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The simplest model of charge storage in single file metallic nanopores

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The problem of voltage controlled accumulation of ions in a narrow nanopore, which can accommodate just one row of ions of an ionic liquid and is filled with ions when the electrode is unpolarised, is mapped on an exactly solvable one-dimensional two state Ising model. Analytical solution of this, presumably simplest, statistical mechanical model reveals the dependence of the electrical capacitance on voltage, pore radius, and temperature. The voltage dependence of capacitance has the character of a smeared resonance, whose position and height is affected by a tiny change of the pore radius. Consequently, even the slightest dispersion of pore radii in the whole electrode, unavoidable in any real system, softens the voltage dependence.

Introduction

Electrochemistry has matured as a physical discipline from the studies of electrical double layer and electrode kinetics at well defined electrodes. In the first half of the 20th century these were liquid metals, such as Hg, with a pure, smooth, self healing atomically flat surface.[1] Such metals were not of great interest for practical applications, and the next big step forward, in the 1970s, was moving to another class of well characterised electrodes – single crystal electrodes, predominantly of noble metals, such as Pt, Ag, and Au.[2] This is how ‘electrochemical surface science’ was born[3,4] and a number of elementary processes at the electrode–electrolyte interface were understood.

On the other hand, because all the events in any industrially important electrochemical processes normally take place at the electrode–electrolyte interface, one generally tends to maximise the interfacial area. In electrochemical engineering, since the middle of the previous century, the use of ‘volume filling’ surfaces, achievable for highly porous electrodes, was mainstream for batteries, fuel cells, or supercapacitors.[5–8] Later, the discovery of various forms of carbon has opened new horizons for engineering nanoporous electrodes of well controlled volume-filling structures, with the surface area many orders of magnitude larger than the projection area.[9,10] For instance, using such electrodes

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for supercapacitors, where the electrical energy is stored in a form of a charge accumulated in electrical double layers, allows to scale up energy storage proportionally to the hugely enhanced interfacial area.[11,12]

A standard way to increase the electrode–electrolyte interface is to decrease the characteristic size of the pores, still accessible to the electrolyte, simultaneously decreasing the thickness of pore walls – altogether increasing the porosity of the electrodes. It was recently found, moreover, that the capacitance *per true unit surface area* increases with pore size, down to the size below which ions can no longer penetrate pores. The effect has been observed both for solvated ions in organic solvents[13] and solvent-free ionic liquids.[14] Although the existence of this effect has been recently questioned[15] on the grounds of possible inaccuracies of the determination of the true internal surface area,[16] the common opinion is that, although there may be some variance in the strength of this effect, qualitatively it will remain valid, *i.e.* the experiments of ref. 13 and 14 demonstrate a real phenomenon, but not an artifact [*cf.* also ref. 17 and 18].

Explanation of this effect was suggested in ref. 19 and 20 on the basis of the following idea. The Coulomb interaction inside a nanoscale pore in an electronically conducting material is exponentially screened, with the decay length proportional to the pore width or radius. The exact laws are different for different pore geometries, *e.g.* cylindrical or slit-like, but the qualitative consequences of such enhanced screening are the same. Pair interaction energies for large ionic liquid ions (or solvated inorganic ions) in a pore of a diameter that is only slightly larger than the diameter of an ion (plus its solvation shell, if applicable) will be just about a couple of k_BT for the nearest neighbors. Interaction of the next nearest neighbors will be less important, and negligible for narrow nanopores. Such suppression of Coulomb interactions allows unbinding of cation–anion pairs packing inside the pore of counterions of predominantly one sign, when polarising the electrode. The findings of ref. 19 based on a mean-field theory and obtained for slit pores have been verified by computer simulations[20] performed in the same geometry of the pores. In the simulations, some features of the capacitance–voltage dependence appeared to be smoothened, but otherwise these simulations approved the qualitative consequences of the enhanced screening in metallic nano-confinement. Some of those findings (effect of pore radius) have been recently confirmed by more involved atomistic molecular dynamic simulations.[21]

The state of ions in the pore in which their Coulomb interactions are replaced by Yukawa-like interactions[22,23] with the decay range proportional to but a few times smaller than the pore width was called a '*superionic state*'.[19,20] The term depicted the ability of ions of the same sign to stay close to each other due to the interaction with polarisable metallic pore walls. Consequently, such a state allows packing into a pore more ions of the same sign for a given voltage, enhancing thereby the capacitance of the pore per unit surface area. With the increase of the pore width, the Coulomb interactions become less screened and the capacitance goes down, as in the experiments of ref. 14.

If one further increases the pore size, a second layer of counterions will be able to sneak into the pore, and this will increase the capacitance. However, further increasing the width of a slit or radius of a cylindrical pore before letting a third layer/line to build up inside the pore will tend to decrease the capacitance. This is because the screening of electrostatic interactions will, as explained above, get weaker and the capacitance will start to go down again. And off these alternations go for a while, leading to decaying ‘oscillations’ of capacitance as a function of the pore size, as was first found in ref. 24–26.

