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One-dimensional Coulomb system in a sticky wall confinement: Exact results

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This work investigates a one-component one-dimensional Coulomb system in sticky wall confinement. Sticky wall is introduced as an alternative and intuitive depiction of charge regulation, the notion that a surface charge is not a fixed but a fluctuating quantity in dynamic equilibrium with its immediate environment. Emphasis is placed on intuitive derivation and expressions are obtained by observing that the partition function of a charge regulated system can be decomposed into a collection of independent equilibriums with different fixed surface charges. Adsorbed particles behave as ideal-gas particles in a one-dimensional box whose length corresponds to the parameter of stickiness. Among various scenarios considered are a single- and two-wall confinement as well as the case of sticky counterions capable of associating into pairs. Exact solutions provide a view of the role and behavior of surface charge fluctuations, which is an important step in the "beyond-mean-field" analysis. Consequently, the model serves as a simple paradigm of the mechanism that gives rise to the Kirkwood-Shumaker interactions detected in real systems.

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I. INTRODUCTION

Recently we studied a sticky-charged wall model [1] as an intuitive interpretation of the mechanism of charge regulation. In that model, nonelectrostatic short-range interactions between free ions and the fixed chemical groups of a surface are represented by the Baxter sticky potential [2]. (Sticky interactions are incorporated into electrostatics since the mid 1970s and can be found in the work of Blum, McQuarrie, and Carnie among others [3–12], strictly, therefore, we did not introduce it but rather revived and considered it in the context of charge regulation.) In the context of charge regulation, the sticky interaction represents covalent or van der Waals bonding between ions in the solution and the chemical groups of the surface.

Because the Baxter potential is just the well potential in the limit of the infinitesimal range and infinite depth, molecular details are suppressed and particles interact with the surface at direct contact. Adsorption, therefore, is proportional to a density at a contact with a surface and the parameter of stickiness (rather than the equilibrium constant as in the original description of charge regulation [13], or the surface energy of adsorption as in [14–18]. However, all these quantities are related.).

Since its introduction in 1968 [2], the Baxter potential has been extensively studied and used to model numerous soft-matter systems. The adhesive hard-sphere model is used to study gelation phenomena in globular proteins [19,20]. In electrolytes, the sticky-charged spheres capture chemical association as in weak acid-base reactions [3]. The sticky-charged wall model that is relevant to the present work has been considered in various works in the past [4–12].

In Ref. [1], we carried out the mean-field analysis for different descriptions of an electrolyte in planar geometry. This amounted to numerical evaluation of different modified Poisson-Boltzmann equations [21–23] for modified boundary conditions. The aim was to determine the dependence of adsorption on different details of the descriptions of an electrolyte.

In the present work, we consider a sticky wall model of a very simple system: a one-component Coulomb model in one dimension [24–29] in confinement between sticky walls. The one-dimensional Coulomb model has been used in the past to gain insight about more complex and realistic systems in higher dimensions. For example, Frydel and Podgornik investigated a one-dimensional Coulomb system of active ions to determine how active dynamics affects stationary distributions [30]. The aim of the present work is to derive exact expressions that could provide insight into the behavior of adsorption. Of special interest is a better understanding of the features "beyond" the mean field such as fluctuations of a surface charge. These monopolar fluctuations not only modify the interaction between charge regulated surfaces, but can give rise to attractive interactions between neutral surfaces [31–34]. This fluctuation mediated interaction is known as the Kirkwood-Shumaker interaction [35–37] after the authors who first described it.

Maggs and Podgornik have previously considered charge regulation in a one-dimensional Coulomb system [31], where the partition function was transformed into functional integral representation [38,39] and then solved by mapping the path integral representation into the Schrödinger formulation. In the present work, we refrain from path integral transformations and other methods of statistical field theory and rely on intuitive procedures similar to those introduced in [40,41] and based on ordering of particles in permanent sequences and by excluding permutations. In the context of the one-dimensional Coulomb system, this transforms a system into a "pseudo-one-body" problem in which each "ideal particle" feels different external potential.

This work is organized as follows. In Sec. II, we introduce a one-dimensional Coulomb model and evaluate the partition function for a single charged (nonsticky) wall system. In Sec. III, we evaluate the partition function for a single sticky-charged wall system using the solution for a nonsticky wall. In Sec. IV, we consider a two-wall confinement with a single sticky wall; then in Sec. V we consider confinement between two sticky walls. In Sec. VI, we briefly consider the case of sticky counterions. Conclusive remarks are provided in Sec. VII.

II. THE MODEL AND A SINGLE-WALL CASE

A one-dimensional (1D) Coulomb model consists of particles moving on a line and interacting via the pair potential

$$\beta u(x_i, x_j) = -\frac{|x_i - x_j|}{\lambda}, \tag{1}$$

where x_i and x_j are the positions of particles i and j, and the length λ determines the interaction strength.

The linear pair potential implies constant force (apart for a singularity at $x_i = x_j$, where the force abruptly changes direction). As long as particles do not exchange their relative positions and retain fixed order, the forces acting on each particle remain constant. This constraint effectively transforms a many-body problem into a “pseudo-one-body” one.

For a single charged wall confinement, with a wall at $x = 0$ and mobile ions confined to a half space $x > 0$, the external potential acting on a single ion k is

$$\beta u^{\text{ext}}(x_k) = \frac{x_k}{\lambda}. \tag{2}$$

For a one-component system of n particles, the interaction between pair of ions is

$$\beta u(x_k, x_l) = -\frac{|x_k - x_l|}{n\lambda}, \tag{3}$$

where the factor $1/n$ ensures the system neutrality: if all particles are at the location of a wall at $x = 0$, the total potential at any point outside a wall is zero. In the limit $n \to \infty$ the system is described exactly by the mean-field approximation, where interactions are not dominated by any particular pair interaction but are determined by the average density of all ions.

