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Screening like charges in one-dimensional Coulomb systems: Exact results

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The possibility that like charges can attract each other under the mediation of mobile counterions is by now well documented experimentally, numerically, and analytically. Yet, obtaining exact results is in general impossible, or restricted to some limiting cases. We work out here in detail a one-dimensional model that retains the essence of the phenomena present in higher-dimensional systems. The partition function is obtained explicitly, from which a wealth of relevant quantities follow, such as the effective force between the charges or the counterion profile in their vicinity. Isobaric and canonical ensembles are distinguished. The case of two equal charges screened by an arbitrary number N of counterions is first studied, before the more general asymmetric situation is addressed. It is shown that the parity of N plays a key role in the long-range physics.

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I. INTRODUCTION

Coulombic effects are often paramount in soft-matter systems, where the large dielectric constant of the solvent (say water) invites ionizable groups at the surface of macromolecules to dissociate [1–3]. While a realistic treatment requires considering three-dimensional systems, interesting progress has been achieved for lower-dimensional problems where the key mechanisms can be studied in greater analytical detail [4–6]. In particular, a one-dimensional model was introduced in the 1960s by Lenard and Prager independently, for which a complete thermodynamic solution was provided [7–9]. This model has been further studied in Ref. [10], but it turns out that some interesting features have been overlooked in relation with the like-charge attraction phenomenon [2,11]. This striking non-mean-field effect, relevant for strongly coupled charged matter [11,12], is the theme of our study.

The paper is organized as follows. The model is first defined in Sec. II. It mimics the screening of charged colloids. The Coulomb potential in one dimension between two charges q and q' located along a line with coordinates $\widetilde{x}$ and $\widetilde{x}'$ is

$$v(\widetilde{x},\widetilde{x}') = -qq'|\widetilde{x} - \widetilde{x}'|. \tag{1}$$

Therefore, the electric field created by one particle is of constant magnitude. This fact simplifies the study of the equilibrium statistical mechanics of such systems, and allows us to obtain some of its properties by simple arguments. Furthermore, it also allows for an explicit computation of the partition function [7,8]. The system under scrutiny can be envisioned as a collection of parallel charged plates, able to move along a perpendicular axis. The salient properties of this system can be obtained by simple arguments, which we present in Sec. II, followed by a more technical analysis where the explicit calculation of the partition function is performed, first in the isobaric and then in the canonical ensemble. After having presented the symmetric case, Sec. III will generalize the investigation to the situations where the two screened charges are different. Noteworthy is that parity of the particle number considerations will play an important role in the remainder.

II. SCREENING OF TWO EQUAL CHARGES BY COUNTERIONS ONLY

Consider two charges q along a line located at $\widetilde{x} = 0$ and $\widetilde{x} = \widetilde{L}$. Between the charges there are N counterions of charge $e = -2q/N$ between them. Consider the equilibrium thermal properties of this system at a temperature T, and as usual define $\beta = 1/(k_B T)$ with k_B the Boltzmann constant. This simple model mimics the screening and effective interaction between two charged colloids in a counterion solution, without added salt. In one dimension, βe^2 has dimensions of inverse length, therefore it is convenient to use rescaled units in which all distances are measured in units of $1/(\beta e^2)$: $x = \beta e^2 \widetilde{x}$. It is also convenient to work with a dimensionless pressure $P = \widetilde{P}/e^2$ where $\widetilde{P}$ is the pressure (equal to the force, in one-dimensional systems).

The potential energy (dimensionless, measured in units of $k_B T$) of the system is

$$U = -\sum_{1 \leqslant i < j \leqslant N} |x_i - x_j| + \left(\frac{N}{2}\right)^2 L. \tag{2}$$

Before presenting the technical analysis, we start by simple and more quantitative considerations.

A. Possibility of attraction between like charges

1. Heuristic argument

The possibility of attraction between the two $+q$ charges at 0 and L is related to the parity of N. If N is odd, $N = 2p + 1$, then p counterions will form a double layer around each charge q. This will form two compound objects with charge $q(1 - 2p/N) = q/N$, each one located around 0 and L. There will be in addition one counterion between these two objects, which is essentially free, as the electric field created by the charges located on each side around 0 and L cancel each other. When L is large enough, consider Fig. 1. The right side of the system composed of one-charge q and p counterions has charge q/N. The left side, which, for the sake of the argument, has the free counterion plus the compound charge, exhibits a

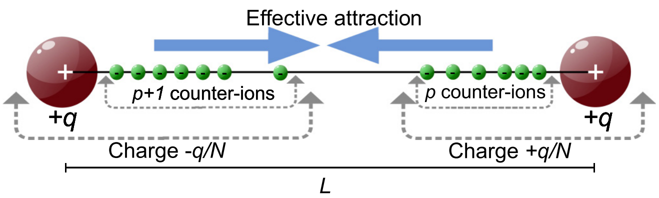

FIG. 1. (Color online) An odd number of mobile counterions screening two like charges. The N mobile ions (counterions) have charge $-2q/N$ and the confining objects have charge q, so that the whole system is electroneutral. Here, $N = 2p + 1$ is odd, so that a single ion (referred to as the misfit since the net electric force acting on it vanishes) floats in between the two screened boundaries, which attract, each, p ions in their vicinity (see also Fig. 4). This single free counterion provides the binding mechanism responsible for long-range attraction. In the canonical treatment, L is held fixed, while in the isobaric situation, it is a fluctuating quantity.

FIG. 3. (Color online) Upon regrouping the $p + 1$ leftmost counterions in Fig. 1, one obtains an ion with charge $-q - q/N$. This newly defined system has the same large distance pressure as that of Fig. 1.

total charge $-q/N$. Thus the force exerted by the left side on the right side is $\widetilde{P} \to -q^2/N^2 = -e^2/4$, an attractive force. Thus one expects that $P \to -1/4$, for $L \to \infty$.

On the other hand, if N is even, there will not be a free counterion between the layers, which will be completely neutral, thus one expects that $P \to 0^+$ when $L \to \infty$, as shown in Fig. 2.

2. *Beyond heuristics*

The previous intuition, providing a large distance attraction for odd N, can be substantiated by a simple calculation. Use will be made here of the contact theorem [10,13–16], an exact relation between the force exerted on the charge q, and the ionic density at contact (stemming from the mobile charges $-2q/N$). Such a relation is particularly useful for discussing the like-charge attraction phenomenon [12,17,18]. The argument allowing us to get the contact density is twofold, and goes as follows.

First, we argue that at large L, the p counterions that are closest to each boundary remain in their vicinity, while the middle free counterion (the misfit in Figs. 1 and 4), which does not experience any electric field by symmetry, tends to be unbounded and no longer contributes to the pressure (discarding $1/L$ terms). In a second step, we thus compute the contact density in a system of an isolated charge $+q$, with a double layer of p ions in the vicinity (the total charge of this composite object, shown on the right-hand side of Fig. 1 is q/N). The solution to this problem is not immediate, but can be found by a convenient mapping onto a more convenient problem, shown in Fig. 3. As illustrated in the figure, we regroup the $p + 1$ leftmost counterions in a single ion, having charge $-q(1 + 1/N)$. At large distances, this regroupment does not influence the distribution of counterions around the rightmost ion $+q$, and thus leaves the large L pressure unaffected. The next important argument is that the pressure can be equivalently computed from the contact density at the rightmost, or leftmost charge $+q$. It is thus simpler to perform the calculation in the newly defined regrouped system (left-hand side of Fig. 3). The regrouped ion with charge $-q(1 + 1/N)$ is in the electric field of the charge q on its left, and of the composite system on its right having charge q/N. This amounts to a field $q(1 - 1/N)$. Hence, the electric potential energy reads $q^2(1 - 1/N)\tilde{x}(1 + 1/N)$. The corresponding Boltzmann weight gives the density of the regrouped ion

$$\rho(\tilde{x}) = \beta q^2\left(1 - \frac{1}{N^2}\right) \exp\left[-\beta q^2 \tilde{x}\left(1 - \frac{1}{N^2}\right)\right], \quad (3)$$

where due account was taken of normalization ($\int \rho \, d\tilde{x} = 1$). The contact density $\rho(0) = \beta q^2(1 - 1/N^2)$ finally yields the pressure through the contact theorem $\beta\widetilde{P} = \rho(0) - \beta q^2$. We get here $\widetilde{P} = -q^2/N^2$ (or equivalently $P = -1/4$), a result, which by construction holds in the large L limit. The reason for a nonvanishing pressure at large distance is that the p counterions cannot exactly screen the charge of an ion q. It is no longer the case when N is even, in which case $P \to 0$ for $L \to \infty$. The present results will be fully corroborated by direct partition function calculations.