The voltage dependence of the specific capacitance of nanoporous electrodes is a separate important issue that was first analyzed theoretically in ref. 19, 20 and 27. The results revealed a dramatic dependence of the capacitance–voltage curves on the nanopore width. This effect was later shown to have important consequences for the choice of the pore size for maximising energy storage.[28]

On the other hand, the power of the capacitor is determined by how fast we can charge/discharge the pore. Energy capacity and the speed of charging are generally competing with each other.[29] Energy storage scales up with the surface area. The surface area increases with the length of the pores and with the decrease of their radius, as one may then have more pores per projection surface area. But the longer the pores, the more time it will take to transport the ions to fully charge them. Energy storage devices are characterised by Ragone plots: the deliverable power *vs.* the storable energy, and relative to batteries, modern supercapacitors lie on this diagram towards higher power, but lower energy. In batteries, the rate-limiting step is, in most cases, the elementary act of electrochemical reaction. Because of that, they charge and discharge much slower than supercapacitors, in which the reaction stage is absent and where the end task is gathering the counterions at the corresponding electrode; in the case of a porous electrode, inside that electrode. With that picture in mind, the baseline for the development of supercapacitors is the increase of the energy storage per unit volume/weight of the device at, however, minimal losses in the power delivery.

Leaving the kinetics of nanoporous electrodes for a separate study[30,31] let us concentrate on the electrical capacitance of porous electrodes, important for the energy capacity.[29,28] Earlier reported models and simulations[19–21,24–28] were instrumental for understanding the capacitance behavior of nanoporous electrodes, but the studies based on them are numerical in implementation. Can one work out some simple model that could lead to a *transparent*, *analytical*, *tutorial textbook-like formula*, which would illuminate the main features of the capacitance dependence on voltage and the pore-size dependence? Such a model is possible for a particular case which has its own, although limited, relevance. Namely, for the capacitance of ultra narrow quasi single-file pores, in which the ions may be assumed to settle at or close to the main axis of a pore that can accommodate just one row of ions, whose arrangement in the pore can be considered as one dimensional, as sketched in Fig. 1. We present this model for the case of a pure, solvent-free ionic liquid, which will be restricted even further, subject to the assumptions formulated below.

The model

Basic assumptions

1. There is a propensity for cations and anions to occupy the pore in the electrode, even when the latter is not polarised. When it becomes polarised, co-ions will tend to be replaced by counterions.[32]

2. This propensity for ions to fill the pore is so strong that a non-polarised pore is densely packed with ions, with no empty voids between them. This simplification may not generally be valid; the more general case is mathematically more sophisticated and is to be studied.

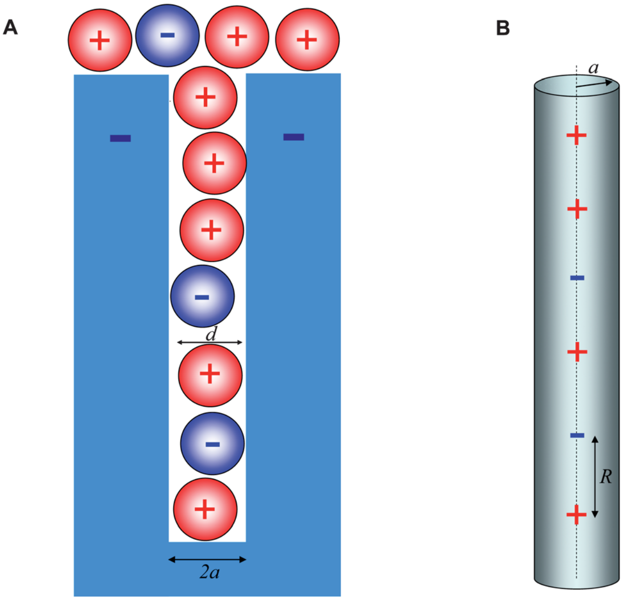

Fig. 1 A 'single-file' pore in a (negatively) polarised electrode: (A) a schematic cross-section, (B) a one dimensional lattice representation of distribution of ions. The pore is assumed to accommodate, roughly, one line of ions, ($d < 2a < 2d$).

3. Electrostatic interactions of ions in the pore are screened by the electronic polarisation of pore walls, and only the interactions of the nearest neighbors must be taken into account.

The study of this simple case results in a compact analytical formula for capacitance, which has a number of lessening consequences. Before formulating the model mathematically, we need to substantiate and discuss the last assumption.

Interionic interaction potential

Electrostatic interaction between charges in a cylindrical pore inside a metal is a classical problem of electrostatics, solved long ago (see *e.g.* a textbook[33]). For two unit point charges $U(R)$ sitting on an axis of a pore of radius a at a distance R from each other, the interaction energy scaled to the thermal energy, k_BT, is given by

$$\frac{U(R)}{k_BT} = \pm\frac{L_B}{R}\left\{1 - \frac{2}{\pi}\int_0^\infty \frac{dx}{I_0(x)^2}\frac{\sin[(R/a)x]}{x}\right\}. \tag{1}$$

Here ± corresponds to the interaction of ions of the same or opposite sign, respectively. L_B is the Bjerrum length; in Gaussian units used throughout the paper, $L_B = e^2/\varepsilon k_BT$, where e is the elementary charge and ε the effective dielectric constant inside the pore due to electronic polarisability of ions (if we assume the latter to be ≈ 2, at room temperature $L_B \approx 28$ nm). $I_0(x)$ is the modified cylindrical Bessel function of zero order. Using residue theory, the integral in the r.h.s. was calculated exactly to give the result in the form of a series,

$$\frac{U(R)}{k_{\mathrm{B}}T} = \pm 2\frac{L_{\mathrm{B}}}{a}\sum_{m=1}^{\infty}\frac{e^{-\frac{k_m R}{a}}}{k_m[J_1(k_m)]^2}. \tag{2}$$

Here $J_1(k_m)$ is the first order cylindrical Bessel function and k_m are zeros of Bessel function of zero order, $J_o(k_m) = 0$; hence $k_1 = 2.4$; $J_1(y_1) = 0.52$; $k_2 = 5.52$, $J_1(y_2) = -0.34$, …[34] Notably, for $R > a$ it is sufficient to keep only the first term of the series,

$$\frac{U(R)}{k_{\mathrm{B}}T} \underset{R>a}{\approx} \pm 3.08\frac{L_{\mathrm{B}}}{a}\exp\left\{-\frac{R}{(a/2.4)}\right\}. \tag{3}$$

Fig. 2 shows that this approximation works amazingly well. Thus, interaction in a cylindrical pore with metallic walls decays exponentially with the decay length $a/2.4$.

