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} - PFZ_1(1)R^2\kappa^2\right] \tag{7.54}$$

that is

$$\left(\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}}\right)^{-2} \tag{7.55}$$
$$= D(R^2\kappa^2)\exp\left[\left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0}\right]\exp\left[-\mathrm{FP}Z_1(1)R^2\kappa^2 - R^2\kappa^2 Z^0(1) + R^2\kappa^2 Z_1(1)\right]$$

now, using the definition of finite part given in (7.52) we notice that the term in square brackets in the second exponential can be written as

$$-R^2\kappa^2\left[\lim_{\in\to 0} Z_1(1+\in) - \frac{\mathrm{Residue}\left[Z_1(1)\right]}{\in}\right] - R^2\kappa^2 Z^0(1) + R^2\kappa^2 Z_1(1) \tag{7.56}$$
$$= \lim_{\in\to 0}\left(\frac{\mathrm{Residue}\left[Z_1(1+\in)\right]}{\in} - Z^0(1)\right)R^2\kappa^2$$
$$= -\lim_{\in\to 0}\left(Z^0(1+\in) - \frac{\mathrm{Residue}\left[Z^0(1)\right]}{\in}\right)R^2\kappa^2 \tag{7.57}$$
$$= -\mathrm{FP}Z^0(1)R^2\kappa^2 \tag{7.58}$$

note that

$$\mathrm{Residue}\left[Z^0(1)\right] = \mathrm{Residue}\left[Z_1(1)\right] = \frac{c_{i_0}}{\Gamma(i_0)} \tag{7.59}$$

where c_{i_0} is the first coefficient in the expansion of the heat kernel (7.9). Remembering that the function $Z^0(1)$ is the Zeta function for the bulk eigenvalues we can find explicitly its finite part since

$$Z^0(s) = \sum_{k=0}^{\infty} \frac{1}{\left(-\lambda_k^0\right)^s} = \frac{A'}{(2\pi)^2} \int \frac{d\mathbf{k}}{\left(-\lambda_k^0\right)^s} \tag{7.60}$$
$$= \frac{A'}{2\pi} \int_{k_{\min}}^{k_{\max}} \frac{kdk}{k^{2s}}$$
$$= \frac{A'}{2\pi} \int_{k_{\min}}^{k_{\max}} k^{1-2s} dk$$
$$= \frac{A'}{2\pi} \left. \frac{k^{2-2s}}{2-2s} \right|_{k_{\min}}^{k_{\max}}$$
$$= \frac{A'}{4\pi} \left(k_{\max}^{2-2s} - k_{\min}^{2-2s}\right) \frac{1}{1-s}$$

where $k_{\min}$ is the lower integration limit that we found in (A.5) for the case of a non-confined system in two dimensions

$$k_{\min} = \frac{2e^{-\gamma}}{L}\,. \tag{7.61}$$

Now, taking the approximation $s \gtrapprox 1$, the term $k_{\max}^{2-2s}$ vanishes for large values of $k_{\max}$. The term that remains can be expanded in this approximation to have

$$Z^0(s) = \frac{A'}{4\pi} \left[\frac{1}{1-s} - 2\ln k_{\min} + O((s-1)) \right] \tag{7.62}$$

from (7.62) and the definition of FP (7.52) we see that the finite part of $Z^0(1)$ equals $-2\frac{A'}{4\pi} \ln k_{\min}$.

Summarizing, we have probed that (7.55) can be written as

$$\left(\frac{\Xi_\Lambda(\beta, \varsigma)}{e^{\sum_\alpha \Lambda \varsigma_\alpha}} \right)^{-2} = D(R^2\kappa^2) \exp\left[\left. \frac{\partial Z_R(s,a)}{\partial s} \right|_{s=0,a=0} \right] \exp\left[\frac{A'}{2\pi} R^2 \kappa^2 \ln k_{\min} \right] \tag{7.63}$$

taking logarithm of both sides of (7.63) and using the definitions of $D(\kappa^2)$ and $Z'(0)$ we find

$$-2\ln\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}} = \ln D(R^2\kappa^2) + \left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} + \frac{A'}{2\pi}R^2\kappa^2\ln k_{\min}$$
$$= \left.\frac{\partial Z_R(s,a)}{\partial s}\right|_{s=0,a=0} - \left.\frac{\partial Z_R(s,R^2\kappa^2)}{\partial s}\right|_{s=0} + \frac{A'}{2\pi}R^2\kappa^2\ln k_{\min} \quad (7.64)$$

finally (7.25) and (7.42) lead to

$$-2\ln\frac{\Xi_\Lambda(\beta,\varsigma)}{e^{\sum_\alpha \Lambda\varsigma_\alpha}} = -\frac{A'\kappa^2R^2}{4\pi}(2\ln\kappa-1) - \frac{B'}{4}\kappa R + \frac{1}{3}\chi\ln R + \frac{A'}{2\pi}R^2\kappa^2\ln k_{\min} + O(R^0) \quad (7.65)$$

writing $\Lambda = A'R^2$ we have finally that the general expansion for the grand potential $\beta\Omega = -\ln\Xi_\Lambda$ becomes

$$\beta\Omega = -\frac{\kappa^2\Lambda}{8\pi}\left[2\ln\left(\frac{\kappa}{k_{\min}}\right) - 1 - 8\pi\sum_\alpha \varsigma_\alpha\right] - \frac{\kappa}{8}B'R + \frac{1}{6}\chi\ln R + O(R^0) \quad (7.66)$$

this is the relationship between the grand potential and the geometry we where looking for.

Comparison with (7.42) allow to say that, in general, the substraction of the self energies causes the inclusion of a bulk term depending on $k_{\min}$. This was expected since just the same situation was encountered when we calculated the expansion for the specific examples in two dimensions. In (7.66) we can also identify the surface tension, which coincide with the value that we found in the examples. Finally we recognize the universal logaritmic expression depending only on $\frac{1}{6}\chi$ as expected.

7.5 System Confined in a Square Domain

As an illustration of the above result consider the case of a system confined in an square domain. Conformal field theory predicts that in the case of a system confined in a geometry with corners in the boundary, appears a contribution

$$\frac{\gamma}{24\pi}(1-(\pi/\gamma)^2)\ln R \tag{7.67}$$

to the grand potential for each corner with interior angle γ [22]. In the case of a square $\gamma = \pi/2$ and the contribution per corner equals

$$\frac{\pi/2}{24\pi}(1-(2\pi/\pi)^2)\ln R = \frac{1}{48}(1-4)\ln R = -\frac{3}{48}\ln R \tag{7.68}$$

then the total contribution is $-\frac{1}{4}\ln R$. As discussed before, for a Coulomb system the sign will change.

On the other hand the eigenvalues for this case can be found easily by separation of variables. Expressing the Laplace operator in rectangular coordinates the eigenvalue equation can be written as

$$\frac{\partial^2\Psi(x,y)}{\partial x^2} + \frac{\partial^2\Psi(x,y)}{\partial y^2} = \lambda\Psi(x,y) \tag{7.69}$$

let $\lambda = -\lambda_x - \lambda_y$, $\Psi(x,y) = X(x)Y(y)$

$$\frac{X''}{X} + \frac{Y''}{Y} = -\lambda_x - \lambda_y \tag{7.70}$$

we find two independent eigenvalue problems

$$X'' + \lambda_x X = 0 \tag{7.71}$$

$$Y'' + \lambda_y Y = 0 \tag{7.72}$$

the solution of the first equations can be written as

$$X(x) = A\cos\sqrt{\lambda_x}x + B\sin\sqrt{\lambda_x}x \tag{7.73}$$

with Dirichlet boundary conditions $X(0) = X(a) = 0$ for all y, where a is the length of each side of the square. Then we have $A = 0$ and $B \sin \sqrt{\lambda_x} a = 0$. We conclude that $\lambda_x = \lambda_n = \left(\frac{n\pi}{a}\right)^2$, $n = 0, 1, 2...$ And in a similar fashion $\lambda_y = \lambda_l = \left(\frac{l\pi}{a}\right)^2$, $l = 0, 1, 2...$ Finally

$$\lambda_{n,l} = -\lambda_n - \lambda_l = -\frac{2\pi^2}{a^2}\left(n^2 + l^2\right), \; n = 0, 1, 2..., l = 0, 1, 2... \tag{7.74}$$

Let us take for simplicity $a = 1$, then $\lambda_{n,l} = -2\pi^2\left(n^2 + l^2\right)$. The heat kernel for this spectrum is by definition

$$\Theta(t) = \sum_{n,l=0}^{\infty} e^{t\lambda_{n,l}} = \left(\sum_{n=0}^{\infty} e^{-2\pi^2 n^2 t}\right)^2 \tag{7.75}$$

and satisfy the asymptotic expansion for $t \to +0$ [39]

$$\begin{aligned} \Theta(t) &= \left(\frac{\sqrt{\pi}}{2}\left(2\pi^2 t\right)^{-1/2} - \frac{1}{2} + O(e^{-\pi^2/t})\right)^2 \\ &= \frac{1}{8\pi t} - \frac{1}{\sqrt{8\pi} t^{1/2}} + \frac{1}{4} + O(e^{-\pi^2/t}) \end{aligned} \tag{7.76}$$

Applying the same argument developed above for the general case to this heat kernel, we find the finite size correction $\frac{1}{4}\ln R$ as expected. This is easily seen from (7.29) since the summand that doesn't depend on t is the one that gives the coefficient of the logarithmic finite size correction at the end.

