

**Configurational and energy landscape in one-dimensional Coulomb systems**

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We study a one-dimensional Coulomb system, where two charged colloids are neutralized by a collection of point counterions, with global neutrality. With temperature being given, two situations are addressed: Either the colloids are kept at fixed positions (canonical ensemble) or the force acting on the colloids is fixed (isobaric-isothermal ensemble). The corresponding partition functions are worked out exactly, in view of determining which arrangement of counterions is optimal. How many counterions should be in the confined segment between the colloids? For the remaining ions outside, is there a left-right symmetry breakdown? We evidence a cascade of transitions as system size is varied in the canonical treatment or as pressure is increased in the isobaric formulation.

DOI: [10.1103/PhysRevE.95.022112](https://doi.org/10.1103/PhysRevE.95.022112)**I. INTRODUCTION**

In condensed matter physics, interactions due to electrostatic forces are essential. Since matter is made of protons and electrons, special properties of materials are ultimately due to the electric and magnetic interactions at the atomic and molecular scales. Plasmas exhibit as well strong electromagnetic interactions that are responsible for their behavior. Their understanding sheds light on the physics at work in the interior of a star [1] or on the conducting properties of liquid metals such as gallium-based alloys, which are used for industrial purposes. Substances with polar solvents (e.g., colloids, polymers, and membranes) give another example of systems where including electric interactions is paramount to describing thermodynamic properties [2].

Coulomb systems are the ensembles that model the interaction between charges with the Coulomb potential energy. In three dimensions this potential reads

$$U_{C_{3D}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{-q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (1)$$

Yet an analytic expression for a partition function of a Coulomb system is impossible to obtain. Mean field theories provide an approach to this problem but fail when the electric correlations are important, which is the case for many systems of interest in soft condensed matter [1,2]. The two most important phenomena they fail to account for are charge reversal (overcharging) and like-charge attraction. The first occurs when a colloid (large ion) is screened by enough counterions (small ions with opposite charge) such that the net charge opposes the one of the colloid. Like-charge attraction happens when two colloids of the same bare charge sign are attracted to each other due to the interactions with the medium (counterions).

Another powerful method that has proven operational predicting the behavior of Coulomb systems, especially the qualitative one, is to study a lower-dimension model. In lower dimensions, the electrostatic potential is easier to manipulate while keeping important features of the three-dimensional (3D) case such as its long range. They can also be mapped

to some three-dimensional systems with a translational invariance in one direction. For example, the 2D logarithmic potential given by

$$U_{C_{2D}}(\mathbf{r}_1, \mathbf{r}_2) = -q_1 q_2 \ln \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{L} \quad (2)$$

is used to model the interaction between vortices in quantum fluids (e.g., superfluid  $^4\text{He}$  and  $^3\text{He}$  films), two-dimensional crystalline solids, and  $XY$  (classical rotor) magnets [1]. Another example is the analogy between the Laughlin trial wave function for the fractional quantum Hall effect [3] and the Boltzmann factor for the two-dimensional one-component plasma [4]. This analogy has proven fruitful to understand the properties of both systems. For example, in [5,6], the authors considered a special case that allows an analytic solution. This led them to find that a plasma forms a double-layer structure that causes an excess density as the edge of the leading support is approached from the inside of the plasma. Furthermore, these two-dimensional models have been used to study important physical phenomena such as charge renormalization and the Onsager-Manning-Oosawa counterion condensation [7,8], which is reviewed in [9].

In one-dimensional Coulomb systems, charged particles interact via the potential

$$U_{C_{1D}}(x_1, x_2) = -q_1 q_2 |x_1 - x_2|. \quad (3)$$

For these systems, analytical expressions for the canonical and isobaric partition functions can be obtained. These were first investigated independently by Lenard [10] and Prager [11]. Although a one-dimensional model is a simplification or fictitious model, it gives insights into the qualitative behavior of the three-dimensional problem. As Prager remarks in [11]: “It is these [long-range] forces which make the statistical mechanics of plasmas and electrolyte solutions so extraordinarily difficult to treat. . . . The one-dimensional plasma, where this can be done exactly, should thus serve as a useful testing-ground for approximations developed to treat the three-dimensional case.” The fact that an exact analytical resolution is possible is indeed of particular interest, for it heralds non-mean-field effects such as overcharging and



FIG. 1. Sketch of the model studied in [13].

like-charge attraction. These properties were found in a one-dimensional model first introduced in [12] and analytically solved in [13]. It consists of two colloidal charges separated by a distance  $L$  and  $N$  neutralizing counterions bounded by the colloids (Fig. 1). Depending on whether the colloidal charges are integer multiples of the counterion charges and the parity of the number of counterions, it was found that both overcharging and like-charge attraction were possible. One-dimensional Coulomb systems have also been used as simple models that mimic some properties of electrolytic soap films and can exhibit their collapse mechanism into Newton black films [14].

The present work extends the analysis of Ref. [13]. We wish here to explore the situation where a variable number of counterions may become unbounded (Fig. 2). Two questions then arise. Which is the optimal configuration and do the non-mean-field phenomena still occur for the new configurations? We will answer these questions, providing a complete thermodynamical solution and interpretation for the canonical and isobaric ensembles that arise from this modification.

Our problem bears some similarities with some three-dimensional studies [15,16] where ions of both signs may be exchanged with a salt reservoir. In our case, counterions may escape the segment interior by populating the outside regions. It is shown in [16] that electroneutrality breakdown may occur in a slab interior, between two parallel charged planar surfaces.

The scheme we use to compute the canonical partition function consists in rearranging the terms of the Coulomb potential and writing it as a convolution product of some auxiliary functions. Then we compute the Laplace transform of the canonical partition function, which is the product of the Laplace transforms of each auxiliary function by virtue of the convolution theorem. By performing the Laplace transform, we obtain the isobaric partition function, which gives us information about the system in this ensemble. Finally, to obtain the canonical partition function, we use the inversion formula for the Laplace transform, which is computed by using the residue theorem.

The outline is as follows. In Sec. II, following Prager [11] and Lenard [10], we start by studying the isobaric ensemble, where the partition function and ensuing quantities are easier to compute and interpret. Special interest is given to finding the configuration of particles that minimizes the Gibbs energy. We then calculate in Sec. III the canonical partition function from its isobaric counterpart, performing an inverse Laplace transform. In each section, the form of the thermodynamic quantities in each ensemble is analyzed by analytical and graphical means. We summarize in Sec. IV.



FIG. 2. Representation of the modified model studied here.

## II. ISOBARIC ENSEMBLE

Both Lenard [10] and Prager [11] noticed that for a one-dimensional plasma with global neutral charge, the potential energy could be expressed as a sum of the relative distance between charges. We follow this technique to rewrite the canonical partition function in a form in which the Laplace transform (isobaric partition function) is readily obtained.

### A. Isobaric partition function

Consider two charges  $q$  along a line located at  $\tilde{x} = 0$  and  $\tilde{x} = \tilde{L}$ . They play the role of the colloids depicted in Figs. 1 and 2. There are also  $N$  counterions of charge  $e = -2q/N$  with positions  $\tilde{x}_i$ . The potential energy of this neutral system is denoted by  $\tilde{U}$ . The system is in thermal equilibrium at a temperature  $T$ . It is convenient to introduce the dimensionless quantities  $x = \beta e^2 \tilde{x}$ , for the positions, and  $U = \beta \tilde{U}$ , for the potential energy, where  $\beta = (k_B T)^{-1}$  and  $k_B$  is the Boltzmann constant. With this notation, the dimensionless potential energy takes the form

$$U(x_1, \dots, x_N) = \frac{N}{2} \sum_{i=1}^N (|x_i| + |x_i - L|) - \sum_{1 \leq i < j \leq N} |x_i - x_j| - \left(\frac{N}{2}\right)^2 L, \quad (4)$$

where the summands from left to right are due to colloid-counterion, counterion-counterion, and colloid-colloid interactions, respectively.

For the computation of the canonical partition function, it is convenient to separate the dimensionless potential energy in three summands. Let  $\ell$  and  $r$  be the number of unbounded counterions to the left and right, i.e., for  $i \leq \ell$ ,  $x_i < 0$  and for  $i > N - r$ ,  $x_i > L$ , respectively. Then  $U_L$  and  $U_R$  are the contributions due to the unbounded counterions and  $U_B$  is due to the counterions bounded by the colloids. The expression in terms of the separated potentials is

$$U(x_1, \dots, x_N) = U_L(x_1, \dots, x_\ell) + U_B(x_{\ell+1}, \dots, x_{N-r}) + U_R(x_{N-r+1}, \dots, x_N). \quad (5)$$

To simplify the expressions for the potentials the particles are ordered as  $x_1 < x_2 < \dots < x_N$ . Writing the distance between particles as the sum of the distances between first neighbors, the following expressions are obtained:

$$U_L(x_1, \dots, x_\ell) = \sum_{k=1}^{\ell} k^2 (x_{k+1} - x_k) \quad (6)$$

with the convention  $x_{\ell+1} \equiv 0$ ,

$$U_B(x_{\ell+1}, \dots, x_{N-r}) = - \sum_{k=\ell}^{N-r} k(N-k)(x_{k+1} - x_k) + \frac{N(N-4r)L}{4} \quad (7)$$

with  $x_\ell = x_{N-r+1} \equiv 0$ , and

$$U_R(x_{N-r+1}, \dots, x_N) = \sum_{k=N-r}^N (N-k)^2 (x_{k+1} - x_k) \quad (8)$$

with  $x_{N-r} \equiv 0$ .