It is also interesting to compare the interaction potentials in a cylindrical pore and the one in a flat gap (employed in the theory of charge accumulation in slit pores[19,20]). Fig. 3 shows this comparison using the asymptotic laws, perfectly sufficient for this study.

In both cases the screening is exponential, but in a cylindrical pore it is stronger than in a slit pore, because in a cylindrical pore the interacting charges are surrounded by metal ‘from all sides’.[35] In a cylindrical pore, the decay range is 1/4.8 of the pore diameter, whereas in a slit pore it is 1/3.14 of the pore width.

Exponential screening in a nanogap or nanopore is a result of the infinite set of image charges that counterbalance the charges inside the nanopore. The importance of this effect in the theory of adsorption at a flat electrode has been studied decades ago (for review see ref. 1); their role in the double layer theory at

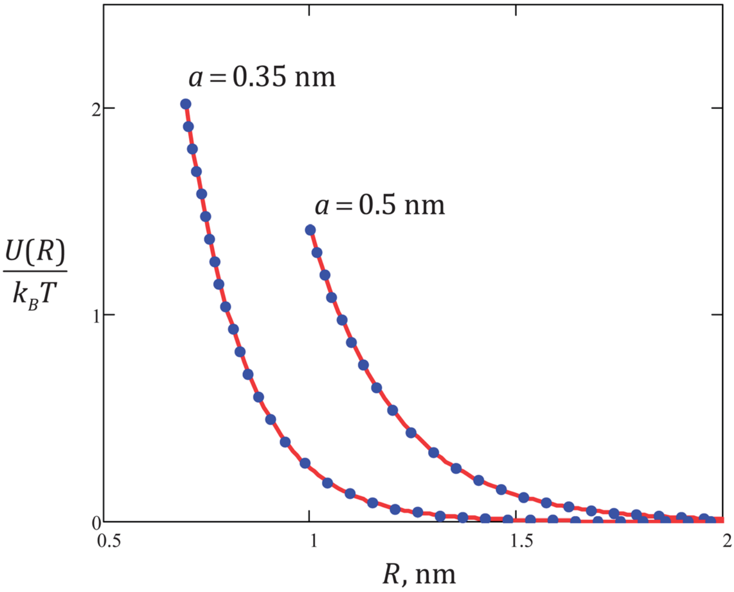

Fig. 2 Interaction potential scaled to thermal energy: comparison between the exact eqn (1) (lines), and its asymptotic form (dots), eqn (3). The graphs were plotted for two indicated pore radii, a, with the absolute values determined by $L_{\mathrm{B}} \approx 28$ nm. For each of the two cases the results are shown down to distances of the pore diameter, $R = 2a$.

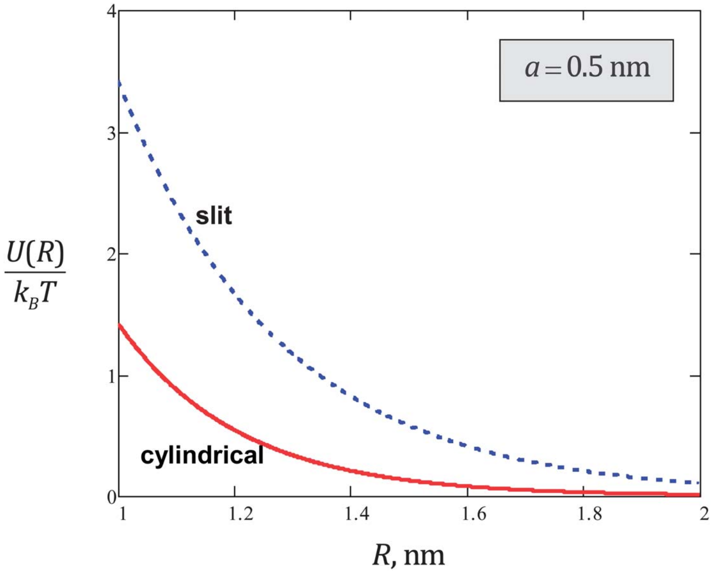

Fig. 3 Comparison of the interaction potentials in a cylindrical pore of *radius a* and a slit pore of *half-width a*. The plots calculated using eqn (3) for cylindrical and $\frac{U(R)}{k_\mathrm{B}T} \simeq 2\frac{L_\mathrm{B}}{\sqrt{aR}}\exp\left\{-\frac{R}{2a/\pi}\right\}$ for slit pore[19] geometry.

flat interfaces has recently been emphasised and explored in ref. 36 and 37. Note that the effect of image charges in gap geometry is much stronger than at a flat interface. Indeed, a charge located at distance a near a flat interface, creates one mirror image of opposite sign in the metal at point $-a$; the charge and its image create together a potential which at long distances $R > a$ takes the form of an effective dipole-type potential $e\,\frac{2a^2}{\varepsilon R^3}$ instead of the Coulomb potential $e\,\frac{1}{\varepsilon R}$. It is the multiple set of image charges that emerge in the metal in a pore geometry that provide a much stronger, exponential screening.

