

# Like-charge attraction in a one-dimensional setting: the importance of being odd

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## Abstract

From cement cohesion to DNA condensation, a proper statistical physics treatment of systems with long-range forces is important for a number of applications in physics, chemistry, and biology. We compute here the effective force between fixed charged macromolecules, screened by oppositely charged mobile ions (counterions). We treat the problem in a one-dimensional configuration that allows for interesting discussion and derivation of exact results, remaining at a level of mathematical difficulty compatible with an undergraduate course. Emphasis is put on the counterintuitive but fundamental phenomenon of like-charge attraction, which our treatment brings for the first time to the level of undergraduate teaching. The parity of the number of counterions is shown to play a prominent role, which sheds light on the binding mechanism at work when like-charge macromolecules do attract.

Keywords: electrostatics, like-charge attraction, colloids

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Soft matter refers to a wealth of systems that may seem disparate at first sight: foams, glues, paints, liquid crystals, colloids, polymers etc [1]. What they have in common is threefold: (a) they are sensitive to ‘gentle’ mechanical or thermal fluctuations; (b) they feature at least two distinct lengthscales (one being microscopic, the other being intermediate between microscopic and macroscopic); (c) they often exhibit strong collective effects, such as the property to self assemble into complex entities. As a consequence, their properties are often difficult to rationalise and the sole knowledge of the basic interaction forces between the individual components is not enough to understand the resulting properties. Here, our interest goes to one such collective effect, that challenges intuition and takes place when

charges are considered. It is at the root of key phenomena, outlined below. Soft matter is in itself a relatively new field, but it is starting to enter the classroom [2–8].

In vacuum, two like-charges interact via Coulomb law, which yields a repulsive force. In a solvent like water, containing mobile cations and anions, the situation becomes more complex. It is highly relevant in soft matter physics [1], and more precisely for colloidal suspensions, where large charged macromolecules, typically of micron-size, are surrounded by much smaller ions, called microions. As microions move on a much shorter time scale than the macromolecules, the relevant concept to discuss interactions is that of *effective potential*: the direct interactions between the charged macromolecules are modified as a result of the fluctuations of the medium. This yields an effective interaction which is mediated by the microions, and it is obtained by performing a thermal equilibrium average over the fluctuations of the positions of the microions [9]. A first effect of the microions is to screen the bare Coulomb repulsion, resulting in a short range effective interaction between the macromolecules [10]. In a small coupling regime (when the typical electrostatic energy is smaller than the thermal one), the effective interaction remains nevertheless repulsive between like-charges. However at large couplings, counterintuitive effects appear such as attraction between like-charge bodies.

The phenomenon of like-charge attraction and its rationale are an old controversy in physico-chemistry literature. While it surfaced as early as the 1930s [11], it appears that early accounts were flawed (as e.g. pointed out in [12, 13]<sup>3</sup>). A breakthrough was realised in the 1980s when numerical evidences demonstrated that equivalently charged surfaces could attract each other, at short distances and under high enough Coulombic coupling [14, 15]<sup>4,5</sup>. It is now realised that like-charge attraction is the root of a wealth of phenomena in man-made or natural systems, among which the formation of DNA condensates [16, 17], or the cohesion of cement [18, 19]<sup>6</sup>. We refer in particular the reader to [17] for an interesting and non technical introduction to these questions pertaining to electrostatics.

The motivation for our paper is that like-charge attraction, in spite of its importance, is absent from educational textbooks. The reason is that it is a complex phenomenon, and that analytical treatments are difficult. On the other hand, computational studies are highly non-trivial and thus not an educational option, since one first has to learn how to deal with Coulomb forces, and more generally, long-range interactions [20]. In this article, we present a model where like-charge attraction is put in evidence, in terms that are accessible to an undergraduate student having only basic notions of electrostatics, and of statistical physics. To this end, a simplified model in one dimension will be worked out, which has the advantage to be tractable analytically. In real applications, in three dimensions, the situation is more involved. Nevertheless, the model presented here not only gives a simple introduction to the basic mechanisms behind like-charge attraction in colloidal systems, but also allows to recover exact results, as we shall emphasise below. In this sense, our treatment is true to experimental reality. The outline of the paper is as follows. The model will be presented in section 2. For the sake of simplicity, we will address the situation where one type only of microion is present and neutralises the charge of two

<sup>3</sup> It is noteworthy that such a controversy spans more than 50 years, involving in part the same protagonists.

