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ABSTRACT

We develop a theory of charge storage in ultranarrow slitlike pores of nanostructured electrodes. Our analysis is based on the Blume-Capel model in an external field, which we solve analytically on a Bethe lattice. The obtained solutions allow us to explore the complete phase diagram of confined ionic liquids in terms of the key parameters characterizing the system, such as pore ionophilicity, interionic interaction energy, and voltage. The phase diagram includes the lines of first- and second-order, direct and re-entrant phase transitions, which are manifested by singularities in the corresponding capacitance-voltage plots. Testing our predictions experimentally requires monodisperse, conducting ultranarrow slit pores, to permit only one layer of ions, and thick pore walls, to prevent interionic interactions across the pore walls. However, some qualitative features, which distinguish the behavior of ionophilic and ionophobic pores and their underlying physics, may emerge in future experimental studies of more complex electrode structures.

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I. INTRODUCTION

Supercapacitors store energy via charge separation between the cathode and anode in electrical double layers at the corresponding electrodes.¹ Since the stored energy scales up with the electrode/electrolyte contact area, highly porous electrodes with “volume-filling” surfaces are used to improve their capacitive

performance. If the pores of an electrode are much wider than the double layer thickness, the capacitance *per surface area*, provided by this electrode, will be comparable to the corresponding capacitance of a flat electrode.² However, if the double layers on the opposite sides of the pores overlap or if the pores are so narrow that they can accommodate only one layer of ions, then the physics and the laws of charge storage become different.^{3–6} The need to maximize the

capacitance and energy storage motivates the use of electrodes with such a fine porosity and, since the modern nanotechnology allows one to build well-defined nanoporous structures,^{7–13} understanding the laws of charge storage in nanosized pores has become in great demand.^{6,14–22}

While in computer simulations the pores of various types,^{17,18,20} or even nanoporous networks,¹⁵ are modeled in a conceptually similar way,²³ analytical theories of ultranarrow porous electrodes, comparable in size to the size of a bare ion, require special modeling, which can, however, benefit from the “reduced dimensionality” of the system. For instance, a narrow slit nanopore may be treated as a quasi-two-dimensional system of ions, which are drawn into the pore by electrode polarization; for a single-file cylindrical pore, the system is even quasi-one-dimensional (1D).

Such quasi-1D systems can be studied by mapping them on the corresponding models of statistical mechanics, and many of them have exact analytical solutions.^{24–33} The simplest appropriate model is a classical two-state antiferromagnetic Ising model with nearest neighbor interactions in an external field.²⁹ In this model, ± 1 spins correspond to positive and negative ions, i.e., cations and anions, respectively, and the external magnetic field is the potential drop between an electrode and a bulk electrolyte; the approximation of nearest neighbor interactions is reasonable due to the superionic state emerging in conducting nanoconfinement⁶ in which the interionic interactions are exponentially screened.³⁴ The solution to this model is well known and can be found in textbooks,³⁵ but it allowed a compact analytical expression for the capacitance and the in-depth analysis of its behavior.²⁹ Despite its simplicity, this model and its extensions have turned out to capture relatively well the qualitative behavior of the voltage-dependent capacitance, as compared to simulations.^{30,31}

While for 1D models, describing single-file cylindrical pores, there are exact analytical solutions, the analytical solutions to 2D (and higher dimension) problems are limited, particularly in an “external field,” the role of which is played by the applied potential. It seems, therefore, rewarding to resort to approximate but reliable approaches, which provide analytical solutions and hence allow new physical insights to be more easily developed. In this work, we present a three-component model for ionic liquids (ILs) (and solvent, or voids) confined into narrow slits, which are subject to externally applied voltage. We solve this model *exactly* on a Bethe lattice³⁶ with coordination number q , which approximate lattices with the same coordination number (it can also be seen as an approximation to off-lattice systems with, on average, q neighbors).³⁷ This model can be mapped onto the well-known antiferromagnetic Blume-Capel model,^{38–42} which has been treated by the Bethe-lattice approach,⁴³ cluster-variation method,⁴⁴ and simulations^{45–49} in the context of magnetic systems. However, the aspects of the phase diagram related to the response to electric field as well as charging and capacitive characteristics, relevant to confined ionic liquids and supercapacitors, have not been investigated.

In our previous work,⁵⁰ we have applied this model to analyze the phase behavior of ions in *nonpolarized* slit nanoconfinement. We demonstrated the emergence of ordered and disordered phases, and first- and second-order phase transitions, which could be induced by changing the temperature and slit width. Herein, we extend this analysis to a much more complex case of polarizable electrodes and study the *voltage-dependent* phase behavior and how it projects onto

the charging properties. The introduction of the electrode potential is not only necessary to study the capacitive characteristics, but we shall see that it also leads to a far richer phase behavior with a variety of direct and re-entrant phase transitions, giving rise to remarkable charging properties. Since the ordered phases are known to exhibit slow dynamics,^{21,51,52} our work may also have an important practical implication in that the knowledge of the parameter space corresponding to such phases may help avoid potential slowdown of charging.

This paper is organized as follows: The model is formulated in Sec. II in which we also discuss its shortcomings and possible extensions (Sec. II C); the Bethe-lattice solution to this model is presented in the Appendix. The results are discussed in Sec. III, and we summarize and conclude in Sec. IV.

II. MODEL

We consider an ultranarrow metallic slit-shaped pore, just one molecular diameter thick, such that it can accommodate only one layer of ions [Fig. 1(a); for simplicity, we assume the cations and anions to be of comparable size]. We also assume that the ions inside the pore reside on the sites of a regular lattice with coordination number q (we note that lattice models are frequently used for ionic liquids and seem to capture their behavior qualitatively well^{24–26,28–31,50,53–55}). The lattice is thus populated by a mixture of cations, anions, and voids (empty, unoccupied sites). To describe the occupation of site i , it is convenient to introduce Boolean variables $n_i^\pm = 0$ or 1, such that $n_i^+ = 1$ ($n_i^- = 1$) means that site i is occupied by a cation (an anion), and $n_i^+ = n_i^- = 0$ means that site i is vacant; the configuration $n_i^+ = n_i^- = 1$ is prohibited due to hard-core exclusion (i.e., each site can be occupied either by a cation or an anion, or be empty). This system can be described by the following Hamiltonian:⁵⁰

$$\mathcal{H} = I \sum_{\langle ij \rangle} (n_i^+ n_j^+ + n_i^- n_j^- - n_i^+ n_j^- - n_i^- n_j^+) - \sum_i (h_- n_i^- + h_+ n_i^+), \quad (1)$$

where $\langle ij \rangle$ denotes nearest neighbor sites, $I > 0$ is the interaction energy between two *neighboring* ions, and the interactions between the next-nearest and further neighbors are neglected (this is seemingly an acceptable approximation due to the superionic state, i.e., an exponential screening of ionic interactions, emerging in conducting nanoconfinement;⁶ see, however, Sec. II C 1). In Eq. (1), “external” fields $h_\pm$ are

$$h_\pm = w_\pm \pm eu, \quad (2)$$

where u is the applied potential (with respect to the bulk electrolyte outside of the pore), e is the elementary charge, and $w_\pm$ is the energy of transfer of a $\pm$ ion *from* the pore into the bulk, which includes the image forces and other interactions of the ions with the pore walls.⁶ We note that the definition used here differs by sign from the resolution energy used in other works^{6,56,57} (here, positive w corresponds to ionophilic pores and negative to ionophobic pores). In the following, we assume $w_+ = w_- = w$ and note that the results for an asymmetric ionic liquid ($w_+ \neq w_-$) can be obtained by shifting the applied voltage by $-(w_+ - w_-)/2e$ and taking the transfer energy equal to $(w_+ + w_-)/2$.