The expression for the canonical partition function is given by

$$\begin{aligned}
 Z_c(N, L) &= \int_L^\infty dx_N \int_L^{x_N} dx_{N-1} \cdots \int_L^{x_{N-r+2}} dx_{N-r+1} \\
 &\times \int_0^L dx_{N-r} \int_0^{x_{N-r}} \cdots \int_0^{x_{\ell+2}} \int_{x_{\ell-1}}^0 \cdots \\
 &\times \int_{x_1}^0 dx_2 \int_{-\infty}^0 e^{-U(x_1, \dots, x_N)} dx_1. \quad (9)
 \end{aligned}$$

This expression can be split into a product of three terms, in a similar way to the potential energy with the aid of the Fubini theorem

$$\begin{aligned}
 Z_c(N, L) &= \left( \int_{x_{\ell-1}}^0 \cdots \int_{-\infty}^0 e^{-U_L} \prod_{j=1}^{\ell} dx_j \right) \\
 &\times \left( \int_0^L \cdots \int_0^{x_{\ell+2}} e^{-U_B} \prod_{j=\ell+1}^{N-r} dx_j \right) \\
 &\times \left( \int_{x_{N-1}}^\infty \cdots \int_L^\infty e^{-U_R} \prod_{j=N-r+1}^N dx_j \right). \quad (10)
 \end{aligned}$$

Grouping the integrals of the left, right, and bounded positions of the counterions, a product of the form

$$Z_c = Z_L Z_B Z_R \quad (11)$$

is obtained. To compute each term, the following auxiliary functions are introduced:

$$g_k(x) \equiv e^{k^2 x} H(-x), \quad (12)$$

$$f_k(x) \equiv e^{k(N-k)x} H(x), \quad (13)$$

where  $H(x)$  is the Heaviside step function. With these functions, the partition function can be recast as a convolution product. The left partition function  $Z_L$  is naturally expressed in terms of the  $g_k$  functions. To write the right term  $Z_R$  in terms of the  $g_k$  functions, a change of variables is performed

$y_k = x_k - L$ . This translation only adds a factor due to the term that does not cancel out,  $x_{N-r+1} = L + y_{N-r+1}$ . The results for  $Z_L$  and  $Z_R$  are

$$Z_L(\ell) = \mathcal{L} \left\{ \bigotimes_{k=1}^{\ell} g_k(-x_1) \right\} (0) = \left( \frac{1}{\ell!} \right)^2, \quad (14)$$

$$Z_R(r) = e^{-r^2 L} \mathcal{L} \left\{ \bigotimes_{k=1}^r g_k(-y_N) \right\} (0) = \left( \frac{1}{r!} \right)^2 e^{-r^2 L}, \quad (15)$$

where  $\mathcal{L}\{f(x)\}(0)$  is the one-sided Laplace transform of  $f(x)$  evaluated at 0.

The partition function  $Z_B$ , corresponding to the counterions bound in between the two colloids, is essentially the same as for the configuration of equally charged colloids studied in [13]. There is a subtle difference from [13]: When writing it as a convolution product, an extra factor  $\exp[r(N-r)L]$  appears. The expression for the partition function  $Z_B$  is

$$Z_B(N, \ell, r, L) = e^{-r(N-r)L - N(N-4r)L/4} \bigotimes_{k=\ell}^{N-r} f_k(L). \quad (16)$$

Putting together all these results, the canonical partition function is then written as

$$Z_c(N, L) = \frac{e^{-(N^2/4)L}}{(\ell!r!)^2} \bigotimes_{k=\ell}^{N-r} f_k(L). \quad (17)$$

It is convenient to switch to the isobaric partition function, which is the Laplace transform of expression (17). This is done using the convolution theorem, obtaining a simple expression in terms of products of the Laplace transforms of the functions  $f_k$  evaluated at  $P + N^2/4$  due to the exponential factor

$$Z_p(N, P) = \frac{1}{(\ell!r!)^2} \prod_{k=\ell}^{N-r} \frac{1}{P + N^2/4 - k(N-k)}. \quad (18)$$

To analyze the structure of the isobaric partition function, we examine the effects of the parity of  $N$  separately. We distinguish the even  $N = 2n$  and odd  $N = 2n + 1$  cases. It is also convenient to introduce the parameters  $M = \max(\ell, r)$  and  $m = \min(\ell, r)$ . In the even case  $N = 2n$ , depending on the values of  $M$  and  $n$ , we have

$$Z_p(2n, P) = \begin{cases} \frac{1}{(M!m!)^2} \frac{1}{P} \left( \prod_{k=1}^{n-M} \frac{1}{P+k^2} \right)^2 \prod_{k=n+1-M}^{n-m} \frac{1}{P+k^2} & \text{if } n - M - \frac{1}{2} > 0 \\ \frac{1}{(M!m!)^2} \prod_{k=M-n}^{n-m} \frac{1}{P+k^2} & \text{if } \frac{1}{2} + M - n > 0. \end{cases} \quad (19)$$

Several important properties can be seen from these equations. When there is an even number of counterions, second-order poles are present for  $M < n$ . The leading (largest) pole is  $P = 0$  for  $M \leq n$ . For  $M > n$  the leading pole is  $P = -(M-n)^2$ . For any value of  $M$  and  $m$  the leading pole is always simple.

In the odd case  $N = 2n + 1$ , the partition function is

$$Z_p(2n + 1, P) = \begin{cases} \frac{1}{(M!m!)^2} \left( \prod_{k=0}^{n-M} \frac{1}{P+(k+\frac{1}{2})^2} \right)^2 \prod_{k=n+1-M}^{n-m} \frac{1}{P+(k+\frac{1}{2})^2} & \text{if } n - M + \frac{1}{2} > 0 \\ \frac{1}{(M!m!)^2} \prod_{k=M-n-1}^{n-m} \frac{1}{P+(k+\frac{1}{2})^2} & \text{if } M - \frac{1}{2} - n > 0. \end{cases} \quad (20)$$

For the odd case the second-order poles appear for  $M \leq n$  and the leading pole is  $P = -1/4$  until  $M \leq n + 1$ . For  $M > n + 1$  the leading pole is  $P = -(M - n - 1/2)^2$ . In the odd case the leading pole has order 2 for  $M < n + 1/2$  and for  $M > 1/2 + n$  it becomes simple.

### B. Equivalent model

Consider the model studied in [13]. It consists of  $N'$  counterions all bounded without chance to escape and two colloidal charges surrounding them. These colloids have different charge magnitudes  $Q_1$  and  $Q_2$ . As considered here, the system is neutral. After comparing the isobaric partition function (18) with the expression obtained for the screening of two unequal charges in [13], we find that they are proportional by a factor  $(M!m!)^2$ ,

$$Z_p(N, P) = \frac{1}{(M!m!)^2} \mathcal{Z}_p(N' = N - M - m, P, Q_1, Q_2), \quad (21)$$

where

$$\begin{aligned} \mathcal{Z}_p(N', P, Q_1, Q_2) &= \prod_{k=M}^{N-m} \frac{1}{P + N^2/4 - k(N-k)} \\ &= \prod_{k \in \{-Q_<, -Q_<+1, \dots, Q_>-1, Q_>\}} \frac{1}{P + k^2} \end{aligned} \quad (22)$$

is the partition function found in [13] for a system with  $N' = N - \ell - r = N - m - M$  counterions confined

between charges  $Q_1 = \frac{N}{2} - \ell$  and  $Q_2 = \frac{N}{2} - r$ . We have defined  $Q_> = \max(Q_1, Q_2) = \frac{N}{2} - m$  and  $Q_< = \min(Q_1, Q_2) = \frac{N}{2} - M$ . Note that  $Q_1$  and  $Q_2$  are the global charges of the colloidal particles plus the counterions outside the corresponding edge. The relation between the two ensembles comes from the nature of the one-dimensional Coulomb electric field. As far as the electric field is concerned, the only thing that matters is the net charge at each side of the point where the field is computed and not the detailed position of each charge in the system. Then it is equivalent to have charges spatially distributed or one point charge as long as the net charge is the same. The proportionality factor only adds up a constant factor to the Gibbs energy, which accounts for the zero-pressure (infinite length in the canonical ensemble) energy of the additional unbounded counterions.