Effects of the field penetration into the massive metal plates, which we did not touch above, has been intensively studied in the past both at the interface and in the flat gap geometry (see *e.g.* ref. 1 and 38–40). Unless $\varepsilon \gg 1$, all these effects effectively extend distance a, but otherwise they will lead to very nontrivial consequences.[38,41,42] In our problem, $\varepsilon \approx 2$ and such consequences will be of no or minor importance.

Mapping the problem on a 1-dimensional Ising model

Considering the dense packing of cations and anions of the same size, we may assume the 1d lattice constant to be equal to their diameter. Had they been of different size, the lattice constant would be voltage dependent. For instance, in a typical case of ionic liquids with cations larger than anions, when the pore is occupied predominantly by cations, the lattice constant will be larger than when the pore is packed with anions. We will not consider this complication in this study.

The idea of the model is sketched in Fig. 4. It uses the lexicon of spin models, standard in statistical mechanics.[43] When the site i of the 1d lattice is occupied by a cation it is assigned the value of 'spin' $S_i = 1$, when it is an anion, $S_i = -1$ (as mentioned in the introduction of the model, the sites are assumed to be always occupied by either cations or anions).

The Hamiltonian of the system (in the units of k_BT) can be written in terms of a *one-dimensional Ising model with nearest neighbour interaction between 'spins' in the presence of an external 'field'*[41]

$$\frac{H}{k_B T} = \sum_i \left\{ \frac{\alpha}{2}(S_i S_{i+1} + S_i S_{i-1}) + uS_i \right\}, \tag{4}$$

where the coupling constant characterising interactions of the neighbouring 'spins'

$$\alpha = |U(d)|/k_B T \tag{5}$$

with d, the ion diameter, taken the lattice constant.

Subject to eqn (3) $U(2d) \approx U(d)\exp\{-2.4\ d/a\}$. Since in the case we are considering in our model, $d < 2a < 2d$, *i.e.* the pore can accommodate ions but only one row of ions, the assumption of the nearest neighbour interactions is well justified.

The first item under the sum in eqn (4) favors cations and anions to neighbour each other. The last term, u, is the electrostatic potential drop between the electrode and the bulk of electrolyte, again taken in the units of k_BT/e (at room temperature $k_BT/e \approx 25.6$ mV). The value of u is constant across and along the pore. This term favours occupation of the sites in the pore by counterions and expulsion of co-ions from the pore.

Recall that in the theory of magnetism, α (often denoted there by letter J) is the so called spin-coupling parameter, which characterises interactions of real magnetic spins of atoms; $\alpha > 0$ favours antiferromagnetic order, whereas $\alpha < 0$ corresponds to ferromagnetic order; u characterises the interaction of spins with the external magnetic field.[43] In our problem $\alpha > 0$, because the anion–cation

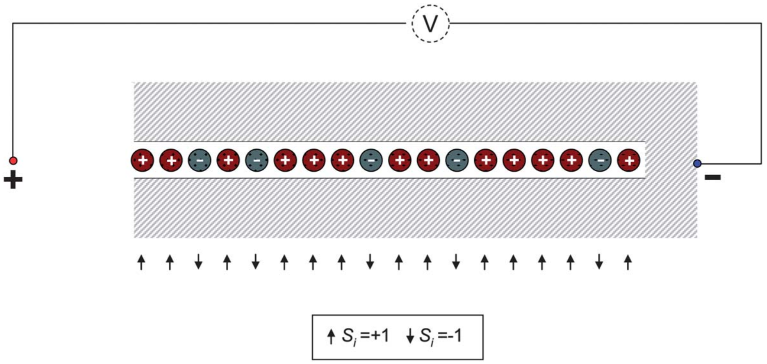

Fig. 4 1d spin description of the occupation of a cylindrical pore. Each site of a 1d lattice is occupied either by a cation (the state with spin +1) or anion (the state with spin −1). Voltage is controlled relative to the exterior of the pore. Nonzero polarisation of the electrode favors one of the spin-states over the other for each site. In this sketch the electrode is negatively polarised and spin +1 states are more favourable. The temperature tends to smear up this trend favoring equal distribution of spin +1 and spin −1 states.

pairs of neighbours are favoured (analogy with anti-ferromagnetism); a nonzero voltage u competes with that trend, at very large voltage the pore will contain only ions of one sign – the counterions. Note that in our problem u is the voltage, not electric field.

If the ions have different propensity to settle in an unpolarised pore due to specific interaction with the walls depending on the sort of ions, u must be replaced by

$$u \Rightarrow \tilde{u} = u - w \tag{6}$$

where $-w$ is half of the difference between the free energy of transfer of a cation and of an anion from the bulk into the interior of the pore, scaled to k_BT. $w > 0$ would mean preferential adsorption of cations.

The value of w will be affected by the difference in the size of cations and anions, but it may be nonzero even if they are of the same size, but of different chemical nature. Consideration of ions of different size will require a more sophisticated model, because the size of the ions enters the model only through the voltage-independent lattice constant. The simplest extension of the model will be making the lattice constant voltage-dependent, as the distance of closest approach between cations, between anions, and between cations and anions may be different. The corresponding extension of the model will be considered elsewhere. Here, we will still adopt correction (6) reminding ourselves that the value of w may be, generally, nonzero, even for the simplest case considered below.