Thermodynamic properties can be calculated from the grand-canonical partition function

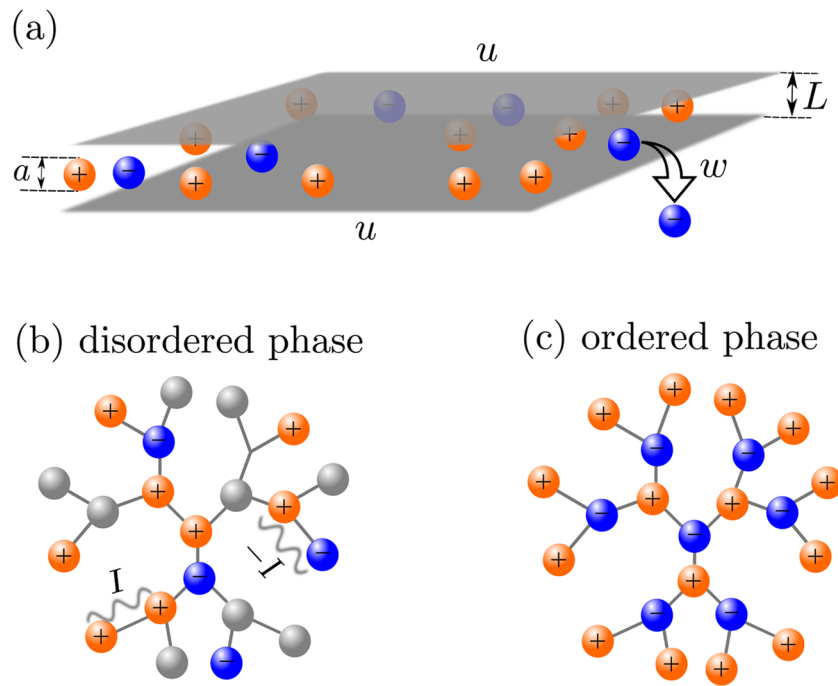


FIG. 1. Model of ions inside a slit nanopore and the Cayley tree representation. (a) Ions are confined into a narrow metallic slit of width L . Ion diameter is $a = a_{\pm}$, which is assumed the same for cations and anions. Potential u is applied at the pore walls with respect to the bulk electrolyte (not shown). The energy of transfer of ions from a pore into the bulk is $w = w_{\pm}$ and is assumed the same for both ions (see text). (b) Fragment of the Cayley tree with coordination number $q = 3$, illustrating a possible arrangement of ions (blue and orange spheres) and voids/solvent (gray spheres) in the disordered phase. Interaction energy between the same type of ions is I and between oppositely charged ions is $-I$ [see Eq. (1)]. (c) The same fragment of the Cayley tree as in (a), but showing an example of the ordered phase in the case of high transfer energy ($\beta w \gg 1$) and zero applied potential ($u = 0$); in this case, the ordered phase consists of an equal amount of cations and anions occupying two sublattices of the Cayley tree.

$$\Xi = \sum_{(n_i^+, n_i^-)} \exp\{-\beta \mathcal{H}\}, \quad (3)$$

where $\beta = 1/k_B T$, with k_B being the Boltzmann constant and T being the temperature, and the sum runs over all possible allowed configurations (n_i^+, n_i^-) of the occupation variables. We have calculated the partition function (3) by using the Bethe-lattice approach, which relies on approximating the actual (lattice) structure by a Bethe lattice³⁶ with the same coordination number³⁷ [Figs. 1(b) and 1(c)]; the partition function on the Bethe lattice can then be evaluated exactly⁵⁸ (see the Appendix for details).

A. Charging characteristics

Having calculated the partition function (3), one can compute the charge accumulated in a pore

$$Q = -\frac{1}{\beta} \frac{d \ln(\Xi)}{du} \quad (4)$$

and the differential capacitance

$$C = \frac{dQ}{du}. \quad (5)$$

Note that per definition, both Q and C are measured per surface area (since we consider a quasi two-dimensional problem); both quantities can be assessed experimentally.⁵⁹

We shall also calculate the charging parameter^{60,61}

$$X_D = \frac{e}{C} \frac{d\rho}{du} = e \frac{d\rho}{dQ}, \quad (6)$$

where $\rho(u)$ is the total (two-dimensional) ion density in a pore. This parameter describes charging mechanisms taking place at the given applied voltage u . In particular, $X_D = 0$ means that the in-pore total ion density does not change with u , which implies that charging, in the thermodynamic sense, is driven by swapping the in-pore coions for the counterions from the reservoir (bulk electrolyte). $X_D = 1$ indicates that charging proceeds by electrosorption of new counterions from the bulk electrolyte, implying that the in-pore total ion density increases along with the charge. $X_D = -1$ means that charging is due to the desorption of the in-pore coions, and hence, the total ion density decreases as the charge increases. For $|X_D| < 1$, charging is a combination of swapping and adsorption/desorption, with the contribution from swapping $1 - |X_D|$. It is also possible that $X_D > 1$, which means that, in addition to counterions, also coions are adsorbed into a pore; similarly, $X_D < -1$ implies that, alongside the in-pore coions, also the counterions are removed from a pore.

B. Ordered and disordered phases

By using the appropriate change of variables and of the interaction parameters (see, e.g., Ref. 50), the lattice model given by Eq. (1) can be mapped onto the classical spin-1 Blume-Capel (BC) model with the Hamiltonian given by^{38–42}

$$\mathcal{H} = I \sum_{\langle ij \rangle} S_i S_j - w \sum_i S_i^2 - eu \sum_i S_i, \quad (7)$$

where “spin” $S_i = \{\pm 1, 0\}$ at site i describes a cation/anion or void (or solvent, if present), respectively. The BC model has been studied by cluster-variation⁴⁴ and Bethe-lattice approaches⁴³ and by Monte Carlo (MC) simulations.^{45–49} Based on these results, we expect rich phase behavior, involving direct and re-entrant symmetry-breaking phase transitions between “ordered” and “disordered” phases. In the context of ionic liquids, the disordered phase is a homogeneous mixture of ions and voids [Fig. 1(b)], while the “ordered” phase means that the ions of one type predominantly occupy one of the two “sublattices.” At zero applied potential, $u = 0$, the ordered phase consists of an equal amount of cations and anions [possibly mixed with voids, depending on the transfer energy w , see Fig. 1(c) for the case $\beta w \gg 1$]; in the corresponding continuous system, this likely corresponds to in-plane crystal-like ordering of ions.⁵⁰ At a nonzero potential and in the ordered phase, the charge on one sublattice exceeds that on the other so that the pore is overall charged. A particular example is an ordered phase consisting of counterions and voids, achievable at sufficiently high potentials. Other ordered configurations are also possible within the underlying lattice structure.

C. Discussion of model limitations

As mentioned, we have solved model (1) on the Bethe lattice, which allowed us to calculate various charging characteristics *analytically*. Before describing the results of these calculations, however, it is important to discuss the limitations of the model, its possible extensions, and the relation to charging real nanoporous electrodes.