### C. Gibbs free energy and optimal configuration

#### 1. General results

We now turn our attention to the Gibbs energy, which will allow us to determine the fundamental configuration (minimum Gibbs energy configuration). First we consider the even case  $N = 2n$ . The Gibbs energy is given by the usual expression  $\tilde{G} = -\beta^{-1} \ln Z_p$ . Using the dimensionless free energy  $G = \tilde{G}\beta$ , we have

$$G_{2n}(M, m) = \begin{cases} 2 \ln(M!m!) + \ln P + 2 \sum_{k=1}^{n-M} \ln(P + k^2) + \sum_{k=n+1-M}^{n-m} \ln(P + k^2) & \text{if } n - M - \frac{1}{2} > 0 \\ 2 \ln(M!m!) + \sum_{k=M-n}^{n-m} \ln(P + k^2) & \text{if } \frac{1}{2} + M - n > 0. \end{cases} \quad (23)$$

First we examine the situation when the total number of unbounded ions is fixed. To this end, consider the exchange of one particle from one side to the other

$$\begin{aligned} \Delta G_{2n}(M \rightarrow M+1, m \rightarrow m-1) \\ = 2 \ln \left( \frac{M+1}{m} \right) + \ln \left( \frac{P + (n+1-m)^2}{P + (n-M)^2} \right), \end{aligned} \quad (24)$$

$$\begin{aligned} \Delta G_{2n}(M \rightarrow M-1, m \rightarrow m+1) \\ = 2 \ln \left( \frac{m+1}{M} \right) + \ln \left( \frac{P + (n+1-M)^2}{P + (n-m)^2} \right). \end{aligned} \quad (25)$$

As  $n+1-m > n-M$  and  $n+1-M \leq n-m$ , from (24) and (25) it can be concluded that  $\Delta G_{2n}(M \rightarrow M+1, m \rightarrow m-1) > 0$  and  $\Delta G_{2n}(M \rightarrow M-1, m \rightarrow m+1) \leq 0$ . This means that the configuration where there is the same number of left and right charges  $m = M$  is the one that minimizes the Gibbs energy. The most probable configuration when the number of unbounded particles is fixed is for  $m = M$  or, in other words,  $r = l$ .

Now we consider transitions where an extra particle becomes unbounded, that is,  $M \rightarrow M+1$  at fixed  $m$  or  $m \rightarrow m+1$  at fixed  $M$ . The Gibbs free-energy differences are

$$\Delta G_{2n}(M \rightarrow M+1, m \rightarrow m) = \ln \left( \frac{(M+1)^2}{P + (n-M)^2} \right), \quad (26)$$

$$\Delta G_{2n}(M \rightarrow M, m \rightarrow m+1) = \ln \left( \frac{(m+1)^2}{P + (n-m)^2} \right). \quad (27)$$

From these two expressions, it appears that for large enough value of  $P$ , the Gibbs energy difference will always be negative regardless of the values of  $n$ ,  $m$ , and  $M$ . This means that for a regime of high pressure the configuration where all particles are between the colloids is the one with highest energy and thus the least probable. This can be seen physically as follows: High pressure implies small volume (length in this case). If the ions are confined tightly together, the entropic cost of confinement becomes overwhelming and it is more favorable to have ions unbounded, in the leftmost or rightmost regions. This can be seen as a phenomenon of counterion evaporation.

For low pressure we analyze first the equality (26). The following inequality guarantees an endergonic ( $\Delta G \geq 0$ ) reaction:

$$M \geq \frac{P + n^2 - 1}{2(n+1)}. \quad (28)$$

On the other hand,  $2n - m - M$  needs to be a positive integer since it is the number of particles in the inner region between the colloids. Therefore,  $2n - 1 - m \geq M$ . Putting this together with (28), we have  $\Delta G_{2n}(M \rightarrow M+1,$

$m \rightarrow m) \geq 0$  when

$$2n - 1 - m \geq M \geq \frac{P + n^2 - 1}{2(n + 1)}. \quad (29)$$

From this relation we can define a special value of the pressure

$$\begin{aligned} P_H(m) &= 3n^2 + 2n(1 - m) - (2m + 1) \\ &= \frac{3}{4}N^2 + N(1 - m) - (2m + 1), \end{aligned} \quad (30)$$

$$M_{2n}^c(P, m) = \begin{cases} \lceil \frac{P+n^2-1}{2(n+1)} \rceil & \text{if } P \leq P_H(m) \\ 2n - m & \text{if } P > P_H(m) \text{ (no ions remain in the inner region),} \end{cases} \quad (31)$$

where  $\lceil x \rceil$  is the ceiling function.

From relation (27) one can obtain more information in a similar fashion. When  $m \rightarrow m + 1$ ,  $\Delta G \geq 0$  if

$$n - 1 \geq m \geq \frac{P + n^2 - 1}{2(n + 1)}. \quad (32)$$

The first inequality stems from the fact that  $2n - M - m \geq 1$  and  $M \geq m$ . Now an intermediate regime is obtained from this last inequality. Let us define  $P_I$  such that  $\frac{P_I+n^2-1}{2(n+1)} = n - 1$ , that is,

$$P_I = n^2 - 1. \quad (33)$$

If  $P_I < P \leq P_H$  and  $M$  satisfies (29), then freeing ions to the side that contains the largest number of ions ( $M \rightarrow M + 1$  and  $m \rightarrow m$ ) will increase the Gibbs energy. However, if ions are freed to the other side (the one with the smallest number of ions,  $m \rightarrow m + 1$  and  $M \rightarrow M$ ), the Gibbs energy will decrease.

## 2. Optimal ionic configurations

We are now in a position to identify the fundamental energy or configuration. Note that we only need to compare the energies of the configurations that have  $M = m$  or  $M = m + 1$ . These were found to be the configurations with minimal energy among the systems with a fixed number of free ions. First let us compare the transitions in which the number of free ions is kept even, that is,  $M \rightarrow M + 1$  and  $m \rightarrow m + 1$  with  $M = m$ . This is given by

$$\Delta G_{2n}(M \rightarrow M + 1, m \rightarrow m + 1) = 2 \ln \left( \frac{(m + 1)^2}{P + (n - m)^2} \right). \quad (34)$$



FIG. 3. Fundamental configuration for  $P = 0$  and  $N = 2n = 26$  (even) and  $n = 13$  (odd). In this case, the first threshold is precisely  $P_0 = 0$ . As soon as  $P$  increases and  $0 < P \leq P_1$ , one particle from each interior side will go to the outside, leaving  $(n - 1)/2$  particles in each interior side of the colloid and  $(n + 1)/2$  on each outer side.

which satisfies  $2n - 1 - m = \frac{P_H(m)+n^2-1}{2(n+1)}$  and will be important in the following analysis. Suppose now that  $M$  is small enough such that (29) is not satisfied and therefore by increasing it, while the other parameters  $P$  and  $m$  are kept fixed, the Gibbs energy will decrease. One can continue to take out ions successively from the inner region to the outer region with the largest number of ions ( $M \rightarrow M + 1$ ) and decrease the Gibbs energy until  $M$  reaches a value that satisfies (29). From there, increasing  $M$  will start to increase the Gibbs energy. Therefore, the value of  $M = M_{2n}^c(P, m)$  for which the system reaches the minimum Gibbs energy, at given pressure  $P$  and value of  $m$ , is

The argument of the logarithm is the same as in (26). Then, following the same analysis done for Eq. (26) but restricting the value of  $m$  such that  $m < n - 1$ , we find that the value for which  $m$  minimizes the energy is

$$m_{2n}^c(P) = \begin{cases} \lceil \frac{P+n^2-1}{2(n+1)} \rceil & \text{if } P \leq P_I \\ n & \text{if } P > P_I. \end{cases} \quad (35)$$

Since  $m_{2n}^c(P)$  and  $M_{2n}^c(P)$  are the same when  $M = m$ , it follows that any configuration with an odd number of unbounded particles must be more energetic than the configuration with  $M = m = m_{2n}^c(P)$ . Then the fundamental configuration has an even number of unbounded ions, with  $M = m = m_{2n}^c(P)$ .