3. *Correction to large distance asymptotics and crossover pressure*

Returning to the case when $N = 2p + 1$ is odd, we can also estimate the first correction to the pressure for large L. Consider that L is fixed (canonical ensemble) and large. Since the system is somehow equivalent to two double layers with a free counterion in between, this counterion will contribute to the pressure (denoted as P_c in the canonical, fixed-L ensemble) with a correction $1/L$. This estimate can be made more

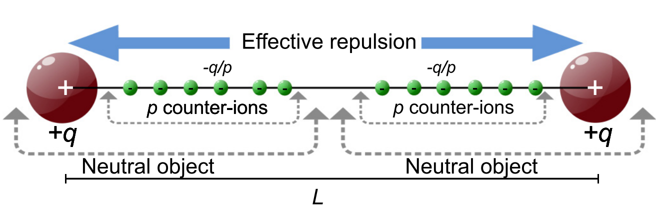

FIG. 2. (Color online) An even number of counterions screening two like charges ($N = 2p$). At large distance, the two double layers (made up of an ion q and p counterions) decouple since they are neutral. No misfit ion is present to mediate attraction, and the pressure is repulsive at all distances.

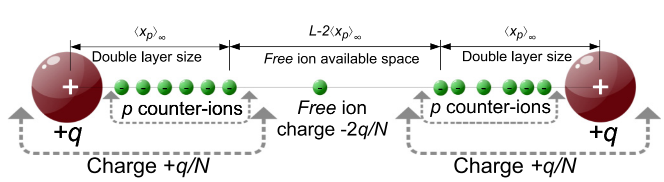

FIG. 4. (Color online) An odd number of counterions screening two like charges. The free misfit ion is singled out.

quantitative. The available space for the free counterion is not L, but it is rather L minus the space occupied by the diffuse counterion layers, given by $\langle x_p\rangle_\infty$ the thermal average position of the pth counterion if they have been ordered $x_1 < x_2 < \cdots < x_p < x_{p+1} < \cdots < x_{2p+1}$, in the limit $L \to \infty$. Thus

$$P_c = -\frac{1}{4} + \frac{1}{L - 2\langle x_p\rangle_\infty} + o\left(\frac{1}{L}\right). \quad (4)$$

This is illustrated in Fig. 4. In the following section, we evaluate explicitly $\langle x_p\rangle_\infty$ and find

$$\langle x_p\rangle_\infty = \frac{p}{p+1} = \frac{N-1}{N+1}. \quad (5)$$

Then, for large L, we expect

$$P_c = -\frac{1}{4} + \frac{1}{L - 2\,\frac{N-1}{N+1}} + o\left(\frac{1}{L}\right). \quad (6)$$

In the other limiting case $L \to 0$, the result is [10] $P_c = N/L$, that can be understood as all the N counterions are squeezed in a small distance L. Thus we see that the pressure is positive (repulsive force) for small separations $L \to 0$ then changes to negative pressure (attractive force) for large L.

We will show in the following section that the $o(1/L)$ corrections in (6) are actually exponentially small, in the canonical ensemble, therefore equation (6) gives a fairly good approximation for the pressure for a large set of values of the separation L. From this, one can estimate the distance L^*, at which the effective force between the two charges becomes attractive

$$L^* \simeq 4 + 2\langle x_p\rangle_\infty = 4 + 2\,\frac{N-1}{N+1}. \quad (7)$$

Figure 5 shows pressure P_c as a function of L, for $N = 25$ and for $N = 26$ particles. For $N = 25$ (odd) the pressure changes its sign at $L^* = 4 + 2 * 24/26 \simeq 5.85$, while for $N = 26$ the pressure is always positive.

Summarizing, in the case of odd N, the possibility of having an effective attraction for large separations L is due to the sharing of the free ion, which leads to the creation of opposite charged objects (ions q plus their counterion clouds). Although the analytical results presented here are valid only for this one-dimensional model, the same physical mechanism has also been observed in three-dimensional systems [19,20]. It

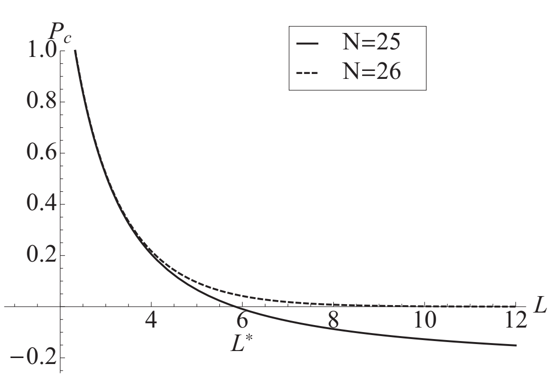

FIG. 5. The (canonical) pressure P_c as a function of the separation L, for $N = 25$ (continuous bottom line) and $N = 26$ (dashed top line). For N odd the pressure becomes negative at large distances.

can also be surmised that in situation of odd N where the free counterion has a varying charge, attraction will be all the stronger as the charge will increase in absolute value. In addition, the very mechanism brought to the fore here indicates that at mean-field level, where the discrete nature of ions is discarded, attraction should be suppressed, which indeed is the case [21–23].

B. Explicit exact calculation of the partition function

1. Preliminary observations

The equilibrium thermodynamics of the one-dimensional two-component Coulomb gas was solved simultaneously but independently by Lenard [7] and Prager [8]. In the present model, only one type of identical particles (the counterions) are present. It is convenient to order the particles as $0 \leqslant x_1 \leqslant \cdots \leqslant x_N \leqslant L$. Then, rearranging the terms in (2), the potential energy of the system can be written as

$$U = \frac{N^2 L}{4} - 2\sum_{j=0}^{p-1}(p-j)(x_{2p+1-j} - x_{1+j})$$
$$\text{for } N = 2p+1 \text{ odd}, \quad (8)$$

and

$$U = \frac{N^2 L}{4} - \sum_{j=0}^{p-1}(2p-2j-1)(x_{2p-j} - x_{1+j})$$
$$\text{for } N = 2p \text{ even}. \quad (9)$$

Notice that in the case $N = 2p+1$, the particle with position x_{p+1} does not appear in the potential energy. It is the free counterion (misfit) discussed in the previous section, whose role is crucial for the possibility of like-charge attraction.

The canonical configuration integral is

$$Z_c(N,L) = \int_0^L dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_3} dx_2 \int_0^{x_2} dx_1\, e^{-U}. \quad (10)$$

As mentioned by Lenard in his seminal paper [7] "the (configuration) integral is elementary (because) the class of functions consisting of exponential of linear functions is closed under the operation of indefinite integral (...) however the task of evaluating (it) is not trivial." For small N one can compute by hand Z_c, and for larger given values of N it can be obtained numerically with the aid of a computer algebra system software program. By inspection of the integral (10), one can deduce that Z_c is a linear combination of products of exponentials of L and linear functions of L. One can also deduce the argument of each exponential function of L by keeping track of the factor that multiplies each x_k in the integral (10). These come from the explicit term in U (for instance, for x_{j+1} it is $2(p-j)$ in the case N odd), but after each successive integration, the factor of x_k will be added to the one of x_{k+1} due to the upper limit of integration. Taking that into account, one realizes that the exponentials of L in Z_c are of the form $\exp[-(j+\frac{1}{2})^2 L]$ in the case N odd, and $\exp(-j^2 L)$ in the case N even. Thus, the configuration canonical integral is expected to be of the form

$$Z_c(N,L) = \sum_{j=0}^{p} e^{-(j+\frac{1}{2})^2 L}(A_j L + B_j) \quad \text{for } N = 2p+1 \text{ odd}, \tag{11}$$

and

$$Z_c(N,L) = \sum_{j=0}^{p} e^{-j^2 L}(C_j L + D_j) \quad \text{for } N = 2p \text{ even}. \tag{12}$$

The nontrivial task is to evaluate explicitly the coefficients A_j, B_j, C_j, and D_j. This is done in Sec. II B 5.

2. Previous results

In Ref. [10], the present system was studied, but an exact analytical explicit evaluation of the partition function for an arbitrary number of particles was not achieved. Rather, an interesting reformulation of this model was proposed by mapping it into a quantum mechanical problem, following a technique put forward by Edwards and Lenard [9]. It was shown in Ref. [10] that the configuration integral is given by

$$Z_c(N,L) = b(N/2,N/2,L), \tag{13}$$

where $b(n,N/2,x)$ is the solution of a set of N coupled elementary linear differential equations

$$\frac{db(n,N/2,x)}{dx} = -(n^2/2)\, b(n,N/2,x) + b(n-1,N/2,x) \tag{14}$$

with the initial condition $b(n,N/2,0) = \delta_{n,-N/2}$. Integrating this equation one has

$$b(n,N/2,x_n) = \int_0^{x_n} e^{-(n^2/2)(x_n - x_{n-1})} b(n-1,N/2,x_{n-1}) \times dx_{n-1}. \tag{15}$$

Then, starting from the known $b(-N/2,N/2,x_1)$ one has to perform successively N integrals (15) to obtain $b(N/2,N/2,L)$ and the configuration integral. This task is equivalent to performing directly the N integrals of the configuration integral (10). Thus, unfortunately, the method proposed in Ref. [10] does not provide any computational advantage over a direct numerical evaluation of the partition function.