1. Next-nearest and further neighbors

We have assumed that only the nearest-neighbor ions interact with each other. This assumption has been made because of the superionic state emerging in conducting nanoconfinement. Indeed, for perfectly metallic walls of a slit pore, the interaction energy between two ions, situated in the slit’s midplane and separated by distance r , is $U_{\alpha\beta}(r) = z_{\alpha}z_{\beta}\phi(r)$, where⁶

$$\phi(r) = \frac{4e^2}{\epsilon L} \sum_{n=1}^{\infty} K_0(\pi nr/L). \quad (8)$$

Here, $K_0(x)$ is the modified Bessel function of the second kind of order zero; $\alpha, \beta = \{+, -\}$, z_{α} is the ion charge, measured in units of the elementary charge e , L is the pore width, and ϵ is the dielectric constant inside the pore (we use Gaussian units throughout this paper). For this system and monovalent ions ($z_{\pm} = \pm 1$), the coupling constant in Eq. (1) is $I = \phi(a)$, where a is the lattice constant. In this case, the value of I varies in the range from a few $k_B T$ to about $15k_B T$, depending on the ion size ($\approx$ lattice constant), pore width, and dielectric constant.⁵⁰

For large separations, $r \gg L$, the large-argument asymptotic expression for the Bessel function⁶² gives

$$\phi(r) = \frac{4e^2}{\epsilon\sqrt{2Lr}} e^{-\pi r/L}, \quad (9)$$

i.e., $\phi(r)$ decays exponentially with r . For the lattice constant $a = 1$ nm and slit width $L = a$, and taking the dielectric constant $\epsilon = 2$ (see Sec. II C 2), one finds $I = \phi(a) \approx 3.3k_B T$, while $\phi(2a) \approx 0.1k_B T$ (both at room temperature); thus, the interaction between the next-nearest-neighbor ions is $\alpha = \phi(a)/\phi(2a) \approx 33$ times smaller than the interaction between the neighboring ions. This seemingly justifies the approximation made above. However, if the pore widths are just below two ion diameters, the decay length becomes two times larger, and hence, $\alpha \approx 7$; then, the next-nearest interactions are not necessarily so negligible any more. Badedah *et al.* have demonstrated that inclusion of the second neighbors can lead to the appearance of new states and multicritical points.⁶³ It would be interesting to investigate such effects in future work.

2. Ion polarizability

It is known that ion polarizability can play an important role in the formation of electrical double layers^{64–67} and its *bona fide* modeling can be essential, particularly at high ion concentrations and for low dielectric media.⁶⁵ In our classical statistical-mechanical model, the conformational and electronic degrees of freedom (of ions), responsible for ion polarizability, are not considered explicitly, but enter the model only through the effective dielectric constant ϵ of the interior of a pore [see Eq. (8)]. For pores densely packed with ions, and in the absence of solvent, we expect ϵ to be in the range between 2 and 5, depending on the slit width; however, the dielectric constant presumably decreases and approaches unity as the in-pore ion density decreases.⁵⁷ In other words, the dielectric constant in Eq. (8) depends on the total ion density, which leads to complicated transcendental equations for ion densities. While such changes in the ion polarizability may affect the location (and the order) of the phase transitions discussed in this work, we do not expect the transitions to disappear and anticipate a similar qualitative behavior. (However, it is interesting to note, in this respect, that the pore-width dependence of the dielectric constant has been shown to have a potentially vivid effect on the charging behavior.⁵⁷)

3. Presence of solvent

It might be tempting to interpret vacant sites (voids) as solvent molecules by appropriately adjusting the effective dielectric constant inside a pore, particularly for systems with nonpolar or weakly polar solvents, comparable in size to ions. This has been done in the previous work on charging cylindrical pores^{30,31} and even the solvent/ion size asymmetry was taken into account.³¹ Although similar reasoning applies also to our model, we note that such interpretations shall be made with caution. Indeed, in real systems, there are both “voids” and solvent present, and the ions may interact with the solvent not only by the excluded volume interactions. Solvent polarizability may also play an important role.^{68,69} For instance, it has been shown that polar solvents may affect charging significantly, leading to an increase in the capacitance, which is not captured by

models with the ions and solvent interacting sterically only.⁷⁰ Thus, while our model may be applicable in the case of some solvents, it would be really interesting to extend it to treat the solvent more rigorously.

4. van der Waals interactions

We have assumed that the ion-ion interactions are determined solely by the screened electrostatics in the superionic state [Eq. (8)]. In reality, the ions and the solvent molecules, if present, interact also via dispersion (van der Waals) forces. It is known that such forces may influence the charging behavior vividly.^{71–74} Since, for a superionic liquid, the electrostatic interactions are exponentially screened,⁶ the van der Waals forces may, in fact, become dominant, thus determining the system behavior, particularly at zero potential.

In the presence of van der Waals forces, our model Hamiltonian [Eq. (1)] will be modified in that the coupling constant I will depend on the types of ions, i.e., $I_{++} \neq I_{--} \neq I_{+-}$ in general. This will likely shift the locations of the phase transitions and may make the phase behavior even richer than that reported below. In addition, since the dispersion forces decay algebraically with the distance, it might be necessary to incorporate higher order neighbors in the Hamiltonian (1) (see Sec. II C 1).

Thus, including van der Waals interactions appears to be a compelling and complex problem, and it will be interesting to account for such interactions in future work.

5. On the lattice nature of the model and Bethe-lattice approach

Model (1) is formulated on a bipartite lattice with coordination number q (the number of nearest neighbors; $q = 3$ in this work). This allowed us to define unambiguously the order parameter, viz., the difference in the ion densities on two sublattices, and hence determine the locations of various phase transitions. In reality, however, the ions are not confined to reside on lattice sites, particularly in the disordered phase, and, upon transition to an ordered phase, may adopt a structure different from the prescribed lattice.

However, to solve our model, i.e., to calculate the partition function (3), we have used the Bethe-lattice approach, which is based on the reformulation of the original lattice model onto a Bethe lattice [Figs. 1(b) and 1(c)]; the only information contained in the Bethe lattice about the lattice structure is the number of nearest neighbors. In this respect, our model may also be considered as an approximation to off-lattice systems in which ions have q neighbors separated by distance a (on average). We emphasize that the partition function and hence the ion densities and the capacitance, as calculated on the Bethe lattice, are *exact*. It thus seems reasonable to expect that our analytical results reflect properly some physics of real ionic liquids in conducting slit nanoconfinements.

6. Carbonic vs metallic pore walls

We have assumed that the pore walls are perfectly metallic surfaces, but this is not generally the case, as the majority of porous electrodes are fabricated from carbon materials.⁷⁵ This has three important implications in the context of our model:

1. The screening of ionic interactions [Eq. (8)] is expected to be different for carbonic pore walls.³⁴ However, it has been shown by quantum density functional calculations that a similar expression for a metallic cylinder is in fact a good approximation for single-wall carbon nanotubes.^{76,77} Although such calculations have not been performed for slits, it is reasonable to expect a similar agreement also in this case. It must be noted, however, that depending on the pore-wall thickness, screening might be weaker for carbonic walls, as compared to the metallic one. Thus, the interaction energy between the next-nearest (and higher) neighboring ions may increase, which may produce a substantial effect on the phase behavior and capacitance (see Sec. II C 1).
2. There is a contribution to the total (measurable) capacitance $C_{\text{tot}}^{-1} = C_{\text{QC}}^{-1} + C_{\text{IL}}^{-1}$ from quantum capacitance C_{QC} of carbonic walls^{78–80} ($C_{\text{QC}} = \infty$ for metallic walls; $C_{\text{IL}} \equiv C$ is the capacitance of an ionic liquid calculated in this work [Eq. (5)]). Thus, the capacitance-voltage curves, as computed in this work, will be modified by C_{QC} , which is also voltage-dependent. However, since the phase transitions, discussed here, are manifested by strong peaks or divergencies in C_{IL} (Sec. III), they shall, in principle, be present in the total capacitance; it will be beneficial to account for C_{QC} explicitly in future work.
3. Thin carbonic pore walls can be “transparent” to electrostatic (and other) interactions. Indeed, Mendez-Morales *et al.* modeled a pore wall as a single layer of Gaussian charges and observed that the ions from neighboring pores are strongly correlated.²⁰ Juarez *et al.*⁸¹ used quantum density functional calculations and reported on similar correlations between the ions from the inside and outside of a single-wall carbon nanotube.⁸¹ Recently, it has been shown that such interactions may have a profound effect on the capacitance and energy storage.⁸² In this work, we neglect the interpore ionic interactions, but it would be interesting to study how they influence the phase transitions discussed below; we note, however, that such effects shall be negligible for sufficiently thick pore walls.