The evolution of the fundamental configuration as  $P$  varies is the following. For  $P = 0$ , which corresponds to a large average separation  $\langle L \rangle$  between the colloids, the number of unbound ions on both sides of the colloids is

$$m_{2n}^c(0) = \left\lceil \frac{n - 1}{2} \right\rceil = \begin{cases} n/2 & \text{if } n \text{ is even} \\ (n - 1)/2 & \text{if } n \text{ is odd.} \end{cases} \quad (36)$$

The remaining bound ions will be divided in two and locate themselves in the vicinity of each colloid. This number of bound ions around each colloid is

$$n - m_{2n}^c(0) = \begin{cases} n/2 & \text{if } n \text{ is even} \\ (n + 1)/2 & \text{if } n \text{ is odd.} \end{cases} \quad (37)$$

These configurations are shown in Figs. 3 and 4. Essentially, there is one-quarter of the total number of counterions on each side of each colloid. For the case when  $n$  is even it is exactly one-quarter ( $n/2 = N/4$ ) and in the case when  $n$  is odd there is a frustration to achieve this and there is one counterion more on each inside side than on the outside sides. This configuration can be understood by a simple argument. For  $P = 0$ ,  $\langle L \rangle \rightarrow \infty$ , so each colloid is like an isolated system that will attract  $N/2$  counterions to neutralize it. Since the effect of the other



FIG. 4. Fundamental configuration for  $P = 0$  and  $N = 2n = 28$  (even) and  $n = 14$  (even).

TABLE I. Values of the pressure  $P_k$  at which a jumping transition occurs.

Parameter	$N = 2n$		$N = 2n + 1$	
	$n$ even	$n$ odd	$n$ even	$n$ odd
pressure threshold $P_k$	$(N + 2)(k + \frac{1}{2})$	$(N + 2)k$	$(N + 2)(k + \frac{1}{4})$	$(N + 2)(k + \frac{3}{4})$
number of unbound ions $M_N^c$	$\frac{n}{2} + k$	$\frac{n-1}{2} + k$	$\frac{n}{2} + k$	$\frac{n+1}{2} + k$
index $k$ range	$k \in \{0, 1, \dots, \frac{n}{2} - 1\}$	$k \in \{0, 1, \dots, \frac{n-1}{2}\}$	$k \in \{0, 1, \dots, \frac{n}{2}\}$	$k \in \{0, 1, \dots, \frac{n-1}{2}\}$

colloid will be negligible, the left and right sides of each colloid are equivalent and the  $N/2 = n$  counterions will distribute themselves in equal numbers around each side (parity of  $n$  permitting).

Then, as  $P$  increases,  $\langle L \rangle$  decreases and it becomes more entropically favorable for the counterions in the inside region to “jump out” to the outside regions.<sup>1</sup> There is no symmetry breaking between the left and right outside regions, so at each transition two counterions simultaneously jump to the outside, one on each side. These transitions occur when the argument of the ceiling function in Eq. (35),  $(P + n^2 - 1)/2(n + 1)$ , is an integer. The values of the pressure at which a transition occurs ( $P = P_k$ ) can be indexed by an integer  $k$ . Table I shows the values of  $P_k$  that depend on the parity of  $N$  and  $n$ . At each transition  $P = P_k$  there is a fourfold degeneracy where the configurations  $(\ell, r)$  corresponding to  $(m_{2n}^c(P_k) - 1, m_{2n}^c(P_k) - 1)$ ,  $(m_{2n}^c(P_k), m_{2n}^c(P_k) - 1)$ ,  $(m_{2n}^c(P_k) - 1, m_{2n}^c(P_k))$ , and  $(m_{2n}^c(P_k), m_{2n}^c(P_k))$  all have the same Gibbs energy.

These transitions continue as  $P$  increases until all particles are outside. This occurs for  $P = P_l = n^2 - 1$ . At this value, the last two counterions that are in the inside region jump to the outside region. The corresponding Gibbs energies of these configurations are

$$G_{2n}(n - 1, n - 1) = 4 \ln(n - 1)! + 2 \ln(P + 1) + \ln P \quad (38)$$

<sup>1</sup>We use the word “jump” figuratively, since the system is really one dimensional and the particles go through the colloids at each transition rather than jumping over them.

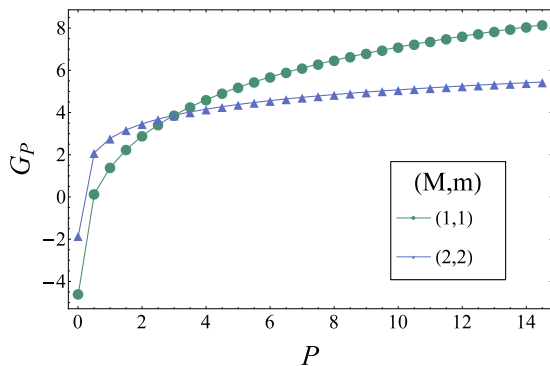


FIG. 5. Gibbs energies for  $N = 4$ . The solid lines represent the configurations with minimal Gibbs energy for a fixed number of unbounded particles.

(there remain only two counterions inside) and

$$G_{2n}(n, n) = 4 \ln n! + \ln P \quad (39)$$

(all counterions out). When  $P = P_l = n^2 - 1$  we have  $G_{2n}(n - 1, n - 1) = G_{2n}(n, n) = G_{2n}(n, n - 1)$ .

Figures 5 and 6 illustrate this situation when  $N = 4$  ( $n = 2$ ). In that case  $P_l = 3$ , which is the value of the pressure above which it is more favorable to take all four particles unbounded outside (two on each side) than to have two outside and two confined in the inner region. The discussion of the present results comes with a word of caution. When  $n = M = m$ , as for the curve labeled (2,2) in Fig. 5, the force experienced by each of the colloids at  $x = 0$  and  $x = L$  vanishes. This is because the electric field acting on a colloid (say, at  $x = 0$ ) reads simply  $-n$  (it tends to repel the colloid from the other located at  $x = L$ ), so the resulting force is  $-n^2$ . On the other hand, the osmotic pressure stemming from counterions on the left-hand side of the colloid creates a contribution  $n^2$ , which is exactly opposite. The fact that the pressure vanishes makes the isobaric ensemble more subtle to analyze and the quantity  $P$  involved in the Laplace transformation to obtain the partition function is not the physical pressure of the system. As a consequence, the curve (2,2) in Fig. 5, which admits a simple analytical expression [ $G_P = \ln(16P)$ ], indicates by its domain of prevalence ( $P > 3$ ) a region that is physically forbidden (in a canonical description). We will see when discussing canonical ensemble results that this scenario is confirmed and that the pressure is indeed always smaller than 3 in the case  $N = 4$ . A similar phenomenon appears when  $N$  is odd and all ions are unbounded (meaning that  $N = 2n + 1$ ,  $M = n + 1$ , and  $m = n$ ). In this case, one can show that  $P$  is again  $L$  independent (and more precisely that  $P = -1/4$ , irrespective

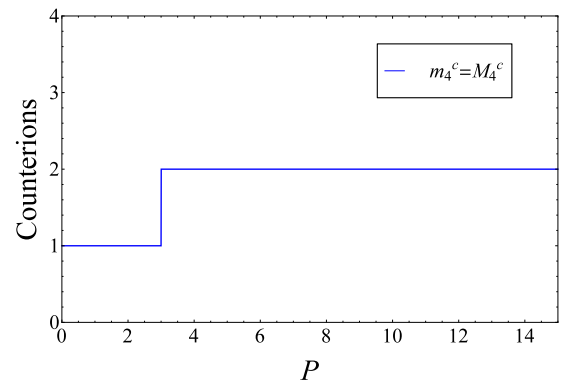


FIG. 6. Configuration that minimizes the Gibbs energy for  $N = 4$ . The figure shows the value of  $m = M$ , which is half the number of unbounded counterions.

of  $N$ ). The canonical and isobaric descriptions yield distinct results: When the canonical pressure is size independent, the system cannot adjust its volume to adapt to the externally imposed pressure  $P$ . The isothermal-isobaric ensemble then exhibits an instability, leading the system to adopt a vanishing volume, or an infinite one, dependent on  $P$ . This suppresses the equivalence of ensembles. One can be slightly more precise

$$G_{2n+1}(M, m) = \begin{cases} 2 \ln(M!m!) + 2 \sum_{k=0}^{n-M} \ln \left[ P + \left( k + \frac{1}{2} \right)^2 \right] + \sum_{k=n+1-M}^{n-m} \ln \left[ P + \left( k + \frac{1}{2} \right)^2 \right] & \text{if } n - M + \frac{1}{2} > 0 \\ 2 \ln(M!m!) + \sum_{k=M-n-1}^{n-m} \ln \left[ P + \left( k + \frac{1}{2} \right)^2 \right] & \text{if } M - \frac{1}{2} - n > 0. \end{cases} \quad (40)$$

The energy changes for a fixed number of free ions are given by

$$\Delta G_{2n+1}(M \rightarrow M+1, m \rightarrow m-1) = 2 \ln \left( \frac{M+1}{m} \right) + \ln \left( \frac{P + (n-m+3/2)^2}{P + (n-M+1/2)^2} \right) \geq 0, \quad (41)$$

$$\Delta G_{2n+1}(M \rightarrow M-1, m \rightarrow m+1) = 2 \ln \left( \frac{m+1}{M} \right) + \ln \left( \frac{P + (n-M+3/2)^2}{P + (n-m+1/2)^2} \right) \leq 0. \quad (42)$$

From these expressions we obtain again a behavior in which the system tends to be with the same number of counterions on each side. In the case in which the number of free ions is odd, the fundamental configuration is degenerated because changing the exceeding ( $m = M - 1$ ) ion from left to right is indifferent to the Gibbs energy.