Appendix A

The Bulk

For reference proposes, in this appendix we summarize the results found in chapter 5 concerned to the grand potentials for non-confined systems.

In three dimensions, the result for the bulk grand potential per unit volume is

$$\frac{\beta\Omega}{\Lambda} = -\frac{\kappa^3}{12\pi} - \sum_\alpha \varsigma_\alpha. \tag{A.1}$$

In two dimensions we found that the interparticle energy gives

$$V_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi}\int_0^{2\pi}\int_0^\infty \frac{ke^{ik|\mathbf{r}-\mathbf{r}'|\cos\theta}}{k^2} dk d\theta = \int_0^\infty \frac{dk}{k} J_0(k\left|\mathbf{r}-\mathbf{r}'\right|) \tag{A.2}$$

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 $k \to 0$

$$V_2(\mathbf{r}, \mathbf{r}') = \int_{k_{\text{min}}}^\infty \frac{dk}{k} J_0(k\left|\mathbf{r}-\mathbf{r}'\right|) \tag{A.3}$$

$$= -\gamma + \ln\frac{2}{|\mathbf{r}-\mathbf{r}'|\, k_{\text{min}}} + o(1) \tag{A.4}$$

where $k_{\text{min}} \to 0$ and γ is the Euler constant. Since we know that $V_2(\mathbf{r}, \mathbf{r}') = -\ln\frac{|\mathbf{r}-\mathbf{r}'|}{L}$ we can find the expression for k_{min} by comparison: $V_2(|\mathbf{r}-\mathbf{r}'|) = -\ln\left(\frac{|\mathbf{r}-\mathbf{r}'|k_{\text{min}}}{2e^{-\gamma}}\right) = -\ln\frac{|\mathbf{r}-\mathbf{r}'|}{L}$;

then

$$k_{\rm min} = \frac{2e^{-\gamma}}{L} \,. \tag{A.5}$$

Finally, the result for the bulk grand potential in two dimensions is

$$\frac{\beta\Omega}{\Lambda} = \frac{\kappa^2}{4\pi}\left[-\ln\frac{\kappa L}{2} - \gamma + \frac{1}{2}\right] - \sum_\alpha \zeta_\alpha \tag{A.6}$$

where all terms that vanish when $L \to \infty$ have been omitted.

Appendix B

The Disk

In this appendix we present the details of the calculation of the grand potential for a Coulomb system on a disk studied in chapter 5. First we need to find the eigenvalues of the Laplace operator for this geometry. Let $\Psi(r,\varphi) = f(r)\Phi(\varphi)$, we look for the solution of the equation $\mathbf{\Delta}\Psi(r,\varphi) = \lambda\Psi(r,\varphi)$. Using the explicit form of the Laplace operator in polar coordinates $\mathbf{\Delta} \equiv \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}$, we find

$$\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} + l^2\Phi(\varphi) = 0 \tag{B.1}$$

$$r\frac{\partial}{\partial r}\left(r\frac{\partial f(r)}{\partial r}\right) - \left(\lambda r^2 + l^2\right) f(r) = 0 \tag{B.2}$$

The solution of (B.1) is trivial. In (B.2) we recognize the modified Bessel equation which solutions are the modified Bessel functions $I_l(x)$ of order l. Then, solving these differential equations for $f(r)$ and $\Phi(\varphi)$ we obtain

$$\Psi(r,\varphi) \propto e^{il\varphi} I_l(\sqrt{\lambda}r) \tag{B.3}$$

Using the Dirichlet boundary condition $\Psi(R,\varphi) = 0$; $\Psi(r,0) = \Psi(r,2\pi)$, we find $l = 0, \pm1, \pm2...$ and $I_l\left(\sqrt{\lambda_k}R\right) = 0$. This means that $\sqrt{\lambda_k}R = \nu_{l,n}$ is the n-th cero of I_l or what is the same

$$\lambda_k = \frac{\nu_{l,n}^2}{R^2} \text{ with } \nu_{l,n} \text{ n-th cero of } I_l(x),\ l = 0, \pm1, \pm2... \tag{B.4}$$

Next we replace this eigenvalues for the Laplace operator for this geometry in the expression for the grand partition function (4.35). Then we have

$$\Xi_\Lambda(\beta,\varsigma) = \left(\prod_k \left[\left(1 - \frac{R^2\kappa^2}{\nu_{l,n}^2}\right) e^{\frac{\kappa^2}{\lambda_k^0}}\right]\right)^{-1/2} e^{\sum_\alpha \Lambda\varsigma_\alpha} \tag{B.5}$$

where $\kappa^2 = \sum_\alpha s_d\varsigma_\alpha\beta q_\alpha^2 = 2\pi\beta\sum_\alpha \varsigma_\alpha q_\alpha^2$ for the case of a two dimensional system and λ_k^0 are the eigenvalues of the Laplace operator for a non-confined two-dimensional system as discussed before.

Now we proceed directly to evaluate the grand potential $\Omega = -k_BT\ln\Xi_\Lambda$. Taking the logarithm of (B.5) we find

$$\beta\Omega = \frac{1}{2}\ln\left[\prod_{l=-\infty}^{\infty}\prod_{n=1}^{\infty}\left(1 - \frac{R^2\kappa^2}{\nu_{l,n}^2}\right)\right] + \frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha \tag{B.6}$$

then, the infinite product involved in the expression that we found for Ξ_Λ became a double product in the indexes n and l denoting the root and the order of the modified Bessel function $I_l(x)$ respectively. To evaluate this double product we introduce the non dimensional parameter $\alpha = R\kappa$ then we can write

$$\frac{1}{2}\ln\left[\prod_{l=-\infty}^{\infty}\prod_{n=1}^{\infty}\left(1 - \frac{\alpha^2}{\nu_{l,n}^2}\right)\right] = \frac{1}{2}\sum_{l=-\infty}^{\infty}\ln\prod_{n=1}^{\infty}\left(1 - \frac{\alpha^2}{\nu_{l,n}^2}\right) \tag{B.7}$$

The infinite product in the index n converges. In fact it is nothing but the infinite product representation of the modified Bessel function, multiplied by a factor depending on l [44]

$$\prod_{n=1}^{\infty}\left(1-\frac{\alpha^2}{\nu_{l,n}^2}\right)=l!\left(\frac{2}{\alpha}\right)^l I_l(\alpha) \tag{B.8}$$

Note that the pre-factor assures that both sides of (B.8) tend to 1 when $\alpha \to 0$. Then using (B.7) we can write

$$\frac{1}{2}\ln\left[\prod_{l=-\infty}^{\infty}\prod_{n=1}^{\infty}\left(1-\frac{\alpha^2}{\nu_{l,n}^2}\right)\right]=\sum_{l=1}^{\infty}\ln\left(l!\left(\frac{2}{\alpha}\right)^l I_l(\alpha)\right)+\frac{1}{2}I_0(\alpha) \tag{B.9}$$

where we have used the modified Bessel functions' property $I_l(x)=I_{-l}(x)$. The right hand side of (B.9) can be expanded to have

$$\sum_{l=1}^{\infty}\ln(l!)+\sum_{l=1}^{\infty}l\ln\left(\frac{2}{\alpha}\right)+\sum_{l=1}^{\infty}\ln I_l(\alpha)+\frac{1}{2}I_0(\alpha) \tag{B.10}$$

these sums are obviously divergent. However these divergences exactly cancel with the other divergence that appears in (B.6) due to the second summand of the right side, the divergence that appears due to the substraction of the self energy form the Hamiltonian of the system. To see how this works let us introduce an upper cutoff N for these sums. Then we have

$$\begin{aligned}\sum_{l=1}^{N}\ln l! &= \ln(1!)+\ln(2!)+\cdots+\ln(N!) \\ &= \ln\left[(1!)(2!)\cdots(N!)\right] \\ &= (N+1)\ln(N!)-\sum_{l=1}^{N}l\ln l\end{aligned} \tag{B.11}$$

the first term of the right side is easily evaluated using the Stirling approximation: $\ln N! \simeq N\ln N - N + \frac{1}{2}\ln(2\pi N)$ valid for large values of N. To find the second term we use the Euler-McLaurin summation formula:

$$\sum_{l=1}^{N}f(l)\simeq\int_1^N f(l)dl+\frac{1}{2}\left[f(1)+f(N)\right]+\frac{1}{12}\left[f'(N)-f'(1)\right] \tag{B.12}$$

After performing the integrations and simplifying we find

$$\sum_{l=1}^{N} \ln l! = \frac{1}{2}N^2 \ln N + N \ln N + \frac{5}{12} \ln N - \frac{3}{4}N^2 - N + \frac{1}{2}N \ln 2\pi + O\left(N^0\right) \tag{B.13}$$

the truncated second sum in (B.10) is easily evaluated

$$\sum_{l=1}^{N} l \ln\left(\frac{2}{\alpha}\right) = \frac{N(N+1)}{2} \ln\left(\frac{2}{\alpha}\right). \tag{B.14}$$