To facilitate calculations and eliminate absolute brackets in Eq. (3), we assume that free ions are permanently ordered as

$$0 \leqslant x_1 \leqslant x_2 \leqslant \cdots \leqslant x_{n-1} \leqslant x_n < \infty. \tag{4}$$

Using Eq. (3), the potential acting on a particle k due to interactions with other particles is

$$\beta u_k^{\text{int}}(x) = -\frac{1}{\lambda}\sum_{i=1}^{k-1}(x - x_i) + \frac{1}{\lambda}\sum_{i=k+1}^{n}(x - x_i). \tag{5}$$

This is rearranged into

$$\beta u_k^{\text{int}}(x) = \left(\frac{n - 2k + 1}{n\lambda}\right)x + \left[\frac{1}{n\lambda}\left(\sum_{i=1}^{k-1} x_i - \sum_{i=k+1}^{n} x_i\right)\right]. \tag{6}$$

Since the second term is a constant that does not affect the interaction force $f_k = -\frac{\partial u_k^{\text{int}}}{\partial x}$, it is enough to write

$$\beta u_k^{\text{int}}(x) = \left(\frac{n - 2k + 1}{n\lambda}\right)x. \tag{7}$$

The final expression of the potential must include the external potential of a confining wall in Eq. (2), leading to

$$\beta u_k(x) = \left(\frac{2n - 2k + 1}{n\lambda}\right)x. \tag{8}$$

The forced ordering of the particle allows us to write the partition function as

$$Z_n = \frac{1}{\Lambda^n}\prod_{k=1}^{n}\int_0^{x_{k+1}} dx_k\, e^{-\frac{(2n-2k+1)x_k}{n\lambda}}, \tag{9}$$

where the upper limit for the last particle is $x_{n+1} = \infty$, as that particle is not bounded from above. Λ is the length scale required to make Z dimensionless, otherwise there is no physical significance attributed to it.

The limits of the multi-integral in Eq. (9) ensure that all configurations are sampled, while precluding sequence permutations. For the position of a particle k, these limits are $x_k \in (0, x_{k+1}]$. As permutations are precluded, there is no need for the Gibbs factor $1/n!$ normally required for describing a liquid state.

An interesting feature of the system represented by the partition function in Eq. (9) is its similarity to an ideal-gas model due to an apparent absence of particle-particle interactions. What sets it apart from the ideal-gas model is that each particle, in addition to being confined by its nearest neighbors, experiences different “external” potential: particles closer to a wall experience stronger attraction. The “pseudo-one-body” character of the system raises the expectation that it is trivially solved. But as shown below, obtaining an analytical solution turns out not to be so trivial.

Before evaluating the partition function in Eq. (9), we make one last simplification and rescale the integration variables as $y_k = x_k/n\lambda$, where y_k is a dimensionless variable, resulting in a simpler integral,

$$Z_n = \left(\frac{n\lambda}{\Lambda}\right)^n \prod_{k=1}^{n}\int_0^{y_{k+1}} dy_k\, e^{-(2n-2k+1)y_k}. \tag{10}$$

To evaluate the above integral, we introduce the recursion relation

$$f_m^n(y) = \int_0^y dy'\, e^{-(2n-2m+1)y'} f_{m-1}^n(y'), \tag{11}$$

where the subscript $0 \leqslant m \leqslant n$ indicates the number of recursions, and the superscript indicates the total number of particles. The recursion is initiated by $f_0^n(y) = 1$. Alternatively, the recursion equation can be expressed as a differential equation,

$$\frac{df_m^n(y)}{dy} = e^{-(2n-2m+1)y} f_{m-1}^n(y). \tag{12}$$

Using the recursion in Eq. (11), the partition function in Eq. (10) can be expressed simply as

$$Z_n = \left(\frac{n\lambda}{\Lambda}\right)^n \lim_{y\to\infty} f_n^n(y). \tag{13}$$

The functions $f_m^n(y)$ can be considered as building blocks in constructing different solutions. And as these functions are not standard, we need a procedure for evaluating them.

To this end, we use the Laplace transform, where the Laplace transformed functions are

$$\tilde{f}_m^n(z) = \int_0^\infty dy\, f_m^n(y) e^{-zy}, \tag{14}$$

and the initial function $f_0^n(y) = 1$ transforms into

$$\tilde{f}_0^n(z) = \frac{1}{z}. \tag{15}$$

The remaining functions are transformed using the recursion relation in Eq. (11). Using the relations

$$\int_0^\infty dy \left[\frac{df_m^n(y)}{dy}\right] e^{-zy} = z\tilde{f}_m^n(z) \tag{16}$$

and

$$\int_0^\infty dy \left[f_m^n(y) e^{-\alpha y}\right] e^{-zy} = \tilde{f}_m^n(z+\alpha), \tag{17}$$

the recursion equation in Laplace space becomes

$$\tilde{f}_m^n(z) = \frac{\tilde{f}_{m-1}^n[z + 2(n-m) + 1]}{z}. \tag{18}$$

We use this relation to obtain $\tilde{f}_1^n(z)$,

$$\tilde{f}_1^n(z) = \frac{1}{z(z+2n-1)}. \tag{19}$$

By continuing the recursion up to an arbitrary $m \leqslant n$, we find

$$\tilde{f}_m^n(z) = \frac{1}{\prod_{k=0}^m [z + 2k(n-m) + k^2]}. \tag{20}$$

The last step involves transforming $\tilde{f}_m^n(z)$ back into physical space. This is done using the inverse Laplace transform,

$$f_m^n(y) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dz\, \frac{e^{zy}}{\prod_{k=0}^m [z + 2k(n-m) + k^2]}, \tag{21}$$

given by the complex integral, where z represents the complex variable. [The constant c is a real number and is introduced to ensure that the contour path of integration is in the region of convergence of $\tilde{f}_m^n(z)$.]