The Gibbs energy differences when only  $M$  or  $m$  is changed are

$$\Delta G_{2n+1}(M \rightarrow M+1, m \rightarrow m) = \ln \left( \frac{(M+1)^2}{P + (n-M+1/2)^2} \right), \quad (43)$$

$$\Delta G_{2n+1}(M \rightarrow M, m \rightarrow m+1) = \ln \left( \frac{(m+1)^2}{P + (n-m+1/2)^2} \right). \quad (44)$$

Performing a similar analysis as in the even case, we conclude that  $M \rightarrow M+1$  with  $m$  fixed yields  $\Delta G \geq 0$  if

$$2n - m \geq M \geq \frac{P + n^2 + n - 3/4}{2n + 3}. \quad (45)$$

We can define a special value of the pressure as before:  $P_H(m) = 3n^2 + 5n + 3/4 - m(3 + 2n)$ . In terms of  $N = 2n + 1$ , this is the same as (30). The  $M$  such that the system has the minimum energy  $M_{2n+1}^c(P)$  for a given pressure and a



FIG. 7. Fundamental configuration for  $P = -1/4$  (meaning that the intercolloid distance is large) and  $N = 2n + 1 = 27$  (odd) and  $n = 13$  (odd).

and state that the ensemble equivalence is lost when the canonical free energy does not diverge for  $L = 0$ . We therefore anticipate that for the  $N = 5$  results to be shown below (Fig. 9), the domain of prevalence of the (3,2) configuration also signals a region that is, canonically, unphysical.

Now the odd case ( $N = 2n + 1$ ) is examined. The dimensionless Gibbs energy is given by the following expression:

given  $m$  is

$$M_{2n+1}^c(P) = \begin{cases} \left\lceil \frac{P+n^2+n-3/4}{3+2n} \right\rceil & \text{if } P \leq P_H \\ 2n + 1 - m & \text{if } P > P_H. \end{cases} \quad (46)$$

On the other hand, when  $m \rightarrow m+1$  with  $M$  fixed, we have  $\Delta G \geq 0$  if

$$n \geq m \geq \frac{P + n^2 + n - 3/4}{2n + 3}. \quad (47)$$

Let us define  $P_I$  such that  $\frac{P_I+n^2+n-3/4}{2n+3} = n$ , that is,

$$P_I = n^2 + 2n + 3/4. \quad (48)$$

The same analysis done to obtain the fundamental configuration for  $N = 2n$  is valid for the case  $N = 2n + 1$ . The fundamental configuration for  $P \leq P_I$  is given by  $M = m = m_{2n+1}^c(P)$  with

$$m_{2n+1}^c(P) = \begin{cases} \left\lceil \frac{P+n^2+n-3/4}{3+2n} \right\rceil & \text{if } P \leq P_I \\ n & \text{if } P > P_I. \end{cases} \quad (49)$$

The evolution of the fundamental configuration as  $P$  increases is similar to the case of  $N$  even. The smallest physical value for the pressure is  $P = -1/4$ , which corresponds to  $\langle L \rangle \rightarrow \infty$ . As before, the counterions will arrange themselves in four quarters around each side of the colloids. Nevertheless, since  $N = 2n + 1$  there is a “misfit” counterion that roams in the inside region between the two colloids, responsible for the effective attractive force ( $P = -1/4$ ) between the colloids. The role of this counterion is analyzed in more detail in Ref. [13]. It should be noted that this delocalized ion is a fundamental piece of the mechanism to generate an effective attractive force and this mechanism is also valid for three-dimensional systems in the strong-coupling regime [17,18].

Figures 7 and 8 show the possible fundamental configurations for  $P = -1/4$ . As  $P$  increases, the transitions where two inside counterions jump to the outside region will occur each time  $(P + n^2 + n - 3/4)/(3 + 2n)$  is an integer, accompanied by the fourfold degeneracy previously discussed. Notice that



FIG. 8. Same as Fig. 7, with still an odd  $N = 2n + 1$ , but now even:  $P = -1/4$ ,  $N = 29$ , and  $n = 14$ .

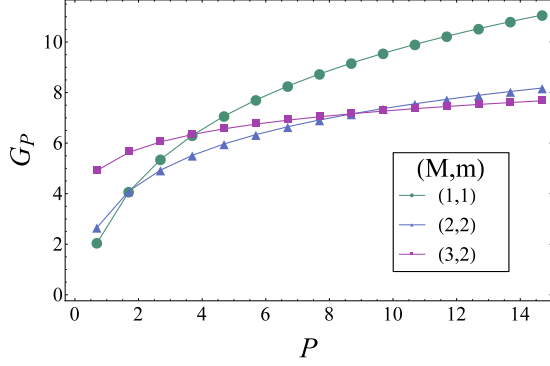


FIG. 9. Gibbs energies  $N = 5$ . The solid lines represent the configurations with minimal Gibbs energy for a fixed number of unbounded particles.

the first transition will occur for a value of  $P > 0$ , therefore the configuration discussed in the preceding paragraph is the fundamental one for all the region of attractive effective force ( $P < 0$ ) and also for small pressures. Table I shows the values of the pressure at the transitions thresholds and the number of counterions  $M_{2n+1}^c$  outside.

Finally, when  $P = P_I = n^2 + 2n + 3/4$  we have  $G_{2n+1}(n, n) = G_{2n+1}(n + 1, n)$ . The last inside counterion will jump to one of the outside regions. For  $P > P_I$  the lowest energy is degenerated for the configurations determined by  $M = n + 1$  and  $m = n$ .

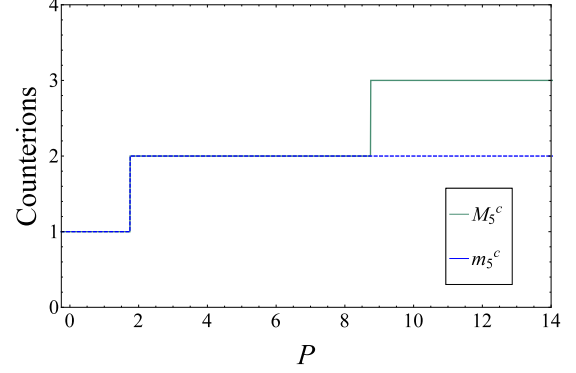


FIG. 10. Configuration that minimizes the Gibbs energy  $N = 5$ . The values of both  $m$  and  $M$  are reported; the total number of unbounded ions is  $m + M$ .

The situation is illustrated in Figs. 9 and 10 for  $N = 5$  ( $n = 2$ ). In this case  $P_I = 35/4 = 8.75$ . Equation (49) predicts two transitions: first from having one particle at each outer side to having two particles at each outer side (at  $P_0 = 1.75$ ) and then the remaining particle goes to one outer region when  $P = P_1 = P_I = 8.75$ .

#### D. Isobaric length

The isobaric length is given by the usual relation  $\langle L \rangle = -\frac{\partial \ln Z_P}{\partial P}$ :

$$\langle L \rangle_{2n}(M, m) = \begin{cases} \frac{1}{P} + 2 \sum_{k=1}^{n-M} \frac{1}{P+k^2} + \sum_{k=n+1-M}^{n-m} \frac{1}{P+k^2} & \text{if } n - M - \frac{1}{2} > 0 \\ \sum_{k=M-n}^{n-m} \frac{1}{P+k^2} & \text{if } \frac{1}{2} + M - n > 0, \end{cases} \quad (50)$$

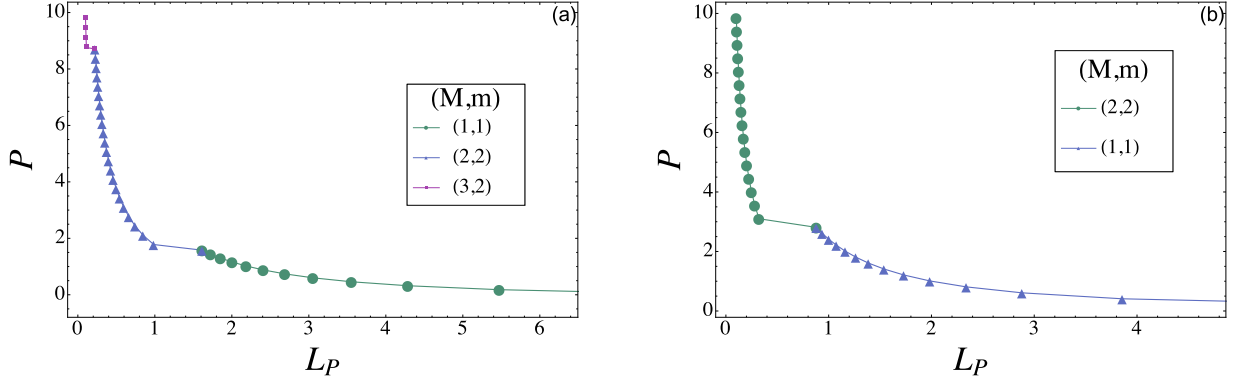
$$\langle L \rangle_{2n+1}(M, m) = \begin{cases} \sum_{k=n+1-M}^{n-m} \frac{1}{P+(k+\frac{1}{2})^2} + 2 \sum_{k=0}^{n-M} \frac{1}{P+(k+\frac{1}{2})^2} & \text{if } n - M + \frac{1}{2} > 0 \\ \sum_{k=M-n-1}^{n-m} \frac{1}{P+(k+\frac{1}{2})^2} & \text{if } M - \frac{1}{2} - n > 0. \end{cases} \quad (51)$$