<sup>4</sup> This requires for instance the screening by microions of large enough charge, which is the reason why, as a rule of thumb, monovalent microions such as  $\text{Na}^+$  or  $\text{Cl}^-$  are not charged enough to trigger the phenomenon.

<sup>5</sup> For more recent theoretical progress, see e.g. [10, 15].

<sup>6</sup> In cement, calcium silicate hydrates are an essential constituent. These hydrates have a debated structure and microstructure, but they can schematically be viewed as forming large and to first approximation planar layers, sandwiching divalent microions. The cohesion between neighbouring layers is to a large extent due to like-charge attraction.

macromolecules. In such a case, the microions are referred to as counterions, since their charge is opposite in sign to that of the macromolecule. While this is a simplification, it is important to stress that certain experimental conditions come close to this so-called *de-ionised* limit [21]. After having defined the model, we will turn in section 3 to the simplest situation where the system has only  $N = 1$  counterion. Comparison to the  $N = 2$  case in section 4 will reveal that the parity of  $N$  plays a fundamental role. This feature will be elucidated in section 5, and highlights the fact that odd values of  $N$  only can lead to attractive interactions. Finally, section 6 will be for the relevant large  $N$  limit and section 7 for our concluding remarks.

## 2. The model

### 2.1. From 3D to a 1D setting

Consider two charged parallel plates. These will mimic the surface of two colloidal charged particles (the ‘macromolecules’). Between them, there is a given number of counterions of opposite charge that screen the macromolecules. The system is globally electro-neutral, and considered in thermal equilibrium at a temperature  $T$ .

We will be interested in computing the effective force between the plates after averaging over the microscopic configurations of the microions<sup>7</sup>. This can be obtained by several means. One way is through the derivative of the free energy of the system with respect to the separation of the plates. The free energy can be computed from the canonical partition function [9]. An alternative but of course equivalent route is through the use of a relation between the density of counterions at the plates and the pressure, which is known as the contact theorem [22], to be explained later on.

Due to the translational symmetry along the planes of the charged plates, the density profile of the counterions depends only on the coordinate perpendicular to the plates. Let us call this direction  $x$ , and locate the first plate at  $x = 0$  and the second one at  $x = L$  where  $L$  is the distance between the plates. A further simplification that will allow us to obtain analytical results is the smear out of the charge of each counterions in a plane parallel to the charged plates. With this (*a priori* unphysical but as will appear below fruitful) approximation the system becomes effectively one dimensional. The interaction between the ‘smeared out’ counterions depends only on the  $x$  coordinate and it is given by the one-dimensional Coulomb potential. At this point, it is instructive to review some basic facts about electrostatics in 1D.

### 2.2. One-dimensional specifics

It is well-known that the electric field created by a charged infinite plane is perpendicular to this plane, proportional to its surface charge, and independent of the distance to the plane. The associated electrostatic potential  $v(x)$  at a distance  $x$  from the plane is [23]

$$v(x) = -\frac{\sigma}{2\epsilon_0}|x|, \quad (1)$$

<sup>7</sup> In an experimental system, solvent molecules would also be present. They are discarded from our discussion, since in the simplest approximation, a solvent like water can be treated as a dielectric and structureless continuum. What matters is that the dielectric permittivity of the solvent is not the same as that of vacuum, but apart from the change in the main text  $\epsilon_0 \rightarrow \epsilon$ , the solvent can be left aside.

where  $\sigma$  is the surface charge density of the plane and  $\epsilon_0$  is the permittivity of vacuum. It is a solution of Poisson equation in one dimension

$$\frac{d^2v}{dx^2} = -\frac{\sigma}{\epsilon_0} \delta(x), \quad (2)$$

where the Dirac distribution reflects the presence of the source of the electric field at  $x = 0$ . With the model presented in the previous section, we consider a collection of parallel charged planes interacting through the potential (1). Equivalently one can think of a one-dimensional world where point charges live on a line and interact with the same potential. In this one-dimensional view, it is more natural to work in units where the potential is

$$v(x) = -q|x| \quad (3)$$

and  $q$  will be called the charge of the particle. The corresponding electric field is simply  $\mathbf{E} = -v'(x)\hat{\mathbf{x}}$  with

$$-v'(x) = \begin{cases} +q & \text{for positions at the right side of the charge } (x > 0), \\ -q & \text{for positions at the left side of the charge } (x < 0). \end{cases} \quad (4)$$

