Impedance of nanocapacitors from molecular simulations to understand the dynamics of confined electrolytes

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Abstract

Nanoelectrochemical devices have become a promising candidate technology across various applications, including sensing and energy storage, and provide new platforms for studying fundamental properties of electrode/electrolyte interfaces. In this work, we employ constant-potential molecular dynamics simulations to investigate the impedance of gold-aqueous electrolyte nanocapacitors, exploiting a recently-introduced fluctuation-dissipation relation. In particular, we relate the frequency-dependent impedance of these nanocapacitors to the complex conductivity of the bulk electrolyte in different regimes, and use this connection to design simple but accurate equivalent circuit
models. We show that the electrode/electrolyte interfacial contribution is essentially capacitive and that the electrolyte response is bulk-like even when the interelectrode distance is only of a few nanometers, provided that the latter is sufficiently large compared to the Debye screening length. We extensively compare our simulation results with spectroscopy experiments and predictions from analytical theories. This work opens new avenues for the molecular interpretation of impedance measurements, and offers valuable contributions for future developments of accurate coarse-grained representations of confined electrolytes.

Keywords

molecular simulation, impedance, nanocapacitors, confined electrolytes, conductivity

In recent decades, fueled by technological advances, the miniaturization of electrochemical devices has made tremendous progress. In this context, micro- and nanogap devices have demonstrated peculiar properties and promising performances in nanofluidics,\textsuperscript{1,2} sensing,\textsuperscript{3–5} as well as energy storage and conversion applications.\textsuperscript{6,7} Beyond their technological importance, nanoelectrochemical devices serve as valuable platforms for acquiring fundamental insights into solid-liquid interfaces,\textsuperscript{8,9} highlighting how microscopic phenomena can impact macroscopic properties. For instance, nanofluidic experiments\textsuperscript{10} (later corroborated by theoretical and computational studies\textsuperscript{11,12}) have shown how friction can be massively modified at water/carbon interfaces because of the coupling of electronic and dielectric fluctuations between the solid and the liquid. Recent studies have also focused on the dielectric properties of confined liquids between planar walls, revealing the influence of the inter-plane separation on the static dielectric response\textsuperscript{13–15} and its anisotropy.\textsuperscript{16,17}

In electrochemical devices, and in particular for capacitors, the dynamical dielectric/electrical
response is assessed through electrochemical impedance spectroscopy (EIS) experiments. Here, the impedance $Z(\omega)$ (or equivalently the admittance $Y(\omega) = 1/Z(\omega)$) quantifies the system’s electric current response $I(\omega)$ to an oscillating voltage $\Delta \Psi(\omega)$, under linear response conditions. EIS results are commonly interpreted through equivalent circuit (EC) models, which are fitted to the experimental data to extract parameters such as the electrical resistance $R$, capacitance $C$, and, more broadly, the distribution of relevant time scales governing polarization and charge transport. One of the most commonly used EC models is the transmission line model (TLM), which is employed to model the charging dynamics of capacitors with porous electrodes. Despite their popularity, the physical interpretation of such representations is not always straightforward and has occasionally led to long-standing debates. For this reason, coupling experiments with theoretical and computational investigations is crucial to elucidate the physical mechanisms behind a given electrochemical signal.

 Popular approaches to model the dynamical response of capacitors include analytic mean-field theories and numerical simulations at the mesoscale. The tractability of such approaches, however, relies on strong assumptions that often neglect important molecular details. In recent years, molecular simulations have proven a powerful tool to investigate the electrode-electrolyte interface that retain details about relevant molecular correlations. In particular, classical constant-potential molecular dynamics (MD) simulations have been extensively used to uncover the microscopic mechanisms that underlie macroscopic properties of electrochemical devices, such as supercapacitors. In this kind of simulation, the electrode charges fluctuate in response to changes in the electrolyte configuration, subject to the constraints of constant applied potential and global neutrality.

 The dynamical behavior of the total charge $Q(t)$ of an electrode, which fluctuates in the constant-potential ensemble, provides a means to obtain important electrochemical information about the system. For example, following the classic approach of Johnson and Nyquist, one can then use the equilibrium charge or current fluctuations to compute the
electrical response of an electrochemical system. Indeed, previous works have shown how the differential capacitance, which describes how the average electrode charge changes with applied potential $\Delta \Psi$, can be calculated from the charge fluctuations using a fluctuation-dissipation relation $C_{\text{diff}} = \partial \langle Q \rangle / \partial \Delta \Psi = \beta \langle \delta Q^2 \rangle$, where brackets denote an ensemble average, $\delta Q = Q - \langle Q \rangle$ and $\beta = 1/k_B T$ with $k_B$ the Boltzmann constant and $T$ the temperature. Furthermore, in recent work, this fluctuation-dissipation relation was extended to dynamical properties, in particular, to calculate the whole impedance spectrum from the total charge autocorrelation function $\langle \delta Q(0) \delta Q(t) \rangle$ (QACF). This approach was illustrated for the case of nanocapacitors with pure water confined between electrodes.

In this work, we leverage this approach to investigate the frequency-dependent impedance of nanocapacitors based on gold electrodes and aqueous electrolytes. First, we discuss the response of nanocapacitors in the time domain and validate our bulk simulations by comparing with spectroscopic measurement. Then, we discuss how the impedance spectrum is related to the bulk conductivity and suggest the design of simple EC models based on capacitive elements and a bulk impedance. We discuss the validity of this approach to EC modelling in different regimes by varying the ionic concentration and the distance between the electrodes. We also discuss the timescales of charge relaxation obtained in MD simulations and compare them to analytical predictions. Finally, we calculate the contributions of solvent and ionic fluctuations to the total impedance, and discuss how the interplay between the two influences the dielectric response.