Exact solution

General equations of the model. The expression for differential capacitance

The 1d Ising model with nearest neighbour interactions in an external field has a simple exact solution described in textbooks. Namely, the statistically averaged value of ‘spin’ is given by,[44]

$$\langle S_i \rangle = -\frac{\sinh(u-w)}{\sqrt{[\sinh(u-w)]^2 + e^{4\alpha}}} \tag{7}$$

The derivative

$$\chi(u) = \frac{d\langle S_i \rangle}{du} = -\frac{e^{-2\alpha}\cosh(u-w)}{\left\{1 + e^{-4\alpha}[\sinh(u-w)]^2\right\}^{3/2}} \tag{8}$$

characterises the response function. Whereas in magnetism χ is proportional to magnetic susceptibility, in our system this derivative characterises the response to the electrode polarisation. This response function determines the voltage-dependent differential capacitance. Given per its unit surface area it is called *specific* differential capacitance, and it is related to $\chi(u)$ as[45]

$$C(u) = -\frac{\varepsilon L_B}{2\pi a d}\chi(u). \tag{9}$$

Following eqn (3) and (5), the coupling constant can be approximated by

$$\alpha \simeq 3.08\frac{L_{\mathrm{B}}}{a}e^{-2.4d/a}. \tag{10}$$

Linear/low voltage response

As a particular case of the above expression for capacitance, one can obtain its value close to the voltage when the row of ions in the pore is electroneutral as a whole:

$$C(u)\big|_{u=w} \equiv \overline{C} = \frac{\varepsilon L_{\mathrm{B}}}{2\pi ad}e^{-2\alpha} \simeq \frac{\varepsilon L_{\mathrm{B}}}{2\pi ad}\exp\left\{-6.16\frac{L_{\mathrm{B}}}{a}e^{-2.4d/a}\right\}. \tag{11}$$

When $w \neq 0$, but the electrode is not polarised

$$C(u)\big|_{u=0} = \overline{C}\frac{\cosh(w)}{\left\{1+e^{-4\alpha}[\sinh(w)]^2\right\}^{3/2}}. \tag{12}$$

The two expressions coincide when there is no preferential adsorption of ions into the pore ($w = 0$).

Understanding absolute values (scaling factor estimates)

If all the lengths in the dimensional pre-factor $\frac{\varepsilon L_{\mathrm{B}}}{2\pi ad}$ in eqn (9) or (11) are taken in nm, in order to get the capacitance in μF/cm^2 one must multiply the result by 11.11.

To get a feeling about an order of magnitude of this prefactor, let us take $\varepsilon = 2$, $L_{\mathrm{B}} = 28$ nm, $a = 0.35$ nm, and $d = 0.7$ nm. We then obtain 36.4 nm^{-1} or 404.37 μF/cm^2. This example corresponds to $\alpha = 2.04$, and the exponential term $e^{-2\alpha}$ will contribute a factor 0.0169 reducing the capacitance to 6.82 μF/cm^2, but a slight increase of α will make this value much smaller.

It is interesting to compare $C_0^{(\mathrm{cylindrical})} = C(u)\Big|_{u=w=0} = (\varepsilon L_{\mathrm{B}}/2\pi ad)e^{-2\alpha}$ with the linear response specific compact layer capacitance of a flat electrode, in Helmholtz approximation,[1] $C_0^{(\mathrm{flat})} = \varepsilon/(2\pi d)$. Their ratio, $C_0^{(\mathrm{cylindrical})}/C_0^{(\mathrm{flat})} = [L_{\mathrm{B}}/a]e^{-2\alpha}$, for the above set of parameters comprises 1.4. For larger pore radii, α will increase, and the ratio will rapidly become much smaller than 1.

Thus the nanopore capacitance is extremely sensitive to the interionic interaction parameter, affected by the radius of the pore and screening properties of the pore walls if the latter are not ideally metallic.[1] On the contrary, the limit of the classical Helmholtz model is valid for the case of a highly concentrated electrolyte, which corresponds to 'zero' Gouy length;[1] there, everything is screened (electric field is zero beyond the compact layer), and ion–ion interactions do not enter the expression for the capacitance.

Results and discussion

Pore size effect and the voltage dependence

The shape of the function $\chi(u)$ is determined by the coupling parameter α, the whole function being symmetric about the point $u = w$. In the illustration below we show the case of $w = 0$, but if different, the zero point on the abscissa would correspond to $u = w$.

Following eqn (3) and (5), for $d = 0.7$ nm, and $a = 0.35$ nm, $\alpha = 2.04$; with the pore radius increasing just by 0.2 nm the coupling constant increases more than twice, to $\alpha = 4.622$. The larger the value of α, the higher the voltages required to charge the pore. The graphs in Fig. 2 illustrate this. We see that when the pore diameter is just a little larger than the diameter of an ion, the capacitance becomes almost negligible for small voltages. The reason for this is clear: it requires some voltage to start accepting the charge into the pore.

Non-monotonic capacitance–voltage dependence lies in two competing trends dominating in different voltage domains. With initial increase of the voltage, one unbinds cation–anion pairs, progressively facilitating charge accumulation, and the capacitance increases. However, at further voltage increase the majority of co-ions will get expelled outside of the pore and be replaced by counterions. Indeed, in eqn (7), at $u \rightarrow \pm\infty$, $\langle S_i \rangle \rightarrow \mp 1$, and, following eqn (8) and (9), the response function $\chi(u)$ and capacitance $C(u)$ vanish $\propto \exp(-2|u|)$, *i.e.* approaching saturation, further charging becomes increasingly difficult. The two regimes are separated by the maxima of capacitance, which lie close to $u_{\max} \approx w \pm (2\alpha + ½\ln 2)$; at this voltage $\langle S_i \rangle \approx \mp 1/\sqrt{2}$, *i.e.* $\approx 50\%$ of the maximal charge is already accumulated in the pore.

