Transient response of an electrolyte to a thermal quench

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We study the transient response of an electrolytic cell subject to a small, suddenly-applied temperature increase at one of its two bounding electrode surfaces. An inhomogeneous temperature profile then develops, causing, via the Soret effect, ionic rearrangements towards a state of polarized ionic charge density \( q \) and local salt density \( c \). We derive analytical approximations to \( q, c \), and the electrostatic potential \( \psi \) for early \((t \ll \tau_T)\) and late \((t \gg \tau_T)\) times as compared to the relaxation time \( \tau_T \) of the temperature. We challenge the conventional wisdom that the typically large Lewis number, the ratio \( a/D \) of thermal to ionic diffusivities, of most liquids implies a quickly-reached steady-state temperature profile onto which ions relax slowly. Though true for the evolution of \( c \), it turns out that \( q \) (and \( \psi \)) can respond much faster. This is because the ratio \( \tau_T/\tau_q \) of thermal to ionic charge relaxation times involves, besides \( a/D \), the salt concentration-dependent Debye length \( \kappa_L \), which can be varied over many decades. Consequently, one can access both \( \tau_q \gg \tau_T \) (if \( \kappa L \approx 1 \), with \( 2L \) being the electrode separation), for which the temperature relaxes quickly and our analytical expressions apply for most of the transient response, as well as \( \tau_q \ll \tau_T \) (if \( \kappa L \gg 1 \)). In the latter scenario, corresponding to several prior experimental setups, a significant portion of the transient response of the cell falls in the \( t \ll \tau_T\)-regime, for which our approximated \( q \) (corroborated by numerics) exhibits a density wave that has not been discussed before in this context.

I. INTRODUCTION

The well-known Soret effect refers to the phenomenon that ions dissolved in a nonisothermal fluid can show preferential movement along or against thermal gradients, characterized by their heats of transport \([1, 2]\). Determining these ionic heats of transport, both experimentally \([3,5]\) and numerically \([6,8]\) is an ongoing scientific endeavor. When ionic thermodiffusion is impeded, for instance by blocking electrodes, local accumulations of either ionic species can be generated. Since such accumulations are not necessarily charge neutral, applying a temperature difference over an electrolyte can generate a so-called thermovoltage \( V_T \). This thermovoltage, the ionic analogue of the Seebeck potential in semiconductors, opens the door to energy scavenging from temperature differences \([9,11]\). Since an electric current in an external circuit is only present during the transient build-up of \( V_T(t) \) \([12]\), it is of interest to study how electrolytic cells respond shortly after a temperature difference is imposed. Bonetti et al. \([13]\) experimentally found that \( V_T(t) \) develops on the diffusion time scale \( L^2/D \), with \( 2L \) being the electrode separation and \( D \) the ionic diffusion constant.

Theoretical models were developed by Agar and Turner \([14]\) and later by Stout and Khair \([15]\). Motivated by the typically large ratio \( a/D \approx 100 \), with \( a \) being the thermal diffusivity, their analyses departed from the ansatz that the steady-state temperature profile develops instantaneously \( [T(x, t) = T(x), \text{with} \ x \text{ being the spatial coordinate of their one-dimensional model electrolytic cells}] \), after which ions relax slowly. With this ansatz, an exact expression for the transient response of the neutral salt density \( c \) \([14]\) and approximate expressions for the corresponding electrostatic potential \( \psi \) and the ionic charge density \( q \) \([15]\) were found. As we show in the present article, the corresponding exact solutions to \( q \) and \( \psi \) decay at late times with a common timescale \( \tau_q = L^2/(D[(\kappa L)^2 + \pi^2/4]) \), with \( \kappa \) being the inverse Debye length. However, the appearance of \( \kappa L \) in \( \tau_q \) signals a problem with the ansatz \( T(x, t) = T(x) \). To see this, consider the ratio of the time scales of the pure thermal relaxation of the cell in the absence of ions \( \text{timescale} \tau_T = 4L^2/(\pi^2a) \), c.f. Eq. \((6)\) to that of the ionic relax-