The third sum in (B.10) requires more work since it involves the modified Bessel functions. To be able to use the Euler-McLaurin summation formula (B.12) we first use the Debye expansion for $I_l(\alpha)$ valid for large values of l and the argument. For clarity and keeping in mind that this part of the calculation will appear in other examples, the detailed procedure is presented in appendix D. There we apply (B.12) to each one of the sums that appear when we use the referred Debye expansion for $I_l(\alpha)$. After doing that we find a huge expression in terms of analytic functions of the argument α. Adding to this expression the contribution of (B.13), (B.14) and $\frac{1}{2}I_0(\alpha) \simeq \frac{1}{2}\frac{e^\alpha}{\sqrt{2\pi\alpha}}$ [44], we obtain the result of the truncated expression (B.10) in terms of the cut N. Then we expand this expression for large values of N and collect terms in powers of $\alpha = \kappa R$. Finally we find

$$\frac{1}{4}\left(1 + \ln\frac{2N}{\kappa R} - \frac{4\pi\varsigma}{\kappa^2}\right)\kappa^2 R^2 - \left(\frac{\pi}{4}\right)\kappa R + \frac{1}{6}\ln R + O(R^0) \tag{B.15}$$

as we see, this expression is still dependent on N, that is, it is divergent. However to obtain $\beta\Omega$ we still have to add the terms $\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha \Lambda\varsigma_\alpha$ that appear in (B.6). To do that we remember that the spectrum $\left\{\lambda_k^0\right\}$ is constituted by the eigenvalues of Δ calculated without boundaries. Then we can approximate the sum on k by an integration as follows

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^2}\int \frac{d\mathbf{k}}{\mathbf{k}^2} = -\frac{1}{2}\frac{\kappa^2\Lambda}{(2\pi)^2}\int_0^{2\pi} d\phi \int_{k_{\min}}^{k_{\max}} \frac{kdk}{k^2} \tag{B.16}$$

then we have

$$\frac{1}{2}\sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{\kappa^2\Lambda}{4\pi}\ln\left(\frac{k_{\max}}{k_{\min}}\right) \tag{B.17}$$

the value of $k_{\min}$ was found when we studied the case of a bulk system in two dimensions. Using equation (A.5) to replace this value and $\Lambda = \pi R^2$ for the total extension of the system we find

$$\beta\Omega = \left[\frac{\kappa^2}{4\pi}\left(1 + \ln\left(\frac{2e^{-\gamma}}{\kappa L}\frac{2N}{k_{\max}R}\right)\right) - \sum_\alpha \varsigma_\alpha\right]\pi R^2 - \frac{\kappa\pi}{4}R + \frac{1}{6}\ln R + O(R^0) \tag{B.18}$$

to evaluate the value of $k_{\max}$ we identify the term in square brackets with the value of the grad potential calculated for the bulk term in two dimensions (A.6). Thus

$$\frac{\kappa^2}{4\pi}\left[-\ln\frac{\kappa L}{2} - \gamma + \frac{1}{2}\right] - \sum_\alpha \varsigma_\alpha = \frac{\kappa^2}{4\pi}\left(1 + \ln\left(\frac{2e^{-\gamma}}{\kappa L}\frac{2N}{k_{\max}R}\right)\right) - \sum_\alpha \varsigma_\alpha \tag{B.19}$$

solving for $k_{\max}$ we find

$$k_{\max} = \frac{2N}{R}e^{1/2} \tag{B.20}$$

replacing this value in (B.18) we finally find the expansion for the grand potential

$$\beta\Omega = \left[\frac{1}{4\pi}\kappa^2\ln\left(\frac{2e^{-\gamma+\frac{1}{2}}}{L\kappa}\right) - \sum_\alpha \varsigma_\alpha\right]\pi R^2 - \left[\frac{\kappa}{4}\right]\pi R + \frac{1}{6}\ln R + O(R^0) \tag{B.21}$$

Appendix C

The Annulus

In a way similar to the case of the disk, we proceed to calculate the eigenvalues of the Laplace operator for this geometry. From the case of the disk we know that the angular part of the wave functions is simply $e^{il\varphi}$ with $l = 0, \pm 1 \pm 2...$ In consequence let $\Psi(r,\varphi) = f(r)e^{il\varphi}$, we need to solve $\mathbf{\Delta}\Psi(r,\varphi) = \lambda\Psi(r,\varphi)$ where $\mathbf{\Delta} \equiv \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}$ is the Laplace operator in polar coordinates. Replacing $\Psi(r,\varphi)$ we find the following differential equation for the radial part $f(r)$

$$r^2 f''(r) + rf'(r) - (l^2 + \lambda r^2)f(r) = 0 \tag{C.1}$$

This is the modified Bessel equation. It is well known that for non integer l the functions $\left\{I_l(\sqrt{\lambda}r), I_{-l}(\sqrt{\lambda}r)\right\}$ are a set of linearly independent solutions for this equation. However, for integer l these solutions are not linearly independent and another set of solutions must be constructed [47]. Two solutions linearly independent for this equation are

$$f_1(r) = I_l(\sqrt{\lambda}r) \tag{C.2}$$

$$f_2(r) = K_l(\sqrt{\lambda}r) = \lim_{\upsilon\to l} \frac{\pi}{2\sin\nu\pi}\left[I_{-\nu}(\sqrt{\lambda}r) - I_\nu(\sqrt{\lambda}r)\right] \tag{C.3}$$

Finally $\Psi(r,\varphi)$ will be a linear combination of f_1 and f_2 multiplied by the angular factor $e^{il\varphi}$

$$\Psi(r,\varphi) = \left[AI_l(\sqrt{\lambda}r) + BK_l(\sqrt{\lambda}r)\right]e^{il\varphi}$$

to find the eigenvalues we apply the Dirichlet boundary conditions

$$AI_l(\sqrt{\lambda}a) + BK_l(\sqrt{\lambda}a) = 0 = \Psi(a,\varphi) \tag{C.4}$$

$$AI_l(\sqrt{\lambda}b) + BK_l(\sqrt{\lambda}b) = 0 = \Psi(b,\varphi) \tag{C.5}$$

where a is the inner radius of the annulus and b its outer radius. Equations (C.4) and (C.5) can be seen as a system of two coupled linear equations in A and B. They have a non-trivial solution only if the determinant of its coefficients equals zero

$$\det\begin{pmatrix} I_l(\sqrt{\lambda}a) & K_l(\sqrt{\lambda}a) \\ I_l(\sqrt{\lambda}b) & K_l(\sqrt{\lambda}b)\end{pmatrix} = 0 \tag{C.6}$$

that is to say

$$I_l(\sqrt{\lambda}a)K_l(\sqrt{\lambda}b) - K_l(\sqrt{\lambda}a)I_l(\sqrt{\lambda}b) = 0 \tag{C.7}$$

we conclude that for the annulus the eigenvalues of the Laplace operator subject to Dirichlet boundary conditions are

$$\lambda_k = \upsilon_{l,n} \ \text{: n-th root of equation (C.7)}, \quad l = 0, \pm 1 \pm 2... \tag{C.8}$$

introducing these eigenvalues in the expression (4.35) we have for the grand potential

$$\begin{aligned}\beta\Omega &= \frac{1}{2}\sum_{l=-\infty}^{\infty}\ln\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l,n}^2}\right)+\frac{1}{2}\sum_k\frac{\kappa^2}{\lambda_k^0}-\sum_\alpha\Lambda\varsigma_\alpha \\ &= \frac{1}{2}\sum_{l=-\infty}^{\infty}\ln\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l,n}^2}\right)-\frac{\Lambda\kappa^2}{2\,(2\pi)^2}\int_0^{2\pi}d\phi\int_{k_{\min}}^{k_{\max}}\frac{kdk}{k^2}-\sum_\alpha\Lambda\varsigma_\alpha\end{aligned} \tag{C.9}$$

In writing (C.9) we have approximated the sum on k by an integral as in (B.16). Similarly, the infinite product in the index n, which denotes the n-th root of equation (C.7) converges to the expression

$$\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{l,n}^2}\right)=\frac{[I_l(\kappa a)K_l(\kappa b)-K_l(\kappa a)I_l(\kappa b)]}{\frac{1}{2l}\left(\left(\frac{a}{b}\right)^l-\left(\frac{b}{a}\right)^l\right)}\quad\text{for } l\neq 0 \tag{C.10}$$

as detailed in chapter 5. In the case $l=0$ the denominator changes but is equally simple

$$\prod_{n=1}^{\infty}\left(1-\frac{\kappa^2}{\upsilon_{0,n}^2}\right)=\frac{K_0(\kappa b)I_0(\kappa a)-I_0(\kappa b)K_0(\kappa a)}{\ln\frac{a}{b}}\qquad\text{for } l=0 \tag{C.11}$$