Results and discussion

Electrode charge dynamics and salt concentration

We consider NaCl(aq)-gold nanocapacitors at five different salt concentrations: 0 M (pure water), 0.1 M, 0.5 M, 1.0 M, and 1.5 M. The simulation results for the pure water case are the same as published in our recent work. A representative snapshot for the 1 M case is
Figure 1: (a) Snapshot of the 1.0 M NaCl system, with the color of Au electrode atoms representing their instantaneous charge, as indicated by the color bar. Hydrogen, oxygen, sodium and chloride atoms are represented as white, red, cyan and green spheres, respectively. (b) Differential capacitance $C_{\text{diff}}$ divided by the electrode area $A_{\text{el}}$, as a function of NaCl concentration. (c) Electrode charge autocorrelation function divided by $A_{\text{el}}$ for the five salt concentrations we considered. (d) Comparison of the responses to a voltage change from $\Delta \Psi = 0$ to 1 V (symbols) with the equilibrium charge ACFs $\langle \delta Q(0) \delta Q(t) \rangle$, normalized as $(f(t) - f(\infty))/(f(0) - f(\infty))$, where $f(t)$ is either $Q(t)$ recorded during the charging process (symbols), or $\langle \delta Q(0) \delta Q(t) \rangle$ at equilibrium (solid lines), for the 0.1 M and 1 M systems. The uncertainty, calculated as 95% confidence intervals, is represented as error bars in panels (b) and (d), and with shaded areas in panel (c).

shown in Figure 1(a). In this work, all simulations are performed with a constant number of atoms, temperature (298 K) and applied electrostatic potential difference $\Delta \Psi$ between the two electrodes. As a preliminary step, we equilibrate the distance between the electrodes at constant atmospheric pressure, obtaining the interelectrode distances $d = 4.94, 4.93, 4.98, 5.06$, and $5.10$ nm for the 0 M, 0.1 M, 0.5 M, 1.0 M, and 1.5 M systems, respectively. After
constant-pressure equilibration, we perform constant volume simulations. In all cases, the applied potential is enforced with the fluctuating charge method, where the atomic charges of electrode atoms are calculated self-consistently depending on the instantaneous electrolyte configuration at each simulation step. The consequences of such a Born-Oppenheimer (BO) approximation on charge fluctuations and electrochemical properties were discussed in previous works. We perform two types of simulations: (i) we characterize the equilibrium fluctuations of the system with $\Delta \Psi = 0$ V; (ii) we interrogate the nonequilibrium response of the solution to a voltage step by instantaneously switching $\Delta \Psi = 0 \to 1$ V. More simulation details are provided in Methods and SI (sec. S1).

Figure 1(b) shows the differential capacitance, $C_{\text{diff}}$, estimated from the fluctuations of the total charge $Q$ on one of the two electrodes as a function of salt concentration. Note that these results do not account for the empty capacitor contribution $C_{\text{diff}}^{\text{empty}}$, which results from the fluctuations neglected by the BO approximation. This contribution depends in particular on the distance between the electrodes and typically amounts to $\sim 10\%$ of the BO capacitance for the systems considered in the present work. The capacitance values for the pure water and 1 M cases are in excellent agreement with recent simulation results on the same setup and compare favorably with simulations performed with different force-fields. Our results show that the presence of ions introduces a positive contribution to capacitance. However, the capacitance does not depend on the salt concentration beyond 1 M in the considered range. A similar trend was found in simulations of supercapacitors and in recent impedance results for NaCl solutions at planar electrodes, where $C_{\text{diff}}$ was found to be almost constant for salt concentrations spanning six orders of magnitude. Interestingly, these results are in stark contrast with the capacitance values predicted by Debye-Hückel (DH) theory,

$$C_{\text{DH}} = A_{\text{el}} \varepsilon_0 \varepsilon_w \frac{1}{\lambda_D},$$

(1)
where $A_{el}$ is the surface area of the electrode, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_w$ is the permittivity of the solvent, and the Debye screening length is given by

$$\lambda_D = \left( \frac{\varepsilon_w \varepsilon_0 k_B T}{e^2 \sum_\alpha c_\alpha Z_\alpha^2} \right)^{\frac{1}{2}},$$ (2)

where $e$ is the electron charge and the sum runs over the species $\alpha$ with concentration $c_\alpha$ and valency $Z_\alpha$. Using $\varepsilon_w = 70.7$ for SPC/E water,\textsuperscript{54} Eq. 1 predicts capacitances that are $\sim$25 to $\sim$100 times larger (at 0.1 M and 1.0 M, respectively) than the values obtained from simulations. This mismatch is not unexpected, given that DH theory implies a very simplified picture of the electrode/electrolyte interface. Furthermore, at sufficiently high salt concentrations (0.5 M and beyond, in our case), $\lambda_D$ becomes comparable to the ionic size, a regime where ionic correlations and molecular features of the solvent, which are neglected entirely in DH theory, are known to become important.\textsuperscript{36,55} More sophisticated capacitance models could be used to fit MD results,\textsuperscript{52} but this falls beyond the scope of the present work.

Fig. 1(c) shows $\langle \delta Q(0) \delta Q(t) \rangle$ for the different salt concentrations we consider. The QACFs in the presence of ions share some qualitative similarities with the pure water case. However, for finite salt concentrations, we observe an additional exponential-like slow mode with a decay rate that depends on concentration (see SI sec S2, and below for a discussion concerning the relevant time scales). In particular, the relaxation rate of the slow mode is faster for higher salt concentrations. In the considered concentration range, it is known (and we will confirm later) that the ionic conductivity increases with salt concentration.\textsuperscript{56} The observed long-time behavior of the QACFs therefore suggests an intuitive connection with the ionic conductivity.

In addition to our equilibrium simulations at $\Delta \Psi = 0$ V, we have also performed simulations where we instantaneously change the voltage $\Delta \Psi = 0 \rightarrow 1$ V, and measure $Q(t)$ as it relaxes to its new equilibrium value. Fig. 1(d) shows a direct comparison between the normalized QACF obtained directly from the equilibrium fluctuations at $\Delta \Psi = 0$ V and from
the normalized charge response to the voltage step, for the 0.1 M and 1.0 M systems. The excellent agreement between the equilibrium and nonequilibrium results demonstrates that linear response is a valid approximation (see SI sec. S3), at least up to $\Delta \Psi = 1$ V, consistent with previous results for water/gold nanocapacitors.\(^{49}\) In other words, this agreement confirms that our analysis of equilibrium charge fluctuations $\langle \delta Q(0) \delta Q(t) \rangle$ (including the impedance, discussed in the following sections) is fully representative of the nonequilibrium charge/discharge dynamics of nanocapacitors in the voltage range we consider.

**Impedance of nanocapacitors as bulk impedance and interfacial capacitance**

The global response of the confined systems shown in Fig. 1 implicitly includes all the molecular correlations that contribute to the total polarization or charge dynamics. Intuitively, we expect the global response to comprise “interfacial contributions” from electrolyte proximate to the electrodes, and a bulk-like contribution from the remaining electrolyte far from the electrodes. Experimentally, it can be challenging to rigorously disentangle such interfacial and bulk contributions to the charging dynamics.\(^{60}\) Here, we exploit the fact that molecular simulations allow us to characterise the bulk response, by performing simulations of the electrolyte in the absence of any explicit interfaces (see SI sec. S1). In particular, we use bulk simulations to estimate the electric conductivity $\sigma$ in two distinct ways: (i) at finite frequencies ($\sigma(\omega)$) using a Green-Kubo (GK) approach;\(^{61}\) (ii) at zero frequency ($\sigma(0)$, which has no imaginary part) using the Einstein-Helfand (EH) approach.\(^{62}\) More details on these calculations are provided in the Methods section. We numerically verified the consistency between the two methods at low frequencies in all systems (see SI sec. S4 and S5).