We define  $L_P^F$  as the value of  $\langle L \rangle$  corresponding to the minimal Gibbs energy configuration for a given pressure  $P$ . This quantity  $L_P^F$  is obtained from Eqs. (50) and (51) by replacing the appropriate values of  $m$  and  $M$  that correspond to the minimal Gibbs energy configuration. By doing this, we are considering a situation where the system is quenched at that fundamental configuration. In Fig. 11 we show graphically the relation between the length  $L_P^F$  and the pressure  $P$ .

The behavior of the fundamental isobaric length shown in Fig. 11 is consistent with the physical intuition for small pressures. The only unexpected behavior is the asymptotic approach to zero length as  $P$  tends to infinity. It would be expected that it reaches zero (for even  $N$ ), or  $-1/4$  (for  $N$  odd) for a finite value of  $P$ , when all particles become unbounded, as discussed after Fig. 5. The fact that this does not happen is due to the characteristic that the pressure of the isobaric ensemble includes the right colloidal charge, unlike the canonical ensemble. We assume here, for the sake of the argument, that the left colloid is held fixed without fluctuations allowed. Thus, a barostat acting on the rightmost colloid has to work against the fluctuations of the colloid itself, which

contributes to the barostatic pressure. As alluded to above, we emphasize that the branch with  $P > 3$  in Fig. 11, having all counterions out, is such that the equivalence of canonical and isobaric ensembles is lost. This will be confirmed in Fig. 14, where it will appear that the value of 3 is the upper bound for the canonical pressure. Note also that for  $N = 4$  the pressure never reaches negative values, while for  $N = 5$  it is negative for  $L_P^F > 80/9$ . For an arbitrary  $n$  such that  $N = 2n + 1$  we have a similar behavior with  $P$  becoming negative for  $L_0^F(n)$ . The function  $L_0^F(n)$  as a function of  $n$  is shown in Fig. 12 and it can be obtained exactly by substituting  $P = 0$  in Eq. (51). It is a monotonically increasing function for  $n \in \mathbb{N}^*$ , bounded from below and from above by 8 and 10, respectively. The lower bound is realized for  $n = 1$ . Note that each value of  $L_0^F$  is repeated twice when  $n$  is increased by one, a behavior that can be explained by analyzing the corresponding number of unbound particles. When  $n$  is increased to  $n + 1$  and the number of unbounded particles remains the same  $m_n^c = m_{n+1}^c$ , in the system of  $n + 1$  there are two additional particles in the bounded region. The only way to maintain the same pressure with more bounded particles is by increasing the




 FIG. 11. Fundamental isobaric length  $L_p^F = \langle L \rangle$  for (a)  $N = 4$  and (b)  $N = 5$ .

length. Then, for an  $n$  such that  $m_n^c = m_{n+1}^c$  the length for  $n + 1$  increases  $L_0^F(n) < L_0^F(n + 1)$ . If, on the other hand, the number of unbounded particles increases, there is the same number of counterions inside, leaving the pressure and length unchanged. Remember that the fundamental configurations are for  $M = m$  and thus if  $m$  increases by 1, so does  $M$ . This means that either both particles become unbounded or none at all are. For  $N = 2n$ , the fundamental pressure is always positive. Consequently, like-charge attraction only occurs for an odd number of counterions.

### III. CANONICAL ENSEMBLE

#### A. Canonical partition function

The canonical partition function is obtained by computing the inverse Laplace transform of Eq. (18). This is done with the aid of the residue theorem. It is more convenient to work with expressions (19) and (20), from which it is easier to identify the first- and second-order poles of the isobaric partition function. For  $M < n$  and  $N = 2n$  (even number of counterions) there are both first- and second-order poles, which leads to the expression

$$Z_c(2n, L) = \frac{1}{(M!m!)^2} \left\{ \frac{1}{[(n-M)!(n-m)!]^2} - \sum_{j=n+1-M}^{n-m} \frac{e^{-j^2L}}{j^2} \left( \prod_{k=1}^{n-M} \frac{1}{j^2 - k^2} \right)^2 \prod_{\substack{k=n+1-M \\ k \neq j}}^{n-m} \frac{1}{k^2 - j^2} - \sum_{j=1}^{n-M} \frac{e^{-j^2L}}{j^2} \right. \\ \left. \times \left( \prod_{\substack{k=1 \\ k \neq j}}^{n-M} \frac{1}{j^2 - k^2} \right)^2 \left( \prod_{k=n+1-M}^{n-m} \frac{1}{k^2 - j^2} \right) \left[ L + \frac{1}{j^2} - 2 \sum_{\substack{k=1 \\ k \neq j}}^{n-M} \frac{1}{k^2 - j^2} - \sum_{k=n+1-M}^{n-m} \frac{1}{k^2 - j^2} \right] \right\}. \quad (52)$$

If  $M \geq n$  and  $N$  is even, the isobaric partition function only contains simple poles, leading to

$$Z_c(2n, L) = \frac{1}{(M!m!)^2} \sum_{j=M-n}^{n-m} e^{-j^2L} \prod_{\substack{k=M-n \\ k \neq j}}^{n-m} \frac{1}{k^2 - j^2}. \quad (53)$$

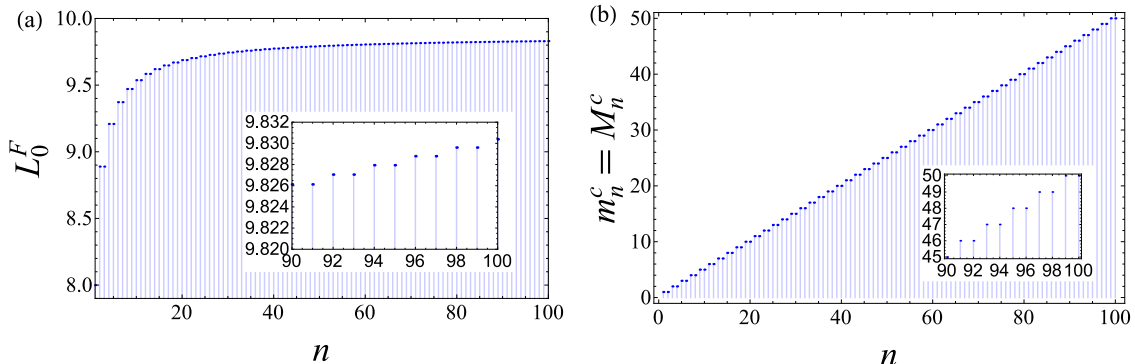


FIG. 12. (a) Isobaric fundamental length  $L_p^F(n)$  when  $P = 0$  as a function of  $n$ . Here  $L_p^F(n) \in [8, 10)$ , approaching asymptotically 10. (b) Corresponding values of  $m_n^c = M_n^c$  as a function of  $n$ . Both graphs emphasize the large- $n$  region, where a doublet structure is apparent.

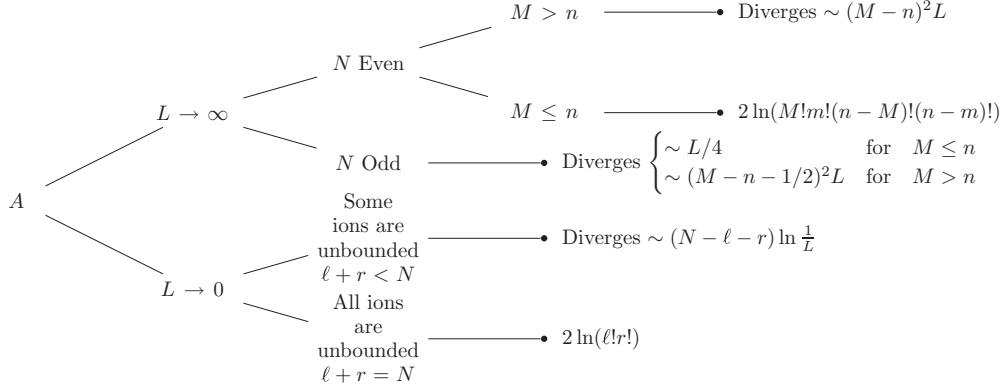


FIG. 13. Behavior of the Helmholtz free energy.