Here, our goal is to obtain an explicit analytical expression for the configuration integral for an arbitrary number of particles N. Using Lenard [7] and Prager [8] method, we will first compute the partition function of the constant pressure ensemble

$$Z_P(N,P) = \int_0^{\infty} e^{-PL} Z_c(N,L)\, dL, \tag{16}$$

which is the Laplace transform of the canonical configuration integral Z_c. This is a straightforward application of the technique of Lenard and Prager, and it is actually much simpler than the complete work presented in Refs. [7,8], since all particles are identical and we will not have to deal with the combinatorial problem of studying the different configurations of charges.

Then, we shall invert the Laplace transform to obtain the canonical, constant volume L, configuration integral $Z_c(N,L)$. Since we are interested in finite systems, the results from the canonical ensemble and the constant pressure ensemble will differ, and it is of interest to compare them.

3. Evaluation of the diffuse layer size $\langle x_p \rangle_\infty$

To introduce the technique used to compute the partition function, we undertake in this section a preliminary, simpler task, based on the same technique: the exact evaluation of the diffuse layer size $\langle x_p \rangle_\infty$. This quantity appeared in the discussion of Sec. II A. Consider here that $L \to \infty$ and $N = 2p+1$. The double layer composed by the charge q at L and its corresponding p counterions are thereby sent to infinity. The remaining $p+1$ counterions, however, still feel the electric field created by this far charged double layer. The potential energy part, which depends on the position of the remaining counterions is

$$U_\infty = 2\sum_{j=0}^{p-1}(p-j)x_{1+j}. \tag{17}$$

We wish to evaluate

$$\langle x_p \rangle_\infty = \frac{\int_{0<x_1<x_2<\cdots<x_p} x_p\, e^{-U_\infty} \prod_{k=1}^{p} dx_k}{\int_{0<x_1<x_2<\cdots<x_p} e^{-U_\infty} \prod_{k=1}^{p} dx_k}. \tag{18}$$

Let

$$F(s) = \int_{0<x_1<x_2<\cdots<x_p} e^{-U_\infty - s x_p/2}\, dx_1 \ldots dx_p. \tag{19}$$

Then $\langle x_p \rangle_\infty = -2\, d \ln F(s)/ds|_{s=0}$. Following Lenard [7] and Prager [8] it is convenient to rewrite the potential energy as

$$U_\infty = \frac{1}{2}\Bigg[\sum_{j=1}^{p}((p-j+1)^2 + (p-j+2)^2) \times (x_j - x_{j-1}) - x_p\Bigg] \tag{20}$$

with the convention that $x_0 = 0$. Let us define

$$f_j(x) = e^{-[(p-j+1)^2+(p-j+2)^2]x/2}\, H(x), \tag{21}$$

where $H(x)$ is the Heaviside step function. Then

$$F(s) = \int_0^\infty dx_1 \cdots \int_0^\infty dx_p \prod_{j=1}^{p} f_j(x_j - x_{j-1})\, e^{-(s-1)x_p/2}. \tag{22}$$

We notice that $F(s)$ is the Laplace transform [evaluated at $(s-1)/2$] of the p-fold convolution product $f_1 * f_2 * \cdots * f_p$. The Laplace transform $\mathcal{L}f_j$ of f_j is elementary

$$\mathcal{L}f_j\left(\frac{s-1}{2}\right) = \frac{2}{(p-j+1)^2 + (p-j+2)^2 + s - 1} = \frac{2}{2(p-j+1)(p-j+2) + s}. \tag{23}$$

Then

$$F(s) = \prod_{j=1}^{p} \frac{2}{2(p-j+1)(p-j+2)+s} = \prod_{k=1}^{p} \frac{2}{2k(k+1)+s}. \tag{24}$$

Computing the derivative of $\ln F(s)$ we obtain

$$\langle x_p\rangle_\infty = -2\left.\frac{d\ln F(s)}{ds}\right|_{s=0} = \sum_{j=1}^{p}\frac{1}{(p-j+1)(p-j+2)}$$
$$= \sum_{k=1}^{p}\frac{1}{k(k+1)} = \sum_{k=1}^{p}\left(\frac{1}{k}-\frac{1}{k+1}\right)$$
$$= \left(1-\frac{1}{p+1}\right) = \frac{p}{p+1}. \quad (25)$$

Thus proving (5).

4. Isobaric ensemble

Consider now the finite system with $L<\infty$. We will detail the calculations in the case $N=2p+1$ odd, the case N even can be obtained by a simple adaptation of the same technique. As it was done in the previous section, it is convenient to rewrite the potential energy (8) as

$$U = -\frac{L}{4} + \frac{1}{2}\sum_{j=1}^{p+1}[(p-j+1)^2+(p-j+2)^2]$$
$$\times\left(x_{2p-j+3}-x_{2p-j+2}+x_j-x_{j-1}\right), \quad (26)$$

where, by convention, we defined $x_0=0$ and $x_{2p+2}=L$. With f_j defined in (21), we notice again that the canonical partition function is a convolution product of $2p+2$ functions f_j

$$Z_c(2p+1,L) = e^{L/4}\left(\mathop{*}_{j=1}^{p+1} f_j * f_j\right)(L). \quad (27)$$

The isobaric partition function Z_P is the Laplace transform of Z_c, and we have

$$Z_P(2p+1,P) = \prod_{j=1}^{p+1}\left[\mathcal{L}f_j\left(P-\frac{1}{4}\right)\right]^2$$
$$= \prod_{k=0}^{p}\frac{4}{[2k(k+1)+s]^2}$$
$$= \prod_{k=0}^{p}\frac{1}{\left[\left(k+\frac{1}{2}\right)^2+P\right]^2}, \quad (28)$$

where $s=(4P+1)/2$. Factoring $(k+\frac{1}{2})^2+P = (k+\frac{1}{2}-i\sqrt{P})(k+\frac{1}{2}+i\sqrt{P}) = |k+\frac{1}{2}+i\sqrt{P}|^2$, the above product can be expressed in terms of gamma functions

$$Z_P(2p+1,P) = \left(\frac{1}{P+\frac{1}{4}}\right)^2\left|\frac{\Gamma\left(\frac{3}{2}+i\sqrt{P}\right)}{\Gamma\left(p+\frac{3}{2}+i\sqrt{P}\right)}\right|^4. \quad (29)$$

The average length of the system is given by the usual thermodynamic relation

$$\langle L\rangle = -\frac{\partial\ln Z_P}{\partial P} = \frac{2}{P+\frac{1}{4}} + \sum_{k=1}^{p}\frac{2}{\left(k+\frac{1}{2}\right)^2+P} \quad (30)$$
$$= \frac{2}{P+\frac{1}{4}} + \frac{2}{\sqrt{P}}\Im m\left[\psi\left(p+\frac{3}{2}+i\sqrt{P}\right)\right.$$
$$\left.-\psi\left(\frac{3}{2}+i\sqrt{P}\right)\right], \quad (31)$$

where $\psi(z)=d\ln\Gamma(z)/dz$ is the digamma function. We can notice that this expression has a pole for $P=-1/4$, from which we obtain the behavior when $\langle L\rangle\to\infty$, $P\to-1/4$, in agreement with the general discussion of Sec. II A. When N is even this pole is absent (see below).

If $N=2p$ is even, similar calculations lead to

$$Z_c(2p,L) = e^{L/4} f_{p+\frac{3}{2}} * \left(\mathop{*}_{j=1}^{p} f_{j+\frac{1}{2}} * f_{j+\frac{1}{2}}\right)(L) \quad (32)$$

and

$$Z_P(2p,P) = \frac{1}{P}\prod_{k=1}^{p}\frac{1}{(k^2+P)^2} = \frac{1}{P}\left|\frac{\Gamma(1+i\sqrt{P})}{\Gamma(p+1+i\sqrt{P})}\right|^4. \quad (33)$$

Notice an important difference in the analytic structure of the partition function in the case N odd (27)–(28) and N even (32)–(33): for N even, there is a single function $f_{p+3/2}$ in the convolution product, leading to a pole of order one for $P=0$, in contrast to the case N odd, where the functions f_{p+1} appear twice in the convolution product and the pole for the smallest value of $|P|$ is of order two and it is for $P=-1/4$, rather than $P=0$. In the case N even, the term $f_{p+1}*f_{p+1}$ corresponds to the coupling of the left diffuse layer with the free counterion and the coupling of this same free counterion with the right diffuse layer. On the other hand in the case N odd, the term $f_{p+3/2}$ corresponds to the direct coupling of the left and right diffuse layers.

The average length, for $N=2p$ even, is

$$\langle L\rangle = \frac{1}{P} + \sum_{k=1}^{p}\frac{2}{k^2+P}. \quad (34)$$

We note that $\langle L\rangle\to\infty$ when $P\to 0^+$, in contrast to what happens when N is odd, where $\langle L\rangle\to\infty$ when $P\to-1/4$.