Consider now a collection of charged particles on the line. One can obtain the electric field at a given position by applying Gauss's law and the superposition principle [23]. The result is simple: the electric field is given by the difference of the sum of the charges at the left and the right sides of the considered position. This field remains constant as long as one does not cross a particle, in which case it will change by an amount  $\pm 2q$ , where  $q$  is the charge that has been crossed, and the sign depends on whether the cross was from left to right (+) or right to left (-).

In our one-dimensional picture, the situation is that of two charges  $Q > 0$  located at  $x = 0$  and  $x = L$ . Between them, there are  $N$  counterions, which are particles with charge  $e = -2Q/N$  at positions  $x_1, \dots, x_N$ . Overall, the system is thus neutral. The charges  $Q$  are at fixed positions, but the counterions can freely move, and are at thermal equilibrium at temperature  $T$  [9]. The natural framework to study this system is the canonical ensemble [9]. Let us denote  $Z(N, L, T)$  the canonical partition function of the system. The corresponding free energy is  $F(N, L, T) = -k_B T \ln Z(N, L, T)$  where  $k_B$  is Boltzmann constant. The effective force between the (macromolecular) charges  $Q$  located at  $x = 0$  and  $x = L$  is  $\mathbf{F} = P(N, L, T)\hat{\mathbf{x}}$  where  $\hat{\mathbf{x}}$  is a unit-vector along the  $x$ -axis and

$$P(N, L, T) = -\frac{\partial F(N, L, T)}{\partial L} = k_B T \frac{1}{Z} \frac{\partial Z}{\partial L}. \quad (5)$$

Before considering some particular cases for a few values of  $N$ , it is instructive to state the contact theorem, that provides a sometimes useful alternative to the force calculation along the lines of equation (5).

### 2.3. Contact theorem

Consider an arbitrary ensemble of charges confined between two parallel plates (charges on a segment between two points as in our 1D setting, or charges in a slab between two parallel lines in 2D, or charges between parallel planes etc). We denote by  $\rho(x)$  the equilibrium average density of ions, that depends on position  $x$ . The contact theorem [22], states that the force  $P$  and the density  $\rho$  are related by

$$P = k_B T \rho(0) - Q^2. \quad (6)$$

The density  $\rho(0)$  is evaluated at contact with the confining boundary at  $x = 0$ . Each contribution can be understood as follows. The term  $k_B T \rho(0)$  stems from the force due to the collisions of the counterions against the wall at  $x = 0$ . It takes an ideal gas form here [24]<sup>8</sup>, and is always repulsive. The second term,  $-Q^2$ , is attractive since global neutrality requires that the total charge, excluding that of the ‘macromolecule’ ( $Q$ ), is exactly the opposite of  $Q$ . This electrostatic contribution to the force is more familiar<sup>9</sup> when written in terms of quantities such as  $\epsilon_0$ ; it is known as the electrostatic pressure, of paramount importance in the physics of conductors [23].

It will turn useful for our purposes to generalise the contact theorem to the case of confinement by asymmetric boundaries, with charge  $Q_1$  at  $x = 0$  and charge  $Q_2$  at  $x = L$ . The force can indifferently be computed using the densities and charges at either boundary, with the result

$$P = k_B T \rho(0) - Q_1^2 = k_B T \rho(L) - Q_2^2. \quad (7)$$

This will be used in section 5, in a situation where asymmetry does not come from  $Q_1 \neq Q_2$  but from the presence of counterions of different charges. Note that the difficulty with the contact theorem is that, in general, the contact densities  $\rho(0)$  and  $\rho(L)$  are not known. Yet, equation (7) amounts to a remarkable connection between them that should always hold.