The complex integral in Eq. (21) is conveniently solved using the residue theorem, which requires identification of the poles and their order, and where $f_n(y)$ can be represented as a sum of residues at all poles z_k,

$$f_m^n(y) = \sum_{\{z_k\}} \mathrm{Res}\left(\tilde{f}_m^n, z_k\right). \tag{22}$$

From Eq. (21), we know that all the poles lie on the negative branch of the real axis including zero, $z_k = -k^2 - 2k(n-m)$ for $k = 0, 1, \ldots, m$. As none of the poles are repeated, there are, in total, $m+1$ simple poles. The residue of $\tilde{f}_m^n$ at a simple pole z_k is given by

$$\mathrm{Res}\left(\tilde{f}_m^n, z_k\right) = \lim_{z \to z_k} (z - z_k) \tilde{f}_m^n(z). \tag{23}$$

Obtaining all the residues, the function $f_m^n(y)$ becomes

$$\begin{aligned} f_m^n(y) = {} & \frac{(2n-2m)!}{m!(2n-m)!} \\ & + \sum_{k=1}^m \frac{(-1)^k (2n-2m+k)!\, e^{-k^2 y} e^{-2k(n-m)y}}{k!(m-k)!(2n-m+k)!} \\ & \times \frac{2n-2m+2k}{2n-2m+k}. \end{aligned} \tag{24}$$

The result does not possess a simple form that we might have hoped for, but at least it is analytic. To evaluate the partition function in Eq. (10), we only need $f_n^n(y)$, which is

$$f_n^n(y) = \frac{1}{n!n!} + 2\sum_{k=1}^n \frac{(-1)^k e^{-k^2 y}}{(n+k)!(n-k)!}, \tag{25}$$

and, in the limit $y \to \infty$, it further reduces to a single term,

$$\lim_{y \to \infty} f_n^n(y) = \frac{1}{n!n!}, \tag{26}$$

and the partition function in Eq. (13) becomes

$$Z_n = \left(\frac{n\lambda}{\Lambda}\right)^n \frac{1}{n!n!}. \tag{27}$$

This is a rather trivial result compared to the procedure that produced it. We compare this result to the partition function of noninteractive particles attracted to a wall by the same external potential, that is, $u(x_k) = \frac{x_k}{\lambda}$ as in Eq. (2),

$$Z_n^{\mathrm{id}} = \frac{1}{\Lambda^n} \prod_{k=1}^n \int_0^{x_{k+1}} dx_k\, e^{-\frac{x_k}{\lambda}}.$$

This evaluates to

$$Z_n^{\mathrm{id}} = \left(\frac{\lambda}{\Lambda}\right)^n \frac{1}{n!},$$

where the preclusion of positional permutations, generates the Gibbs factor $1/n!$. Using the Sterling approximation $n! \approx n^n e^{-n}$, Eq. (27) for an interactive system can be written as

$$Z_n \approx \left(\frac{e\lambda}{\Lambda}\right)^n \frac{1}{n!}.$$

This suggests that interactions effectively reduce the strength of external potential such that $\lambda \to e\lambda$, which might be regarded as a screening effect.

III. STICKY SINGLE WALL

In this section, we consider a system where a confining wall is charged and sticky. The sticky potential is represented using the Baxter potential $u_s(x)$ obtained from the square-well potential [1,2],

$$\beta u_{\mathrm{well}}(x) = \begin{cases} -\varepsilon & \text{for } 0 < x < a \\ 0 & \text{for } x > a, \end{cases} \tag{28}$$

in the limit $a \to 0$ and $\varepsilon \to \infty$, such that $ae^{\varepsilon} = l_s$. The Boltzmann factor of the Baxter potential is given by

$$e^{-\beta u_s(x)} = 1 + l_s \delta(x), \tag{29}$$

where the length l_s defines the strength of the surface stickiness. The zero range of interactions implies that the sticky potential interacts with particles only when at direct contact with a wall.

We first write the partition function without the assumption of a fixed positional order,

$$Z_s = \frac{1}{n!\Lambda^n}\int_0^\infty dx_1\cdots\int_0^\infty dx_n\, e^{-\beta u_{\rm el}}\prod_{i=1}^n e^{-\beta u_s(x_i)}, \tag{30}$$

where

$$\beta u_{\rm el}(x_1,\dots,x_n) = -\frac{1}{2}\sum_{i,j}^n \frac{|x_i-x_j|}{n\lambda} + \sum_{i=1}^n \frac{x_i}{\lambda} \tag{31}$$

is the total electrostatic contribution to the interactions. Applying Eq. (29), the partition function is written as

$$Z_s = \frac{1}{n!\Lambda^n}\int_0^\infty dx_1\dots\int_0^\infty dx_n\, e^{-\beta u_{\rm el}}\prod_{i=1}^n [1+l_s\delta(x_i)]. \tag{32}$$

The systematic way of evaluating the above partition function requires expanding it and then organizing the terms into expansion in powers of l_s. The same result, however, can be obtained using an alternative intuitive procedure. We note that adsorbed ions behave as ideal-gas particles in a 1D box of length l_s, in which case the partition function of m adsorbed particles is

$$Z_m^{\rm id} = \left(\frac{l_s}{\Lambda}\right)^m \frac{1}{m!}. \tag{33}$$

The parameter of stickiness in this case takes on the role of the box size. The larger the box, the more likely to find a particle inside it and, consequently, more likely is the adsorption.

The partition function of the remaining $n-m$ free ions is provided by Eq. (27),

$$Z_{n-m}^{\rm el} = \left(\frac{n\lambda}{\Lambda}\right)^{n-m} \frac{1}{(n-m)!(n-m)!}. \tag{34}$$

Note that the interaction strength $n\lambda$ does not change with the number of adsorbed particles; the parameter $n\lambda$ was introduced to ensure that the total charge of counterions is independent of the total number of ions.

The partition functions for m adsorbed ions, combining the two subsystems, is

$$Z_{\rm tot} = Z_m^{\rm id} Z_{n-m}^{\rm el}. \tag{35}$$

The complete partition function must account for all redistributions of ions. This leads to

$$Z_s = \sum_{m=0}^n Z_m^{\rm id} Z_{n-m}^{\rm el}, \tag{36}$$

and the explicit result is

$$Z_s = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m=0}^n \left(\frac{l_s}{n\lambda}\right)^m \frac{1}{(n-m)!(n-m)!m!}. \tag{37}$$

The resulting partition function recalls a grand canonical ensemble with the fugacity of adsorption l_s/λ, or the chemical potential of adsorption $\beta\mu_s = \ln(l_s/\lambda)$. It represents a system comprised of a number of contributing equilibriums.