Recall again that in Fig. 2 we have shown the case $w = 0$. Had it been different, the curves would have been shifted by the value of w (*i.e.* to the right when $w > 0$, or to the left when $w < 0$).

Temperature dependence

Temperature appears in the capacitance expression (eqn (8) and (9)) in several places: the values of voltage, u is scaled to the, so called, 'thermal voltage' k_BT/e (25.6 mV at room temperature), whereas the energy of interionic interaction, α, and the free energy of preferential adsorption, w, are both scaled to thermal energy k_BT. To make things even more complicated, the temperature dependence is also inherent in the free energy of preferential adsorption through the entropic term. If, however, we neglect the latter (which is admissible for the case of strong specific adsorption of both cations and anions, the keystone of the two state model), the resulting trends appear to be simple (*cf.* Fig. 6). With the temperature increase the capacitance peaks become lower and broaden; the capacitance at low polarisation increases, because the structures that the voltage needs to break down in order to charge the pore get softer. The overall effect is noticeable but is not and cannot be large, because in the nanopore the pertinent 'energies' are larger than k_BT. The saturation regimes (the wings) are unaffected.

The effect of pore radii distribution

The sharp maxima in Fig. 5 and 6 refer to a single pore capacitance. But even the slightest dispersion of pore radii has a dramatic effect on the capacitance plots, due to the resonance character of a single pore capacitance–voltage dependence. Fig. 7 and 8 show that for any physically meaningful dispersion of pore radii, the values of the capacitance in the maxima reduce from anomalously large to more 'reasonable' values, *i.e.* closer to the observable ones. The second message is that the wings decrease much less steeply, and the overall capacitance–voltage dependence becomes less 'dramatic'.

Pore size and temperature effects on the linear response capacitance

It is remarkable that in a single file pore, the capacitance close to $u = w$ (or $u = 0$ when $w = 0$) appears to be very small, unless the interionic interactions are very strongly screened. The effect of the pore size that eqn (11) predicts (Fig. 9) is qualitatively similar to that experimentally observed,[14] but at pore radius only slightly larger than the ion radius, the single file capacitance practically vanishes. To the best of our knowledge, such small values of specific capacitance have never been reported. This is different in the case of slit pores,[19,20] where non-polarised pores delivered substantial capacitance. Thus this can mean that in

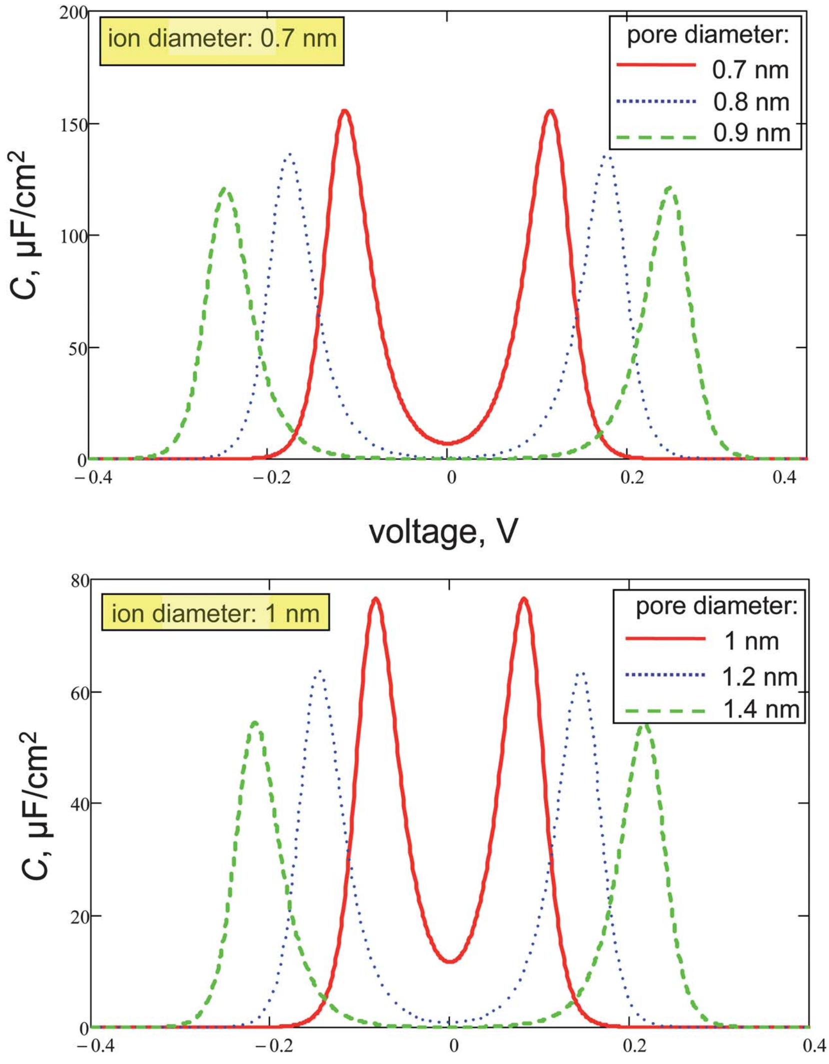

Fig. 5 Ising model results for the specific voltage-dependent differential capacitance of a single pore per its unit surface area, calculated *via* eqn (8)–(10). The effect of the diameter of the pore, shown for ion diameter 0.7 nm (upper panel) and 1 nm (lower panel); the effective dielectric constant of the pore interior, $\varepsilon = 2$. Remarkably, the capacitance vanishes very quickly with voltage because of the saturation of charge density in a single file geometry.