### 3. One counterion $N = 1$

Let first consider the simplest case when there is only one counterion ( $N = 1$ ) located at a position  $x_1 \in [0, L]$ . For the system to be globally neutral, we require the counterion charge to be  $-2Q$ , thereby balancing the two charges  $Q$ . In the region  $[0, L]$  where the counterion is confined, the electric field created by the charge  $Q$  at  $x = 0$  is cancelled by the field due to the other charge  $Q$  at  $x = L$ . Thus the counterion does not feel any electric force and it is free to move in  $[0, L]$ . The electric field felt by the charge  $Q$  located at  $x = 0$  is obtained simply by summing the charges that are located at its right: the counterion at position  $x_1$  (charge  $-2Q$ ) and, at  $L$ , the charge  $Q$ . In total, the electric field is  $-(-2Q + Q)\hat{\mathbf{x}} = Q\hat{\mathbf{x}}$  and the force on the charge  $Q$  located at  $x = 0$  is  $Q^2\hat{\mathbf{x}}$ . By the same argument, the electric field felt by the charge  $Q$  located at  $x = L$  is  $-Q\hat{\mathbf{x}}$  and the corresponding force is  $-Q^2\hat{\mathbf{x}}$ . These three forces derive from the potential energy

$$U = Q^2 L. \quad (8)$$

It can be easily checked that the force on each particle are reproduced computing minus the gradient of the potential energy with respect to each of the particles positions.

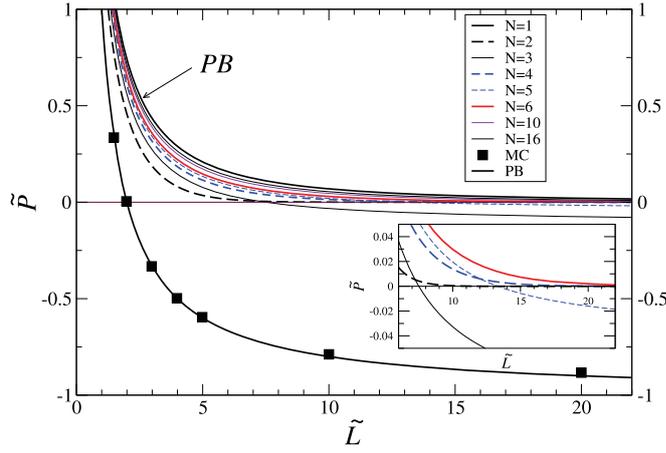
The partition function of the system is

$$Z(1, L, T) = \frac{1}{\lambda} \int_0^L e^{-\beta Q^2 L} dx_1, \quad (9)$$

where  $\beta = 1/(k_B T)$  and  $\lambda = h/\sqrt{2\pi m k_B T}$  is the de Broglie thermal wavelength of the counterion of mass  $m$ , and  $h$  is the Planck constant. This quantum mechanics intrusion in the problem is immaterial, and it will be important to check *a posteriori* that it does not affect physical observable like the force  $P$ . Since  $U$  does not depend on  $x_1$ , the calculation of the

<sup>8</sup> Yet, this expression is also valid when microions feature a hard-core interaction with the confining boundary.

<sup>9</sup> It may be useful to rewrite the contact theorem in terms of more standard quantities pertaining to usual three-dimensional electrostatics. The pressure at a flat interface having uniform surface charge  $\sigma$  then reads  $P = k_B T \rho(0) - \sigma^2/(2\epsilon_0)$ , where  $\epsilon_0$  is the permittivity of vacuum. The (attractive) contribution in  $\sigma^2$  is the so-called electrostatic pressure, see e.g. [23], chapter 1, section 1.11.