The denominators in the expressions (C.10) and (C.11) assure that both sides of the equations tend to 1 when $\kappa\to 0$. Then the first term of the right side of (C.9) equals

$$\begin{aligned}&\sum_{l=1}^{\infty}\ln\left[2l\left(\left(\frac{a}{b}\right)^l-\left(\frac{b}{a}\right)^l\right)^{-1}[K_l(\kappa b)I_l(\kappa a)-I_l(\kappa b)K_l(\kappa a)]\right] \\ &+\frac{1}{2}\ln\left[\left(\ln\frac{a}{b}\right)^{-1}[K_0(\kappa b)I_0(\kappa a)-I_0(\kappa b)K_0(\kappa a)]\right]\end{aligned} \tag{C.12}$$

where we have used the property of the modified Bessel functions $I_l(x)=I_{-l}(x)$ and $K_l(x)=K_{-l}(x)$. The contribution of $K_l(\kappa b)I_l(\kappa a)$ is exponentially smaller than the one from the term $I_l(\kappa b)K_l(\kappa a)$ when $b\to\infty$, $a\to\infty$ and $b-a>0$. For example in the case for $l=0$, using the asymptotic form for $I_0(z)$ and $K_0(z)$ for large values of the argument

$$I_0(z)\sim\frac{e^z}{\sqrt{2\pi z}},\qquad K_0(z)\sim\frac{\sqrt{\pi}e^{-z}}{\sqrt{2z}} \tag{C.13}$$

we have $K_0(\kappa b)I_0(\kappa a) = \frac{e^{-\kappa(b-a)}}{2z} \ll K_0(\kappa a)I_0(\kappa b) = \frac{e^{\kappa(b-a)}}{2z}$, remember that $b-a>0$. This also holds in the general case for $l \neq 0$ as seen from Debye formulas for $K_l(x)$ and $I_l(x)$ given in appendix D. Then we can correctly approximate (C.12) to

$$\sum_{l=1}^{\infty} \ln \left[2l \left(\left(\frac{b}{a}\right)^l - \left(\frac{a}{b}\right)^l \right)^{-1} I_l(\kappa b)K_l(\kappa a) \right] + \frac{1}{2} \ln \left[\left(\ln \frac{b}{a} \right)^{-1} I_0(\kappa b)K_0(\kappa a) \right] \tag{C.14}$$

again, the sum on l diverges, but like in the case of the disk the divergence due to this sum is cancelled by the divergence of the second term of the right side in expression (C.9). Proceeding similarly to the case of the disk we introduce an upper cutoff N. Then we have for the term involving the sums in (C.14)

$$\sum_{l=1}^{N} \ln \left[2l \left(\left(\frac{b}{a}\right)^l - \left(\frac{a}{b}\right)^l \right)^{-1} \right] + \sum_{l=1}^{N} \ln \left[I_l(\kappa b) \right] + \sum_{l=1}^{N} \ln \left[K_l(\kappa a) \right] \tag{C.15}$$

the first sum is easily evaluated since

$$\begin{aligned}
&\sum_{l=1}^{N} \ln \left[2l \left(\left(\frac{b}{a}\right)^l - \left(\frac{a}{b}\right)^l \right)^{-1} \right] \\
&= -\sum_{l=1}^{N} \ln \left(\left(\frac{b}{a}\right)^l - \left(\frac{a}{b}\right)^l \right) + \sum_{l=1}^{N} \ln 2l \\
&= -\sum_{l=1}^{N} \ln \left[\left(\frac{b}{a}\right)^l \left(1 - \left(\frac{a}{b}\right)^{2l} \right) \right] + \sum_{l=1}^{N} \ln 2l \\
&= -\sum_{l=1}^{N} l \ln \left(\frac{b}{a}\right) - \sum_{l=1}^{N} \ln \left(1 - \left(\frac{a}{b}\right)^{2l} \right) + \sum_{l=1}^{N} \ln 2l \\
&\simeq \sum_{l=1}^{N} \ln 2l - \sum_{l=1}^{N} l \ln \left(\frac{b}{a}\right) + O(1)
\end{aligned} \tag{C.16}$$

In the last equation we use the fact that $\sum_{l=1}^{N} \ln \left(1 - \left(\frac{a}{b}\right)^{2l}\right)$ converges to a finite function of $a/b < 1$ for $N \to \infty$, which constitute a term of $O(1)$. Using the Euler-McLaurin summation formula $\sum_{l=1}^{N} f(l) \simeq \int_1^N f(l)dl + \frac{1}{2}[f(1) + f(N)] + \frac{1}{12}[f'(N) - f'(1)]$ to evaluate these two sums we have

$$\sum_{l=1}^{N} \ln 2l = N(\ln 2 + \ln N - 1) + \frac{1}{2}\ln N + O(N^0)) \tag{C.17}$$

and

$$\sum_{l=1}^{N} l \ln\left(\frac{b}{a}\right) = \frac{1}{2}\ln\left(\frac{b}{a}\right)\left(N^2 + N\right) \tag{C.18}$$

putting (C.17) and (C.18) together we have

$$\begin{aligned} &\sum_{l=1}^{N} \ln\left[2l\left(\left(\frac{b}{a}\right)^l - \left(\frac{a}{b}\right)^l\right)^{-1}\right] &\text{(C.19)}\\ = \;& N\left(\ln 2 + \ln N - 1\right) + \frac{1}{2}\ln N - \frac{1}{2}\ln\left(\frac{b}{a}\right)\left(N^2 + N\right) + O(N^0) \end{aligned}$$

To evaluate the second and third sums in (C.15) we use the Debye asymptotic formula for $I_l(\kappa b)$ and $K_l(\kappa a)$ and apply the Euler-McLaurin summation formula to each term. The detailed calculations are presented in appendix D. Note that the third sum is the same involved in the calculation for the disk. We still have to take charge of the second summand in (C.14). Using the asymptotic expression (C.13) for $I_0(\kappa b)$ and $K_0(\kappa a)$ [44] we have

$$\frac{1}{2}\ln\left[I_0(\kappa b)K_0(\kappa a)\right] = \frac{1}{2}\ln\left[\frac{e^{\kappa b}}{\sqrt{2\kappa b}}\frac{e^{-\kappa a}}{\sqrt{2\kappa a}}\right] = \frac{1}{2}\ln\left[\frac{e^{\kappa(b-a)}}{\kappa\sqrt{ab}}\right] + O(N^0) \tag{C.20}$$

Finally, putting all this together and expanding the result for large values of N we find for the grand potential given in (C.9)

$$
\begin{aligned}
&(k_B T)^{-1}\,\Omega \qquad\qquad (C.21)\\
= &\ \frac{1}{24}\left(-6\alpha^2+6\alpha+6\beta^2-6\beta-\alpha^2\ln 64+\beta^2\ln 64+2\ln\alpha+6\ln\alpha\right)+\\
&\frac{1}{24}\left(-2\ln\left[\frac{\alpha}{1+\sqrt{1+\alpha^2}}\right]-2\ln\left[1+\sqrt{1+\alpha^2}\right]+6\alpha^2\ln\left[1+\sqrt{1+\alpha^2}\right]\right)+\\
&\frac{1}{24}\left(-2\ln\beta+6\ln\beta+2\ln\left[\frac{\beta}{1+\sqrt{1+\beta^2}}\right]+2\ln\left[1+\sqrt{1+\beta^2}\right]\right)\\
&\frac{1}{24}\left(-6\beta^2\ln\left[1+\sqrt{1+\beta^2}\right]+12\ln\left[\frac{e^{-\alpha+\beta}}{\sqrt{\alpha\beta}}\right]+6\alpha^2\ln\frac{1}{N}-6\beta^2\ln\frac{1}{N}\right)\\
&+\frac{1}{24}\left(-6\alpha\pi-6\beta\pi\right)-\frac{(\beta^2-\alpha^2)}{4}\left(\ln k_{\max}-\ln k_{\min}\right)-\frac{\pi(\beta^2-\alpha^2)}{\kappa^2}\sum_\alpha\varsigma_\alpha+O(N^0)
\end{aligned}
$$

where we have used $\Lambda=\pi(b^2-a^2)$ for the total extension of the system and the non dimensional parameters $\alpha=a\kappa$ and $\beta=b\kappa$. To find the thermodynamic limit we still have to expand the terms $6\alpha^2\ln\left[1+\sqrt{1+\alpha^2}\right]$ and $6\beta^2\ln\left[1+\sqrt{1+\beta^2}\right]$ for large values of α and β

$$
6\alpha^2\ln\left[1+\sqrt{1+\alpha^2}\right] = 6\alpha^2\ln a+6\alpha-O(\alpha^{-1}) \qquad (C.22)
$$

$$
6\beta^2\ln\left[1+\sqrt{1+\beta^2}\right] = 6\beta^2\ln\beta+6\beta-O(\alpha^{-1}) \qquad (C.23)
$$

after simplifying we find for the bulk term

$$
\begin{aligned}
&(k_B T)^{-1}\,\Omega_{bulk} \qquad\qquad (C.24)\\
= &\ \frac{1}{4}\left(-\alpha^2+\beta^2-\alpha^2\ln 2+\beta^2\ln 2+\alpha^2\ln\alpha-\beta^2\ln\beta+\alpha^2\ln\frac{1}{N}-\beta^2\ln\frac{1}{N}\right)+\\
&-\frac{(\beta^2-\alpha^2)}{4}\left(\ln k_{\max}-\ln k_{\min}\right)-\Lambda\sum_\alpha\varsigma_\alpha
\end{aligned}
$$

simplifying

$$(k_BT)^{-1}\,\Omega_{bulk} = \tag{C.25}$$
$$\frac{1}{4} \quad \left[\alpha^2 \ln\frac{\alpha k_{\max}}{2N} - \beta^2 \ln\frac{\beta k_{\max}}{2N} - \alpha^2 + \beta^2\right] + \frac{1}{4}\left[(\beta^2-\alpha^2)\ln k_{\min} - 4\Lambda\sum_\alpha \varsigma_\alpha\right]$$