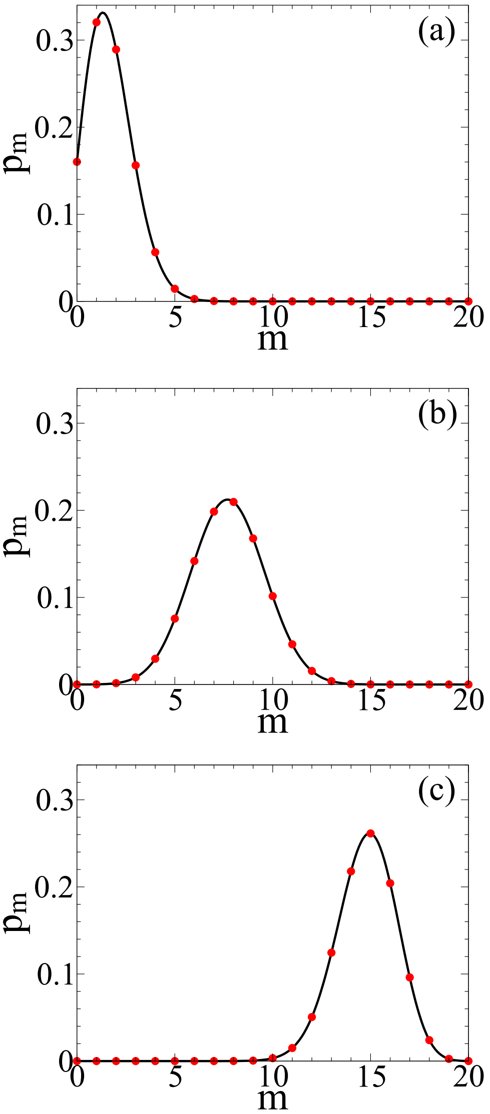

FIG. 1. Probabilities p_m, defined in Eq. (38), for $n = 20$ and for three different values of the stickiness: (a) $l_s/\lambda = 0.1$, (b) $l_s/\lambda = 1$, and (c) $l_s/\lambda = 10$. The solid lines are guides to the eye.

From the partition function, we can obtain the probability for m adsorbed particles,

$$p_m = \frac{1}{c}\frac{n!n!}{(n-m)!(n-m)!m!}\left(\frac{l_s}{n\lambda}\right)^m, \tag{38}$$

where c is the normalization constant that ensures $\sum_{m=0}^n p_m = 1$. The probability in Eq. (38) does not correspond to any of the usual discrete probability distributions. It bears some resemblance to the Fisher's noncentral hypergeometric distribution p_m^f used for models of biased sampling, where $p_m/p_m^f = m!c^f/c$.

Figure 1 shows the distribution p_m for different parameters of stickiness for $n = 20$. The distribution shifts toward higher m for larger stickiness of a wall. The variance is largest if the distribution finds itself in the central location of the interval $m \in [0, n]$.

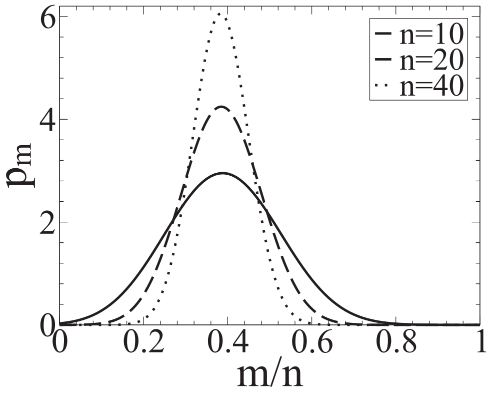

FIG. 2. Probabilities p_m, defined in Eq. (38), as a function of the fraction of adsorbed particles for $l_s/\lambda = 1$ and different number of particles, $n = 10, 20, 40$.

In Fig. 2, we plot the distributions p_m as a function of the fraction of adsorbed particles, m/n, for a single value of stickiness $l_s/\lambda = 1$, but for different number of counterions n. The purpose is to illustrate the effect of the number of particles on fluctuations in the number of adsorbed particles. Fluctuations, defined as $\delta m/n = (m - \langle m\rangle)/n$, are suppressed as the number of particles increases. The limit $n \to \infty$ recovers the mean-field behavior, that is, the system is exactly described by the mean-field theory. The convergence toward the mean-field limit, however, is slow where the fluctuations decay like

$$\frac{\langle \delta m^2\rangle}{n^2} \propto \frac{1}{n}. \tag{39}$$

The mean adsorption $\langle m\rangle/n$ and fluctuations $\langle \delta m^2\rangle/n^2$ are plotted in Fig. 3 as a function of l_s/λ for different n corresponding to the three distributions in Fig. 2. The average adsorption is effectively unaffected by the change in the number of particles, suggesting that the mean-field approximation can be relied on in its prediction. The fluctuations, on the other hand, are highly dependent on n.

The fact that a realistic description of charge regulated surfaces is more accurately represented by a distribution p_m rather than the mean value $\langle m\rangle$ suggests a dynamic picture of charge regulation. The dynamic connection can be seen if we consider the response of adsorption to system parameters. If we define the average number of adsorbed particles as

$$\langle m\rangle = l_s \frac{\partial \ln Z_s}{\partial l_s}, \tag{40}$$

then the variation of $\langle m\rangle$ with l_s can be found to be related to fluctuations as

$$\frac{\partial \langle m\rangle}{\partial l_s} = \frac{\langle \delta m^2\rangle}{l_s}; \tag{41}$$

therefore, the larger the fluctuations, the larger the response of a system to changes in the environment. Alternatively, the system response to the variation in λ is

$$\frac{\partial \langle m\rangle}{\partial \lambda} = -\frac{\langle \delta m^2\rangle}{\lambda}. \tag{42}$$