**Figure 1.** Force  $\tilde{P} = P/Q^2$  as a function of the charges separation  $\tilde{L} = 2LQ^2/(k_B T)$ , for different number of counterions. Close inspection reveals that odd  $N$  only can lead to attractive interactions ( $\tilde{P} < 0$ ). The results are compared to Monte Carlo simulation data of a *bona fide* three-dimensional system where counterions are confined by uniformly charged parallel plates, in a situation where Coulombic coupling is large (square symbols, data from [25]). The curve denoted PB is for the result of Poisson–Boltzmann theory, where the calculation of the force is different in spirit, and follows from the solution of a nonlinear differential equation. The inset provides a zoom into the region where some pressure curves become negative (cases  $N = 3$  and  $N = 5$ ), while the even  $N$  cases remain positive for all distances.

integral in (8) is straightforward:

$$Z(1, L, T) = \frac{L}{\lambda} e^{-\beta Q^2 L}. \quad (10)$$

The effective force between the charge is then obtained applying (5)

$$P(1, L, T) = \frac{k_B T}{L} - Q^2. \quad (11)$$

The contact theorem, equation (6), would have readily provided us with the very same information, since the counterionic density is  $x$ -invariant in our case (no electric field acting on the counterion): thus,  $\rho(x)$  is uniform in  $[0, L]$ , and normalisation tells us that  $\rho(x) = k_B T/L$ . This force, as expected independent of the Planck constant, is plotted as a function of  $L$  in figure 1. Note that for short separations  $L$ , it is repulsive ( $P > 0$ ) but as  $L$  increases, the force decreases and eventually becomes attractive ( $P < 0$ ) for  $L > L^* = \beta Q^2$ . This is a simple illustration of the counterintuitive phenomenon of like-charge attraction. The asymptotic behaviours for short and large distances are

$$P(1, L, T) \sim \frac{k_B T}{L}, \quad L \rightarrow 0 \quad (12)$$

and

$$P(1, L, T) \rightarrow -Q^2, \quad L \rightarrow \infty. \quad (13)$$

In figure 1, we show Monte Carlo (MC) simulations results for the effective force between two parallel charged plates sandwiching a large number of point counterions, in the

strong coupling regime [25]<sup>10</sup>. Note how accurately this simple one-dimensional model captures the behaviour of the more realistic situation in three dimensions. Thus, although the MC 3D simulations are run with a large value of  $N$ , the distance range corresponding to figure 1 is such that the typical inter-counterion distance is much larger than  $L$ , the inter-plate distance. Then, counterions become decoupled and the physics is equivalent to that of our  $N = 1$  counterion in a slab [26, 27]. We emphasise that upon further increasing the distance range in the figure (so as to exceed the typical distance between counterions), the MC symbols would eventually reach the line  $\tilde{P} = 0$ . For the corresponding very large distances, our one-dimensional model ultimately becomes irrelevant. The fact that we find that  $\tilde{P}$  does not vanish for  $L \rightarrow \infty$  is a peculiarity of one-dimensional electrostatics, which does not transpose to higher dimensions.

#### 4. Two counterions $N = 2$

Let us now turn our attention to the case where there are two counterions, each of them with a charge  $-Q$ , at positions  $x_1$  and  $x_2$ . Without loss of generality, we order the particles' positions as  $0 < x_1 < x_2 < L$ . The electric field at  $x = 0$  and  $x = L$  is the same as in the previous section. The electric field at the position  $x_1$  of the first counterion is obtained by counting the charges at its left ( $Q$ ) and its right ( $-Q + Q = 0$ ). The electric field is then  $Q\hat{x}$ . For the particle at  $x_2$  it is simply the opposite. From this, we obtain the potential energy of the system:

$$U = -Q^2|x_2 - x_1| + Q^2L. \quad (14)$$

The partition function reads

$$Z(2, L, T) = \frac{1}{\lambda^2} \iint_{0 < x_1 < x_2 < L} e^{\beta Q^2(x_2 - x_1 - L)} dx_1 dx_2. \quad (15)$$

Once the integrals are computed, the result can be cast as

$$Z(2, L, T) = \frac{1 - e^{-\beta Q^2 L}(1 + \beta Q^2 L)}{(\beta Q^2 \lambda)^2}. \quad (16)$$