7. Nanoporous electrodes

Frequently used nanoporous electrodes for supercapacitors are activated and carbide-derived carbons.⁷⁵ Such electrodes do not consist of perfectly aligned monodisperse slits, but they are random porous media, containing interconnected pores of various shapes and sizes.^{83–87} Clearly, our model is not directly applicable to these electrodes.

However, recently, there has been a significant progress in developing low-dimensional carbon materials, such as quasi-two-dimensional MXene phases^{11–13} and graphenes,^{7–10} which appear to be more suitable to test the predictions of our theory. It is important to note, however, that even in these materials, the pore walls may not be perfectly aligned, the pore width may vary along a pore, and the walls can be rough or contain impurities. This will affect the strength of interionic interactions locally and may allow multi-layer filling of the pore with ions; all these may lead to rounding-off of the transitions, discussed in this work, or to turning them into smooth transformations between the “ordered” and disordered

phases. Nevertheless, it seems reasonable to expect that some features of these transitions, such as strong peaks manifested in the differential capacitance (Sec. III), shall still be present in the capacitance curves.

8. Concluding remark on the model

As discussed, the presented model [Eq. (1)] neglects many aspects of charge storage in nanoporous electrodes, and its predictions may not be easily verified in experiments due to the enormous complexity of real nanoporous electrode/electrolyte systems. Nevertheless, this model lends itself to be the *simplest analytically solvable model* for quasi-2D slit pores, likely capturing the basic physics of ionic liquids in ultranarrow conducting slits and thereby providing a reference frame for future theoretical, experimental, and numerical analysis.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the global phase diagram, drawn in the space of ion's transfer energy w , ion-ion interaction energy I , and applied potential u . It consists of two phases, ordered and disordered [Sec. II B, Figs. 1(b) and 1(c)], which are separated by two nonoverlapping surfaces of first- and second-order phase transitions. These surfaces meet at a line of tricritical points. It is important to note that the surface of second-order transitions bends down for increasing u such that the disordered phase is always on top of the ordered phase [cf. also Fig. 2(c)]. This means that, at sufficiently high applied potentials, the disordered phase becomes stable, independently of the values of w and I .

To better understand the topology of the global phase diagram, we combined the phase diagram at zero potential, $u = 0$, with the *orthogonal projection* of the phase transition surfaces onto the $u = 0$ plane [Fig. 2(b)]. This projection divides the $u = 0$ plane into two basic regions:

1. The region onto which the transition surface does not project [zone 0 in Fig. 2(b)]. A system with I and w belonging to this zone does not undergo any voltage-induced phase transition. In other words, the systems are, and remain, in the disordered state at any applied potential.
2. The region onto which the transition surface projects at least once [if the surface bends or makes zigzags, it can project twice or more [cf. Fig. 2(c)]]. This region is most interesting as it contains a number of voltage-induced phase transitions. Depending on the number of these transitions, it can be further divided into three zones. A system from zone 1 experiences only one second-order voltage-induced phase transition from the ordered into the disordered phase (cf. Fig. 3). (Note that since our system is symmetric, there are in fact two transitions, at a positive potential, u_1 , and at a negative potential $-u_1$; the same concerns all zones. Hence, hereafter, we focus only on positive u .) Zone 2 contains two transitions (for $u > 0$). This is because the transition surface makes a zigzag for increasing voltage [Figs. 2(a) and 2(c)], and the system first undergoes a transition from the disordered to the ordered phase and then back to the disordered phase (cf. Fig. 4) (we recall that, at sufficiently high potentials, the system is in the disordered phase, independently of I and w). Finally, in zone 3, there are three transitions. One is either of first-order or second-order from the ordered to the disordered phase and then two second-order transitions to the ordered phase and back to the disordered phase [see Figs. 2(b) and 2(c), cf. Fig. 5].

Figure 2(c) shows all four zones in the (w, u) plane for a constant value of $\beta I = 2.18$; the cuts at constant w are shown in Figs. 3(a), 4(a), and 5(a). We shall discuss below the charging and capacitive characteristics of a superionic liquid in each of these four zones. It will be convenient, however, to discuss them separately for positive and negative transfer energies, which roughly correspond to ionophilic and ionophobic pores, respectively.

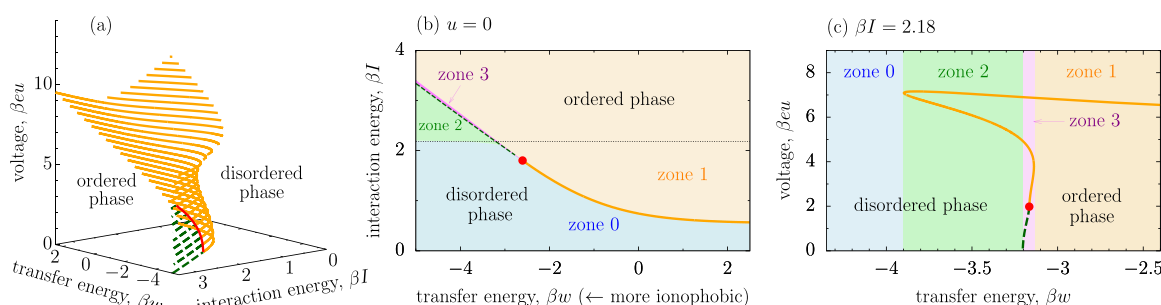


FIG. 2. Phase diagram of a model superionic liquid described by Eq. (1). (a) Phase diagram drawn in the (w, I, u) space, where w is the ion transfer energy, I is the ion-ion interaction parameter, and u is the applied voltage. Ordered and disordered phases are separated by surfaces of the first-order (dashed green lines) and second-order (solid orange lines) phase transitions, which meet at a line of tricritical points (thick solid red line). At high voltages, the surface of the second-order transitions (solid orange lines) bends down such that the disordered phase is always on top of the ordered phase [cf. panel (c)]. (b) Phase diagram at zero applied voltage ($u = 0$). The red filled circle denotes a tricritical point. Differently colored zones are numbered according to the number of phase transitions, which the systems belonging to these zones experience, as the voltage increases. The thin horizontal line shows the value of βI used in (c). (c) Phase diagram in the (w, u) plane for $\beta I = 2.18$ (which lies close to the border line between zones 0 and 2). Voltage is measured in units of thermal voltage $(\beta e)^{-1}$ (≈ 26 mV at room temperature).