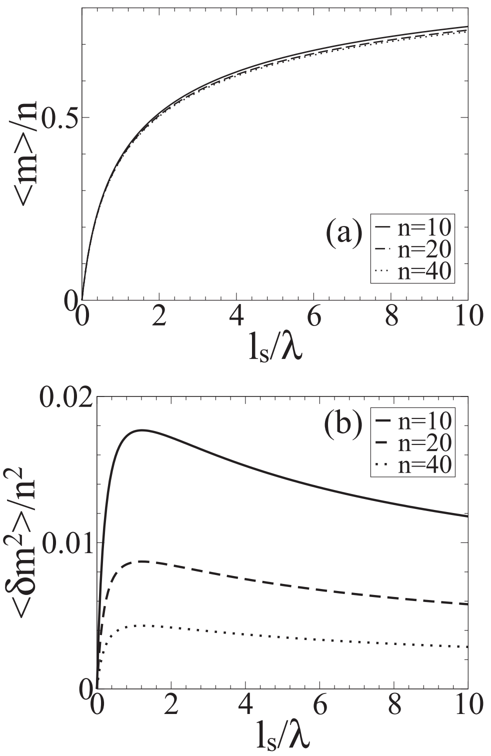

FIG. 3. (a) The average fraction of adsorbed particles and (b) the average fluctuations as a function of l_s/λ for varying number of particles, $n = 10, 20, 40$.

Variation of a sticky surface

The intuitive procedure used to obtain the partition function for a system with an adsorbing wall can be modified in a straightforward manner to provide different characterization of an adsorbing wall. If we substitute the ideal-gas partition function in Eq. (33) with the partition function of the Tonks gas given by

$$Z_m^{\text{tonks}} = \left(\frac{l_s - ma}{\Lambda}\right)^m \frac{1}{m!}, \tag{43}$$

which represents particles as cylinders of length a moving on a line, we can incorporate the overcrowding effect of adsorption by reducing the effective size of a system,

$$l_s \to l_s - ma = l_s\left(1 - \frac{m}{n_s}\right), \tag{44}$$

or an effective stickiness which depends on the number of adsorbed particles. The quantity $n_s = l_s/a$ represents the maximum number of adsorbed particles. The total partition function becomes

$$Z_s' = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m=0}^{n} \left(\frac{l_s}{n\lambda}\right)^m \frac{(1 - m/n_s)^m}{(n-m)!(n-m)!m!}. \tag{45}$$

The surface is now characterized by three parameters: λ, l_s, and n_s. In the limit $n_s \gg n$, the above result recovers the partition function in Eq. (37).

Another alternative is to use, in place of an ideal-gas partition function, a lattice-gas entropy,

$$Z_m^{\mathrm{lg}} = \left(\frac{l_s}{\Lambda}\right)^m \frac{n_s!}{m!(n_s-m)!}, \tag{46}$$

and the complete partition function becomes

$$Z_s' = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m=0}^{n} \left(\frac{l_s}{n\lambda}\right)^m \frac{n_s!}{m!(n-m)!(n-m)!(n_s-m)!}. \tag{47}$$

IV. TWO-WALL CONFINEMENT: ONE STICKY WALL

Next we consider the two-wall confinement with walls at $x=0$ and $x=L$. To proceed by steps, we first consider the case where only a wall at $x=0$ is charged and sticky, while the sole role of a neutral and nonsticky wall at $x=L$ is to confine ions. The partition function can still be represented by the general form $Z_s=\sum_{m=0}^{n} Z_m^{\mathrm{id}} Z_{n-m}^{\mathrm{el}}$; however, the part representing free ions needs to take into account the finite size of the confinement. This is represented by

$$Z_{n-m}^{\mathrm{el}} = \left(\frac{n\lambda}{\Lambda}\right)^{n-m} f_{n-m}^{n-m}\left(\frac{L}{n\lambda}\right), \tag{48}$$

and the complete partition function becomes

$$Z_s = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m=0}^{n} \left(\frac{l_s}{n\lambda}\right)^m \frac{1}{m!} f_{n-m}^{n-m}\left(\frac{L}{n\lambda}\right), \tag{49}$$

where the function $f_{n-m}^{n-m}(y)$ is defined in Eq. (25).

In the limit $\lambda \to \infty$, which effectively switches off particle interactions, the above expression reduces to the ideal-gas system,

$$\lim_{\lambda\to\infty} Z_s = \sum_{m=0}^{n} \left(\frac{l_s}{\Lambda}\right)^m \left(\frac{L}{\Lambda}\right)^{n-m} \frac{1}{m!(n-m)!}, \tag{50}$$

with n particles variously distributed between two boxes of size l_s and L. Another limit that recovers an ideal-gas behavior is $L \to 0$. In this case the partition function reduces to

$$\lim_{L\to 0} Z_s = \left(\frac{l_s}{\Lambda}\right)^m \frac{1}{n!}, \tag{51}$$

where all particles exist in an adsorbed state.

The partition function in Eq. (49) can be used to obtain the probability for m adsorbed particles,

$$p_m = \frac{1}{c}\left(\frac{l_s}{n\lambda}\right)^m \frac{1}{m!} f_{n-m}^{n-m}\left(\frac{L}{n\lambda}\right), \tag{52}$$

or in exclusive form,

$$p_m = \frac{1}{c}\left(\frac{l_s}{n\lambda}\right)^m \frac{1}{m!}\left[\frac{1}{(n-m)!(n-m)!} + \sum_{k=1}^{n-m} \frac{2(-1)^k e^{-k^2 L/n\lambda}}{(n-m+k)!(n-m-k)!}\right], \tag{53}$$

where c is the normalization constant.

In Fig. 4, we plot the distributions p_m for different degrees of confinement, $L/\lambda = \infty$, 1, 0.5. The smaller the space available to ions, the greater adsorption, which shifts the distributions toward $m/n=1$. In the limit $L/\lambda \to 0$, all ions must be adsorbed.