For the odd case,  $N = 2n + 1$ , something analogous happens. For  $M \leq n$  there are second-order poles and for  $M > n$  there are only simple poles, as can be seen in the expressions

$$\begin{aligned}
 Z_c(2n+1, L) = \frac{1}{(M!m!)^2} & \left\{ \sum_{j=n+1-M}^{n-m} e^{-(j+1/2)^2 L} \left( \prod_{k=0}^{n-M} \frac{1}{j^2 + j - k^2 - k} \right)^2 \prod_{\substack{k=n+1-M \\ k \neq j}}^{n-m} \frac{1}{k^2 + k - j^2 - j} \right. \\
 & + \sum_{j=0}^{n-M} e^{-(j+1/2)^2 L} \left( \prod_{\substack{k=0 \\ k \neq j}}^{n-M} \frac{1}{k^2 + k - j^2 - j} \right)^2 \left( \prod_{k=n+1-M}^{n-m} \frac{1}{k^2 + k - j^2 - j} \right) \\
 & \left. \times \left[ L - \sum_{\substack{k=0 \\ k \neq j}}^{n-M} \frac{2}{k^2 + k - j^2 - j} - \sum_{k=n+1-M}^{n-m} \frac{1}{k^2 + k - j^2 - j} \right] \right\}, \quad (54)
 \end{aligned}$$

$$Z_c(2n+1, L) = \frac{1}{(M!m!)^2} \sum_{j=M-n-1}^{n-m} e^{-(j+1/2)^2 L} \prod_{\substack{k=M-n-1 \\ k \neq j}}^{n-m} \frac{1}{(k-j)(k+j+1)}. \quad (55)$$

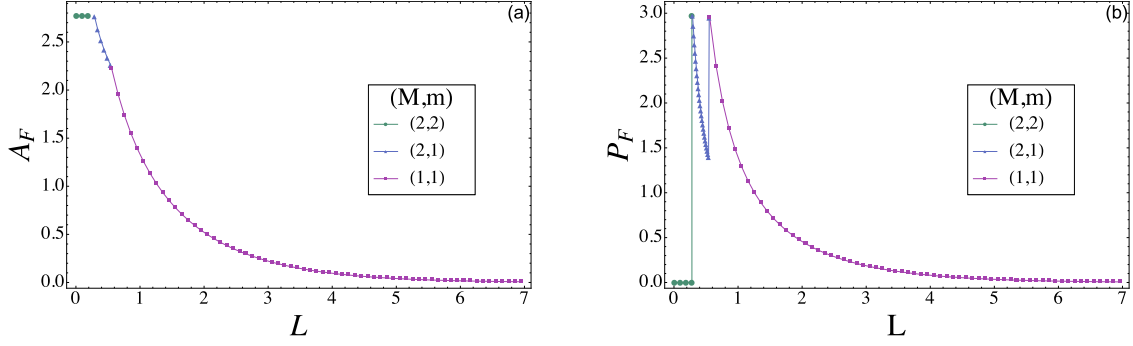
### B. Helmholtz free energy

To discuss the configuration that will be adopted in the canonical ensemble, we analyze the Helmholtz free energy  $\tilde{A}$ . We use the relation  $\tilde{A} = -\beta^{-1} \ln Z_c$  and we introduce the dimensionless free energy  $A = \beta \tilde{A}$ . The analytic expression for  $A$  is hard to analyze, but its physical interpretation is straightforward. First consider small values of the length  $L$ . There are two different behaviors as  $L$  approaches zero. If all counterions are unbounded, they screen the colloids, behaving effectively as two charges of opposite sign, decreasing their energy as they get closer. If at least one particle is bounded, again the two colloids are screened, but as the distance between them decreases, the pressure increases, making  $A$  diverge. Now consider the asymptotic behavior when  $L \rightarrow \infty$ . If  $N$  is odd the energy diverges because the ensemble decouples in two charges of opposite sign. Separating them requires work, which gives an increase of  $A$  as  $L$  grows. This is due to the fact that  $A$  can be interpreted as the energy required to assemble the

system. However, if  $N$  is even, two behaviors are observed. If  $M < n + 1$ , all the ions screen the opposite colloid, creating two neutral systems, which will require a finite amount of energy to be separated an infinite distance. If  $M \geq n + 1$ , this screening is not successful and we have the same situation as in the case when  $N$  is odd. A summary of the behavior of  $A$  for  $L \rightarrow 0$  and  $L \rightarrow \infty$  is shown in Fig. 13.

### C. Canonical pressure

The canonical pressure is given by  $P = \frac{d \ln Z_c}{dL}$ . We are interested in the behavior of the fundamental (energy-minimizing) configuration. In Figs. 14 and 15 one can see the essential traits for  $N = 4$  and  $N = 5$ . For the even case note that the fundamental pressure is always positive, while for an odd number of ions, it can be negative. We stress again that like-charge attraction is only possible for an odd numbers of counterions. The pressure exhibits discontinuities when a


 FIG. 14. (a) Fundamental Helmholtz energy  $A_F$ . (b) Pressure  $P_c^F$  for  $N = 4$ .

configuration transition occurs. The Helmholtz free energy is always continuous regardless of the parity of  $N$ . The most notable difference between the free energies due to the parity is the asymptotic behavior as  $L \rightarrow \infty$ . For  $N$  even,  $A$  approaches 0 as  $L \rightarrow \infty$ , while when  $N$  is odd,  $A$  tends to infinity for  $L \rightarrow \infty$ . This behavior was explained in Sec. III B and it has to do with the formation of two effective opposite charges made by the colloids and the ions that screen them.

#### D. Density profiles

The density profile of the counterions is obtained by computing the expression

$$n(x, L) = \frac{1}{Z_c(N, L)} \sum_{k=1}^N \int_{x_1 < \dots < x_k = x < \dots < x_N} e^{-U(x_1, \dots, x_N, L)} \times \prod_{\substack{j=1 \\ j \neq k}}^N dx_j. \quad (56)$$

The sum in Eq. (56) can be separated into three sums, one per region [in the spirit of the decomposition in Eq. (5)]. Due to the characteristics of the one-dimensional Coulomb potential, the integrals of each region depend only on the ions that reside in it. The parts of the integral that depend on ions that are not in the region do cancel out and the expression for the density

profile for  $x < 0$  is given by

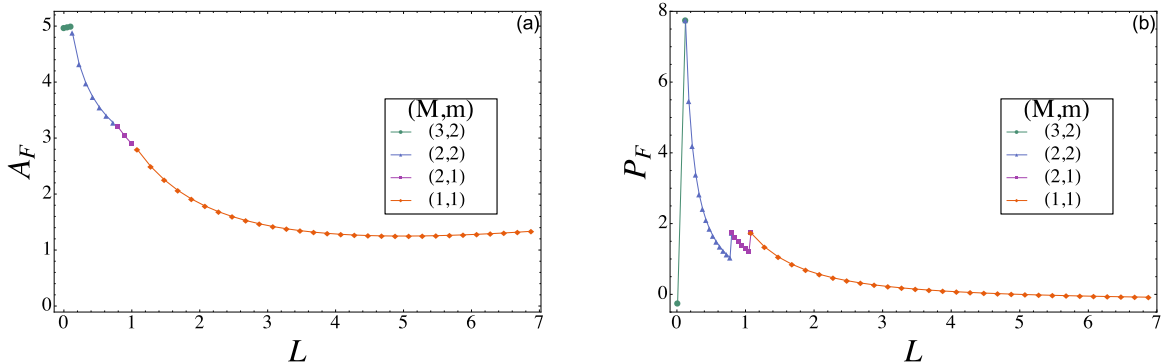
$$n_\ell(x < 0, \ell) = \frac{1}{Z_L} \sum_{k=1}^{\ell} \int_{x_1 < \dots < x_k = x < \dots < x_\ell} e^{-U_L(x_1, \dots, x_\ell)} \times \prod_{\substack{j=1 \\ j \neq k}}^{\ell} dx_j \quad (x < 0). \quad (57)$$