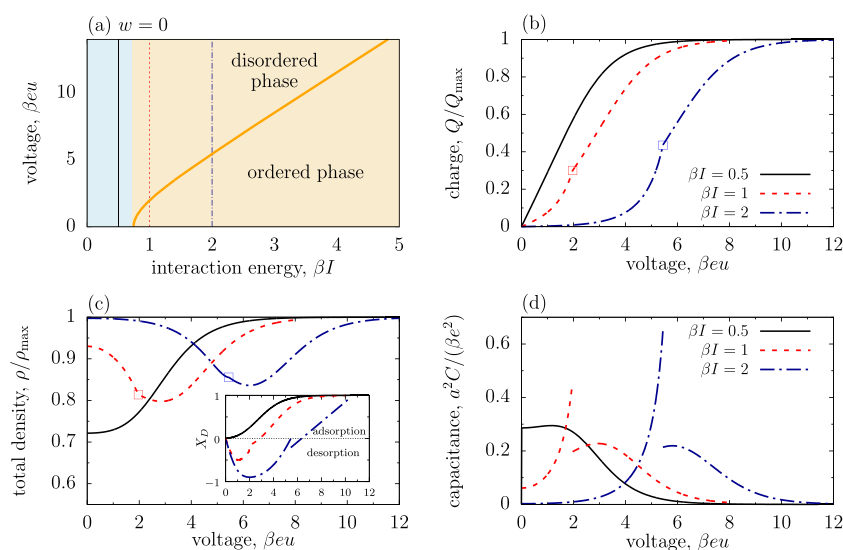


FIG. 3. Charging, capacitive, and phase behavior of a superionic liquid in ionophilic pores ($w = 0$). (a) Phase diagram in the (I, u) plane, where I is the ion-ion interaction parameter and u is the applied voltage. Ordered and disordered phases are separated by a line of second-order phase transitions (solid orange line). The thin vertical lines show the values of βI used in (b)–(d). The light yellow region indicates zone 1 and the blue domain is zone 0 [see Figs. 2(b) and 2(c)]. (b) Accumulated charge, (c) total ion density, and (d) differential capacitance as functions of voltage for three chosen values of βI . The inset in (c) shows the charging parameter [Eq. (6)]. The open squares in (b) and (c) indicate the transition points, where the charge and the total ion density show cusps. Voltage is measured in units of thermal voltage $(\beta e)^{-1}$ (≈ 26 mV at room temperature), and capacitance is measured in units of thermal electric capacitance⁸⁸ $(\beta e^2 \approx 6.2$ aF at room temperature) per a^2 , where a is the lattice constant; for $a = 1$ nm, $\beta e^2/a^2 \approx 620$ $\mu\text{F}/\text{cm}^2$.

A. Positive transfer energies

In Fig. 3(a), we present the phase diagram in the (I, u) plane for $w = 0$, which consists of zones 0 and 1. In zone 0, an ionic liquid is in the disordered phase at any applied potential [blue region in Fig. 3(a)]. In zone 1 [light yellow region in Fig. 3(a)], it is in the ordered phase at $u = 0$, but undergoes a *second-order* phase transition to the disordered phase as the voltage increases. Thus, one can distinguish two types of behavior: (i) the charge, total ion density, and capacitance are all smooth functions of u [0-zone, solid lines in Figs. 3(b) and 3(c)]; (ii) the charge and total ion density exhibit cusps at the transition, whereas the capacitance and the charging parameter X_D show discontinuities [zone 1, dashed and long-dashed lines in Figs. 3(b) and 3(c)].

It is interesting to note that, in zone 0, charging is driven by swapping coions for counterions and by counterion adsorption, i.e., $X_D > 0$. In zone 1, however, the system first expels the in-pore coions via swapping and coion *desorption* ($X_D < 0$), and only then the counterion adsorption commences; this point virtually coincides with the transition voltage [the inset in Fig. 3(c)]. Remarkably, the charge remains nearly constant (and the capacitance is low or vanishes) in the ordered phase before the onset of the transition [dashed lines in Figs. 3(b) and 3(d)]. This is likely because changing the ion density (significantly) can distort the ordered phase, which is thermodynamically unfavorable.

It is instructive to compare the charging behavior predicted by our model with the results of other models considered in the literature. In particular, a continuous mean-field model of Ref. 6 predicted a first-order phase transition between coion rich and coion deficient phases, with the total ion density and charge experiencing a jump

(rather than a cusp) at the transition.^{6,89} However, *charging* behavior was similar in that the counterion adsorption starts only after the system expels the coions via swapping and/or desorption. A similar charging behavior was observed in molecular dynamics (MD) and Monte Carlo (MC) simulations. Vatamanu *et al.*¹⁷ studied a few ionic liquids by atomistic molecular dynamics simulations and found that charging is often accompanied by a first-order transition, as predicted in Ref. 6. Similarly, in a combined MC and MD study, Breitsprecher *et al.*⁶¹ also observed that the counterion adsorption was preceded by coion desorption, although they did not report on any phase transition.

B. Negative transfer energies and multiple re-entrance phenomena

The region of negative transfer energies mainly corresponds to ionophobic pores, whose existence is yet to be demonstrated experimentally. However, this region includes all four zones and is far more interesting than the region of conventional, ionophilic pores. Since charging in zones 0 and 1 appears to be very similar to the case of positive w , our primary focus will be on zones 2 and 3, although we shall discuss zone 0 as well.

1. Zones 0 and 2

Figure 4(a) shows the phase diagram in the (I, u) plane for $\beta w = -4$. There are ordered and disordered phases, as before, but here they are separated by lines of first-order (dashed line) and second-order (solid line) phase transitions, which meet at a tricritical point (full circle). This phase diagram, in fact, includes all four zones; in this section, however, we shall focus on zones 0 and 2 only.

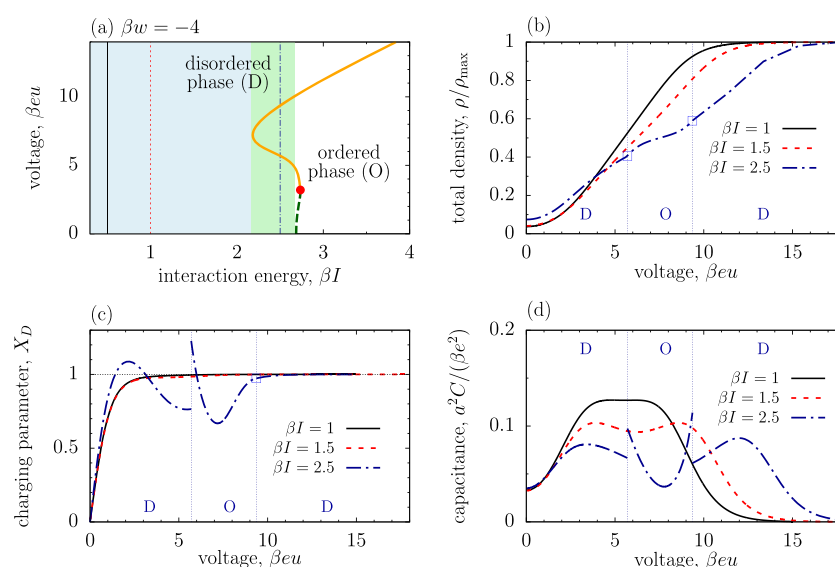


FIG. 4. Capacitive, charging, and phase behavior of a superionic liquid in ionophobic pores with $\beta w = -4$. (a) Phase diagram in the (I, u) plane, where I is the ion-ion interaction parameter and u is the applied voltage. Ordered (O) and disordered (D) phases are separated by a line of second-order transitions (solid line) and by a line of first-order transitions (dashed line), which meet at a tricritical point (full circle). Thin vertical lines show the values of βI used in (b)–(d). This phase diagram contains all four zones, but only 0-zone (light blue) and zone 2 (green) are highlighted. (b) Total ion density, (c) differential charging parameter X_D , and (d) differential capacitance as functions of voltage for three chosen values of βI . The open squares and thin vertical lines indicate the location of the transitions for $\beta I = 2.5$. Voltage is measured in units of thermal voltage $(\beta e)^{-1}$ (≈ 26 mV at room temperature), and capacitance is measured in units of thermal electric capacitance⁸⁸ ($\beta e^2 \approx 6.2$ aF at room temperature) per a^2 , where a is the lattice constant; for $a = 1$ nm, $\beta e^2/a^2 \approx 620$ $\mu\text{F}/\text{cm}^2$.

To study them, we have chosen the values of βI such that the system is in the disordered phase at no applied voltage [thin vertical lines in Fig. 4(a)]. For these values of βI , the pores are (almost) empty at $u = 0$ [Fig. 4(b)].