In Figure 2, we compare our simulations with experimental results obtained with different spectroscopic techniques.\(^{56-59}\) The experimental datasets were converted from permittivity to conductivity using the relation\(^{61,63}\) $\sigma(\omega) = i \omega \varepsilon_0 [\varepsilon(\omega) - 1]$. The simulation results for the 1 M system reported in Fig. 2(a) show that $\sigma(\omega)$ reaches a global maximum at $\omega \approx 1.5 \times 10^{14}$
Figure 2: (a) Conductivity calculated from bulk simulations (symbols), as a function of frequency, for the 1 M system compared with experimental optical measurements (solid lines).\textsuperscript{57-59} (b) Comparison of conductivity from bulk simulations (symbols) and experimental measurements (solid lines) from Ref. 56 for all the concentrations we considered. (c) Conductivity at zero frequency $\sigma(0)$ from bulk simulations (symbols) and from experimental measurements\textsuperscript{56,57} (dashed lines).

At lower frequencies, we find a shoulder resembling the Debye-like modes of polar fluids and a plateau corresponding to the static conductivity $\sigma(0)$. The same panel also shows a semi-quantitative agreement between simulations and experiments, across the whole frequency range. Minor discrepancies are expected due \textit{e.g.} to the limitations of the model we use for the electrolyte, which does not capture all
polarization modes expected for real solutions in this frequency range, in particular at high
frequency (as recently discussed for the SPC/E water model\textsuperscript{64}). In panel (b), we find a simi-
lar agreement between simulations and experiments for all the concentrations we considered
in the low frequency limit (note that in this case the experimental results were obtained at
$T = 293$ K,\textsuperscript{56} while our simulations are performed at 298 K). Finally, in Fig. 2(c), we show
that $\sigma(0)$ computed from simulations is in quantitative agreement with experimental results
at low salt concentrations but it progressively underestimates it at higher concentrations.
This discrepancy is expected, since the model we consider for the electrolyte was originally
optimized for dilute systems.\textsuperscript{65} Notwithstanding the limitations of the underlying model,
the above analyses suggest that our bulk simulations faithfully capture the experimental
conductivity of NaCl solutions. Having established this fact, we will now use these results
to analyze the impedance in nanocapacitors.

Following the approach used in Ref. 49, we obtain $Z(\omega)$ from the QACF sampled at
$\Delta \Psi = 0$ V. As in this previous work, and for consistency with the BO contribution to the
differential capacitance (see above), we limit our analysis to the impedance contributions
within the BO approximation. Figs. 3(a) and (b) report the real and imaginary parts of $Z(\omega)$,
respectively. Here, to represent intensive quantities, the impedance results are multiplied by
$A_{el}/d_{DDS}$, where $d_{DDS} = d - 2w_{DDS}$ is the effective width of the confined electrolyte, based
on the positions of the dielectric dividing surface at each electrode/electrolyte interface.\textsuperscript{16}
Roughly speaking, $w_{DDS}$ is the width of the vacuum layer between the first atomic plane
of the electrode and the closest water molecules. In this work, we use $w_{DDS} = 1.27$ Å as
it was found in a previous work for water/gold nanocapacitors using the same force field.\textsuperscript{49}
The impedance results display some distinctive features of capacitors at low frequencies.\textsuperscript{18}
In particular, the real part of $Z(\omega)$ plateaus at $\omega \to 0$, corresponding to the total electrical
resistance of each electrochemical system. For finite salt concentrations, resistance decreases
with increasing salt concentration, suggesting an intuitive link with bulk conductivity, which
will be further discussed below. Furthermore, the imaginary part of $Z(\omega)$ displays a clear
Figure 3: (a) Real part of the total impedance $Z(\omega)$ as calculated from confined simulations for all the salt concentrations we considered, as a function of frequency. (b) Imaginary part of $Z(\omega)$. (c) Real part of interfacial impedance $Z_{\text{int}}(\omega)$. (d) Imaginary part of $Z_{\text{int}}(\omega)$. The insets in panels (c) and (d) are used to zoom the respective plots in the low-frequency parts (see the dashed lines). In the inset of panel (d), the symbols correspond to simulation results, the solid lines represent $1/\omega C_{\text{diff}}$ for each system, and the dotted line represents $-\Im[Z(\omega \to 0) - Z_{\text{bulk}}(\omega \to 0)]$ for the pure water case (see Eq. 5 and SI sec. S6). In all the panels, the colors indicate the same salt concentrations. All the results are multiplied by the electrode area $A_{\text{el}}$ and scaled by the $d_{\text{DDS}}$ distance.

$\omega^{-1}$ scaling behavior at low frequencies, which is typical of capacitive systems. Interestingly, above $10^{11}$ rad/s, the impedance results do not depend on salt concentration and follow the same profiles consistently with pure water results. This overlap at high frequencies suggests that, in this regime, the impedance reflects the individual motion of solvent molecules and ions, which is dominated by water molecules, since the number of ions is at least $\sim 40$ times smaller than the number of water molecules in the considered systems (see SI sec. S1).

To discern the interfacial and bulk-like contributions to the impedance, we adopt a sub-
traction technique similar to that used in experiments. Specifically, we suppose that the total impedance can be written as a simple sum of bulk and interfacial contributions,

\[ Z(\omega) = Z_{\text{int}}(\omega) + Z_{\text{bulk}}(\omega), \]

which corresponds to an EC with bulk and interfacial elements in series. Note that \( Z_{\text{int}} \) implicitly includes the two electrode/electrolyte interfaces. Therefore, in our symmetric setup, one can calculate the contribution of a single interface as \( Z_{\text{int}}(\omega)/2 \). Assuming that the relevant width of the confined slab is \( d_{\text{DDS}} \), we can write \( Z_{\text{bulk}} \) using the bulk conductivity as

\[ Z_{\text{bulk}}(\omega) = \frac{d_{\text{DDS}}}{A_{\text{el}}} \frac{1}{\sigma(\omega)}. \]