The effective force is then

$$P(2, L, T) = \frac{\beta Q^4 L}{e^{\beta Q^2 L} - 1 - \beta Q^2 L}, \quad (17)$$

once more independent of the de Broglie wavelength  $\lambda$ , and thus of Planck's constant, as it should be. Since the exponential is a convex-up function, we have  $e^x > 1 + x$  for all  $x$ , so that now  $P(2, L, T) > 0$  for all values of  $L$ : the force is repulsive. At short distances

$$P(2, L, T) \sim \frac{2k_B T}{L}, \quad L \rightarrow 0, \quad (18)$$

which is readily recovered from the contact theorem (6). Indeed, for strong confinement (small  $L$ ), the repulsive contribution in  $\rho(0)k_B T$  is dominant since the counterion density  $\rho$  diverges, the latter being given by  $2/L$ . For large distances, the force decays exponentially

$$P(2, L, T) \sim \beta Q^4 L e^{-\beta Q^2 L}, \quad L \rightarrow \infty. \quad (19)$$

<sup>10</sup> For the Monte Carlo simulations shown, the coupling parameter defined in [25] is  $\Xi = 10^5$ . It is large enough to qualify the system as 'strongly coupled'.

This exponential form is a fingerprint of complete screening of the macromolecule charges by the counterions.

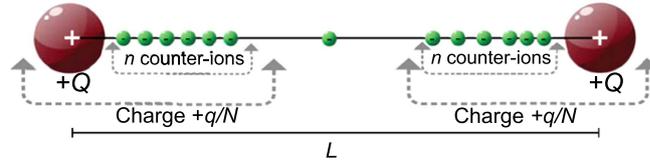
For  $N = 2$ , like-charge attraction is thus ruled out. What is the physical mechanism behind like-charge attraction with  $N = 1$  counterion, but discarded with  $N = 2$ ? An important difference between these two cases is the ‘sharing’ of a counterion between the fixed macromolecules  $Q$  at  $x = 0$  and  $x = L$ . For  $N = 1$ , the counterion does not feel any electric field, as the field created by both macromolecules cancels out. The counterion thus does not have any preference and can roam in the full region between the charges  $Q$ . This counterion shared by the charges creates a bond between them, that in turn, leads to attractive interactions at large enough distance. Note that attraction cannot hold at short separation, since as noticed above, the repulsive (entropic) contribution embodied in the contact density of counterions  $\rho(0)$  becomes divergent, with a resulting dominant repulsive squeezing effect.

When  $N = 2$ , on the contrary, the left ion at  $x_1$  feels an electric field that pushes it to the leftmost macromolecule  $Q$  located at  $x = 0$ . Similarly, the counterion on the right-hand side (position  $x_2$ ) is subject to an electric field that pushes it to the rightmost charge  $Q$  at  $x = L$ . At large enough distance  $L$ , the resulting picture is that of two *decoupled* neutral objects without the possibility of presenting an effective attractive force. We can surmise at this point that a counterion can be shared whenever  $N$  is an odd number, with a foreseeable attraction, while the sharing (or coupling) effect will disappear whenever  $N$  is even. In a nutshell, we expect to observe like-charge attraction for odd  $N$ , and none for even  $N$ . This is indeed correct [26]. In the following section, we focus on the situation where the number of counterions  $N$  is arbitrary but odd, in an effort to compute exactly the large distance force between the macromolecules.

## 5. An odd number of counterions $N = 2n + 1$

For arbitrary  $N$ , the computation of the partition function becomes involved, although it can be performed explicitly [26–29]. However, it is not necessary to do the explicit calculation to grab interesting characteristics of the effective force: a ‘trick’, that we now present, allows to find the exact force at large distances. The argument goes in two steps and we start by a qualitative discussion. If  $N = 2n + 1$ ,  $n$  being an integer, global neutrality demands that each counterion bears a charge  $-2Q/(2n + 1)$ . The first  $n$  counterions at the left-hand side of the system are in an electric field oriented to the left and they will be attracted to the charge  $Q$  located at  $x = 0$ . This creates a charged object with charge  $Q - n \frac{2Q}{2n+1} = Q/(2n + 1)$ . Similarly, the  $n$  counterions at the rightmost region will be attracted to the charge  $Q$  located at  $x = L$  creating an object with the same charge  $Q/(2n + 1)$ . In the middle, there remains a ‘misfit’ counterion, see figure 2. Since its right and left neighbours bear the same total charge, the electric field in the corresponding region is zero, by symmetry. Apart from confinement effects (that will become less and less important as  $L$  increases), the misfit counterion is free to roam, without any electric force acting on it. The situation is then reminiscent of that when  $N = 1$ . This counterion will create a bond between the two charged objects, which will result in an effective attraction if  $L$  is large enough. Let us show this in a more quantitative way.