For βI corresponding to 0-zone (solid and dashed lines in Fig. 4), no phase transition occurs, and the total ion density, charge, charging parameter X_D , and capacitance are all continuous functions of u , similarly as in the 0-zone for $w > 0$ [the solid lines in Figs. 3(b)–3(d)]. Here, however, the capacitance shows a *transformation* (not a transition) between one- and two-peak shapes, which we had not observed for positive w . This behavior can be understood as follows: At small voltages, the system has to overcome an energy barrier for the ions to enter a pore; the potential at which this happens corresponds to the first peak. The second peak appears above a threshold voltage at which the system overcomes an unfavorable interaction between the ions of the same sign; this threshold voltage decreases for decreasing I so that the first and the second peaks merge into a single peak at low values of I . Clearly, no energy barrier exists for ions to enter an ionophilic pore; hence, only one peak is observed in that case [the solid line in Fig. 3(d)].

In zone 2, the capacitance shows a similar two-peak behavior [blue long-dashed line in Fig. 4(d)]. In this case, however, charging is discontinuous at two second-order phase transitions, as the system experiences a transition from the disordered to the ordered phase and then *re-enters* the disordered phase for increasing voltage. After the onset of the first transition, both counterions and coions enter a pore, in response to the applied potential,

as evidenced by the charging parameter X_D , which becomes larger than unity [Fig. 4(c)]. At the transition voltage, the system overcomes an energy barrier for ions to enter the pore (similarly as for $\beta I = 1.5$, see the red short-dashed lines in Fig. 4), and both sorts of ions are adsorbed into the pore, likely in order for the ions to be able to form an “antiferromagnetic” type of ordering. Interestingly, the total ion density and hence the charge do not change appreciably within the ordered phase, which is possible because the excess ions would distort the ordered phase. This, in fact, occurs at the second transition [at $\beta eu \approx 9.4$, see the squares in Figs. 3(b) and 3(c)].

2. Zone 3

We first note that in zone 3 (and in zone 1, not shown), despite the negative transfer energies ($w < 0$), a pore is nearly fully occupied by ions at $u = 0$ [Fig. 5(b)]. This is because of the strong interaction between the ions of the opposite sign (i.e., large βI), which promotes the formation of an ordered phase, characterized by a high density. However, as the voltage increases, *both* types of ions are expelled from the pore, as manifested by *negative* $X_D < 1$ [Fig. 5(c)], so that the pore becomes effectively ionophobic. This process is characterized by a drastic jump in the total ion density [Fig. 5(b)] and by a deltalike peak in the charging parameter [$X_D \rightarrow -\infty$ at the transition, which occurs at $\beta eu \approx 1.9$, Fig. 5(c), not shown for clarity].

After having expelled both co- and counterions, the charging proceeds via *coadsorption* of cations and anions, i.e., both types of ions are adsorbed into the pore again, but in a different

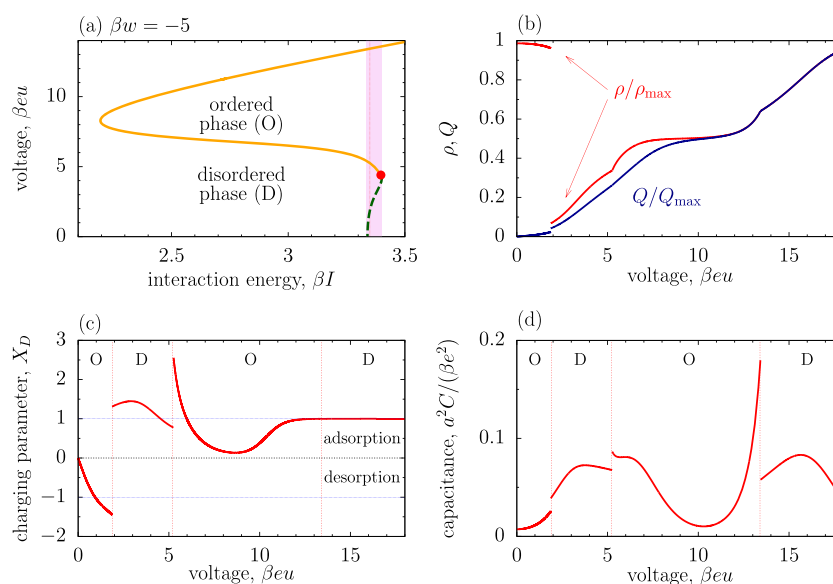


FIG. 5. Capacitive, charging, and phase behavior of a superionic liquid in zone 3 with $\beta w = -5$. (a) Phase diagram in the (I, u) plane, where I is the ion-ion interaction parameter and u is the applied voltage. Ordered (O) and disordered (D) phases are separated by a line of second-order transitions (solid line) and by a line of first-order transitions (dashed line), which meet at a tricritical point (full circle). The thin vertical line shows the value of $\beta I = 3.25$ used in (b)–(d). The shaded region denotes zone 3. (b) Accumulated charge and total ion density, (c) differential charging parameter X_D , and (d) differential capacitance as functions of voltage for $\beta I = 3.35$. Thin vertical lines denote the locations of the transitions. Voltage is measured in units of thermal voltage $(\beta e)^{-1}$ (≈ 26 mV at room temperature), and capacitance is measured in units of thermal electric capacitance⁸⁸ $(\beta e^2 \approx 6.2$ aF at room temperature) per a^2 , where a is the lattice constant; for $a = 1$ nm, one has $\beta e^2/a^2 \approx 620$ $\mu\text{F}/\text{cm}^2$.

proportion. This process is amplified when the system *re-enters* the ordered phase [note high $X_D > 1$ above the transition at $\beta eu \approx 5.2$, Fig. 5(c)]. This is likely because more coions are required to form an ordered phase than that present in the pore at the transition. As the voltage increases further, these excess coions are removed from the pore via swapping ($0 < X_D < 1$), and eventually, the system *re-enters* the final, disordered phase via another second-order phase transition.

This charging behavior manifests itself in the voltage dependence of the differential capacitance, which exhibits three jumps in the course of charging [Fig. 5(d)]. It is particularly interesting to point out a relatively low capacitance in the ordered phase around $\beta eu \approx 10$, where the main charging mechanism is swapping [$X_D \approx 0$, Fig. 5(c)]. In contrast, above the third transition (which is at $\beta eu \approx 13.3$), the charging is solely due to counterion adsorption and is characterized by a relatively high capacitance. This might seem to be in disagreement with the reasoning presented in Ref. 88, where adsorption has been shown to provide the lowest capacitance, and swapping and desorption the highest (this is due to an additional entropic costs associated with the counterion adsorption). In the present case, however, swapping occurs within the (“antiferromagnetically”) ordered phase, and hence, the system has to overcome an additional barrier of breaking this order, which leads to low capacitances (such ordering effects have not been taken into account in Ref. 88).

Thus, zone 3 appears to be a spectacular region, showing remarkably rich voltage-induced phase and capacitive behavior. We note, however, that it lies in a very narrow domain of I and w and it might be difficult to detect it in experiments or by simulations.

IV. CONCLUSIONS

We have presented a simple model [Eq. (1)] for ionic liquids (ILs) confined to narrow slit-shaped metallic nanopores of nanostructured electrodes, termed superionic liquids. The model was solved *exactly* on a Bethe lattice with coordination number $q = 3$ (Fig. 1). The obtained solutions allowed us to calculate the complete phase diagram of superionic liquids in the space of ion-ion interaction energy, the energy of transfer of ions from a nanopore into the bulk electrolyte, and the potential applied at the pore walls with respect to the bulk. The phase diagram consists of ordered and disordered phases [Figs. 1(b) and 1(c)], separated by surfaces of first- and second-order phase transitions, and a line of tricritical points (Fig. 2).