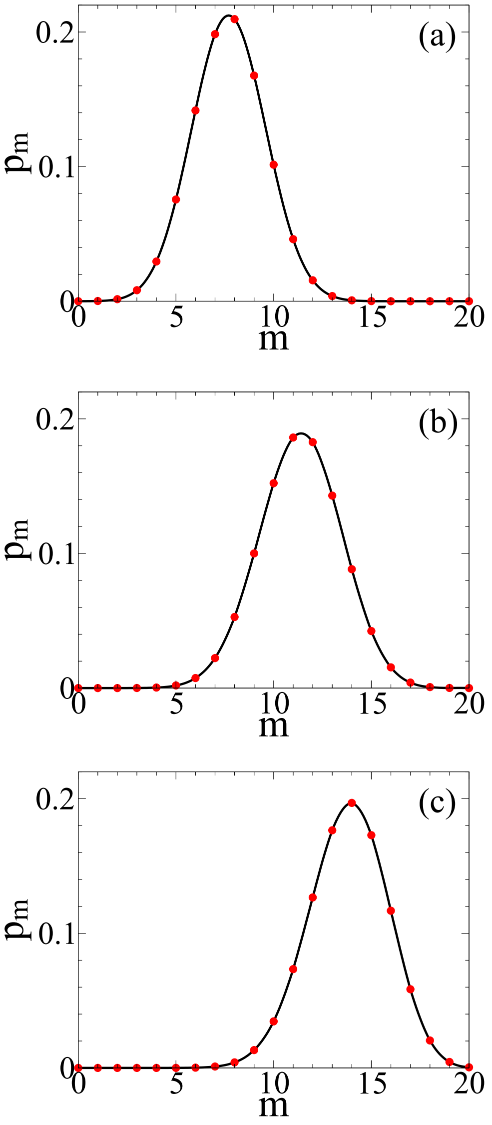

FIG. 4. Probabilities p_m defined in Eq. (53), for $n=20$, $l_s/\lambda = 1$ and three different confinements: (a) $L/\lambda=\infty$, (b) $L/\lambda = 1$, and (c) $L/\lambda = 0.5$. The solid lines are guides to the eye.

It is expected that if more particles are adsorbed, the weaker is the pressure, whose thermodynamic definition is

$$\beta P = \frac{\partial \ln Z_s}{\partial L}. \tag{54}$$

For a nonadsorbing system, pressure is expected to diverge in the limit $L \to 0$ as $\beta P \approx nL^{-1}$. The onset of adsorption eliminates such divergence as all the particles exist in an adsorbed state, leading to a different limiting behavior,

$$\lim_{L\to 0} \beta P = \frac{n}{l_s}, \tag{55}$$

which is the pressure of n ideal particles inside a box of size l_s. The nonzero pressure indicates that particles, even if all of them are adsorbed, continue exerting pressure as the result of their tendency to dissociate.

We next consider a two-wall system with a wall at $x = 0$ charged (but nonsticky) and a wall at $x = L$ sticky and neutral. The general form of the partition function $Z_s = \sum_{m=0}^{n} Z_m^{\mathrm{id}} Z_{n-m}^{\mathrm{el}}$ still applies to this situation. However, the ideal-gas part is slightly modified and is expressed as

$$Z_m^{\mathrm{id}} = \left(\frac{l_s}{\Lambda}\right)^m \frac{e^{-m^2 L/n\lambda}}{m!} \tag{56}$$

because the potential at a wall at $x = L$ does not vanish as is the case of a wall at $x = 0$. The Boltzmann factor $e^{-m^2 L/n\lambda}$ accounts for this potential. The partition function for free electrons is also modified according to

$$Z_{n-m}^{\mathrm{el}} = \left(\frac{n\lambda}{\Lambda}\right)^{n-m} f_{n-m}^{n}\left(\frac{L}{n\lambda}\right), \tag{57}$$

as the recursion relation stops at f_{n-m}^{n}, excluding the adsorbed particles. The complete partition function becomes

$$Z_s = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m=0}^{n} \left(\frac{l_s}{n\lambda}\right)^m \frac{e^{-m^2 L/n\lambda}}{m!} f_{n-m}^{n}\left(\frac{L}{n\lambda}\right). \tag{58}$$

From Eq. (24), we get

$$\begin{aligned} f_{n-m}^{n}(y) = {} & \frac{(2m)!}{(n-m)!(n+m)!} \\ & + \sum_{k=1}^{n-m} \frac{(-1)^k (2m+k)! e^{-(k^2+2km)y}}{k!(n-m-k)!(n+m+k)!} \frac{2m+2k}{2m+k}. \end{aligned} \tag{59}$$

The probability for m adsorbed ions is given by

$$p_m = \frac{1}{c}\left(\frac{l_s}{n\lambda}\right)^m \frac{e^{-m^2 L/n\lambda}}{m!} f_{n-m}^{n}\left(\frac{L}{n\lambda}\right), \tag{60}$$

or, explicitly,

$$\begin{aligned} p_m = {} & \frac{1}{c}\left(\frac{l_s}{n\lambda}\right)^m \frac{e^{-m^2 L/n\lambda}}{m!} \left[\frac{(2m)!}{(n-m)!(n+m)!}\right. \\ & \left. + \sum_{k=1}^{n-m} \frac{(-1)^k (2m+k)! e^{-(k^2+2km)L/n\lambda}}{k!(n-m-k)!(n+m+k)!} \frac{2m+2k}{2m+k}\right]. \end{aligned} \tag{61}$$

The pressure between the two plates in the limit $L \to 0$ reduces to

$$\lim_{L\to 0} \beta P = \frac{n}{l_s} - \frac{n}{\lambda}, \tag{62}$$

where the origin of the positive term was previously discussed in reference to Eq. (55). The negative term arises due to electrostatic attraction between the walls, as the adsorption of counterions on a neutral wall at $x = L$ leads to attractive force toward the charged wall at $x = 0$. As in the limit $L \to 0$ all counterions become adsorbed, this force is proportional to n.

In Fig. 5, we plot pressure and the average adsorption as a function of confinement L for two scenarios: when adsorption occurs on a charged wall and when adsorption occurs on a neutral wall. Even if adsorption is lower for a sticky neutral wall, because counterions prefer the vicinity of the opposite charged wall, the adsorption in this case affects pressure more strongly due to the resulting electrostatic attraction between the two walls.