now, equating with the bulk grand potential in two dimensions (A.6):

$$\begin{aligned} &\frac{(\beta^2-\alpha^2)}{4}\left[\frac{1}{2} + \ln\frac{k_{\min}}{\kappa}\right] - \Lambda\sum_\alpha \varsigma_\alpha \\ = \quad &\frac{1}{4}\left[(\beta^2-\alpha^2)\ln k_{\min} - 4\Lambda\sum_\alpha \varsigma_\alpha\right] - \frac{(\beta^2-\alpha^2)}{4}\ln\kappa + \frac{(\beta^2-\alpha^2)}{8} \end{aligned} \tag{C.26}$$

and simplifying we find

$$\beta^2 \ln\frac{\beta k_{\max}}{2N} - \alpha^2 \ln\frac{\alpha k_{\max}}{2N} = (\beta^2-\alpha^2)C \tag{C.27}$$

where $C = \ln\left(\kappa e^{1/2}\right)$. Solving for $k_{\max}$

$$\begin{aligned} \left(\frac{\beta k_{\max}}{2N}\right)^{\beta^2}\left(\frac{\alpha k_{\max}}{2N}\right)^{-\alpha^2} &= e^{(\beta^2-\alpha^2)C} \\ \left(\frac{k_{\max}}{2N}\right)^{\beta^2-\alpha^2} &= \alpha^{\alpha^2}\beta^{-\beta^2}e^{(\beta^2-\alpha^2)C} \end{aligned} \tag{C.28}$$

then we have

$$k_{\max} = 2Ne^{C}f(\alpha,\beta) = 2N\kappa e^{1/2}f(\alpha,\beta) \tag{C.29}$$

where

$$f(\alpha,\beta) = \alpha^{\frac{\alpha^2}{\beta^2-\alpha^2}}\beta^{-\frac{\beta^2}{\beta^2-\alpha^2}} \tag{C.30}$$

which, using $x = \alpha/\beta$, can be written as

$$\begin{aligned} f(\alpha,\beta) &= \alpha^{\frac{1}{x^2-1}}\beta^{-\frac{x^2}{x^2-1}} && \text{(C.31)} \\ &= \left(\frac{\alpha^{x^2+1-x^2}}{\beta^{x^2}}\right)^{\frac{1}{x^2-1}} && \text{(C.32)} \\ &= \left(\frac{\alpha}{\beta}\right)^{\frac{x^2}{x^2-1}}\left(\alpha^{1-x^2}\right)^{\frac{1}{x^2-1}} && \text{(C.33)} \\ &= \frac{1}{\alpha}x^{\frac{x^2}{x^2-1}} && \text{(C.34)} \end{aligned}$$

replacing the value of $k_{\min}$ we find

$$\kappa^2\frac{1-C+\ln k_{\min}}{4\pi} = \frac{\kappa^2}{4\pi}\left[\frac{1}{2}-\gamma-\ln(2\kappa L)\right] \tag{C.35}$$

finally

$$(k_BT)^{-1}\,\Omega_{bulk} = \frac{\kappa^2}{4\pi}\left[\frac{1}{2}-\gamma-\ln(2\kappa L)-\frac{4\pi}{\kappa^2}\sum_\alpha \varsigma_\alpha\right]\pi\left(b^2-a^2\right) \tag{C.36}$$

From (C.21) and (C.22) the boundary grand potential is

$$\begin{aligned} &(k_BT)^{-1}\,\Omega_{bound} \\ &= \frac{1}{24}\left[6\alpha-6\beta+12\ln\left[e^{-\alpha+\beta}\right]+6\alpha-6\beta-6\alpha\pi-6\beta\pi\right] \\ &= -\frac{1}{4}\pi(\alpha+\beta) && \text{(C.37)} \end{aligned}$$

and the logarithmic corrections

$$\frac{1}{24}\left[6\ln a+6\ln b+12\ln\frac{1}{\sqrt{ab}}\right]=0$$

as expected in the case of an annulus where $\chi = 0$

Appendix D

Calculation of Sums Involved in Specific Examples

D.1 Sums involved in the calculation of $\sum_{l=1}^{N} \ln K_l(\alpha)$

We use the asymptotic expression for $K_l(z)$ valid for large values of the argument [44]

$$K_l(\alpha) \sim \frac{\sqrt{\pi} e^{-\eta(l,\alpha)}}{\sqrt{2}(l^2+\alpha^2)^{1/4}} \left[1 - \frac{3t - 5t^3}{24l} + \cdots\right] \tag{D.1}$$

where $\alpha = a\kappa$ and

$$\eta(l,\alpha) = \sqrt{l^2+\alpha^2} + l \ln\left(\frac{\alpha}{l+\sqrt{l^2+\alpha^2}}\right); \quad t = \frac{l}{\sqrt{l^2+\alpha^2}} \tag{D.2}$$

then we have

$$\sum_{l=1}^{N} \ln K_l(\alpha) = \sum_{l=1}^{N} \ln\left[\frac{\sqrt{\pi}}{\sqrt{2}}\right] + \sum_{l=1}^{N} \ln\left[\frac{1}{(l^2+\alpha^2)^{1/4}}\right] - \sum_{l=1}^{N} l \ln\left(\frac{\alpha}{l+\sqrt{l^2+\alpha^2}}\right) - \sum_{l=1}^{N} \sqrt{l^2+\alpha^2} + \sum_{l=1}^{N} \ln\left[1 - \frac{3t-5t^3}{24l}\right] \quad (D.3)$$

using Euler-McLaurin summation formula to evaluate each of these five sums we find

$$\sum_{l=1}^{N} \ln\left[\frac{\sqrt{\pi}}{\sqrt{2}}\right] = N \ln\left[\frac{\sqrt{\pi}}{\sqrt{2}}\right] \quad (D.4)$$

$$\sum_{l=1}^{N} \ln\left[\frac{1}{(l^2+\alpha^2)^{1/4}}\right] \quad (D.5)$$
$$= -\frac{1}{4} N \ln\left(N^2+\alpha^2\right) - \frac{1}{8}\ln(N^2+\alpha^2) - \frac{1}{2}\alpha \arctan\frac{N}{\alpha} + \frac{1}{2}N + \frac{1}{8}\ln\left(\alpha^2+1\right) + O(N^0)$$

$$\sum_{l=1}^{N} l \ln\left(\frac{\alpha}{l+\sqrt{l^2+\alpha^2}}\right) \quad (D.6)$$
$$= \frac{N}{4}\sqrt{N^2+\alpha^2} + \frac{N^2}{2}\ln\left(\frac{\alpha}{N+\sqrt{N^2+\alpha^2}}\right) - \frac{a^2}{4}\ln\left(N+\sqrt{N^2+\alpha^2}\right)$$
$$-\frac{1}{4}\sqrt{1+\alpha^2} - \frac{1}{2}\ln\left(\frac{\alpha}{1+\sqrt{1+\alpha^2}}\right) + \frac{a^2}{4}\ln\left(1+\sqrt{1+\alpha^2}\right)$$
$$+\frac{1}{2}\left[N\ln\left(\frac{\alpha}{N+\sqrt{N^2+\alpha^2}}\right) + \ln\left(\frac{\alpha}{1+\sqrt{1+\alpha^2}}\right)\right] + O(N^0)$$

$$\sum_{l=1}^{N} \sqrt{l^2+\alpha^2} \quad (D.7)$$
$$= \frac{1}{2}N\sqrt{(N^2+\alpha^2)} + \frac{1}{2}\alpha^2 \ln\left(N+\sqrt{(N^2+\alpha^2)}\right) - \frac{1}{2}\alpha^2\ln\left(1+\sqrt{(1+\alpha^2)}\right) + \frac{1}{2}\sqrt{N^2+\alpha^2}$$

to evaluate the last sum we note that the term $\frac{3t-5t^3}{24l}$ is small for large values of $\alpha = a\kappa$, in consequence we can make the approximation

$$\ln\left[1-\frac{3t-5t^3}{24l}\right] = \ln\left[1-\frac{3}{24}\frac{1}{\sqrt{l^2+\alpha^2}}+\frac{5}{24}\frac{l^2}{(l^2+\alpha^2)^{3/2}}\right] \tag{D.8}$$
$$\sim -\frac{3}{24}\frac{1}{\sqrt{l^2+\alpha^2}}+\frac{5}{24}\frac{l^2}{(l^2+\alpha^2)^{3/2}}$$

and then apply Euler-McLaurin formula to obtain

$$\sum_{l=1}^{N}\ln\left[1-\frac{3t-5t^3}{24l}\right] \tag{D.9}$$
$$= -\frac{1}{24}\left(-2\ln\left(N+\sqrt{(N^2+\alpha^2)}\right)+2\ln\left(1+\sqrt{(1+\alpha^2)}\right)\right)+O\left(\frac{1}{N}\right)+O\left(\frac{1}{\alpha^2}\right)$$

putting all this together, taking the limits $N\to\infty$, and $\alpha\to\infty$ simplifying and collecting terms in powers of N we find

$$\frac{-3+\ln 4-2\ln\frac{\alpha}{N}}{4\left(\frac{1}{N^2}\right)}+\frac{\ln\frac{\pi}{\alpha}}{2\left(\frac{1}{N}\right)}+\frac{-1-\ln\frac{N}{\alpha}-\ln 2}{4\left(\frac{1}{\alpha^2}\right)}+\frac{2-\pi}{4\left(\frac{1}{\alpha}\right)}+\frac{1}{6}\left(\ln\frac{\alpha}{N}\right) \tag{D.10}$$