5. Canonical ensemble

We return to the case $N=2p+1$ odd. To compute the canonical partition function, we need to invert the Laplace transform computed in the previous section

$$Z_c(2p+1,L) = \mathcal{L}^{-1}\left(\prod_{k=0}^{p}\frac{1}{\left[\left(k+\frac{1}{2}\right)^2+P\right]^2}\right)(L). \quad (35)$$

This rather technical part of the analysis is presented in Appendix A, where it is shown that

$$Z_c(2p+1,L) = \sum_{j=0}^{p}\left[\frac{2j+1}{(p-j)!(p+j+1)!}\right]^2 e^{-(j+\frac{1}{2})^2 L}\left[L + \frac{2}{2j+1}\left(\sum_{k=p-j+1}^{p+j+1}\frac{1}{k} - \frac{1}{2j+1}\right)\right]. \tag{36}$$

From this expression, we obtain the canonical pressure $P_c = \frac{d\ln Z_c}{dL}$,

$$P_c = -\frac{\sum_{j=0}^{p}\frac{4(j+\frac{1}{2})^4}{[(p-j)!(p+j+1)!]^2}\left[L + \frac{2}{2j+1}\left(\sum_{k=p-j+1}^{p+j+1}\frac{1}{k} - \frac{3}{2j+1}\right)\right]e^{-(j+\frac{1}{2})^2 L}}{\sum_{j=0}^{p}\left[\frac{2j+1}{(p-j)!(p+j+1)!}\right]^2\left[L + \frac{2}{2j+1}\left(\sum_{k=p-j+1}^{p+j+1}\frac{1}{k} - \frac{1}{2j+1}\right)\right]e^{-(j+\frac{1}{2})^2 L}}. \tag{37}$$

For $N = 2p$ even, the results are

$$Z_c(2p,L) = \frac{1}{(p!)^4} - \sum_{j=1}^{p}\frac{(2j)^2 e^{-j^2 L}}{[(p+j)!(p-j)!]^2}\left[L + \frac{1}{j}\left(\sum_{k=p-j+1}^{p+j}\frac{1}{k} - \frac{1}{2j}\right)\right], \tag{38}$$

and

$$P_c = \frac{\sum_{j=1}^{p}\frac{4j^4 e^{-j^2 L}}{[(p+j)!(p-j)!]^2}\left[L + \frac{1}{j}\left(\sum_{k=p-j+1}^{p+j}\frac{1}{k} - \frac{3}{2j}\right)\right]}{\frac{1}{(p!)^4} - \sum_{j=1}^{p}\frac{(2j)^2 e^{-j^2 L}}{[(p+j)!(p-j)!]^2}\left[L + \frac{1}{j}\left(\sum_{k=p-j+1}^{p+j}\frac{1}{k} - \frac{1}{2j}\right)\right]}. \tag{39}$$

6. *Limiting cases and comparison between the ensembles*

With the exact expressions obtained above, we can prove rigorously the limiting behavior of the pressure when $L \to \infty$ and $L \to 0$ discussed in Sec. II A.

Let us consider first the case $N = 2p+1$ odd. In the canonical ensemble, the behavior of the pressure P_c when $L \to \infty$, is obtained from the term $j = 0$ of (36), confirming the prediction (6) of Sec. II A. Furthermore, we realize that the next to next to leading order correction is exponentially small

$$P_c = -\frac{1}{4} + \frac{1}{L - 2\frac{p}{p+1}} - 2\left(\frac{3p}{p+2}\right)^2 e^{-2L}[1 + O(L^{-1})] + O(e^{-6L}). \tag{40}$$

In contrast, when $N = 2p$, the pressure tends to 0 exponentially fast when $L \to \infty$

$$P_c = \frac{4p^2 e^{-L}}{(p+1)^2}\left(L + \frac{2p+1}{p(p+1)} - \frac{3}{2}\right) + O(e^{-2L}). \tag{41}$$

The behavior of the pressure is different in the isobaric ensemble. Consider again first the case $N = 2p+1$. From (30), we already know that when $P = -1/4$, $\langle L\rangle \to \infty$. Denoting $s = (4P+1)/2$, one can expand (30) for small s and invert the relation to obtain P as a function of $\langle L\rangle$ when $\langle L\rangle \to \infty$. For instance, to order $O(s)$, Eq. (30) is

$$\langle L\rangle = \frac{4}{s} + \frac{2p}{p+1} - sS(p) + o(s), \tag{42}$$

where

$$S(p) = \sum_{k=1}^{p}\frac{1}{[k(k+1)]^2} = 2\mathcal{H}_p^{(2)} - \frac{p(3p+4)}{(p+1)^2}, \tag{43}$$

with $\mathcal{H}_p^{(r)} = \sum_{k=1}^{p} k^{-r}$ the harmonic numbers. Inverting that relation, up to order $O(\langle L\rangle^{-3})$, gives

$$P = -\frac{1}{4} + \frac{2}{\langle L\rangle - 2\frac{p}{p+1}} - \frac{8S(p)}{\left(\langle L\rangle - 2\frac{p}{p+1}\right)^3} + o\left(\frac{1}{\left(\langle L\rangle - 2\frac{p}{p+1}\right)^3}\right). \tag{44}$$

Notice a factor 2 of difference in the next to leading order correction [the $O(\langle L\rangle^{-1})$ term] in the pressure in the isobaric ensemble and the canonical ensemble. Furthermore, in the isobaric ensemble the next to next to leading order corrections are algebraic and not exponential as in the canonical ensemble.

For $N = 2p$, the behavior of the pressure, in the isobaric ensemble, when $\langle L\rangle \to \infty$, is

$$P = \frac{1}{\langle L\rangle - 2\mathcal{H}_p^{(2)}} - \frac{2\mathcal{H}_p^{(4)}}{\left[\langle L\rangle - 2\mathcal{H}_p^{(2)}\right]^3} + O(\langle L\rangle^{-4}). \tag{45}$$

Notice again the different behavior with respect to the canonical ensemble. Here in the isobaric ensemble, the pressure vanishes as $1/\langle L\rangle$, whereas in the canonical ensemble it vanishes exponentially fast, as e^{-L}.

Let us study the other limiting behavior of the pressure, for small separations L. Let us focus on the case $N = 2p+1$ first. It is not completely straightforward to obtain the behavior of the pressure in the canonical ensemble when $L \to 0$ directly from expression (37). Rather, it is better to return to (27), and notice that if $L \to 0$, then the convolution product $f_j * f_j$ behaves as

$$f_j * f_j(x) = xH(x) + O(x^2), \tag{46}$$

which is independent of j. Then,

$$\left(\overset{p+1}{\underset{j=1}{*}} f_j * f_j\right)(x) = \frac{x^{2p+1}}{(2p+1)!} + O(x^{2p+2}) \tag{47}$$

and

$$Z_c(2p+1,L) = \frac{L^N}{N!} + O(L^{N+1}). \tag{48}$$

We deduce that the pressure behaves as

$$P_c \sim \frac{N}{L} \quad \text{when } L \to 0, \tag{49}$$

a result already noticed in Ref. [10]. Eq. (49) also holds when $N = 2p$.

In the isobaric ensemble, when $N = 2p+1$, if $\langle L\rangle \to 0$, then, necessarily, $s = (4P+1)/2 \to \infty$ in (30). Expanding that equation to order $O(s^{-2})$, one obtains

$$P = \frac{N+1}{\langle L\rangle} - \frac{N(N+2)}{12} + O(\langle L\rangle) \quad \text{when } \langle L\rangle \to 0. \tag{50}$$

This result also holds true for $N = 2p$. Notice again the difference between the canonical (49) and isobaric ensemble (50), where the leading term changes from N/L to $(N+1)/L$.

When $N = 2p+1$ is odd, the pressure changes of sign when L varies. It is positive for $L \to 0$ and negative for $L \to \infty$. We already obtained an approximation of the value L^* of L when this occurs in the canonical ensemble, see (7), up to exponentially small corrections. In the isobaric ensemble, one just has to put $P = 0$ in (30) to obtain the exact value

$$\langle L^*\rangle = 8\left(1 + \sum_{k=1}^{p} \frac{1}{(2k+1)^2}\right) = \pi^2 - 2\psi'(p+3/2). \tag{51}$$

For this quantity, the predictions from the canonical ensemble (7) and the isobaric ensemble (51) are again different.

Figure 6 shows the pressure as a function of the separation, for $N = 15$, in the isobaric ensemble and the canonical ensemble. Notice that the pressure from the canonical ensemble is smaller that the one in the isobaric ensemble for the same separation. Figure 7 shows the value of L^* for which the pressure changes of sign as a function of N, when N is odd, in both ensembles. Notice again that in the canonical ensemble, the change of sign of the pressure occurs for smaller values L^* of the separation than in the isobaric ensemble.

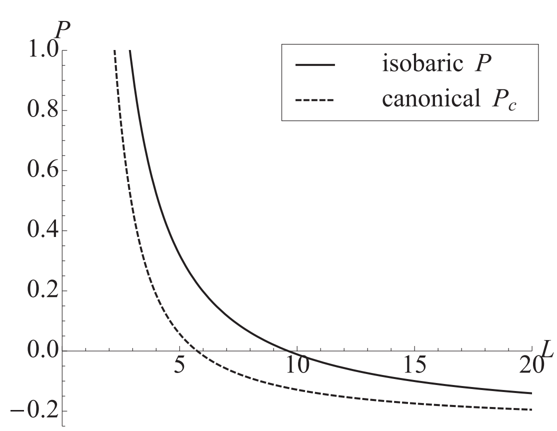

FIG. 6. The pressure P as a function of the separation L, for $N = 15$. The top continuous line represents the result from the isobaric ensemble, and the dotted bottom line those from the canonical ensemble.