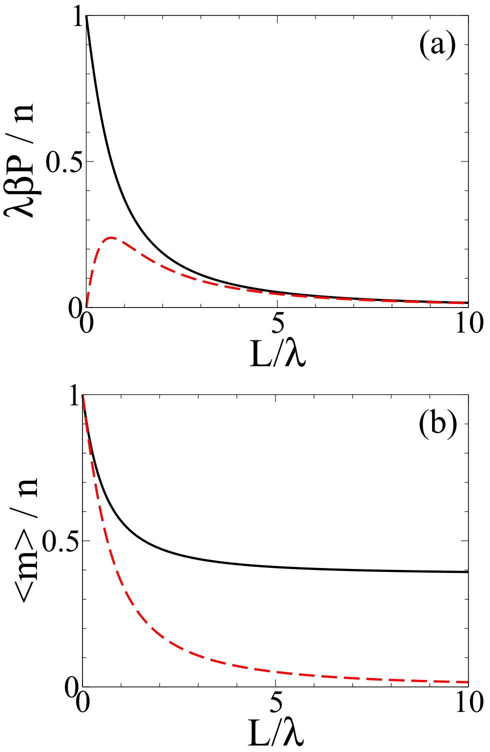

FIG. 5. (a) Pressure and (b) average fraction of adsorbed particles as a function of confinement for two scenarios: adsorption on a charged wall (solid line) and adsorption on a neutral wall (dashed line). The system parameters are $n = 20$ and $l_s/\lambda = 1$.

V. TWO-WALL CONFINEMENT: TWO STICKY WALLS

In this section, we consider a confinement with two sticky walls with a wall at $x = 0$ charged and a wall at $x = L$ neutral. The stickiness of each wall is l_1 and l_2. The general form of the partition function reads as

$$Z_s = \sum_{m_1=0}^{n} \sum_{m_2=0}^{n-m1} Z_{m_1}^{\mathrm{id}} Z_{m_2}^{\mathrm{id}} Z_{n,m_1,m_2}^{\mathrm{el}}, \tag{63}$$

where the ideal parts are

$$Z_{m_1}^{\mathrm{id}} = \left(\frac{l_1}{\Lambda}\right)^{m_1} \frac{1}{m_1!} \tag{64}$$

and

$$Z_{m_2}^{\mathrm{id}} = \left(\frac{l_2}{\Lambda}\right)^{m_2} \frac{e^{-m_2^2 L/n\lambda}}{m_2!}, \tag{65}$$

respectively, and the electrostatic part of free counterions is

$$Z_{n,m_1,m_2}^{\mathrm{el}} = \left(\frac{n\lambda}{\Lambda}\right)^{n-m_1-m_2} f_{n-m_1-m_2}^{n-m_1}\left(\frac{L}{n\lambda}\right). \tag{66}$$

To understand the expression above, it helps to think of the superscript as representing an effective surface charge of a wall at $x = 0$ (that is, a bare surface charge reduced by adsorbed counterions), and a subscript as representing the number of free ions. The functions $f_{n-m_1-m_2}^{n-m_1}(y)$ are defined in Eq. (24). The partition function can be written as

$$Z_s = \left(\frac{n\lambda}{\Lambda}\right)^n \sum_{m_1=0}^{n} \sum_{m_2=0}^{n-m_1} \left(\frac{l_s}{\lambda}\right)^{m_1+m_2} \times \frac{1}{m_1!} \frac{e^{-m_2^2 L/n\lambda}}{m_2!} f_{n-m_1-m_2}^{n-m_1}\left(\frac{L}{n\lambda}\right). \tag{67}$$

To verify the accuracy of the expression, we ensure that it correctly recovers the number of limiting cases. In the limit $\lambda \to \infty$, we recover the ideal-gas behavior given by

$$\lim_{\lambda\to\infty} Z_s = \sum_{m_1=0}^{n} \sum_{m_2=0}^{n-m_1} \left(\frac{l_1}{\Lambda}\right)^{m_1} \left(\frac{l_2}{\Lambda}\right)^{m_2} \left(\frac{L}{\Lambda}\right)^{n-m_1-m_2} \times \frac{1}{m_1!m_2!(n-m_1-m_2)!}, \tag{68}$$

and which corresponds to n ideal particles variously distributed in three boxes of length l_1, l_2, and L. The other limiting situation is the limit $L \to 0$, which yields

$$\lim_{L\to 0} Z_s = \sum_{m_1=0}^{n} \left(\frac{l_1}{\Lambda}\right)^{m_1} \left(\frac{l_2}{\Lambda}\right)^{n-m_1} \frac{1}{m_1!(n-m_1)!}, \tag{69}$$

and which corresponds to n ideal particles distributed in two boxes.

If we look into the behavior of pressure in the limit $L \to 0$, we find

$$\lim_{L\to 0} \beta P = \frac{n}{l_1 + l_2} - \frac{n}{\lambda}\left(\frac{l_2}{l_1 + l_2}\right)^2 \left(1 + \frac{1}{n}\frac{l_1}{l_2}\right). \tag{70}$$

As before, the first term indicates the pressure that adsorbed particles exert as the result of their tendency to dissociate. It has the form of an ideal-gas pressure for n particles inside a box of combined size $l_1 + l_2$. The negative term comes from attractive interactions between the two walls due to their effective charge. This term can be shown to originate from the potential between two walls given by

$$\beta u(L) = \frac{L}{n\lambda}\langle m_2^2\rangle. \tag{71}$$

The second term in Eq. (70) has a contribution that does not depend on n. This is the term that accounts for the Kirkwood-Shumaker force [35,36]. It becomes less significant as the number of counterions increases.

Two charged walls

In the above examples, we limited our investigation to a setup with only one wall charged, as this allowed us to formulate the solutions in terms of the functions $f_m^n(y)$ defined in Eq. (24) for a single-wall system. To consider a situation with two charged walls, a different set of fundamental functions is required, which are more complex as they involve the combination of simple and second-order poles.

However, by considering the limit $L \to 0$, we suppress the electrostatic part and can still point out some interesting features of the model. If the two walls have the same charge and the stickiness parameter, and the total number of counterions is $2n$, with each wall releasing n counterions, in the limit $L \to 0$ all the counterions are adsorbed and the interaction potential between the walls is given by

$$\beta u(L) = -\frac{L(n-m_1)(n-m_2)}{n\lambda}, \tag{72}$$

where $n - m_i$ might be considered as the effective charge on a wall and n/λ is the interaction strength between two ions. If all counterions are adsorbed, then $m_2 = 2n - m_1$ and

$$\beta u(L) = \frac{L(n-m_1)^2}{n\lambda}. \tag{73}$$

The above formula is correct for L that is sufficiently small so that ion dissociation is negligible. The expression indicates that interactions are almost always attractive even if, on average, the walls are neutral. The no interaction case corresponds to a single symmetric configuration when $m_1 = n$. The attraction is therefore strictly the result of fluctuations which produce asymmetric distributions of counterions.