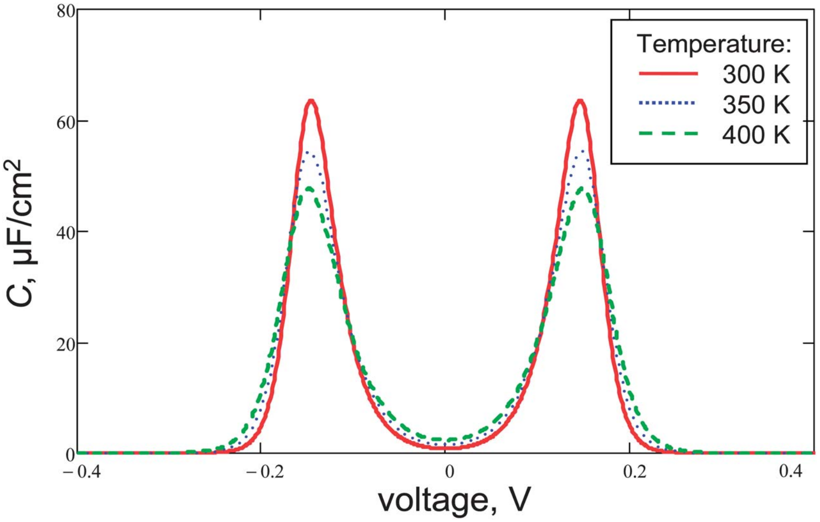

Fig. 6 Temperature effect on the voltage dependence of the specific differential capacitance of a single pore: calculated *via* eqn (8)–(10), shown for ion diameter 1 nm and pore diameter 1.2 nm. As in Fig. 5, $\varepsilon = 2$.

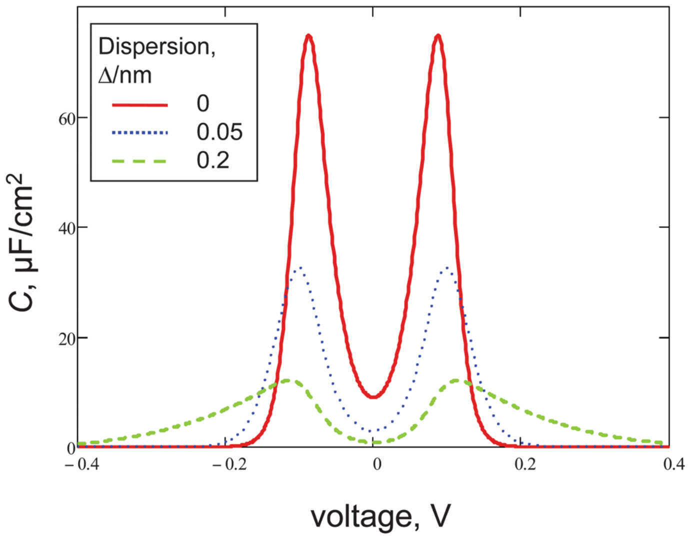

Fig. 7 Specific differential capacitance of a narrow cylindrical pore at dense packing of ions, just about to accommodate one row of ions on its axis, weighted over narrow Gaussian pore size distributions. Ion diameter d = 0.7 nm, pore diameter $2a$ = 0.72 nm; curves correspond to the indicated pore-radii dispersion; $\varepsilon = 2$. Already for minor pore-radii dispersion, the saturation regions move to higher voltages, and the capacitance curve displays moderate values.

experiments reported so far, we may not deal with single-file pores. An alternative explanation may be that there is a preferential adsorption of one sort of ions at a nonpolarised electrode, and the values of $u = 0$ do not actually correspond to the dip between the peaks. Last, but not least, if the pore contains not only ions, but

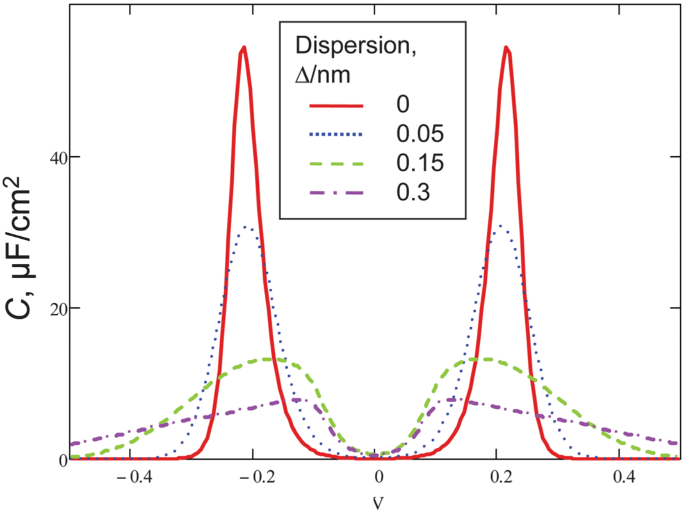

Fig. 8 The same as in Fig. 7 but shown for a larger average diameter of pores, $2a = 1.4$ nm (for the same size of ions, $d = 0.7$ nm), a larger spread of indicated pore-radii dispersion, and slightly larger voltage range. Broadening of pore-radii distribution does not make the linear response capacitance smaller, unlike the examples shown in Fig. 7. There, the range of smaller pores simply cannot accommodate ions, as taken into account in the calculation, and that decreased the capacitance. The role of the latter effect is minor in the curves of this figure.