The interfacial impedance then follows from Eq. 3 as \( Z_{\text{int}}(\omega) = Z_{\text{tot}}(\omega) - Z_{\text{bulk}}(\omega) \). The results for the real and imaginary parts of \( Z_{\text{int}}(\omega) \) are shown in Figs. 3(c) and (d), respectively. Clearly, for all concentrations (including pure water), the real part of \( Z_{\text{int}}(\omega) \) is almost negligible compared to the imaginary part. Only in one case (0.1 M), we notice that \( \Re[Z_{\text{int}}(\omega)] \) becomes slightly negative and in the same order of magnitude as \( \Re[Z(\omega)] \), even though the uncertainty is relatively large due to the error bars in the computed \( \sigma(\omega) \) in this system. A more detailed comparison between the resistance in the confined system \( R = \Re[Z(\omega \to 0)] \), and the bulk resistance \( R_{\text{bulk}} \) computed from \( \sigma(0) \), obtained with the EH approach, is reported in the SI sec. S7. Our results show that in the 0.1 M system, the resistance of the confined electrolyte is \( \sim 4 \) times smaller than the bulk value. Anticipating the following discussion, this suggests that the separation between bulk and interfacial contributions is less straightforward in that case.

Within the DH framework, we can assume that the width of each interfacial region is \( \sim \lambda_D \), despite the known limitations of DH theory in particular at larger concentrations (see e.g. the above discussion of the DH prediction for the capacitance). At 1.5 M, the highest
salt concentration considered, $\lambda_D \approx 2.4$ Å, which is approximately 20 times smaller than the inter-electrode separation $d$. In contrast, at 0.1 M this screening length is $\approx 9.1$ Å, only $\sim 5$ times smaller than $d$. In this scenario, DH theory predicts that the two interfaces occupy a significant fraction of the electrolyte regions, and the two electric double layers (EDL) overlap in the central part of the system. We conclude that, in the limit of thin double-layers ($\lambda_D \ll d$), one should expect the resistance to be dominated by $R_{\text{bulk}}$. Otherwise, for $\lambda_D \sim d$, the resistance is strongly affected by the interfaces, and in general, $R \neq R_{\text{bulk}}$. Therefore, we cannot easily separate interfacial and bulk response, since it is not possible to identify a ‘bulk’ region in this dilute system. For more concentrated electrolytes (0.5 to 1.5 M), the absence of a finite plateau in $\Re[Z_{\text{int}}(\omega \to 0)]$ (see Fig. 3(c) and inset) suggests that any interfacial resistance (if present) is negligible compared to the bulk one in the considered systems. This is in stark contrast with recent findings on electrode/ionic liquid interfaces, where the electric resistance was dominated by interfacial contributions.\textsuperscript{67}

The imaginary part of $Z_{\text{int}}(\omega)$ at finite salt concentrations is well-described by $-1/(\omega C_{\text{diff}})$, with $C_{\text{diff}}$ the (static) differential capacitance, as shown by Fig. 3(d) and highlighted in the inset of the same panel. However, in the case of pure water, the interfacial component cannot be described only by a simple capacitive contribution based on $C_{\text{diff}}$. This is because, in the absence of ions, $\sigma(0) = 0$ and $\Im[Z_{\text{bulk}}(\omega \to 0)] \propto -d_{\text{DDS}}/(\varepsilon_0 \varepsilon_w \omega)$, as predicted from continuum theory for a dielectric capacitor (see SI sec. S6 for more information). In contrast, in the presence of ions $\Im[Z_{\text{bulk}}(\omega \to 0)] = 0$. This limit illustrates how the ‘bulk’ region is the main source of capacitance for a pure dielectric, whereas in the presence of salt, capacitance is an interfacial phenomenon and $\Im[Z_{\text{int}}(\omega \to 0)] = -1/(\omega C_{\text{diff}})$. The same qualitative result was recently discussed in terms of bulk-dominated and interface-dominated static dielectric response.\textsuperscript{68} In the case of pure water, the imaginary part of $Z_{\text{int}} = Z - Z_{\text{bulk}}$ includes a term that depends on the bulk permittivity (see SI sec. S6 for more information):

$$\lim_{\omega \to 0} \Im[Z(\omega) - Z_{\text{bulk}}(\omega)] \approx \frac{d_{\text{DDS}}}{A_{\text{el}} \varepsilon_0 \varepsilon_w \omega} - \frac{1}{C_{\text{diff}} \omega}. \tag{5}$$
Interestingly, this result can be directly related to the impedance of the three-capacitor model introduced in our previous work to describe the capacitance of the same system.\textsuperscript{49} It can be shown that, for the three-capacitor model, Eq. 5 corresponds to the impedance of two capacitors related to interfacial vacuum layers of width $w$ located between water and gold electrodes

$$\frac{2w}{\varepsilon_0\omega A_{el}} = \frac{1}{C_{\text{diff}}\omega} - \frac{d_{\text{DDS}}}{A_{el}\varepsilon_0\varepsilon_w\omega}. \quad (6)$$

A simple rearrangement of this equation leads to $w = 1.6$ Å, which is close to $w_{\text{DDS}} = 1.27$ Å that was directly derived from the dielectric profile in our previous work.\textsuperscript{49}

To summarize, from the above analysis we conclude that for finite salt concentrations the interfacial contribution to the impedance is mostly capacitive and is well described by $Z_{\text{int}}(\omega) \approx 1/i\omega C_{\text{diff}}$, with the (static) differential capacitance $C_{\text{diff}}$. These observations mean that we can model the total impedance of our systems as an equivalent circuit (EC) with a bulk component, parameterized on $\sigma(\omega)$ as in Eq. 4, in series with a purely capacitive element with $C_{\text{diff}} = \beta\langle\delta Q^2\rangle$. Such EC models are already widely used by experimental groups to model macroscopic electrochemical cells with planar blocking electrodes.\textsuperscript{60} It is worth emphasizing, however, that this work brings the first direct evidence of this behavior at the molecular scale and confirms the validity of these EC models to represent nanocapacitors.