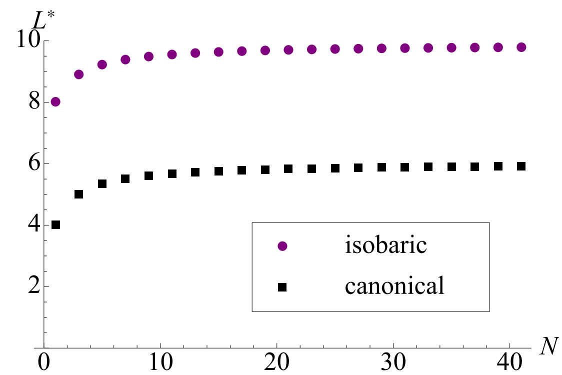

FIG. 7. (Color online) The value of the separation L^* for which the pressure vanishes and changes sign as a function of N for N odd. The (purple) disks represent the results from the isobaric ensemble, and the (black) squares, their canonical counterpart.

The nonequivalence between the two ensembles studied here is due to the fact the system is finite ($L < \infty$). In the thermodynamic limit only should both ensembles present the same results.

III. SCREENING OF TWO UNEQUAL CHARGES

In this section we consider a generalization of the previous model, where the two charges located at $x = 0$ and at $x = L$ are q_1 and q_2, respectively, which can be eventually different. The overall system should be neutral, therefore $q_1 + q_2 = -Ne$, e being charge of one counterion. It is convenient to introduce the notation Q_1 and Q_2 such that $q_1 = -eQ_1$ and $q_2 = -eQ_2$. The electroneutrality relation is $Q_1 + Q_2 = N$. The charge asymmetry can be characterized by the quantity $a = Q_1 - Q_2$, which allows to write $Q_1 = (N+a)/2$ and $Q_2 = (N-a)/2$. The potential energy of the system is now

$$U(N,L,Q_1,Q_2) = -\sum_{1\leqslant i<j\leqslant N} |x_i - x_j| + a\sum_{i=1}^{N} x_i + (Q_2)^2 L. \tag{52}$$

The overall effect of the charge asymmetry is to introduce a global electric field proportional to a (the term in $\sum_i x_i$).

A. Isobaric ensemble

Adapting the ideas of Sec. II B 4 to the present case, we can obtain the isobaric partition function. Once again, the results differ depending on the parity of the number of counterions N. For $N = 2p+1$ odd,

$$Z_P(2p+1,P,Q_1,Q_2) = \prod_{k=0}^{p} \frac{1}{\left[\left(k+\frac{1-a}{2}\right)^2 + P\right]\left[\left(k+\frac{1+a}{2}\right)^2 + P\right]}, \tag{53}$$

while for $N = 2p$ even,

$$Z_P(2p,P,Q_1,Q_2) = \frac{1}{\left(\frac{a}{2}\right)^2 + P} \prod_{k=1}^{p} \frac{1}{\left[\left(k-\frac{a}{2}\right)^2 + P\right]\left[\left(k+\frac{a}{2}\right)^2 + P\right]}. \tag{54}$$

The above formulas highlight the difference between the two cases, depending on the parity of N. However, both formulas can be summarized in a single one as

$$Z_P(N,P,Q_1,Q_2) = \prod_{\ell=0}^{N} \frac{1}{\left(\ell - \frac{N-|a|}{2}\right)^2 + P} = \prod_{l=0}^{N} \frac{1}{(\ell - Q_<)^2 + P} = \prod_{y\in\{-Q_<,-Q_<+1,\ldots,Q_>-1,Q_>\}} \frac{1}{y^2+P}. \tag{55}$$

where we defined

$$Q_< = \frac{N-|a|}{2} = \min(Q_1,Q_2) \quad \text{and} \quad Q_> = \frac{N+|a|}{2} = \max(Q_1,Q_2). \tag{56}$$

Taking the derivative of (55) with respect to P, we obtain the relation between the average length $\langle L\rangle$ of the system and the pressure P in the isobaric ensemble

$$\langle L\rangle = \sum_{\ell=0}^{N} \frac{1}{(\ell - Q_<)^2 + P}. \tag{57}$$

If $a \notin \mathbb{Z}$ is not an integer (q_1 and q_2 are not integer multiples of $-e/2$), or $|a| > N$ (q_1 and q_2 have opposite signs), then Z_P has simple poles. But when $a \in \mathbb{Z}$ is an integer and $|a| \leqslant N$, the partition function Z_P turns out to have some double poles. This corresponds to the case when $2Q_1$ and $2Q_2$ are both positive integers. In that case it is best to reorder the products in (55) to make those double poles more apparent. The result depends on the parity of $2Q_1$ and $2Q_2$ (both have the same parity). If $2Q_1$ and $2Q_2$ are odd, then Q_1 and Q_2 are half integers: $Q_1 = \lfloor Q_1\rfloor + \frac{1}{2}$ and $Q_2 = \lfloor Q_2\rfloor + \frac{1}{2}$. The notation $\lfloor x\rfloor$ denotes the floor function of x (largest integer less or equal than x). The isobaric partition function (55) becomes

$$Z_P(N,P,Q_1,Q_2) = \prod_{\ell=0}^{\lfloor Q_<\rfloor} \frac{1}{\left[\left(\ell+\frac{1}{2}\right)^2 + P\right]^2} \prod_{\ell=\lfloor Q_<\rfloor+1}^{\lfloor Q_>\rfloor} \frac{1}{\left(\ell+\frac{1}{2}\right)^2 + P}, \tag{58}$$

and the corresponding equation of state is

$$\langle L\rangle = \sum_{\ell=0}^{\lfloor Q_<\rfloor} \frac{2}{\left(\ell+\frac{1}{2}\right)^2 + P} + \sum_{\ell=\lfloor Q_<\rfloor+1}^{\lfloor Q_>\rfloor} \frac{1}{\left(\ell+\frac{1}{2}\right)^2 + P}. \tag{59}$$

When Q_1 and Q_2 are positive integers, these expressions become

$$Z_P(N,P,Q_1,Q_2) = \frac{1}{P} \prod_{\ell=1}^{Q_<} \frac{1}{(\ell^2+P)^2} \prod_{\ell=Q_<+1}^{Q_>} \frac{1}{\ell^2+P}, \tag{60}$$

and

$$\langle L\rangle = \frac{1}{P} + \sum_{\ell=1}^{Q_<} \frac{2}{\ell^2+P} + \sum_{\ell=Q_<+1}^{Q_>} \frac{1}{\ell^2+P}. \tag{61}$$

B. Canonical ensemble: Partition function

To compute the canonical partition function, one has to perform the inverse Laplace transform of the expressions obtained in the preceding section. From the above discussion, it is clear that the results will have a different analytical structure depending on whether the isobaric partition function has simple or double poles, that is, depending on whether a is an integer or not. If a is not an integer, or $|a| > N$, all poles of Z_P are simple poles, and we obtain from (55):

$$Z_c(N,L,Q_1,Q_2) = \sum_{j=0}^{N} (-1)^j e^{-(j-\frac{N-|a|}{2})^2 L} \frac{(2j - N + |a|)\,\Gamma(j-N+|a|)}{j!\,(N-j)!\,\Gamma(j+|a|+1)}$$
$$= \sum_{j=0}^{N} (-1)^j e^{-(j-Q_<)^2 L} \frac{2(j-Q_<)\,\Gamma(j-2Q_<)}{j!\,(N-j)!\,\Gamma(j+|Q_1-Q_2|+1)}. \tag{62}$$

This formula is valid whenever $2Q_1$ and $2Q_2$ are not integers, or if Q_1 and Q_2 have opposite signs ($Q_< < 0$ and $Q_> > 0$).