Most interesting and relevant to supercapacitors is the behavior of confined ILs with the applied potential. We have identified four zones, corresponding to the number of phase transitions experienced by an IL for increasing voltage (called zones 0–3). While for conventional ionophilic pores, we found either no transition (zone 0) or a single second-order order-disorder transition (zone 1, see Fig. 3), the phase behavior in ionophobic pores turned out to be far more interesting. In this case, charging can also proceed smoothly without transition; however, in some range of parameters, we revealed the emergence of two types of *re-entrant* behavior. In zone 2, the system is in the disordered state at zero potential and undergoes a second-order phase transition to the ordered phase, as the voltage increases; then, there is a second (second-order) phase transition to the disordered phase at a higher voltage (Fig. 4). In zone 3, the behavior is even richer as the system undergoes three

transitions: From the ordered to disordered phase, then back to the ordered one, and finally to the disordered phase at a high potential (Fig. 5).

This variety of phase transitions is reflected in the charging behavior. For ionophilic pores, we found that the capacitance can be either a continuous function of voltage or experience a divergence in the case of a second-order transition [Fig. 3(d)]. For ionophobic pores, charging is again more interesting. We revealed a *transformation* (not a transition) between the shapes with one and two peaks in the capacitance-voltage curves, which can be linked to the ionophobic nature of the pores and appears because the ions have to overcome an energy barrier due to ionophobicity and another one related to the unfavorable interactions between coions.⁹⁰ In the case when the system experiences two second-order transitions (zone 2), there are additionally two singularities in the capacitance [Fig. 4(d)]; in zone 3, there are three such singularities [Fig. 5(d)].

It is also interesting to note that charging of ionophobic pores often proceeds in a manner in which both types of ions are adsorbed into or removed from a pore. This is manifested by the behavior of the charging parameter, which becomes larger than unity or smaller than -1 , respectively [see Eq. (6) and Figs. 4(c) and 5(c)].

It is known that ordered phases typically exhibit sluggish dynamics, particularly ordered or quasicrystalline ionic liquids in slit nanopores.^{21,51,52} The knowledge of the parameter space corresponding to such phases may guide to avoid a potential slowdown of charging. Clearly, the precise location of the ordered phases in real systems will be affected by many factors, which we have neglected in our model, such as ion-size asymmetry, pore-wall roughness, ion polarizability, etc. (see Sec. II C). However, as most analytical models, our model can serve as a reference point for a further, and more detailed, investigation of superionic liquids and, in particular, of the influence of ordering and phase transitions on charging dynamics.

To solve our model analytically, we have used the Bethe-lattice approach, which assumes that the ions reside on the sites of a Bethe lattice. In this formulation, the partition function, and hence all charging characteristics, can be evaluated *exactly*. We thus expect that our theory captures properly the essential physics of ionic liquids in conducting slit nanoconfinements. However, as we discussed in Sec. II C, our model neglects a number of important aspects of real nanoporous electrodes. In particular, we assumed that an electrode consists of monodisperse perfectly conducting ultranarrow slit pores, while typical electrodes are often random porous media fabricated from carbon.^{83–87} This might make an experimental validation of our predictions currently challenging. Nevertheless, the recent progress in low-dimensional porous materials with well-defined pore structure^{7–13} seems promising in developing the electrodes suitable for our predictions to be tested. We, therefore, hope that the theory presented in this work will guide the future experiments, providing new physical insights into the charge storage in narrow nanoconfinements.

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APPENDIX: DETAILS OF CALCULATIONS

Since the Bethe-lattice calculations for nonzero voltage, $u \neq 0$, are similar to the case $u = 0$, we describe them only briefly and refer an interested reader to Ref. 50, where they have been discussed at length.

For a Cayley tree [Figs. 1(b) and 1(c)] with q branches emanating from the root site, the partition function for model (1) is $\Xi = \lim_{N \rightarrow \infty} \Xi_N$, where N is the number of generations in the Cayley tree and

$$\Xi_N = g_N^q(0) + z_+ g_N^q(+) + z_- g_N^q(-), \quad (\text{A1})$$

where $z_{\pm} = \exp \beta h_{\pm}$, with $h_{\pm}$ given by Eq. (2), and $g_N(0)$ and $g_N(\pm)$ are the partition functions of a branch with the root site being vacant and branches with the root sites being occupied by $\pm$ ions, respectively.

Since each branch consists of $q - 1$ identical sub-branches, one can write the following recursion relations for g_N :

$$\begin{aligned} g_N(0) &= g_{N-1}^{q-1}(0) + z_+ g_{N-1}^{q-1}(+) + z_- g_{N-1}^{q-1}(-), \\ g_N(+) &= g_{N-1}^{q-1}(0) + z_+ e^{-\beta I} g_{N-1}^{q-1}(+) + z_- e^{\beta I} g_{N-1}^{q-1}(-), \\ g_N(-) &= g_{N-1}^{q-1}(0) + z_+ e^{\beta I} g_{N-1}^{q-1}(+) + z_- e^{-\beta I} g_{N-1}^{q-1}(-). \end{aligned} \quad (\text{A2})$$

By introducing new variables,

$$x_N = \frac{g_N(+)}{g_N(0)} \quad \text{and} \quad y_N = \frac{g_N(-)}{g_N(0)}, \quad (\text{A3})$$

one gets a system of two coupled recursion relations

$$\begin{aligned} x_N &= \frac{1 + z_+ e^{-\beta I} x_{N-1}^{q-1} + z_- e^{\beta I} y_{N-1}^{q-1}}{1 + z_+ x_{N-1}^{q-1} + z_- y_{N-1}^{q-1}}, \\ y_N &= \frac{1 + z_+ e^{\beta I} x_{N-1}^{q-1} + z_- e^{-\beta I} y_{N-1}^{q-1}}{1 + z_+ x_{N-1}^{q-1} + z_- y_{N-1}^{q-1}}. \end{aligned} \quad (\text{A4})$$

In the interior part of the Cayley tree, and in the limit $N \rightarrow \infty$, i.e., *on the Bethe lattice*,⁹¹ all sites are equivalent and hence all $\{x_N, y_N\}$ converge to a fixed point or cycle solutions $\{x, y\}$. In this case, excluding the effects of boundary sites by following the procedure of Ref. 92 (see also Ref. 93), we have obtained for the *bulk* free energy per site,⁵⁰

$$-\beta f = \frac{q}{2} \ln(1 + z_+ x^{q-1} + z_- y^{q-1}) - \frac{q-2}{2} \ln(1 + z_+ x^q + z_- y^q). \quad (\text{A5})$$

To take into account the bipartite nature of the Cayley tree, we modified our description to include *sublattices* A and B . Then, instead of Eq. (A4), one has, taking additionally the limit $N \rightarrow \infty$,

$$x_A = \frac{1 + e^w (e^{-I+eu} x_B^{q-1} + e^{-I-eu} y_B^{q-1})}{1 + e^w (e^{eu} x_B^{q-1} + e^{-eu} y_B^{q-1})}, \quad (A6)$$

$$y_A = \frac{1 + e^w (e^{I+eu} x_B^{q-1} + e^{-I-eu} y_B^{q-1})}{1 + e^w (e^{eu} x_B^{q-1} + e^{-eu} y_B^{q-1})},$$

$$x_B = \frac{1 + e^w (e^{-I+eu} x_A^{q-1} + e^{-I-eu} y_A^{q-1})}{1 + e^w (e^{eu} x_A^{q-1} + e^{-eu} y_A^{q-1})}, \quad (A7)$$

$$y_B = \frac{1 + e^w (e^{I+eu} x_A^{q-1} + e^{-I-eu} y_A^{q-1})}{1 + e^w (e^{eu} x_A^{q-1} + e^{-eu} y_A^{q-1})},$$

where we have taken into account the explicit expression for $z_{\pm}$ and assumed $w_+ = w_- = w$. The free energy of the full system is $[f(x_A, y_A) + f(x_B, y_B)]/2$, with expression for $f(x, y)$ given by Eq. (A5). To find x_A, y_A, x_B , and y_B , we have solved Eqs. (A6) and (A7) with $q = 3$ ³⁷ numerically using Mathematica.