**Effect of the inter-electrode distance**

In the previous section, we introduced an EC model defined on a capacitive interfacial element and a bulk impedance. While the interfacial contribution depends implicitly on the size of the system (through any potential size-dependence of $C_{\text{diff}}$), the bulk contribution depends explicitly on the separation between the electrodes (see Eq. 4). When EC models are accurate, they provide a powerful tool to analyze impedance spectra. In this section, following our previous work for pure water,\textsuperscript{49} we therefore further probe the robustness of
Figure 4: (a) Differential capacitance $C_{\text{diff}}$ divided by the lateral area of the electrodes, $A_{\text{el}}$, as a function of $d$ for pure water\textsuperscript{49} (blue) and 1 M NaCl aqueous solution (orange). (b) Electrode charge auto-correlation function, $\langle \delta Q(0)\delta Q(t) \rangle$, divided by $A_{\text{el}}$ as a function of $t$, for all the considered inter-electrode distances (see legends) with the 1 M aqueous electrolyte. Panels (c) and (d): real and imaginary parts of impedance as a function of frequency. In (c) and (d) the simulation results are shown with solid lines and the predictions from the EC model are shown in black dashed lines. In panels (c) and (d) the uncertainty is not shown for clarity.

the above EC model by investigating its dependence on the interelectrode distance, $d$, for a fixed salt concentration (1 M). Upon equilibrating $d$ at constant 1 atm pressure for four systems with various number of ion pairs and solvent molecules, we obtain, including the original system size, $d = 2.56$, 5.07, 9.80, and 19.84 nm. These values are subsequently used for simulations at constant volume.

Fig. 4(a) shows a direct comparison of $C_{\text{diff}}$ (scaled by the lateral area $A_{\text{el}}$ of the electrodes) as a function of $d$, for gold nanocapacitors with pure water and 1 M NaCl solutions. For pure
water, \( C_{\text{diff}} \) decreases with increasing \( d \), in qualitative agreement with what is expected from macroscopic theories of pure dielectrics, \( C = \varepsilon_0 \varepsilon_w A_{el}/d \) (see Ref. 49 for more discussion of this case). In contrast, at 1 M \( C_{\text{diff}} \) only mildly depends on \( d \). This result is in qualitative agreement with mean field theories, which predict that, for finite salt concentrations, the differential capacitance is expected to depend exclusively on the screening length \( \lambda_D \) (see e.g. Eq. 1, despite its limitations at such a concentration) in the limit of large \( d \).

Fig. 4(b) reports the QACF at \( \Delta \Psi = 0 \) V, for all the considered values of \( d \). In all cases, we recognize the same qualitative features discussed in the previous section (see Fig. 1(c)). The short time oscillations, corresponding to the high frequency maximum in conductivity (see Fig. 2(a)), are very similar to that observed for pure water. As described in Ref. 49, they can be ascribed to libration of water molecules. In the present case of electrolytes, this mode is dominated by water molecules residing beyond the adlayer (formed by water molecules in contact with the surface). However, the relative contribution of adlayer and non-adlayer water molecules depends on the distance between the electrodes. As the inter-electrode distance \( d \) increases, these oscillations appear to be progressively attenuated due to the increased dissipation also reflected in the larger real part of the impedance.\(^{49}\) In the presence of ions, we further observe that both the characteristic time and the amplitude of the additional slow relaxation mode increase with \( d \) (see next Section).

Despite the significant changes in relaxation dynamics for the different values of \( d \), for this 1 M system the relaxation dynamics are still well-described by the simple combination of bulk and interfacial contributions to the impedance. This is demonstrated in Fig. 4(c) and (d), where we report the real and imaginary parts of impedance respectively, as a function of frequency. The impedance of our EC models (black dashed lines) are in excellent agreement with the impedance results obtained from simulation, for all considered inter-electrode separations. This suggests that, aside from the capacitive contribution arising from the EDL formation at the interface, the dielectric response of the confined electrolyte remains bulk-like. This observation is consistent with recent works that highlight how the dielectric
response of nanoconfined water is essentially bulk-like, provided that one appropriately ac-
counts for the boundary of the liquid.$^{16,49,69–71}$ Our results extend this conclusion to systems
with dissolved ions.

**Effect of the salt concentration on relaxation times**

Figure 5: Comparison of relevant characteristic times as a function of salt concentration
from simulations (symbols) and analytical theories (dashed lines).$^{29,31–33,72}$ $\tau_Q$ is calculated
as the integral of the normalized QACFs (see Eq. 7). For $\tau_{\text{ion-tot}}$ (blue dots) and $\tau_{\text{diff}}$ (green
dots), the characteristic time is extracted by fitting the data (see Figs. 6(b,c) and SI sec.
S2) with exponential functions. The $RC$ and $R_{\text{bulk}}C$ characteristic times use the resistance
computed from confined and bulk simulations, respectively, and $C = C_{\text{diff}}$ from confined
simulations. Note that $R_{\text{bulk}}$ was calculated using $d_{\text{DDS}}$ instead of $d$, consistently with Eq. 4.
Here, $RC$, $R_{\text{bulk}}C$, $\tau_Q$ and $\tau_{\text{diff}}$ were computed from equilibrium simulations, whereas $\tau_{\text{ion-tot}}$
was estimated from nonequilibrium simulations.

As shown in previous work, for pure water confined between the gold-electrodes, the
relaxation of the QACF is well-characterized by a single exponential with a characteristic
time $\tau_w = \tau_{w,\infty} d/[d + (\varepsilon_w - 1) w_{\text{DDS}}]$,$^{49}$ where $\tau_{w,\infty} \approx 8.6$ ps is close to the bulk value for the
Debye relaxation mode of water. Upon introducing ions, the QACF is broadly characterized
by two timescales: a fast relaxation that is comparable to $\tau_w$, and a much slower relaxation
$\tau_{\text{slow}}$, which depends on salt concentration (see Fig. 1(c)). A global timescale can be defined

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from the integral of the normalized QACF,\(^{49}\)

\[
\tau_Q = \int_0^\infty \frac{\langle \delta Q(0)\delta Q(t) \rangle}{\langle \delta Q^2 \rangle} \, dt,
\]

such that the admittance behaves at low frequency as \(Y(\omega) \approx i\omega C_{\text{diff}}/(1 + i\omega\tau_Q)\). This translates in terms of impedance to \(Z(\omega) \approx R_{\text{eff}} + 1/i\omega C_{\text{diff}}\), with an effective resistance \(R_{\text{eff}} = \tau_Q/C_{\text{diff}}\) that corresponds to the low-frequency limit \(R = \Re[Z(\omega \to 0)]\) in the EC model used above. In practice, \(R\) is estimated from the lowest frequency accessible from simulations, whereas \(R_{\text{eff}}\) refers specifically to \(\omega = 0\).