We now turn to the second step of our argument, that relies first on the definition of an auxiliary useful and asymmetric problem, followed by an application of the contact theorem in that asymmetric setting. We take  $L$  large, meaning more precisely that  $L \gg 1/(\beta Q^2)$ . To compute the density, we consider an auxiliary model where we regroup the leftmost  $n + 1$  counterions into a single composite ion of charge  $-(n + 1)(2Q/N) = -(Q + Q/N)$ . For large  $L$ , we argue that this does not modify the force on the charge  $Q$  located at  $L$  (decreasing



**Figure 2.** Screening of two charges by an odd number  $N = 2n + 1$  of counterions, where  $n$  is an integer. The fixed ‘macromolecules’ both have charge  $+Q$ . For the sake of illustration, they are shown as spheres, but in the present one-dimensional setting, they simply are point-like, located at  $x = 0$  and  $x = L$ . The configuration displayed is relevant at large  $L$ , where the ‘misfit’ central counterion can be seen. It acts as a bridge between its right- and left-hand sides, that are thereby electrostatically bound and coupled. This misfit ion, by symmetry free of electric force, is the mediator of like-charge attraction; see text.

$L$ , the statement becomes less and less correct). The composite ion is in an electric field due to the charge  $Q$  at the left ( $x = 0$ ) and a charge  $-n(2Q/N) + Q = Q/N$  at the right. This electric field is  $Q - Q/N$ . Denoting  $x$  the position of the composite ion, the corresponding potential energy stems from the product of the composite ion charge with the electric field:  $-(Q + Q/N)(Q - Q/N)x = Q^2(1 - (1/N)^2)x$ . The composite ion density then follows from the Boltzmann factor associated to this energy:

$$\rho(x) = Ce^{-\beta Q^2(1 - \frac{1}{N^2})x}. \quad (20)$$

The normalisation constant  $C$  is obtained by requiring that  $\int_0^\infty \rho(x)dx = 1$ . Strictly speaking, the upper bound of integration should not be  $\infty$ , because we always are in a finite  $L$  system. Yet, the error incurring becomes exponentially small in  $L$ , and we finally arrive at

$$\rho(x) = \beta Q^2 \left(1 - \frac{1}{N^2}\right) e^{-\beta Q^2(1 - \frac{1}{N^2})x}. \quad (21)$$

From this, we obtain the contact density  $\rho(0) = \beta Q^2 \left(1 - \frac{1}{N^2}\right)$ . Invoking one last time the contact theorem, in its asymmetric formulation embodied in equation (7), we get the force as

$$P = -\frac{Q^2}{N^2}, \quad L \rightarrow \infty. \quad (22)$$

An attractive interaction ensues for large  $L$ . This is the generalisation of the result derived for  $N = 1$ , to any odd  $N$ . Figure 1 shows the pressure as a function of  $L$  for different  $N$ -values. There, it can be noticed that for  $N$  even, the force is always repulsive ( $P > 0$ ) while on the contrary, when  $N$  is odd, the force becomes attractive for a sufficiently large inter-charge distance  $L$ .

## 6. Large $N$ limit

In the odd number of counterions case, where like-charge attraction is possible, the amplitude of the effect decreases as  $1/N^2$  when  $N$  increases, and practically vanishes whenever  $N$  exceeds a few tens. This is illustrated in figure 1. In the  $N \rightarrow \infty$  limit, the charge of the ions  $e = -2Q/N$  vanishes, but there is a large number of them. An adequate description of the system is to consider that the counterions form a continuous charge density. Furthermore, since in that limit the electrostatic coupling between the ions vanishes ( $e = -2Q/N \rightarrow 0$ ), this situation is described by a so-called mean-field theory, where the field in question refers

to the electrostatic potential<sup>11</sup>. The charge density can be obtained by solving the Poisson–Boltzmann equation [30, 31]<sup>12</sup>. It has been shown that within such a framework, like-charge attraction is impossible [32], as has been illustrated here. The attraction under scrutiny in the previous section was possible due to the ‘sharing’ of one counterion (the misfit). The ‘granularity’ of matter, which is important for this phenomenon to happen, is lost in the mean-field description. An equivalent formulation is to note that replacing a finite number of particles by a field, as useful as it can be in some cases, discards an important length scale related to inter-ionic typical distances. This length plays a key role in the like-charge attraction phenomenon [33]. It is precisely the typical distance between counterions, featured at the end of section 3.