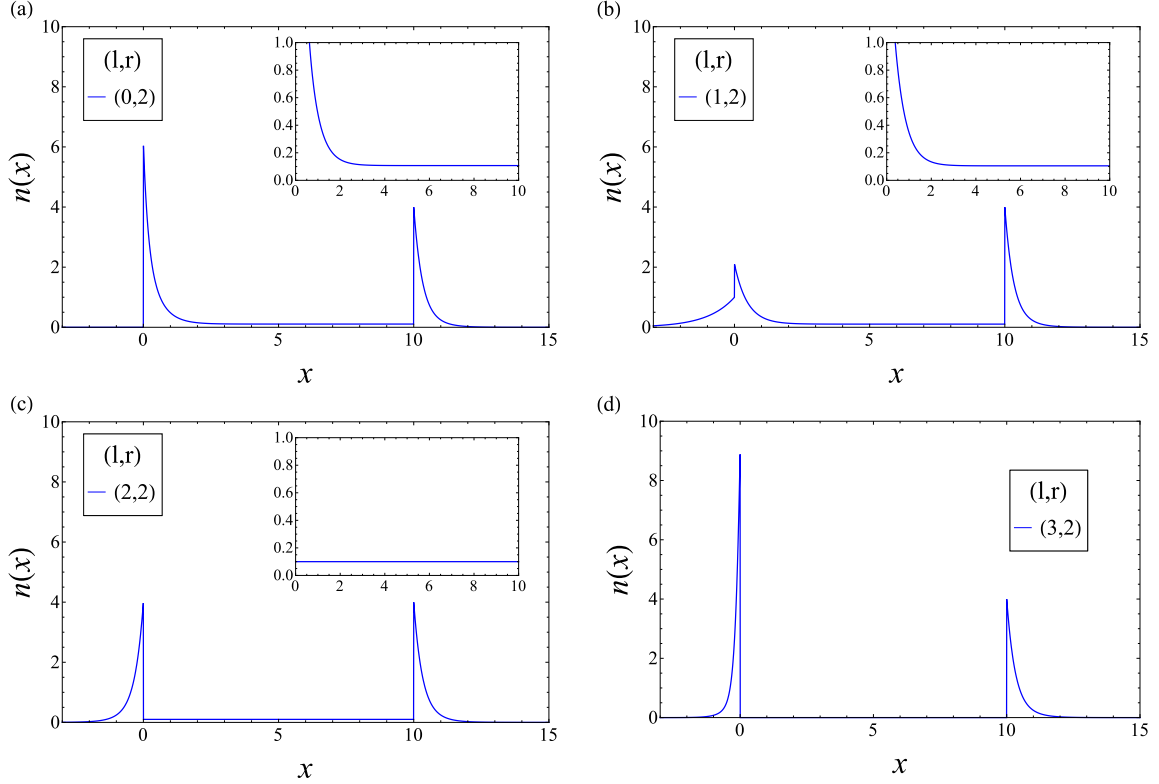
This can be evaluated following similar lines as above. We first introduce the change of variables  $y_j = x_j - x_k$  (for  $1 \leq j < k$ ) and the functions  $\phi_k(x) = H(x) \exp(k^2 x)$ , which yields

$$\int_{x_1 < \dots < x_k = x < \dots < x_\ell} e^{-U_L(x_1, \dots, x_\ell)} \prod_{\substack{j=1 \\ j \neq k}}^{\ell} dx_j = (-1)^{\ell-k} \left( \bigotimes_{j=k}^{\ell} \phi_j(x_k) \right) \mathcal{L} \left\{ \bigotimes_{j=1}^{k-1} g_j(-x_1) \right\} (0). \quad (58)$$

In the second step, we have

$$n_\ell(x, \ell) = (\ell!)^2 \sum_{k=1}^{\ell} \frac{(-1)^{\ell-k} e^{k^2 x}}{[(k-1)!]^2} \times \sum_{i=k}^{\ell} \prod_{\substack{j=k \\ j \neq i}}^{\ell} \frac{e^{i^2 x}}{i^2 - j^2} \quad (x < 0). \quad (59)$$


 FIG. 15. (a) Fundamental Helmholtz energy  $A_F$ . (b) Pressure  $P_c^F$  for  $N = 5$ .

FIG. 16. Density plot for  $r = 2$  and (a)  $\ell = 0$ , (b)  $\ell = 1$ , (c)  $\ell = 2$ , and (d)  $\ell = 3$ .

Analogously, the density profile for the region  $x > L$  is obtained as

$$n_r(x, r, L) = (r!)^2 \sum_{k=0}^r \frac{e^{-(k+1)^2(x-L)}}{[k!]^2} \times \sum_{i=N-k+1}^r \prod_{\substack{j=N-k+1 \\ j \neq i}}^r \frac{e^{-i^2(x-L)}}{j^2 - i^2} \quad (x > L). \quad (60)$$

For the bounded interval  $x \in [0, L]$  the convolution product of the bounded partition function splits into two convolution products. This convolution products can be expressed in terms of canonical partition functions using equality (17):

$$n_B(x, \ell, r, L) = \frac{1}{Z_c(N, \ell, r, L)} \sum_{k=\ell+1}^{N-r} Z_c(N, \ell, N-k+1, x) \times Z_c(N, k, r, L-x) [k!(N-k+1)!]^2. \quad (61)$$

From the three expressions for the three regions it can be observed that for the intervals  $x < 0$  and  $x > L$ , the density is independent of  $L$ . Also  $n_\ell(x, \ell)$  and  $n_r(x, r, L)$  do not depend on  $r$  and  $\ell$ , respectively. All these properties stem from the fact that in the present one-dimensional setting, the presence of colloidal charges at  $x = 0$  and  $x = L$  decouple the corresponding half lines that each of them delimits. In Fig. 16, this is shown for  $N = 5$ . For most of the cases the density is not continuous at the colloids position. In fact, for a given value of  $\ell$  and  $r$  it is only continuous for one value of  $L$ . The values at the fixed points  $x = 0$  and  $x = L$  follow a simple

expression. For the cases  $n(0^+)$  and  $n(L^-)$  the expressions can be obtained using the equivalent model (22) and the contact theorem (see [13])

$$n(0^+) = P + (N/2 - \ell)^2, \quad (62)$$

$$n(L^-) = P + (N/2 - r)^2. \quad (63)$$

For the outside regions, the same equation is valid, however the pressure is zero, giving the expressions

$$n(0^-) = \ell^2, \quad (64)$$

$$n(L^+) = r^2. \quad (65)$$

This is fully compatible with the results displayed in Fig. 16. The above results also call for a number of comments. When no ions are bound, we necessarily have  $n(0^+) = n(L^-) = 0$ . Equations (62) and (63) thus imply that  $(N/2 - \ell)^2 = (N/2 - r)^2$ , which is indeed true since we have  $r + \ell = N$  (all ions out). These equations also immediately yield  $P = 0$  for  $N = 2n$  even,  $m = M = n$  and  $P = -1/4$  for  $N = 2n + 1$  odd,  $M = n + 1$ , and  $m = n$ . These results have already been mentioned in Sec. II C 2.

### E. Charge reversal

Finally, concerning overcharging, there is always a configuration for which this happens independently of parity or  $L$ . This is due to the fact that one can always pick a configuration that has  $M > N/2$ , which will reverse the charge of one colloid. As expected for an odd  $N$  overcharging occurs for all configurations due to the fact that even for  $M \leq N/2$  the

charges cannot be arranged such that the screened colloids are neutral. That is, one of the colloids will have at least one more counterion in its vicinity. That and the fact that the system is neutral implies that one of the colloids will have an effective charge  $q_+ \geq |e|$  and the other  $q_- = -q_+$ .

#### IV. CONCLUSION

We have studied a one-dimensional Coulomb system, which is an extension of the model proposed in [13], where the charge of two colloids is compensated by that of an ensemble of  $N$  counterions, all of the same charge. Our goal was to identify the fundamental (optimal) configuration of charges: How many counterions should be confined, and therefore lying between the two colloids, and how many should be unbound?

We found that for large separation between colloids (or small pressures for the isobaric ensemble), the system separates in two almost independent subsystems. These subsystems are formed by each colloid and a screening cloud with half of the total number of counterions. If  $N$  is odd, there is additionally a single counterion between these subsystems. The structure of the screening cloud of each subsystem is such that approximately half of the counterions of the cloud are on each side of the colloid. The exact number of counterions on each side depends on the parity of  $n$  ( $N = 2n$  or  $N = 2n + 1$ ), which plays a crucial role in determining the subsystem structure. The precise subsystem structure for each case is illustrated in Figs. 3, 4, 7, and 8.

When the colloids are close (high pressure), the interaction between counterions dominates, forcing them to escape in pairs the bounded region. The process is symmetrical, except for the last bounded particle in the odd case, which lacks a pair to jump with. For an arbitrary separation of colloids, we characterize analytically the fundamental configuration in the isobaric ensemble (see Table I).

We observed that this model allows both like-charge attraction and charge reversal, even for the fundamental configuration. As in [13], these phenomena were related to the parity of the number counterions, arising due to the failure to neutralize the colloidal charges. All thermodynamic quantities for the isobaric and canonical ensembles were obtained analytically for all the configurations. The fundamental canonical configuration was examined with computational aid. Within the isobaric ensemble, we explained in detail how the Gibbs energy behaves for all possible configurations and provided the physical interpretation. We also gave asymptotic behaviors for the thermodynamic quantities in the two ensembles.

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