As shown in Fig. 5, \(\tau_Q\) decreases with increasing ion concentration (beyond the initial jump from the pure water case, for which no ions from water autodissociation are captured by the present force field), but remains on the order \(10^{-11}\) s for the considered systems. It is compared with the ‘RC’ times, using the differential capacitances obtained from \(\langle \delta Q^2 \rangle\) (see Fig. 1(b)), and the total resistance estimated either as \(R_{\text{bulk}} = d_{\text{DDS}}/A_{\text{el}}\sigma(0)\) with the DC conductivity from bulk simulations, or from the confined simulations as \(R = Z(\omega \to 0)\) which is computed from the plateau shown in Fig. 3(a). As expected, \(RC\) agrees well with \(\tau_Q\) for the whole range of concentrations, thereby confirming numerically the consistency between \(R_{\text{eff}}\) and \(R\). The agreement obtained with \(R_{\text{bulk}}\) from bulk simulations is also good for the higher concentrations, but for the lowest concentration, 0.1 M, \(R_{\text{bulk}}C\) is approximately 4 times larger than \(\tau_Q\), consistent with the same difference between \(R_{\text{bulk}}\) and \(R\) discussed previously (see also SI sec. S7). Overall, these observations further support the analysis in terms of capacitive interfacial and bulk contributions to the impedance, provided that the effective width of the interfacial region (which is not accurately described by the Debye screening length in this concentration range, except maybe at 0.1 M) is sufficiently small with respect to the interelectrode distance.

While the intermediate and high frequency range of \(Z_{\text{bulk}}(\omega)\) is dominated by the contribution of water, as discussed previously (see e.g. Fig. 4(a)), the behavior at low frequency
significantly depends on the ions. We now examine three timescales frequently considered in the dynamics of ions in confined electrolytes obtained with analytical theories.\textsuperscript{29,31–33,35,72} Since they rely on an implicit solvent description, a common diffusion $D$ for cations and ions, as well as mean-field theory and a simplified representation of the interface, we limit ourselves to examining qualitative trends with salt concentration rather than how well these time scales compare quantitatively with our simulations. The first timescale is $\tau_d = d^2/4D$, which corresponds to ion diffusion over the distance between the electrodes. The second timescale is the Debye relaxation time $\tau_{\text{Debye}} = \lambda_D^2/D$, which corresponds to the relaxation of charge fluctuations in bulk electrolytes, with the diffusion of ions over the corresponding Debye screening length. The third timescale $\tau_{\text{mix}} = \lambda_D(d - 2\lambda_D)/2D$ (which mixes both $\lambda_D$ and $d$ lengths) corresponds to the ‘RC’ charging time assuming Nernst-Einstein conductivity and DH capacitance, including a correction for the width of the two EDLs.\textsuperscript{29} In the limit of thin EDLs, one can consider only the leading order term $\lambda_D d/2D$. The time scales introduced so far can be broadly intended as approximations or limiting cases of the more general solution shown recently by Janssen and Bier in Ref. 31 and obtained within the Debye-Falkenhagen approximation, which we indicate as $\tau_{\text{JB}}$ (see SI sec. S8).

These timescales are reported in Fig. 5 together with the simulation results for $\tau_Q$. For the diffusion coefficient we use $D = 1.41 \times 10^{-9}$ m\(^2\)/s, the average diffusion coefficient of Na\(^+\) and Cl\(^-\) ions computed from bulk simulations at 0.1 M. All the analytical timescales overestimate the relaxation time, but with different orders of magnitudes and trends with salt concentration. The worst estimate is $\tau_d$, by several orders of magnitude and no dependence on salt concentration, as expected because the build-up of EDLs does not require ions to diffuse over the whole electrochemical cell. While the order of magnitude of $\tau_{\text{Debye}}$ is correct for the highest concentrations we consider, the agreement with $\tau_Q$ is worse for the lower concentrations, with $\tau_{\text{Debye}}/\tau_Q \approx 10$ at 0.1 M. Naively, we would expect such a mean-field prediction to improve as concentration is decreased. This discrepancy suggests the observation that $\tau_{\text{Debye}} \sim \tau_Q$ for the higher concentrations is largely coincidental. The mismatch in
the scaling with concentration of $\tau_{\text{Debye}}$ and $\tau_Q$ corroborates this notion. Finally, despite the wrong order of magnitude (not surprising, considering e.g. the failure of Eq. 1 to capture the capacitance at high concentration), only $\tau_{\text{mix}}$ display a trend with concentration similar to that of $\tau_Q$. A more detailed discussion of the concentration dependence of $\tau_{\text{Debye}}$, $\tau_{\text{mix}}$, $\tau_{\text{JB}}$ and $\tau_Q$ is included in the SI sec. S8. Overall, these comparisons further support the idea that $\tau_Q$, and more generally the impedance of the system, reflects the interplay between the dynamics of a bulk-like electrolyte and the interfacial capacitive behavior induced by the blocking electrodes. In a bid to rationalize the quantitative disagreement between theory and simulation, in the the next section, we finally probe the relaxation process in terms of contributions from ions, water and their cross correlations.

**Water and ionic contributions**

As shown in previous works, at $\Delta \Psi = 0$ V and with global electroneutrality, the total electrode charge $Q$ is proportional to the total dipole moment of the solution $M_{\text{tot}}$ in the direction perpendicular to the electrode surface.\(^{49,73}\) For this reason, the behavior of $\langle \delta Q(0)\delta Q(t) \rangle$ is determined entirely by $\langle M_{\text{tot}}(0)M_{\text{tot}}(t) \rangle$. Clearly, in the case of an electrolyte solution, $M_{\text{tot}}(t) = M_{\text{wat}}(t) + M_{\text{ion}}(t)$ has contributions from both the solvent water molecules and the dissolved ions. We can therefore decompose the autocorrelation function of the total dipole moment:

$$
\langle \delta M_{\text{tot}}(0)\delta M_{\text{tot}}(t) \rangle = \langle \delta M_{\text{tot}}(0)\delta M_{\text{ion}}(t) \rangle + \langle \delta M_{\text{tot}}(0)\delta M_{\text{wat}}(t) \rangle \\
= \langle \delta M_{\text{ion}}(0)\delta M_{\text{ion}}(t) \rangle + \langle \delta M_{\text{wat}}(0)\delta M_{\text{wat}}(t) \rangle + 2\langle \delta M_{\text{wat}}(0)\delta M_{\text{ion}}(t) \rangle,
$$

where in the last equality we have used $\langle \delta M_{\text{wat}}(0)\delta M_{\text{ion}}(t) \rangle = \langle \delta M_{\text{ion}}(0)\delta M_{\text{wat}}(t) \rangle$. The correlation functions on the right hand side of Eq. 8 rigorously relate the linear response of $M_{\text{ion}}(t)$ and $M_{\text{wat}}(t)$ to a change in voltage across the cell; consequently, they can be obtained by monitoring the time evolution of $M_{\text{ion}}(t)$ and $M_{\text{wat}}(t)$ upon the step change.
\[ \Delta \Psi = 0 \rightarrow 1 \text{ V.} \]

Figure 6: (a) Static correlations of the water and ionic contributions to the total dipole moment as a function salt concentration. (b,c) Normalized time correlation functions of the contributions to the total dipole moment for 0.1 M and 1.0 M salt concentrations, as a function of time. In all panels, each color indicates the same combination of contributions \( \alpha \) and \( \beta \). In panels (b,c), we compare the results of equilibrium simulations (lines with error bars), those of nonequilibrium simulations (dotted lines), and exponential fits (dashed lines).