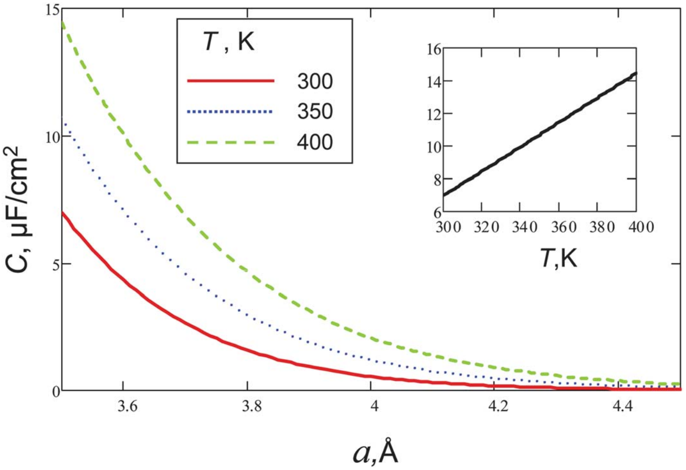

Fig. 9 Differential 'linear response' capacitance of a nanopore as a function of pore radius at different temperatures. Curves are calculated for the packing of ions of 0.7 nm diameter. The inset is the capacitance temperature dependence shown for the pore diameter equal to ion diameter. Other parameters are as in Fig. 2.

empty voids, the two state Ising model will not be applicable, whereas its extension to the three state model may give a different result. All these options remain to be studied.

The temperature dependence of the linear response capacitance is also worth noting. Outlining explicitly the temperature dependence in eqn (10), we get

$$C(u)\big|_{u=w} \simeq \frac{\varepsilon L_{\mathrm{B}}^{(\mathrm{r})}}{2\pi a d}\frac{T_{\mathrm{r}}}{T}\exp\left\{-6.2\frac{L_{\mathrm{B}}^{(\mathrm{r})}}{a}e^{-2.4d/a}\frac{T_{\mathrm{r}}}{T}\right\} \tag{13}$$

where T and T_{r} (=300) are, respectively, running and room temperatures, $L_{\mathrm{B}}^{(\mathrm{r})}$ is the Bjerrum length at $T = T_{\mathrm{r}}$; for $\varepsilon = 2$, $L_{\mathrm{B}}^{(\mathrm{r})} \simeq 28$ nm. The inset in Fig. 9 shows such dependence. Due to competing trends in the pre-exponential and exponential factors, it *linearly* grows with temperature in the relevant interval of temperatures.

Concluding remarks

Ultraporous electrodes with single-file pores may themselves not be practical for supercapacitors because of large ohmic power losses accompanying the charging–discharging process, as swapping co-ions with counterions in a single file may have substantial kinetic hindrance. For the same reason, accurate measurements of the equilibrium differential capacitance in such ultra narrow pores are difficult, and the author is not aware of any data on the voltage dependence reported so far. Still, theoretical results may be useful for understanding what, in principle, ultra nanoporous electrodes could deliver for energy storage.

Formulation of the model presented above was inspired by ref. 47. The latter suggested mapping of the electrical double layer problem in ionic liquids at a semi-infinite flat electrode onto a 1d-three state spin model in an external field with long range Coulomb interactions, for which the authors have obtained a sophisticated exact solution. The model of the present paper and its solution is much simpler, because in the metallic pore electrostatic interactions are exponentially screened, *i.e.* are short range, but most importantly the 1d spin-analogy is literal here.

The resulting 'toy' model of single-file charge storage allows the rationalisation of several interesting features. It shows the interplay between the voltage, temperature and the electrostatic interactions between electrolyte ions inside the nanopore, screened by free electrons of the electrode. The existence of an exact analytical solution for this model reported in this paper, describes all these dependences in the most simple terms. It may trigger new experimental electroanalytical studies of nanotemplated electrodes with ionic liquids, in order to verify the predicted trends. In designing such experiments one should keep in mind the two main limitations of the model:

(i) The description of the electrode as an 'ideal metal' may be fairly good for many metallic electrodes, but it can be questioned for carbon materials. Recent investigation[46] has shown that the reduction of screening will be noticeable with the corresponding effect on α, and subsequently on the capacitance. A similar effect is produced by a slight increase of the radius of the pore, except the latter also increases the denominator in eqn (8), thus affecting not only $\chi(u)$ through the coupling constant α, but also the pre-factor. Hence the main effect of such refinement will be the shift of the maxima to higher voltages. Accounting for a modified screening pattern can be easily implemented through correcting the input value of α.

(ii) We assumed that pores of a nonpolarised electrode are stuffed with ions (the stuffing is neutral, if there is no preferential adsorption of ions of one sign). We assumed furthermore that both sorts of ions are strongly adsorbed in a pore of a nonpolarised electrode. For the latter to be true there must be a strong energetic drive to compensate for the losses of entropy incurred when squeezing the ion into a narrow nanopore. Thus no empty space in the pore was allowed. This made it possible to reduce the description to a *two state model*: each site of the lattice can be in 'spin-up' (occupied by cation) or 'spin-down' (occupied by anion) states. To take into account a balance between cations, anions, and empty voids, one must develop a theory beyond the two state model, namely a three state model in which the 'spin' can also acquire the value 0 to account for the possibility of empty sites in the lattice, call them voids.[47] Such theory is more complicated and leads to a more cumbersome set of equations, providing more sophisticated capacitance curves, which will be reported elsewhere. The above considered 'tutorial' case is, however, not only valuable because it is simpler; it may as well correspond to physical reality, in the limit of strong adsorption of ions.

With all these reservations spelled out, it still made sense to present this model, as simple as it is, as a starting point for future theoretical and experimental developments.

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