1. Ordered and disordered phases

Similarly as in the case of zero voltage,⁵⁰ there are two stable thermodynamic phases for $u \neq 0$, namely:

1. *Disordered phase*, described by $x_A = x_B, y_A = y_B$ [Fig. 1(b)]. The solution for the disordered phase can be obtained from Eq. (A6) by putting $x_B = x_A$ and $y_B = y_A$. Equation (A7) is not needed.
2. *Ordered phase* with $x_A \neq x_B$ and $y_A \neq y_B$ [Fig. 1(c)]. In this case, all four equations, Eqs. (A6) and (A7), must be solved.

Examples of the Bethe-lattice solution for $q = 3$ and for $\beta eu = 0.5$ and two values of I are shown in Fig. 6. Figure 6(a) shows x_A as a function of the transfer energy βw for $\beta I = 1.7$, at which there is a *second-order* phase transition between the ordered and disordered phases. For low values of w , there is no ordering in the system (i.e., $x_A = x_B$ and $y_A = y_B$), but with increasing w to a critical value $\beta w \approx -2.44$ (the crossing point between the two lines in Fig. 6(a), denoted by the symbol), another solution emerges with $x_A \neq x_B$ and $y_A \neq y_B$, which corresponds to the ordered phase (the solution corresponding to the disordered phase becomes unstable).

Figure 6(b) illustrates the case of a first-order phase transition ($\beta I = 2.3$). In the vicinity of the crossing point between two lines in Fig. 6(b), the solution for the ordered phase is *multivalued*. The value of w at which the transition occurs can be found by matching the

free energies (A5) of the disordered and ordered phases [$\beta w \approx -3.4$, denoted by the thin vertical line in Fig. 6(b)].

The above-described procedure has been used to calculate the phase diagrams in Figs. 2–5.

2. Thermodynamic quantities and charging characteristics

The average densities of $\pm$ ions on the root (central) site of the Cayley tree can be obtained via the variables x_N and y_N as follows:⁵⁰

$$\rho_{0,+} = \frac{z_+ x_N^q}{1 + z_+ x_N^q + z_- y_N^q}, \quad \rho_{0,-} = \frac{z_- y_N^q}{1 + z_+ x_N^q + z_- y_N^q}. \quad (A8)$$

Assuming that the central site belongs to sublattice A, Eq. (A8) gives for the average density of ions on sublattice A (in the limit $N \rightarrow \infty$)

$$\rho_+^A = \frac{z_+ x_A^q}{1 + z_+ x_A^q + z_- y_A^q}, \quad \rho_-^A = \frac{z_- y_A^q}{1 + z_+ x_A^q + z_- y_A^q}. \quad (A9)$$

If the central site belongs to sublattice B, the expression for the average density can be obtained from Eq. (A9) by interchanging the indices $A \leftrightarrow B$.

The total ion density and the charge density (in units of the elementary charge e) on sublattice A are

$$\rho^A = (\rho_+^A + \rho_-^A), \quad \delta \rho^A = (\rho_+^A - \rho_-^A) \quad (A10)$$

and similarly for sublattice B. For the whole system, one obviously has

$$\rho = \frac{\rho^A + \rho^B}{2}, \quad \delta \rho = \frac{\delta \rho^A + \delta \rho^B}{2}. \quad (A11)$$

The charge accumulated in a nanopore is [see Eq. (4)]

$$Q = e \delta \rho, \quad (A12)$$

and hence, the differential capacitance [see Eq. (5)]

$$C = \frac{dQ}{du} = e \frac{d \delta \rho}{du} \quad (A13)$$

and the charging parameter [see Eq. (6)]

$$X_D = \frac{e}{C} \frac{d \rho}{du}. \quad (A14)$$

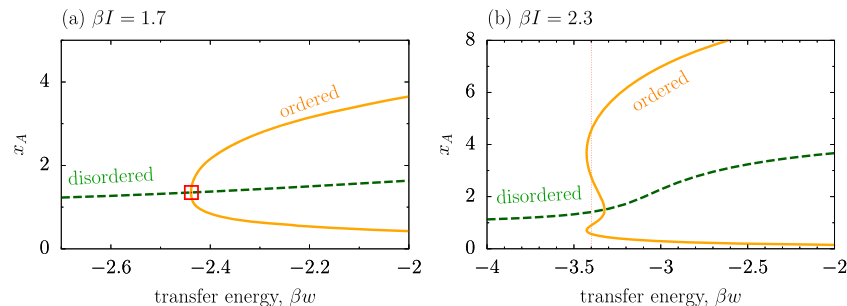


FIG. 6. Bethe-lattice solutions for the ordered and disordered phases. (a) Solutions for disordered (dashed line) and ordered (solid line) phases for $\beta eu = 0.5$ and $\beta I = 1.7$. The crossing point between two lines (denoted by the symbol) determines the location of the second-order phase transition. (b) The same but for $\beta I = 2.3$, at which the transition is of first order. The location of the transition is determined by comparing the free energies of the ordered and disordered phases (thin vertical line).

To calculate these quantities analytically, it is convenient to rewrite Eqs. (A6) and (A7) with $q = 3$ as

$$\begin{aligned}x_{A+}^2 &= \frac{(1-\lambda)(1-x_B) + \lambda(1-y_B)}{x_B + y_B - 2 \cosh(\beta I)}, \\ y_{A-}^2 &= \frac{(1-\lambda)(1-y_B) + \lambda(1-x_B)}{x_B + y_B - 2 \cosh(\beta I)},\end{aligned}\quad (\text{A15})$$

$$\begin{aligned}x_{B+}^2 &= \frac{(1-\lambda)(1-x_A) + \lambda(1-y_A)}{x_A + y_A - 2 \cosh(\beta I)}, \\ y_{B-}^2 &= \frac{(1-\lambda)(1-y_A) + \lambda(1-x_A)}{x_A + y_A - 2 \cosh(\beta I)},\end{aligned}\quad (\text{A16})$$

where $\lambda = e^{\beta I}/(1 + e^{\beta I})$. Plugging these expressions into Eq. (A11), one finds

$$\delta\rho = 1/2 \frac{x_A + x_B - y_A - y_B + 2(\lambda - 1)(x_A x_B - y_A y_B)}{x_A + x_B + y_A + y_B + (\lambda - 1)(x_A x_B + y_A y_B) - \lambda(x_A y_B + x_B y_A) - 2 \cosh(\beta I)} \quad (\text{A17})$$

and

$$\rho = 1/2 \frac{x_A + x_B + y_A + y_B + 2(\lambda - 1)(x_A x_B + y_A y_B) - 2\lambda(x_A y_B + x_B y_A)}{x_A + x_B + y_A + y_B + (\lambda - 1)(x_A x_B + y_A y_B) - \lambda(x_A y_B + x_B y_A) - 2 \cosh(\beta I)}. \quad (\text{A18})$$

To calculate the differential capacitance [Eq. (A13)] and charging parameter [Eq. (A14)], one needs the derivatives dx_A/du , dy_A/du , dx_B/du , and dy_B/du . They can be obtained by differentiating both sides of Eqs. (A15) and (A16) with respect to u and then solving the resulting system of equations for the corresponding derivatives numerically.

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