D.2 Sums involved in the calculation of $\sum_{l=1}^{N}\ln I_l(\alpha)$

We use the asymptotic expression for $I_l(z)$ valid for large values of the argument

$$I_l(\alpha)\sim\frac{e^{\eta(l,\alpha)}}{\sqrt{2\pi}(l^2+\alpha^2)^{1/4}}\left[1+\frac{3t-5t^3}{24l}+\cdots\right] \tag{D.11}$$

then

$$\sum_{l=1}^{N}\ln K_l(\alpha) = -\sum_{l=1}^{N}\frac{1}{2}\ln(2\pi)+\sum_{l=1}^{N}\ln\left[\frac{1}{(l^2+\alpha^2)^{1/4}}\right]+\sum_{l=1}^{N}l\ln\left(\frac{\alpha}{l+\sqrt{l^2+\alpha^2}}\right)$$
$$+\sum_{l=1}^{N}\sqrt{l^2+\alpha^2}+\sum_{l=1}^{N}\ln\left[1+\frac{3t-5t^3}{24l}\right] \tag{D.12}$$

Except for the first term of the right side, sums are exactly the same calculated above when we considered the case for $\sum_{l=1}^{N}\ln K_l(\alpha)$. The complete expression only differs in the signs of the last three terms. Then the results obtained before are applicable taking care of the change in the signs. Putting all these together and taking the limits $N \to \infty$, and $\alpha \to \infty$ we find

$$\frac{3 - \ln 4 + 2\ln\frac{b}{N}}{4\left(\frac{1}{N^2}\right)} + \frac{2 + \ln b - 2\ln N - \ln 4\pi}{2\left(\frac{1}{N}\right)} + \frac{6 + \ln 64 + 6\ln\frac{N}{b}}{24\left(\frac{1}{b^2}\right)} - \frac{2+\pi}{4\left(\frac{1}{b}\right)} - \frac{1}{3}\ln\frac{N}{b} \quad \text{(D.13)}$$

D.3 Sums involved in the calculation of $\sum_{l=0}^{N}(2l+1)\ln I_{l+1/2}(\alpha)$

To be able to use the Euler-McLaurin summation formula we first use the Debye expansion for $I_{l+1/2}(\alpha)$ valid for large values of l and the argument

$$I_{l+1/2}(\alpha) \simeq \frac{e^{\eta(l,\alpha)}}{\sqrt{2\pi}((l+1/2)^2 + z^2)^{1/4}}\left[1 + \frac{3t - 5t^3}{24\,(l+1/2)} + \cdots\right] \quad \text{(D.14)}$$

where

$$\begin{aligned} \eta(l,\alpha) &= \sqrt{(l+1/2)^2 + \alpha^2} + (l+1/2)\ln\left(\frac{\alpha}{l + 1/2 + \sqrt{(l+1/2)^2 + \alpha^2}}\right) \quad \text{(D.15)} \\ t &= \frac{l+1/2}{\sqrt{(l+1/2)^2 + \alpha^2}} \end{aligned}$$

after taking the logarithm of $I_{l+1/2}(\alpha)$ we find

$$\begin{aligned} &\sum_{l=0}^{N}(1+2l)\ln I_{l+1/2}(\alpha) \quad \text{(D.16)} \\ = \; &-\sum_{l=0}^{N}\frac{1}{2}(1+2l)\ln(2\pi) - \frac{1}{4}\sum_{l=0}^{N}(1+2l)\ln\left(\alpha^2 + (l+1/2)^2\right) \\ &+\sum_{l=0}^{N}(1+2l)\,\eta(l,\alpha) + \sum_{l=0}^{N}(1+2l)\ln\left[1 + \frac{3t-5t^3}{24\,(l+1/2)}\right] + O\left(\frac{1}{\alpha^2 + l^2}\right) \end{aligned}$$

similarly

$$\begin{aligned} \sum_{l=0}^{N} 2l\ln I_{l+1/2}(\alpha) &= -\sum_{l=0}^{N} l\ln(2\pi) - \frac{1}{2}\sum_{l=0}^{N} l\ln\left(\alpha^2 + (l+1/2)^2\right) \quad \text{(D.17)} \\ &\quad + \sum_{l=0}^{N} 2l\eta(l,\alpha) + \sum_{l=0}^{N} 2l\ln\left[1 + \frac{3t-5t^3}{24\,(l+1/2)}\right] + O\left(\frac{1}{\alpha^2 + l^2}\right) \end{aligned}$$

applying the Euler-McLaurin summation formula to each one of these sums we find

$$\sum_{l=0}^{N} \ln(2\pi)\,(1+2l) = N\ln(2\pi) + \ln(2\pi)\left(N^2+N\right) \tag{D.18}$$

$$\begin{aligned}
&\sum_{l=0}^{N} (1+2l)\ln\left(\alpha^2+(l+1/2)^2\right) \qquad\qquad (\mathrm{D.19})\\
= \; & \left(N+\frac{1}{2}\right)\ln\left(4N^2+1+4N+4\alpha^2\right) - N\left(2+2\ln 2\right) + 2\alpha\arctan\frac{1}{2}\frac{2N+1}{\alpha}\\
&-\frac{1}{2}\ln\left(1+4\alpha^2\right) - 2\alpha\arctan\frac{1}{2\alpha} + \frac{1}{2}\left[\ln\left(\alpha^2+(N+1/2)^2\right)+\ln\left(\alpha^2+(1/2)^2\right)\right] + O(N^0)\\
&+\left(N^2-\frac{1}{4}+\alpha^2\right)\ln\left(4N^2+1+4N+4\alpha^2\right) - N^2 + N - 2\alpha\arctan\frac{1}{2}\frac{2N+1}{\alpha}\\
&-2N^2\ln 2 - \left(\ln\left(4\alpha^2+1\right)\right)\alpha^2 + \frac{1}{4}\ln\left(4\alpha^2+1\right) + 2\alpha\arctan\frac{1}{2\alpha}\\
&\left[N\ln\left(\alpha^2+(N+1/2)^2\right)\right] + \frac{2}{3}\left[\frac{\left(\ln\left(4\alpha^2+4N^2+4N+1\right)\right)N^2}{4\alpha^2+4N^2+4N+1}\right] + o(N)
\end{aligned}$$

using the explicit for the function $\eta(l,\alpha)$ given in (D.15) we have

$$\sum_{l=0}^{N}\eta(l,\alpha) = \sum_{l=0}^{N}\sqrt{(l+1/2)^2+\alpha^2} + \sum_{l=0}^{N}(l+1/2)\ln\left(\frac{\alpha}{l+1/2+\sqrt{(l+1/2)^2+\alpha^2}}\right) \tag{D.20}$$

and using the Euler-McLaurin formula we have

$$\begin{aligned}
&\sum_{l=0}^{N}(2l+1)\sqrt{(l+1/2)^2+\alpha^2}\\
= \; & \int_0^N \sqrt{(l+1/2)^2+\alpha^2}dl + \frac{1}{2}\left[\sqrt{(N+1/2)^2+\alpha^2}+\sqrt{(1/2)^2+\alpha^2}\right] + O(N^0)\\
&\frac{1}{4}\left(N+\frac{1}{2}\right)\sqrt{(4N^2+1+4N+4\alpha^2)} + \frac{1}{2}\alpha^2\ln\left(2N+1+\sqrt{(4N^2+1+4N+4\alpha^2)}\right)\\
&-\frac{1}{8}\sqrt{(4\alpha^2+1)} - \frac{1}{2}\alpha^2\ln\left(1+\sqrt{(4\alpha^2+1)}\right) + \frac{1}{2}\left[\sqrt{(N+1/2)^2+\alpha^2}+\sqrt{(1/2)^2+\alpha^2}\right] + O(N^0)\\
&+\frac{1}{3}\left(N^2-\frac{1}{8}+\frac{1}{4}N+\alpha^2\right)\sqrt{(4N^2+1+4N+4\alpha^2)} - \frac{1}{2}\alpha^2\ln\left(2N+1+\sqrt{(4N^2+1+4N+4\alpha^2}\right.\\
&-\frac{1}{3}\sqrt{(4\alpha^2+1)}\alpha^2 + \frac{1}{24}\sqrt{(4\alpha^2+1)} + \frac{1}{2}\alpha^2\ln\left(1+\sqrt{(4\alpha^2+1)}\right)\\
&+\left[N\sqrt{(N+1/2)^2+\alpha^2}\right] + \frac{1}{12}\left[\frac{4\alpha^2+8N^2+6N+1}{\sqrt{(4\alpha^2+4N^2+4N+1)}} - \frac{4\alpha^2+1}{\sqrt{(4\alpha^2+1)}}\right] + o(N)
\end{aligned}$$