In Fig. 5(a), we present the static limit of these normalized decomposed dipole correlation functions. For all ion concentrations, the total comprises positive contributions from \( \langle \delta M^2_{\text{ion}} \rangle \) and \( \langle \delta M^2_{\text{wat}} \rangle \) and a large negative contribution from the cross correlation \( \langle \delta M_{\text{ion}} \delta M_{\text{wat}} \rangle \). This anti-correlation between the equilibrium fluctuations of the ionic and solvent contributions to the polarization was also found in bulk systems,\(^{74-76}\) and reflects the well-known Stillinger-Lovett conditions (SL).\(^{77,78}\) While Ref. 76 provided a framework to understand the SL conditions for the total dipole moment in bulk systems in terms of ‘virtual electrodes’ arising
from the imposed boundary conditions, our results demonstrate that these SL conditions are also obeyed in the presence of explicit electrodes held at constant bias. See also Ref. 79.

We now turn our attention to the nonequilibrium relaxation of $M_{\text{ion}}$ and $M_{\text{wat}}$, shown in Fig. 6(b,c) for 0.1 M and 1.0 M, respectively. For both systems, we see an initial fast response of the solvent polarization (see dotted orange lines in Fig. 6(b,c)). In fact, the negative values of $\langle M_{\text{tot}}(0)M_{\text{wat}}(t) \rangle$ for $t \gtrsim 10^{-12}$ s indicate that the solvent polarization overshoots its equilibrium value (see Eq. S7 in the SI). On larger time scales, the ionic polarization begins to relax accompanied by further relaxation of the solvent polarization in an almost equal-and-opposite fashion. The relaxation of $M_{\text{ion}}$ appears to follow a simple exponential time dependence, from which we can obtain an associated time scale $\tau_{\text{ion-tot}}$. In Fig. 5 we plot $\tau_{\text{ion-tot}}$ for all concentrations. Despite being roughly an order of magnitude smaller, we see that the dependence of $\tau_{\text{ion-tot}}$ on concentration closely follows that of $\tau_{\text{mix}}$ and $\tau_{\text{JB}}$. The observed anti-correlations between the solvent and ionic polarization during the system’s nonequilibrium response are reminiscent of the SL conditions at equilibrium, and consistent with recent observations in bulk electrolyte solutions at finite wavevector and frequency. The impact of these anti-correlations appears to manifest as a much faster overall charging dynamics than predicted by ionic relaxation alone, as reflected by the order of magnitude discrepancy between $\tau_{\text{ion-tot}}$ and $\tau_{Q}$. Also shown in Fig. 6(b,c) are the correlation functions $\langle \delta M_{\text{tot}}(0)\delta M_{\text{ion}}(t) \rangle$ and $\langle \delta M_{\text{tot}}(0)\delta M_{\text{wat}}(t) \rangle$ obtained directly from the equilibrium fluctuations at $\Delta \Psi = 0$ V, albeit at a lower time resolution (full lines). As expected, these results agree with those obtained from our nonequilibrium simulations.

In an attempt to quantify the impact of introducing ions, we have computed $\langle \delta Q(0)\delta Q(t) \rangle_{\text{diff}}$, by subtracting the pure water QACF from the QACF at finite salt concentration. We find that, for all investigated concentrations, $\langle \delta Q(0)\delta Q(t) \rangle_{\text{diff}}$ is well described by a simple exponential with characteristic time $\tau_{\text{diff}}$ (see SI sec. S2). The behavior of $\tau_{\text{diff}}$ with concentration is shown in Fig. 5. For all concentrations, $\tau_{\text{diff}}$ is roughly seven times larger than $\tau_{Q}$ and comparable to $\tau_{\text{ion-tot}}$. While it is tempting to attribute fast and slow timescales in the
system into motions that involve ions and those that do not, such a decomposition is not straightforward. This can be seen in Fig. 6(b,c), where we further decompose the equilibrium correlation functions according to Eq. 9. Not only do we see that $\langle \delta M_{\text{ion}}(0)\delta M_{\text{ion}}(t) \rangle$ and $\langle \delta M_{\text{ion}}(0)\delta M_{\text{wat}}(t) \rangle$ decay slowly, but so too does $\langle \delta M_{\text{wat}}(0)\delta M_{\text{wat}}(t) \rangle$. In other words, fast and slow relaxation cannot be separated into purely solvent and ionic contributions.

To summarize, we find that analytical theories and implicit solvent descriptions can describe the qualitative scaling of the relaxation time scales with concentrations, for the systems we considered. However, these predictions are far from a quantitative agreement with simulation results. Our analysis from MD results highlighted that: (i) ion and water polarization are strongly anticorrelated, and this effect is persistent in time; (ii) ion and water polarization relax with different time scales (single exponential with $\tau_{\text{ion-tot}}$, and a combination of $\tau_{\text{w}}$ and $\tau_{\text{ion-tot}}$, respectively). These two features are absent in most analytical theories of electrolytes and present a significant challenge for implicit solvent models to faithfully capture relaxation in EDL capacitors.

**Conclusions**

In this work, we employed molecular dynamics simulations to study electrode charge and polarization dynamics in gold/NaCl(aq) nanocapacitors. Using equilibrium and nonequilibrium simulations, we investigated the impact of ion concentration and interelectrode distance on the charge dynamics. Specifically, ions induce slower dynamics compared to pure water systems, and more concentrated solutions result in faster charge relaxation.