If a is an integer, with $|a| \leqslant N$, then using (58), we obtain, when Q_1 and Q_2 are half integers,

$$Z_c(N,L,Q_1,Q_2) = \sum_{j=0}^{\lfloor Q_< \rfloor} \frac{(2j+1)^2\, e^{-(j+\frac{1}{2})^2 L}}{(\lfloor Q_1\rfloor+1+j)!(\lfloor Q_1\rfloor-j)!(\lfloor Q_2\rfloor+1+j)!(\lfloor Q_2\rfloor-j)!} \times \left[L - \frac{1}{2j+1}\left(\psi(\lfloor Q_1\rfloor-j)-\psi(\lfloor Q_1\rfloor+1+j)+\psi(\lfloor Q_2\rfloor-j)-\psi(\lfloor Q_2\rfloor+1+j)+\frac{2}{2j+1}\right)\right] + \sum_{j=\lfloor Q_<\rfloor+1}^{\lfloor Q_>\rfloor} \frac{e^{-(j+\frac{1}{2})^2 L/4}(j-\lfloor Q_<\rfloor-1)!\,(2j+1)(-1)^{j-\lfloor Q_<\rfloor-1}}{(\lfloor Q_<\rfloor+1+j)!(\lfloor Q_>\rfloor+1+j)!(\lfloor Q_>\rfloor-j)!}, \tag{63}$$

and when Q_1 and Q_2 are integers,

$$Z_c(N,L,Q_1,Q_2) = \sum_{j=1}^{Q_<} \frac{-(2j)^2\, e^{-j^2 L}}{(Q_1+j)!(Q_1-j)!(Q_2+j)!(Q_2-j)!} \times \left[L - \frac{1}{2j}\left(\psi(Q_1+1-j)-\psi(Q_1+1+j)+\psi(Q_2+1-j)-\psi(Q_2+1+j)+\frac{1}{j}\right)\right] + \sum_{j=Q_<+1}^{Q_>} \frac{e^{-j^2 L}(j-Q_<-1)!\,(2j)(-1)^{j-Q_<}}{(Q_<+j)!(Q_>+j)!(Q_>-j)!} + \frac{1}{(Q_1!Q_2!)^2}. \tag{64}$$

The two previous results (63) and (64) show the different analytical structure of the two cases, which depend on the parity of $2Q_1$ and $2Q_2$, in particular the existence of a term independent of L in the case $2Q_1$ and $2Q_2$ even, and the form of the argument of the exponentials $e^{-j^2 L}$ (for $2Q_1$ even), as opposed to $e^{-(j+\frac{1}{2})^2 L}$ (for $2Q_1$ odd). However, both results (63) and (64) can be subsumed in a single formula as follows. Let us define

$$A_j(N,L,Q_1,Q_2) = \frac{[2(Q_<-j)]^2(-1)^{2Q_>+1}}{(2Q_<-j)!\,j!\,(N-j)!(|Q_1-Q_2|+j)!} \times \left[L - \frac{\psi(j+1)-\psi(2Q_<-j+1)+\psi(j+|Q_1-Q_2|+1)-\psi(N-j+1)+\frac{1}{Q_<-j}}{2(Q_<-j)}\right], \tag{65}$$

for $j \neq Q_<$, and, when $Q_<$ is an integer, define

$$A_{Q_<}(N,L,Q_1,Q_2) = \frac{1}{(Q_1!Q_2!)^2}. \tag{66}$$

Also, let

$$D_j(N,Q_1,Q_2) = \frac{j!\,2(j+Q_<+1)(-1)^{j+2Q_>+1}}{(2Q_<+j+1)!(N+j+1)!(|Q_1-Q_2|-j-1)!}. \tag{67}$$

Then, both results (63) and (64) are equivalent to

$$Z_c(N,L,Q_1,Q_2) = \sum_{j=0}^{\lfloor Q_<\rfloor} A_j(N,L,a)\, e^{-(Q_<-j)^2 L} + \sum_{j=0}^{|Q_1-Q_2|-1} D_j(N,a)\, e^{-(j+Q_<+1)^2 L}. \tag{68}$$

C. Canonical ensemble: Asymptotic behavior of the pressure

For small separations L, the results (49), $P_c \sim N/L$ (canonical) and (50), $P \sim (N+1)/\langle L\rangle$ (isobaric), still hold independently of the charge asymmetry a. Thus, the effective interaction is always repulsive at short distance, irrespective of the charges q_1 and q_2, even in the case where these charges are opposite. Indeed, the pressure is dominated here by the entropy cost for confining the ions in a narrow domain.

The behavior for large separations L will depend on whether the charges q_1 and q_2 are multiples of e or not, and their relative signs. There are four cases to consider.

Opposite charges. First, suppose that $q_1 q_2 < 0$, the charges at the edges have opposite signs. This corresponds to the case $|a| > N$, and the canonical partition function is obtained with Eq. (62). From that expression, we deduce that for L large, the leading order is given by the term $j = 0$ of that sum. Therefore, the effective force is attractive and given by

$$P_c \sim -(Q_<)^2, \qquad L \to \infty, \tag{69}$$

where here $Q_< = (N-|a|)/2 < 0$ corresponds to the charge of the edge particle, which has the same sign as the small ions. This result can actually be obtained by simple arguments. The small ions will be repelled by the particle with charge corresponding to $Q_<$ and attracted to the other edge where there is a particle with charge $-eQ_>$ with $Q_> = (N+|a|)/2 > 0$. By electroneutrality, the charge of the compound object formed by the small ions and $-eQ_>$ will be $eQ_<$. The effective force between this object and the other opposite charge $-eQ_<$ is repulsive, equal to $-(eQ_<)^2$, thus recovering (69). Application of the contact theorem of course yields the same result, since the density of counterions vanishes at contact with $Q_<$ (a similar effect was reported in Refs. [24,25]).

Like charges that are not integer multiples of $-e$. To discuss this situation, we keep in mind that $Q_1 > 0$ and $Q_2 > 0$ are not integers. The small ions of charge e will be divided into two parts that will try to screen the charges q_1 and q_2. A number $\lfloor Q_1 \rfloor$ of counterions will partially screen q_1 and $\lfloor Q_2 \rfloor$ ions will partially screen the other charge q_2. Each edge, with its screening cloud of counterions, will have a charge $-e(Q_1 - \lfloor Q_1 \rfloor) = -e\{Q_1\}$ and $-e(Q_2 - \lfloor Q_2 \rfloor) = -e\{Q_2\}$ respectively, where $\{x\} := x - \lfloor x \rfloor$ denotes the fractional part of x. However, since Q_1 and Q_2 are not integers, we have $\lfloor Q_1 \rfloor + \lfloor Q_2 \rfloor = N - 1$: there is still one counterion to take into consideration. This counterion experiences the electric field created by the charge difference $-e(\{Q_1\} - \{Q_2\})$, therefore it will be attracted to the edge that has the largest remaining charge (in the sense of the largest between $\{Q_1\}$ and $\{Q_2\}$). To fix the ideas suppose $\{Q_1\} > \{Q_2\}$. The remaining ion will become part of the screening cloud of q_1, and the charge of that compound object will be $-e(\{Q_1\} - 1)$. Then the effective force between the two edges will be $e^2(\{Q_1\} - 1)\{Q_2\} = -e^2\{Q_2\}^2$, the last equality coming from the fact that $\{Q_1\} + \{Q_2\} = 1$. Summarizing, in general we expect an attractive force at large separations given by

$$P_c \sim -(\min(\{Q_1\},\{Q_2\}))^2, \qquad L \to \infty. \tag{70}$$

This can be verified by identifying the largest argument of the exponentials in the canonical partition function (62) or, equivalently, the largest pole of the isobaric partition function (55). The poles of the isobaric partition function are $-(\ell - Q_<)^2$, with ℓ going from 0 to N. Then, one can notice that $\ell - Q_<$ varies from $-Q_< < 0$ up to $Q_> > 0$ by integer steps of 1. From this one-dimensional array of points, we are interested in the one that is the closest to 0. That is precisely $\min(\{Q_1\},\{Q_2\})$, in agreement with (70). One can also notice from (62) that in the canonical ensemble, the next to leading order correction to (70) is exponentially small of order $O(e^{-|\{Q_1\}-\{Q_2\}|L})$.

Like charges that are half-integer multiples of $-e$. A degenerate case of the previous situation is when Q_1 and Q_2 are half integers, that is $\{Q_1\} = \{Q_2\} = \frac{1}{2}$. In this case the canonical partition function is given by (63) instead of (62). The leading order is still given by (70), specifically $P_c \sim -1/4$. But the correction to leading order is not exponentially small, it can be read from the term $j = 0$ of (63)

$$P_c = -\frac{1}{4} + \frac{1}{L - L_1 - L_2} + O(e^{-2L}), \tag{71}$$

with

$$L_m = 1 - \psi\left(Q_m + \frac{1}{2} + 1\right) + \psi\left(Q_m + \frac{1}{2}\right) = \frac{Q_m - \frac{1}{2}}{Q_m + \frac{1}{2}} = \frac{\lfloor Q_m \rfloor}{\lfloor Q_m \rfloor + 1}, \quad m = 1, 2. \tag{72}$$

We find here the generalization of the charge-symmetric case ($Q_1 = Q_2 = p + \frac{1}{2}$) discussed in Sec. II. Each charge q_1 and q_2 is screened by $\lfloor Q_1 \rfloor$ and $\lfloor Q_2 \rfloor$ ions. The remaining counterion is free to roam in a region of size $L - L_1 - L_2$, and with zero electric field. This ion contributes to the pressure with a term $\frac{1}{L-L_1-L_2}$. Here $L_1 = \langle x_{\lfloor Q_1 \rfloor} \rangle_\infty$ is the size of the screening layer of $\lfloor Q_1 \rfloor$ counterions formed around q_1 and $L_2 = \lim_{L\to\infty}(L - \langle x_{N+1-\lfloor Q_2 \rfloor}\rangle)$ the size of the layer of $\lfloor Q_2 \rfloor$ counterions formed around q_2 [compare (72) to (5), when $\lfloor Q_1 \rfloor = \lfloor Q_2 \rfloor = p$].