similarly

$$\sum_{l=0}^{N}(2l+1)\,(l+1/2)\ln\left(\frac{\alpha}{l+1/2+\sqrt{(l+1/2)^2+\alpha^2}}\right) \tag{D.21}$$

$$\begin{aligned}
= &\int_0^N (l+1/2)\ln\left(\frac{\alpha}{l+1/2+\sqrt{(l+1/2)^2+\alpha^2}}\right)dl \\
&+\frac{1}{2}\left[(3/2)\ln\left(\frac{\alpha}{3/2+\sqrt{(3/2)^2+\alpha^2}}\right)+(N+1/2)\ln\left(\frac{\alpha}{N+1/2+\sqrt{(N+1/2)^2+\alpha^2}}\right)\right] \\
&+\frac{1}{12}\left[\ln\frac{\alpha}{2N+1+\sqrt{(4\alpha^2+4N^2+4N+1)}}-\ln\frac{\alpha}{1+\sqrt{(4\alpha^2+1)}}\right] \\
&+\int_1^N 2l\,(l+1/2)\ln\left(\frac{\alpha}{l+1/2+\sqrt{(l+1/2)^2+\alpha^2}}\right)dl \\
&+\frac{1}{6}\left[2N\ln 2+(2N+1/2)\ln\frac{\alpha}{2N+1+\sqrt{(4\alpha^2+4N^2+4N+1)}}-\frac{2N^2+N}{\sqrt{(4\alpha^2+4N^2+4N+1)}}\right] \\
&-\frac{1}{6}\left[\frac{1}{2}\ln\frac{\alpha}{1+\sqrt{(4\alpha^2+1)}}\right]+o(N)+\left[N\,(N+1/2)\ln\left(\frac{\alpha}{N+1/2+\sqrt{(N+1/2)^2+\alpha^2}}\right)\right]
\end{aligned}$$

finally, using the explicit form for t given in (D.15) and using the approximation $\ln(1+x)\simeq x$ valid for small values of x we have

$$\sum_{l=1}^{N}(2l+1)\ln\left[1+\frac{3t-5t^3}{24\,(l+1/2)}\right] \tag{D.22}$$

$$\simeq \frac{1}{8}\sum_{l=0}^{N}\frac{(2l+1)}{\sqrt{(l+1/2)^2+\alpha^2}}-\frac{5}{24}\sum_{l=0}^{N}\frac{(2l+1)\,(l+1/2)^2}{\left((l+1/2)^2+\alpha^2\right)^{3/2}}$$

applying Euler-McLaurin summation formula to each sum we find

$$\begin{aligned}
&\sum_{l=0}^{N}\frac{(2l+1)}{\sqrt{(l+1/2)^2+\alpha^2}} \\
= \quad & \ln\left(2N+1+\sqrt{(4N^2+1+4N+4\alpha^2)}\right)-\ln\left(1+\sqrt{(4\alpha^2+1)}\right)+ \\
& \frac{1}{2}\left[\frac{1}{\sqrt{(1/2)^2+\alpha^2}}+\frac{1}{\sqrt{(N+1/2)^2+\alpha^2}}\right] \\
& +\sqrt{(4N^2+1+4N+4\alpha^2)}-\ln\left(2N+1+\sqrt{(4N^2+1+4N+4\alpha^2)}\right) \\
& -\sqrt{(4\alpha^2+1)}+\ln\left(1+\sqrt{(4\alpha^2+1)}\right)+\left[\frac{N}{\sqrt{(N+1/2)^2+\alpha^2}}\right]+o(N)
\end{aligned} \tag{D.23}$$

$$\begin{aligned}
&\sum_{l=1}^{N}\frac{(2l+1)\,(l+1/2)^2}{\left((l+1/2)^2+\alpha^2\right)^{3/2}} \\
= \quad & \ln\left(2N+1+\sqrt{(4N^2+1+4\alpha^2+4N)}\right)-\ln\left(1+\sqrt{(4\alpha^2+1)}\right) \\
& +\frac{1}{2}\left[\frac{(N+1/2)^2}{\left((N+1/2)^2+\alpha^2\right)^{3/2}}+\frac{(1/2)^2}{\left((1/2)^2+\alpha^2\right)^{3/2}}\right]+O(N^0) \\
& \frac{4N^2}{\sqrt{(4N^2+1+4N+4\alpha^2)}}-2\ln\left(2N+1+\sqrt{(4N^2+1+4\alpha^2+4N)}\right) \\
& +2\ln\left(1+\sqrt{(4\alpha^2+1)}\right)+\left[\frac{N\,(N+1/2)^2}{\left((N+1/2)^2+\alpha^2\right)^{3/2}}\right]+o(N)
\end{aligned} \tag{D.24}$$

putting all together and taking the limits $N\to\infty$ and $a\to\infty$ we find

$$\begin{aligned}
& \frac{4-\ln 8+3\ln\frac{b}{N}}{9\left(\frac{1}{N^3}\right)}+\frac{9-8\ln 2+8\ln b-10\ln N-2\ln 2\pi}{8\left(\frac{1}{N^2}\right)} \\
& +\frac{\frac{b^2}{4}+\frac{1}{24}\left(11-22\ln 2+22\ln b-34\ln N-12\ln 2\pi\right)}{\left(\frac{1}{N}\right)} \\
& -\frac{b^3}{9}+\frac{1-2\ln\frac{N}{b}}{8\left(\frac{1}{b^2}\right)}+\frac{1}{24}b+o(N)
\end{aligned} \tag{D.25}$$

D.4 Sums involved in the calculation of $\sum_{l=0}^{N}(2l+1)\ln K_{l+1/2}(\alpha)$

We use the asymptotic formula for $K_{l+1/2}(\alpha)$ valid for large values of l and the argument

$$K_{l+1/2}(\alpha) \sim \frac{\sqrt{\pi}e^{-\eta(l,\alpha)}}{\sqrt{2}((l+1/2)^2+\alpha^2)^{1/4}}\left[1-\frac{3t-5t^3}{24\,(l+1/2)}+\cdots\right] \tag{D.26}$$

where $\alpha = a\kappa_D$ and

$$\eta(l,\alpha) = \sqrt{(l+1/2)^2+\alpha^2}+\left(l+\frac{1}{2}\right)\ln\left(\frac{\alpha}{(l+1/2)+\sqrt{(l+1/2)^2+\alpha^2}}\right) \tag{D.27}$$

$$t = \frac{(l+1/2)}{\sqrt{(l+1/2)^2+\alpha^2}}$$

then

$$\begin{aligned}
&\sum_{l=0}^{N}(1+2l)\ln K_{l+1/2}(\alpha) \qquad \text{(D.28)}\\
&= \sum_{l=0}^{N}\frac{1}{2}(1+2l)\ln(2\pi)-\frac{1}{4}\sum_{l=0}^{N}(1+2l)\ln\left(\alpha^2+(l+1/2)^2\right)\\
&\quad -\sum_{l=0}^{N}(1+2l)\,\eta(l,\alpha)+\sum_{l=0}^{N}(1+2l)\ln\left[1-\frac{3t+5t^3}{24\,(l+1/2)}\right]+O\left(\frac{1}{\alpha^2+l^2}\right)
\end{aligned}$$

Except for some changes in the signs in the first, third and fourth terms on the right side, sums are exactly the same calculated above when we considered the case for $\sum_{l=0}^{N}(1+2l)\ln I_{l+1/2}(\alpha)$. Then the results obtained before are applicable taking care of the change in the sings. In this case, taking the limits $N\to\infty$ and $a\to\infty$ we find

$$\begin{aligned}
&\frac{-4+\ln 8-3\ln\frac{b}{N}}{9\left(\frac{1}{N^3}\right)}+\frac{-7-8\ln 2-8\ln b+6\ln N+2\ln\pi}{8\left(\frac{1}{N^2}\right)}\\
&+\frac{-\frac{b^2}{4}+\frac{1}{24}\left(-11+22\ln 2-22\ln b+10\ln N+12\ln\pi\right)}{\left(\frac{1}{N}\right)}\\
&+\frac{b^3}{9}+\frac{-3-2\ln\frac{N}{b}}{8\left(\frac{1}{b^2}\right)}-\frac{1}{24}b+o(N)
\end{aligned} \tag{D.29}$$

Appendix E

Calculations for a Coulomb system Inside a Sphere

After we regularize the infinite divergent sums we have to find the value of

$$\begin{aligned}
&\frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln\left[\Gamma\left(l+\frac{3}{2}\right)\left(\frac{2}{\alpha}\right)^{l+1/2}\right] \\
=\;&\frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln\left[\Gamma\left(l+\frac{3}{2}\right)\right]+\frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln\left(\frac{2}{\alpha}\right)^{l+1/2}. \qquad \text{(E.1)}
\end{aligned}$$