We simulated bulk NaCl(aq) systems to compute the frequency-dependent conductivity and validated the simulation results with extensive experimental datasets. Then, we calculated the frequency-dependent impedance from the electrode charge fluctuations in nanocapacitors. The comparison between the impedance of nanocapacitors and that of bulk showed that the electrode/electrolyte interfacial contribution is essentially capacitive and
that the electrolyte response is bulk-like even when the interelectrode distance is only of a few nanometers, provided that the latter is sufficiently large compared to the Debye screening length. We conclude that, in this scenario, the impedance of nanocapacitors can be represented by EC models based on a bulk impedance in series with capacitors. We tested the ability of these EC models to represent the impedance as we changed the interelectrode distance, and found excellent agreement with our simulation results over the whole frequency range. Future work could focus on the influence of more complicated, possibly heterogeneous electrode/electrolyte interfaces, as well as on the effect of screening within the electrode material.80

Finally, we investigated the most relevant characteristic times of charge and polarization relaxation and how they scale with salt concentration. We found that analytical predictions fail to describe quantitatively the simulation results, but can succeed in reproducing the qualitative behavior. We attribute this discrepancy, in part, to the strong and persistent anticorrelation between water and ion polarization, which is not described in most commonly employed analytical models. Our findings offer valuable contributions to the development of accurate coarse-grained descriptions of confined electrolytes.34 This will help to bridge the gap between molecular simulations and EIS experiments, paving the way for a microscopic interpretation of impedance.

Methods

Numerical simulations

Classical molecular dynamics simulations were performed using MetalWalls81,82 and LAMMPS83 (equipped with the ELECTRODE package84), which allows for the computation of custom properties on-the-fly. Equivalent simulations performed on the two software yielded consistent results, as already checked by other authors on similar systems.84 In this work, we simulated two different kinds of systems: bulk and confined simulations. The force field
parameterization and simulation setups are similar to those used in previous works. Bulk simulations of the electrolyte, described by a simple point charge model (i.e., water with the SPC/E model and NaCl ions modelled as Lennard-Jones particles with point charges), were performed with 3D periodic boundary conditions (PBCs) with “tin-foil” boundary conditions. The confined system also included gold electrodes modelled as Lennard-Jones particles with a gaussian charge density fluctuating in magnitude (see below). Simulations performed with MetalWalls were carried out under 2D PBCs, while those with LAMMPS used 3D PBCs and a finite field to impose $\Delta \Psi$. In all the confined simulations, the spacing between the electrodes $d$ was equilibrated at constant atmospheric pressure and production runs were carried out at fixed separation. All the simulations are performed in the NVT ensemble and the temperature is fixed at 298 K using a Nosé–Hoover chain thermostat, with 5 chained thermostats having all the same time constant of 1 ps. In confined simulations, we enforce the additional constraints of constant applied potential and global electroneutrality. The constant potential condition is ensured by the fluctuating charge method.

More simulation details and a list of all simulation runs can be found in the SI sec. S1.

**Frequency-dependent impedance from charge fluctuations and bulk conductivity spectrum**

The frequency-dependent electrical impedance and admittance were calculated from the dynamics of the equilibrium fluctuations of the electrode charge sampled from MD simulations, using the fluctuation-dissipation relation introduced in our previous work:

$$Y(\omega) = \beta \left[ i\omega \langle \delta Q^2 \rangle + \omega^2 \int_0^\infty \langle \delta Q(0)\delta Q(t) \rangle e^{-i\omega t} dt \right], \tag{10}$$

where $Y = 1/Z$ is the admittance, $Z$ is the impedance, $\beta = 1/k_B T$ with $k_B$ the Boltzmann constant and $T$ the temperature, $\omega$ is the angular frequency, $Q$ is the electrode charge, and $\delta Q = Q - \langle Q \rangle$, with $\langle \cdot \rangle$ denoting the canonical average. The numerical calculation of the
Fourier-Laplace transform in Eq. 10 was performed as in Ref. 49, using Filon-Lagrange integration and by applying a windowing procedure to $\langle \delta Q(0)\delta Q(t) \rangle$ to suppress the numerical noise at large times. In this work, we used a normalized version of the windowing function, which allows preserving the magnitude of the original function at short times. A direct comparison between the raw and windowed autocorrelation functions is shown in the SI sec. 9.

In principle, the frequency-dependent conductivity in bulk systems can be estimated from the dynamics of the total dipole moment $\mathbf{M}$, calculated with unwrapped coordinates and including both salt and solvent species. In particular, the susceptibility $\chi(\omega)$ can be estimated from the total dipole moment via

$$\chi(\omega) = \frac{\beta}{3V} \left[ \langle \delta \mathbf{M}^2 \rangle - i\omega \int_0^\infty \langle \delta \mathbf{M}(0)\delta \mathbf{M}(t) \rangle e^{-i\omega t} dt \right], \quad (11)$$

where $V$ is the system volume. The frequency-dependent conductivity can be then calculated as

$$\sigma(\omega) = i\omega \chi(\omega) = i\omega \chi'(\omega) - \omega \chi''(\omega), \quad (12)$$

where $\chi'$ and $\chi''$ denote the real and imaginary parts of the susceptibility. We used this approach to estimate the frequency-dependent conductivity from bulk water simulations. In the presence of free charge carriers (i.e., for finite salt concentrations), $\langle \mathbf{M}^2 \rangle$ becomes a divergent quantity, so the frequency-dependent conductivity has to be calculated using a different approach. The problem can be circumvented using electric currents $\mathbf{J}(t) = d\mathbf{M}/dt$ instead of the total polarization. The conductivity can be rewritten in the following form

$$\sigma(\omega) = \frac{\beta}{3V} \int_0^\infty \langle \delta \mathbf{J}(0)\delta \mathbf{J}(t) \rangle e^{-i\omega t} dt. \quad (13)$$

The Fourier-Laplace transform in Eqs. 11 and 13 was calculated numerically with the same
windowing and integration scheme used to solve the transform in Eq. 10.

For finite salt concentrations, the DC conductivity ($\sigma(\omega \to 0) = \sigma(0)$) can be estimated from the value of $\sigma(\omega)$ at the lowest frequency accessible, or by numerical integration of the current autocorrelation function. Alternatively, it can be computed using the Einstein-Helfand formalism which relates the total dipole moment of ions $M_{\text{ion}}$ to $\sigma(0)$: \(^{62}\)

$$\lim_{t \to \infty} \langle \Delta M_{\text{ion}}^2(t) \rangle = \frac{6V}{\beta} \sigma(0) t + 2 \langle M_{\text{ion}}^2 \rangle,$$

where $t$ is the time. In practice, we fit $\langle \Delta M_{\text{ion}}^2(t) \rangle$ with a line and extract $\sigma$ from the slope of the fitted line. A direct comparison between the MD results and the fitted lines is shown in the SI sec. S4.

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