As the effective interaction takes into account all possible configurations, we write

$$\beta u(L) = \frac{L}{\lambda}\frac{\langle (n-m_1)^2\rangle}{n}, \tag{74}$$

and since it is easy to guess that $\langle m_1\rangle = n$, the effective interactions between two walls become dependent on fluctuations alone as

$$\beta u(L) = \frac{L}{\lambda}\frac{\langle \delta m_1^2\rangle}{n}. \tag{75}$$

To evaluate the fluctuations $\langle \delta m_1^2\rangle$, we define the partition function valid in the limit $L \to 0$,

$$Z = \left(\frac{l_s}{\Lambda}\right)^{2n} \sum_{m_1=0}^{2n} \frac{e^{-(n-m_1)^2 L/\lambda}}{m_1!(2n-m_1)!}. \tag{76}$$

What is clear from the above expression is that asymmetric configurations are less likely to occur for finite L. In the exact limit $L = 0$, we find

$$\lim_{L\to 0}\langle \delta m_1^2\rangle = \frac{n}{2}, \tag{77}$$

and the interaction potential is

$$\lim_{L\to 0}\beta u(L) = \frac{1}{2}\frac{L}{\lambda}. \tag{78}$$

Based on this, we can next obtain an expression for pressure in the same limit. Since the attractive force is $-1/2\lambda$, the pressure must be

$$\lim_{L\to 0}\beta P = n\left(\frac{1}{l_s} - \frac{1}{2n}\frac{1}{\lambda}\right). \tag{79}$$

As the number of particles increases, the attractive force between walls becomes less relevant, and in the limit $n \to \infty$, it completely vanishes. In that case, pressure is strictly repulsive.

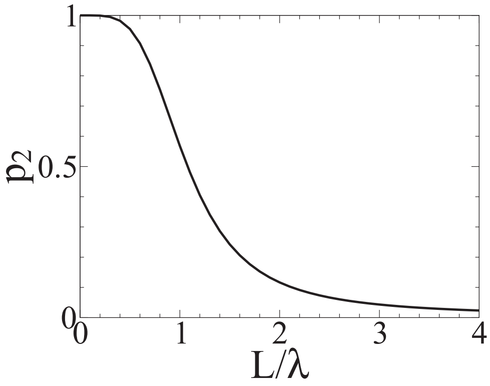

FIG. 6. Probability of ion association into pairs, p_2, as a function of the confinement size L/λ, obtained based on Eq. (82). The system parameters are $n = 10$ and $l_s/\lambda = 0.1$.

VI. STICKY COUNTERIONS

In this section, we briefly consider sticky counterions as a way to model the association of counterions into pairs. Such charge regulation of mobile ions have been recently considered in Refs. [15,16,18].

To simplify things, we assume that all ions are either dissociated or associated into pairs. The partition function accounting for this two different configurations, for a single charged wall case, is

$$Z = \left(\frac{n\lambda}{\Lambda}\right)^n \frac{1}{n!n!} + \left(\frac{n\lambda}{2\Lambda}\right)^{n/2} \left(\frac{l_s}{\Lambda}\right)^{n/2} \frac{1}{(n/2)!(n/2)!}, \tag{80}$$

where we used the partition function in Eq. (27), and where the first term represents dissociated counterions and the second term represents associated counterions into pairs due to sticky interactions between them. Alternatively, we may write

$$Z = \left(\frac{n\lambda}{\Lambda}\right)^n \left[\frac{1}{n!n!} + \left(\frac{l_s}{2n\lambda}\right)^{n/2} \frac{1}{(n/2)!(n/2)!}\right]. \tag{81}$$

To see how confinement affects dissociation of ion pairs, we introduce a neutral and nonsticky wall at $x = L$. The partition function for this situation is

$$Z = \left(\frac{n\lambda}{\Lambda}\right)^n \left[f_n^n\left(\frac{L}{n\lambda}\right) + \left(\frac{l_s}{2n\lambda}\right)^{n/2} f_{n/2}^{n/2}\left(\frac{2L}{n\lambda}\right)\right], \tag{82}$$

with $f_n^n(y)$ given in Eq. (25). In Fig. 6, we plot the probability that all ions are associated into pairs, p_2, as a function of confinement. The smaller the confinement, the more likely it is for ions to exist as pairs. As smaller confinement implies a more concentrated system, this result could be used to obtain the solubility of a given ionic molecule.

VII. CONCLUSION

In this work, we have investigated a one-dimensional one-component Coulomb gas model in a sticky wall confinement as a simple case study of charge regulation. The choice of the system has been motivated by the desire to gain a deeper understanding of, first, the role of fluctuations and, second, the statistical mechanics of more realistic systems in higher dimensions, especially with regard to the structure of a partition function.

Unlike the mean-field analysis, the model provides complete distributions of adsorbed particles. These distributions depend on the interaction strength, the wall stickiness, the number of ions, and the size of the confinement. In consequence, the model provides a simple paradigm for the mechanism of the Kirkwood-Shumaker interactions [35–37].

The view that the complete system is a collection of independent equilibriums with fixed number of adsorbed ions allows us to derive expressions in an intuitive manner. A similar decomposition holds for higher-dimensional models; however, in these systems, adsorbed ions are no longer viewed as ideal particles, as they no longer occupy a single point in space. In two-dimensions, adsorbed ions are moving on a line, and in three-dimensions, they move on a surface. Different configurations of adsorbed particles may lead to spontaneous inhomogeneity of a surface charge, giving rise to local fluctuations of surface charge density, even if the total number of adsorbed ions is fixed. Particles adsorbed on a surface, can, in addition, undergo a phase transition under appropriate conditions [42], leading to additional exotic forces unrelated to the Kirkwood-Shumaker interactions.

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