## 7. Discussion and conclusion

We have studied a simple model of point charges on a line, which mimics the situation of two charged macromolecules of charge  $Q$ , held fixed in space at a distance  $L$ , and screened by a collection of microions. This is a prototypical soft matter question, of paramount importance in various fields of colloid science, from physics to biochemistry, including the food industry. Compared to experimental systems, we made the simplifying assumption that microions are only of one type (the counterions). In reality, microions of both signs are usually present (e.g.  $\text{Na}^+$  and  $\text{Cl}^-$ ), but it is important to stress that the counterions-only limiting case can be approached experimentally, through a process called deionisation.

In our presentation, the contact theorem sketched in section 2 plays a particular role. This exact statistical mechanics relation expresses the force felt by one macromolecule as a tradeoff between the repulsive kinetic pressure due to the collisions with counterions (local interactions), and the attractive electrostatic pressure (long-range, non-local interactions). We started in section 3 with the extreme case where only  $N = 1$  counterion screens the two macromolecules. We could explicitly check that the contact theorem route yields the same force between the macromolecules, as the route going through the calculation of the partition function, with subsequent  $L$ -derivative. Interestingly, these results allow to recover those of 3D numerical simulations, provided two requirements are satisfied: one should be in a regime where the macromolecule charge is large enough (strong coupling condition), and in a distance range where the typical 3D distance between counterions is larger than  $L$  (see the agreement between our  $N = 1$  curve in figure 1 and the exact Monte Carlo data).

Going from the  $N = 1$  case to  $N = 2$  in section 4, we noticed that the effective force turns from long-range attractive to all distance repulsive. This pinpoints the significance of the parity of  $N$ . For odd  $N$ , we indeed showed in section 5, invoking a trick where some carefully chosen counterions are grouped to form a composite ion (so as not to affect the force we aimed at computing), that the large  $L$  force is attractive, given by  $-Q^2/N^2$ . The rationale behind attraction is that for odd  $N$ , there always exists a ‘misfit’ counterion, electric-field free by symmetry, that floats in between its neighbours and which becomes completely

<sup>11</sup> A more rigorous analysis can be found in section 4 of [27], where it is shown that the relevant coupling parameter,  $\Xi$ , behaves in the present 1D problem like  $1/N$ . Hence, the large  $N$  limit is that where mean-field theory becomes exact. This is at variance with the three-dimensional situation.

<sup>12</sup> Within Poisson–Boltzmann theory, first formulated by Gouy and Chapman at the beginning of the 20th century, one first computes the electrostatic potential  $\psi$ , given by a Poisson equation of the (dimensionless) form  $d^2\psi/dx^2 = e^\psi$ . In the present geometry, this differential equation admits an analytical solution, from which the density of counterions  $\rho(x) \propto e^{\psi(x)}$  follows. The force can then be computed from the contact theorem. More details can be found in [31]. Poisson–Boltzmann is a key theory to understand the structure and thermodynamics of soft matter systems [30].

delocalised when  $L$  increases. This delocalized ion has a bridging effect that couples the two moieties of the system; hence the negative force at large  $L$ . On the other hand, no ion can become delocalized when  $N$  is even, and effective interactions are always repulsive. At short distances and for all  $N$ , the force is always repulsive, as a squeezing penalty due to the entropic cost for confining ions, which becomes overwhelming.

We believe that these considerations, relying on simple algebra, can be useful for an undergraduate course in statistical physics. Such a discipline is difficult to marry with long-range interactions like those in Coulomb systems. In particular, our final section (7) on the large  $N$  limit where the relevant approach is no longer particle-based, but field-theoretic, provides interesting additional pedagogical perspectives for a more advanced and comprehensive discussion, still at a level of mathematical complexity that remains affordable.

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