Like charges that are natural integer multiples of $-e$. In this case, the screening is not frustrated as in all the previous situations. Simply Q_1 counterions will screen the charge q_1 forming a neutral object, and similarly around q_2 there will be a screening cloud of Q_2 counterions. Since both objects with their screening clouds are neutral, the effective force between them is expected to be $P_c \to 0^+$. This can be verified from the expression for the partition function applicable here, Eq. (64). If $L \to \infty$, we have

$$Z_c = \frac{1}{Q_1!^2 Q_2!^2} - \frac{4e^{-L}}{Q_1!^2 Q_2!^2}\frac{Q_1}{Q_1+1}\frac{Q_2}{Q_2+1} \times \left[L + \frac{1}{2}\left(\frac{2Q_1+1}{Q_1(Q_1+1)} + \frac{2Q_2+1}{Q_2(Q_2+1)} - 1\right)\right] + O(e^{-4L}). \tag{73}$$

Therefore,

$$P_c = 4e^{-L}\frac{Q_1}{Q_1+1}\frac{Q_2}{Q_2+1} \times \left[L + \frac{1}{2}\left(\frac{2Q_1+1}{Q_1(Q_1+1)} + \frac{2Q_2+1}{Q_2(Q_2+1)} - 3\right)\right] + O(e^{-2L}). \tag{74}$$

D. Density profile

With the above results, we can obtain an explicit expression for the density profile of counterions

$$n(x) = \frac{\sum_{k=1}^{N}\int_{x_1<\cdots<x_{k-1}<x_k=x<x_{k+1}<\cdots<x_N} e^{-U(N,L,Q_1,Q_2)}\prod_{j=1,j\neq k}^{N} dx_j}{Z_c(N,L,Q_1,Q_2)}. \tag{75}$$

Notice that due to the fact that each particle only feels a constant electric field proportional to the difference between the number of charges, which are at its left and right sides, the potential energy has the following property

$$U(N,L,Q_1,Q_2) = U[k-1,x_k,Q_1,Q_2-(N-k+1)] + U(N-k,L-x_k,Q_1-k,Q_2). \tag{76}$$

This can be interpreted as follows. If the particle at position x_k is fixed, the system decouples into two independent systems, one of size x_k with $k-1$ particles, and the other one of size $L-x_k$ with $N-k$ particles, with the appropriate charges at each boundary (obtained by summing the charges at the left side and right sides of x_k of the original system). Then, the computation of the integrals in (75) simply yields the product of the two partition functions of each subsystem,

$$n(x) = \frac{\sum_{k=1}^{N} Z_c(k-1,x,Q_1,Q_2-N+k-1)Z_c(N-k,L-x,Q_1-k,Q_2)}{Z_c(N,L,Q_1,Q_2)}, \tag{77}$$

where each Z_c should be replaced by its appropriate corresponding expression from (62) or (68).

1. Contact density and pressure

From this expression we can verify the known relation between the contact density at $x=0$ (or $x=L$) and the pressure [13]. Indeed, notice that

$$n(0) = \frac{Z_c(N-1,L,Q_1-1,Q_2)}{Z_c(N,L,Q_1,Q_2)}. \tag{78}$$

On the other hand, from Eq. (62) we can verify that

$$\frac{\partial Z_c(N,L,Q_1,Q_2)}{\partial L} = Z_c(N-1,L,Q_1-1,Q_2) - (Q_1)^2, \tag{79}$$

where this last relation was obtained by writing $-(j-\frac{N-a}{2})^2 = (N-j)(j+a) - [(N+a)/2]^2$ in (62), and recalling that $Q_1 = (N+a)/2$. Therefore, we find

$$P_c = n(0) - (Q_1)^2 = n(L) - (Q_2)^2. \tag{80}$$

The last equality is obtained using the same argument on $x=L$ in $n(x)$.

2. Asymptotic behavior of the density

Let us consider the case $a=0$, i.e., $Q_1=Q_2=N/2$. Figure 8 shows a plot of the density profile for $N=25$ and $N=26$. Notice that in the case $N=26$ even, the density falls off quickly to zero far from the boundaries $x=0$ and $x=L$. On the other hand, when $N=25$ is odd, the density does not fall to zero, but goes to a nonvanishing value shown by the horizontal line. This corresponds to the density of the free counterion, responsible for the effective attraction between the two charges q_1 and q_2 as discussed earlier.

To quantify this behavior, consider expression (77) for the density in the case $N=2p+1$, and $Q_1=Q_2=p+\frac{1}{2}$,

$$n(x) = \frac{\sum_{k=1}^{N} Z_c\big(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2}\big)Z_c\big(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2}\big)}{Z_c\big(2p+1,L,p+\frac{1}{2},p+\frac{1}{2}\big)}. \tag{81}$$

In this sum, the partition function $Z_c(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2})$ corresponds to a system with charges $-e(p+\frac{1}{2})$ and $-e(k-p-\frac{3}{2})$ at its boundaries. If $k\leqslant p$, these two charges carry opposite signs, therefore, $Z_c(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2})$ is given by Eq. (62). Then, if $1\ll x\ll L$, $Z_c(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2}) = O[e^{-(p-k+\frac{3}{2})^2 x}]$. On the other hand, the second partition function, $Z_c(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2})$, corresponds to a system with charges $-e(p-k+\frac{1}{2})$ and $-e(p+\frac{1}{2})$ at its edges. If $k\leqslant p$, these two charges carry the same sign and are half-integer multiples of e, therefore $Z_c(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2})$ should be obtained by using Eq. (64). In particular one can notice that if $1\ll x\ll L$, then $Z_c(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2}) = O[e^{-(L-x)/4}]$. Therefore, in the sum (81) all terms with $k\leqslant p$ decay exponentially fast when x is far from the boundaries: they are of order $O(e^{-[(p-k+\frac{3}{2})^2-\frac{1}{4}]x})$. The same argument could be applied to all the terms with $k\geqslant p+2$, with the roles of $Z_c(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2})$ and $Z_c(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2})$ interchanged. Then, only one term in the sum (81) survives, it corresponds to $k=p+1$, which is precisely the index of the position of the free counterion. In this term, both $Z_c(k-1,x,p+\frac{1}{2},k-p-\frac{3}{2})$ and $Z_c(2p+1-k,L-x,p-k+\frac{1}{2},p+\frac{1}{2})$ with $k=p+1$, correspond to a system with charges $-e(p+\frac{1}{2})$ and $e/2$ at its edges (notice the opposite signs), and those partition functions should both be computed using (62). The leading order of these partition functions, when $1\ll x\ll L$, is

$$Z_c\left(p,x,p+\frac{1}{2},-\frac{1}{2}\right) \sim \frac{e^{-x/4}}{p!(p+1)!} \quad \text{and} \quad Z_c\left(p,L-x,-\frac{1}{2},p+\frac{1}{2}\right) \sim \frac{e^{-(L-x)/4}}{p!(p+1)!} \tag{82}$$

while the leading order of the denominator of (81) is

$$Z_c\left(2p+1,L,p+\frac{1}{2},p+\frac{1}{2}\right) \sim \frac{e^{-L/4}}{(p!(p+1)!)^2}\left(L-2\frac{p}{p+1}\right). \tag{83}$$

This gives

$$n(x) \sim \frac{1}{L - 2\frac{p}{p+1}} = \frac{1}{L - 2\langle x_p\rangle_\infty}, \quad \text{for } 1 \ll x \ll L. \tag{84}$$

This is the analytical confirmation of the intuitive analysis of Sec. II A where it was explained that when N is odd, there is one free ion roaming between the two charges with an available space equal to $L - 2\langle x_p\rangle_\infty$, as shown in Fig. 4.

In the case where N is even, a similar analysis shows that all terms of the sum (77) fall of exponentially fast when x is far from the boundaries.

E. Large N limit

It is interesting to consider the limit $N \to \infty$. Due to the electroneutrality condition $q_1 + q_2 + eN = 0$, one needs to consider different situations: whether q_1 and q_2 are kept finite, then necessarily the charge of the counterions e should vanish as $1/N$. Then we notice that this is also a mean-field regime. The other possible limit is to consider that e has a nonvanishing finite value, then q_1 and/or q_2 should go to infinity as N.