Writing $\Gamma\left(l+\frac{3}{2}\right) = \Gamma\left(l+\frac{1}{2}+1\right)$ and using the asymptotic expansion for the Gamma function [44]

$$\Gamma(p+1) \simeq p^p e^{-p}\sqrt{2\pi p}\left(1+\frac{1}{12p}\right) \qquad \text{(E.2)}$$

valid for large values of p we have

$$\ln\Gamma\left(l+\frac{3}{2}\right) \simeq \left(l+\frac{1}{2}\right)\ln\left(l+\frac{1}{2}\right)-\left[l+\frac{1}{2}-\frac{1}{2}\ln\left(2\pi\left(l+\frac{1}{2}\right)\right)\right]+\ln\left(1+\frac{1}{12l+6}\right) \qquad \text{(E.3)}$$

now we apply the Euler-McLaurin summation formula to find the value of each sum involved in the calculation of (E.1). After using the approximation (E.3) we divide the resulting expression in three sums whose values in the Euler-McLaurin approximation are

$$
\begin{aligned}
& \sum_{l=0}^{N} (2l+1)\left(l+\frac{1}{2}\right)\ln\left(l+\frac{1}{2}\right) \qquad \text{(E.4)} \\
= \; & \frac{2}{3}N^3\ln(N+1/2)+\frac{1}{2}N^2\ln(N+1/2)-\frac{1}{24}\ln(2N+1)-\frac{2}{9}N^3-\frac{1}{12}N^2+\frac{1}{12}N \\
& +\left[N\left(N+\frac{1}{2}\right)\ln\left(N+\frac{1}{2}\right)\right]+\frac{1}{6}\left(2N\ln(N+1/2)+\frac{1}{2}\ln(N+1/2)+N\right) \\
& +\frac{1}{2}N^2\left(\ln(N+1/2)-\frac{1}{2}\right)+\frac{1}{2}N\left(\ln(N+1/2)-\frac{1}{2}\right)+\frac{1}{8}\ln(2N+1) \\
& +\frac{1}{2}\left[(N+1/2)\ln(N+1/2)\right]+\frac{1}{12}\ln(2N+1)+O\left(\frac{1}{N}\right)
\end{aligned}
$$

$$
\begin{aligned}
& (2l+1)\sum_{l=0}^{N}\left[l+\frac{1}{2}-\frac{1}{2}\ln(2\pi l+\pi)\right] \qquad \text{(E.5)} \\
= \; & \frac{2}{3}N^3+\frac{1}{8}\ln(2N+1)+\frac{3}{4}N^2-\frac{1}{2}N^2\ln\pi-\frac{1}{2}N^2\ln(2N+1)-\frac{1}{4}N \\
& +N\left[N+\frac{1}{2}-\frac{1}{2}\ln\left(2\pi\left(N+\frac{1}{2}\right)\right)\right]+\frac{1}{6}\left[\frac{4N^2}{2N+1}-\frac{N\ln(2N+1)}{2N+1}\right] \\
& +\frac{1}{2}N^2+N-\frac{1}{2}N\ln\pi-\frac{1}{2}N\ln(2N+1)-\frac{1}{4}\ln(2N+1) \\
& +\frac{1}{2}\left[N-\frac{1}{2}\ln(2\pi N+\pi)\right]+O\left(\frac{1}{N}\right)
\end{aligned}
$$

$$
\begin{aligned}
& \sum_{l=0}^{N}(2l+1)\ln\left(1+\frac{1}{12\,(l+1/2)}\right) \qquad \text{(E.6)} \\
= \; & \frac{1}{12}N+N^2\ln(12N+7)-N^2\ln(2N+1)-N^2\ln 6-\frac{49}{144}\ln(12N+7) \\
& +\frac{1}{4}\ln(2N+1)+N\ln\left(1+\frac{1}{12\,(N+1/2)}\right)-\frac{1}{2}\ln(2N+1)+N\ln(12N+7) \\
& -N\ln(3N+3/2)+\frac{7}{12}\ln(12N+7)+\frac{1}{2}\ln\left(1+\frac{1}{12N+6}\right)+O\left(\frac{1}{N}\right)
\end{aligned}
$$

For the second term in (E.1) we find

$$\frac{1}{2}\sum_{l=0}^{\infty}(1+2l)\ln\left(\frac{2}{\alpha}\right)^{l+1/2} = \frac{1}{2}\ln\left(\frac{2}{\alpha}\right)\left[\frac{1}{2}N^2+N\right]+\ln\left(\frac{2}{\alpha}\right)\left[\frac{1}{3}N^3+\frac{3}{4}N^2+\frac{5}{12}N\right] \tag{E.7}$$

putting all this together, expanding for large values of N and collecting terms we find

$$\begin{aligned} & \frac{1}{2}\sum_{l=0}^{N}(1+2l)\ln\left[\Gamma\left(l+\frac{3}{2}\right)\left(\frac{2}{\alpha}\right)^{l+1/2}\right] \\ = \quad & \frac{\ln 8-3\ln\alpha+3\ln N-4}{9\left(\frac{1}{N^3}\right)}+\frac{\ln 1024-9\ln\alpha+10\ln N+2\ln\pi-9}{8\left(\frac{1}{N^2}\right)} \\ & +\frac{34\ln 2-22\ln a+34\ln N+12\ln\pi-9}{24\left(\frac{1}{N}\right)}+o(N) \end{aligned} \tag{E.8}$$

Appendix F

Calculations for Coulomb System in a Spherical Shell

Expanding the logarithm we have

$$\begin{aligned} & \sum_{l=0}^{N}(2l+1)\ln\left[\frac{1}{2\,(l+1/2)}\left(\left(\frac{b}{a}\right)^{l+1/2}-\left(\frac{a}{b}\right)^{l+1/2}\right)\right] \quad (F.1)\\ = & \sum_{l=0}^{N}(2l+1)\left[-\ln\left(2l+1\right)+\ln\left(\left(\frac{b}{a}\right)^{l+1/2}-\left(\frac{a}{b}\right)^{l+1/2}\right)\right]\end{aligned}$$

we apply the Euler-McLaurin summation formula to the first term in the right side of (F.1) to have

$$\begin{aligned} & -\sum_{l=0}^{N}\left(2l+1\right)\ln\left(2l+1\right) \quad (F.2)\\ = & -N^2\ln\left(2N+1\right)+\frac{1}{4}\ln\left(2N+1\right)+\frac{1}{2}N^2+N\ln\left(\frac{1}{(2N+1)}\right)\\ & +\frac{1}{3}\left[\frac{N\ln\frac{1}{2N+1}}{2N+1}\right]-N\ln\left(2N+1\right)-\frac{1}{2}\ln\left(2N+1\right)+N-\frac{1}{2}N\\ & -\frac{1}{2}\ln\left(2\left(N+1/2\right)\right)+o(N) \quad (F.3)\end{aligned}$$

to evaluate the sum in the second term of (F.1) we note that

$$\begin{aligned}\sum_{l=0}^{N} \ln\left(\left(\frac{b}{a}\right)^{l+1/2} - \left(\frac{a}{b}\right)^{l+1/2}\right) &= \sum_{l=0}^{N} \ln\left(\frac{b}{a}\right)^{l+1/2}\left(1-\left(\frac{a}{b}\right)^{2l+1}\right) \\ &= \sum_{l=0}^{N} \ln\left(\frac{b}{a}\right)^{l+1/2} + \sum_{l=0}^{N} \ln\left(1-\left(\frac{a}{b}\right)^{2l+1}\right) \\ &\simeq \sum_{l=0}^{N} \ln\left(\frac{b}{a}\right)^{l+1/2} + O(1)\end{aligned} \tag{F.4}$$

here we have used the fact that $\sum_{l=0}^{N} \ln\left(1-\left(\frac{a}{b}\right)^{2l+1}\right)$ converges to a finite result of order $O(1)$ for $N \to \infty$. Then we can write

$$\sum_{l=0}^{N}(2l+1)\ln\left(\left(\frac{b}{a}\right)^{l+1/2} - \left(\frac{a}{b}\right)^{l+1/2}\right) \simeq \sum_{l=0}^{N}(2l+1)\ln\left(\frac{b}{a}\right)^{l+1/2}. \tag{F.5}$$

Now, using the Euler-McLaurin formula we find

$$\begin{aligned}&\sum_{l=0}^{N}(2l+1)\ln\left(\frac{b}{a}\right)^{l+1/2} \\ = \;& -\frac{1}{2}(\ln a)N^2 - \frac{1}{2}N\ln a + \frac{1}{2}N^2\ln b + \frac{1}{2}N\ln b \\ & +\frac{1}{2}\left[\ln\left(\frac{b}{a}\right)^{1/2} + \ln\left(\frac{b}{a}\right)^{N+1/2}\right] + \frac{2}{3}(\ln b)N^3 - \frac{2}{3}(\ln a)N^3 \\ & +\frac{1}{2}N^2\ln b - \frac{1}{2}(\ln a)N^2 + \left[N\ln\left(\frac{b}{a}\right)^{N+1/2}\right] \\ & +\frac{1}{6}\left[\ln\left(\frac{b}{a}\right)^{N+\frac{1}{2}} + N\ln\frac{b}{a} - \left(\ln\left(\frac{b}{a}\right)^{\frac{1}{2}}\right)\right] + o(N)\end{aligned} \tag{F.6}$$

putting all this together, taking the limit $N \to \infty$ and collecting term in powers of N we find

$$\frac{\ln\frac{a}{b}}{3\left(\frac{1}{N^3}\right)} + \frac{1-\ln 4 - 4\ln\frac{a}{b} - 2\ln N}{4\left(\frac{1}{N^2}\right)} + \frac{\frac{11}{12}\ln\frac{b}{a} - \ln N - \ln 2}{\frac{1}{N}} + o(N) \tag{F.7}$$

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