1. Mean-field limit, $N \to \infty$ and $e \to 0$.

Momentarily, it is best to return to dimensional units $\widetilde{L}$ and $\widetilde{P}$: the rescaling by e^2 is not appropriate here, because $e \to 0$. Consider the equation of state (57) derived in the isobaric ensemble, which now reads

$$\beta\langle\widetilde{L}\rangle = \sum_{\ell=0}^{N} \frac{1}{(e\ell + q_<)^2 + \widetilde{P}} \sim \frac{1}{e}\int_{q_<}^{-q_>} \frac{dy}{y^2 + P}, \tag{85}$$

where $q_< = -eQ_<$ and $q_> = -eQ_>$. Since $e \to 0$, one can recognize a Riemann sum and replace it by an integral. This finally leads to

$$\beta e\langle\widetilde{L}\rangle\sqrt{\widetilde{P}} = \arctan\frac{q_1}{\sqrt{\widetilde{P}}} + \arctan\frac{q_2}{\sqrt{\widetilde{P}}}. \tag{86}$$

We recover here the implicit relation between $\langle\widetilde{L}\rangle$ and $\widetilde{P}$ from the mean-field theory as described by the Poisson-Boltzmann equation [26,27]. Indeed, referring for instance to Ref. [27], where the mean-field regime of the present problem was considered, Eq. (86) can be directly obtained from a simple linear combination of Eqs. (16) and (17) of Ref. [27]. Notice that the interesting effects, such as like-charge attraction, stemming from the discrete nature of the charges, are lost in this mean-field limit. Like charges will always have a repulsive effective interaction in the mean-field regime [21–23]. A related comment is that the asymptotic negative pressure reported for odd N in Sec. II, $\widetilde{P} = -q^2/N^2$, vanishes in the limiting process addressed here.

It should be noted that the present limit is also the thermodynamic limit, since we have to remember that e is of order $1/N$, therefore in the left-hand side of (86) $\langle\widetilde{L}\rangle$ should be of order N. To make this more apparent, introduce the average distance per ion $\langle\widetilde{\ell}\rangle = \langle\widetilde{L}\rangle/N$ (inverse of the density), then (86) becomes

$$\beta(q_1 + q_2)\langle\widetilde{\ell}\rangle\sqrt{\widetilde{P}} = \arctan\frac{q_1}{\sqrt{\widetilde{P}}} + \arctan\frac{q_2}{\sqrt{\widetilde{P}}}. \tag{87}$$

2. Limit $N \to \infty$ and e fixed.

In this situation, the charges at the edges q_1 and q_2 should be of order N, or at least one of them. Consider the case when both $Q_1 > 0$ and $Q_2 > 0$ are of order N. Then, when $N \to \infty$, Eq. (57) can be put in the following form by shifting the index of the summation by $\lfloor Q_< \rfloor$,

$$\langle L\rangle = \sum_{\ell=-\infty}^{\infty} \frac{1}{(\ell - \{Q_<\})^2 + P}. \tag{88}$$

Notice that by shifting the index ℓ by one, we can replace $\{Q_<\}$ by $\{Q_>\}$ if necessary. One can then write

$$\langle L\rangle = \sum_{\ell=-\infty}^{\infty} \frac{1}{[\ell - \min(\{Q_1\},\{Q_2\})]^2 + P}. \tag{89}$$

Notice that in this analysis, the limit depends on how Q_1 and Q_2 are taken to infinity, and assumes that the fractional part of them is kept fixed as N is increased.

To cover the whole range of values for $\langle L\rangle$ from 0 to $+\infty$, it is necessary that P covers the range from $-\min(\{Q_1\},\{Q_2\})^2$ to $+\infty$. We recover the same phenomenology as in the case N finite, when $\langle L\rangle \to \infty$, $P \to -\min(\{Q_1\},\{Q_2\})^2$. So, the pressure can become attractive, except in the case where Q_1 and Q_2 are integers. Eq. (89) can be made more explicit in two particular cases. When Q_1 and Q_2 are integers,

$$\langle L\rangle = \sum_{\ell=-\infty}^{\infty} \frac{1}{\ell^2 + P} = \frac{\pi\coth(\pi\sqrt{P})}{\sqrt{P}}, \tag{90}$$

and when Q_1 and Q_2 are half integers,

$$\langle L\rangle = \sum_{\ell=-\infty}^{\infty} \frac{1}{\left(\ell + \frac{1}{2}\right)^2 + P} = \frac{\pi\tanh(\pi\sqrt{P})}{\sqrt{P}}. \tag{91}$$

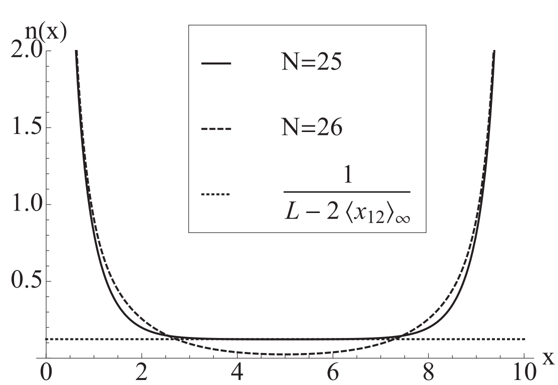

FIG. 8. The density profile for $N = 25$ and $N = 26$ counterions and $L = 10$. Notice that in the case where the number of counterions is odd, $N = 25$, the density far from the edges converges to a nonzero value $1/(L - 2\langle x_{12}\rangle_\infty)$, here close to 0.124.

When Q_1 and Q_2 are not integers, the value of $\langle L\rangle$ for which the pressure changes of sign is given by putting $P=0$ in (89)

$$\langle L^*\rangle = \sum_{\ell=-\infty}^{\infty} \frac{1}{[\ell-\min(\{Q_1\},\{Q_2\})]^2} = \psi'(\{Q_1\})+\psi'(\{Q_2\}). \quad (92)$$

When Q_1 and Q_2 are half-integers this reduces to $\langle L^*\rangle = \pi^2$.

IV. CONCLUSION

We have studied a simple one-dimensional system as a model to understand the effective interaction between charged particles that are screened by counterions only. This model evidences the possibility of attraction between two like charges at large separation. The physical phenomenon behind this attraction is a frustration of the screening process due to the discrete nature of the electric charges. More specifically, if the two like charges are not integer multiples of the charge of the counterions, a perfect screening of the charges is not possible, and there will be a misfit counterion, responsible for the overscreening of one of the like charges, leading to an effective attractive force. A byproduct is that in the mean-field limit where discreteness effects are washed out, no like-charge attraction is possible, a well-known phenomenon.

The present model is in addition interesting from a purely theoretical perspective, since it is exactly solvable: it is possible to compute explicitly its partition functions (isobaric and canonical), the pressure (effective force), and the density profile of the counterions. Although the specific exact results and expression for the effective force are particular to this one-dimensional model, the physical mechanism responsible for the attraction between like charges could also be applicable for three-dimensional situations [19]. In particular the case $N=1$ leads to an equation of state that is equivalent to that found under strong coupling for three-dimensional planar interfaces, screened by point counterions interacting through the standard $1/r$ Coulomb potential [11,12,17].

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APPENDIX: TWO EQUAL CHARGES: CANONICAL EXPRESSIONS

The inverse Laplace transform can be computed with integral inversion formula, which can be evaluated using the residue theorem

$$\mathcal{L}^{-1}\left(\prod_{k=0}^{p}\frac{1}{\left[\left(k+\frac{1}{2}\right)^2+P\right]^2}\right)(L) = \sum_{j=0}^{p} \operatorname*{Res}_{P=-(j+\frac{1}{2})^2} \frac{e^{PL}}{\prod_{k=0}^{p}\left[\left(k+\frac{1}{2}\right)^2+P\right]^2}. \quad (A1)$$

Each residue is straightforward to compute

$$\operatorname*{Res}_{P=-(j+\frac{1}{2})^2} \frac{e^{PL}}{\prod_{k=0}^{p}\left[\left(k+\frac{1}{2}\right)^2+P\right]^2} = \frac{e^{-(j+\frac{1}{2})^2 L}}{\prod_{k=0,k\neq j}^{p}\left[\left(k+\frac{1}{2}\right)^2-\left(j+\frac{1}{2}\right)^2\right]^2}\left(L-\sum_{l=0,l\neq j}^{p}\frac{2}{\left(l+\frac{1}{2}\right)^2-\left(j+\frac{1}{2}\right)^2}\right). \quad (A2)$$

Writing

$$\frac{1}{\left(k+\frac{1}{2}\right)^2-\left(j+\frac{1}{2}\right)^2} = \frac{1}{(k-j)(k+j+1)} = \frac{1}{2j+1}\left(\frac{1}{k-j}-\frac{1}{k+j+1}\right), \quad (A3)$$

the above product and sum can be simplified

$$\frac{1}{\prod_{k=0,k\neq j}^{p}\left[\left(k+\frac{1}{2}\right)^2-\left(j+\frac{1}{2}\right)^2\right]} = \frac{(-1)^j(2j+1)}{(p-j)!(p+j+1)!}, \quad (A4)$$

and

$$\sum_{l=0,l\neq j}^{p}\frac{1}{\left(l+\frac{1}{2}\right)^2-\left(j+\frac{1}{2}\right)^2} = \frac{2}{2j+1}\left(\frac{1}{2j+1}-\sum_{k=p-j+1}^{p+j+1}\frac{1}{k}\right) = \frac{2}{2j+1}\left(\frac{1}{2j+1}+\psi(p-j+1)-\psi(p+j+2)\right). \quad (A5)$$

Gathering all results, the exact explicit result for the canonical partition function is found in the form of Eq. (36).

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