![Figure 1](image-url)

Figure 1. A model thermoelectric cell consisting of a 1:1 electrolyte with Debye length \( \kappa^{-1} \) (solvent not shown) and two flat electrodes separated over a distance \( 2L \). At time \( t = 0 \), the temperature of one electrode increases by a factor \( 1 + \epsilon \).
ation:

\[ \frac{\tau_T}{\tau_q} = \frac{D}{a} \left[ 1 + \frac{4(\kappa L)^2}{\pi^2} \right]. \]

Since \( \kappa \) depends on the salt concentration, this ratio can be varied over many decades, and is by no means restricted to \( \tau_T/\tau_q \ll 1 \) (requiring minute devices and very low salt concentrations). Hence, an instantaneous steady-state temperature profile onto which ions rearrange slowly is a special case of a more general problem. Given the longstanding experimental and theoretical interest in thermodiffusion of electrolytes, it is timely to discuss its solution.

### II. SETUP

We consider an electrolytic cell (see Fig. 1) with two parallel flat electrodes at \( x = \pm L \). Provided that the electrodes are much larger than their separation, we can ignore edge effects and treat this system as being one-dimensional. The electrodes are chemically inert and impermeable to ions and they are not connected by an external circuit, hence, do not acquire a surface charge. The cell is filled with an electrolyte solution at bulk salt concentration \( \rho_s \) in a solvent of dielectric constant \( \varepsilon \).

The valence \( z_i \) of ionic species \( i = \{+,-\} \) amounts to \( z_+ = 1 \) for the cations and \( z_- = -1 \) for the anions, respectively. The electrolyte is further characterized by the diffusion constants \( D_i \), single-ion heats of transport \( Q_i^s \), and the thermal conductivity \( \kappa_\theta \) (\( J \mathrm{kg}^{-1} \mathrm{K}^{-1} \)). For simplicity, we ignore all (salt) density parameter and specify to the case where \( D_+ = D_- \equiv D \). Moreover, we ignore convection here, which is reasonable if temperature differences are small and if the thermal gradient is aligned in the direction opposite to gravity. Alternatively, convection can be minimized in “microgravity”, e.g., onboard the International Space Station.

#### A. Governing equations

The electrostatic potential \( \psi(x, t) \), the local ionic number densities \( \rho_i(x, t) \), and the local temperature \( T(x, t) \) are modeled via the classical Poisson-Nernst-Planck and heat equations,

\[
\begin{align*}
\varepsilon_0 \varepsilon_0 \partial_x^2 \psi &= -eq, \quad (2a) \\
\partial_t \rho_i &= -\partial_x J_i, \quad (2b) \\
J_i &= -D \left( \partial_x \rho_i + \frac{z_i c_p \rho_i}{k_B T} \partial_x \psi + \frac{\rho_i Q_i^s}{k_B T^2} \partial_x T \right), \quad (2c) \\
\partial_t T &= a \partial_x^2 T - \frac{e}{c_p} (J_+ - J_-) \partial_x \psi, \quad (2d)
\end{align*}
\]

with \( e \) being the proton charge and \( \varepsilon_0 \) being the vacuum permittivity. First, in the Poisson equation \( (2a) \), appears the ionic unit charge density \( q = \rho_+ - \rho_- \). Next, the Nernst-Planck equations \( (2b) \) account for diffusion, electromigration, and thermodiffusion. Finally, in the heat equation \( (2c) \) appears \( \kappa_\theta / (c_p e^2) \), the thermal diffusivity, and a heat source term that was discussed at length in Refs. [18, 19].

Initially, the ionic density profiles and temperature are homogeneous:

\[
\rho_i(x, t < 0) = \rho_s, \quad T(x, t < 0) = T_0. \quad (3)
\]

Thereafter, at \( t = 0 \), the temperature of the electrode at \( x = L \) is suddenly increased to \( T(L, t = 0) = T_0 + \Delta T \), with \( \Delta T > 0 \). For \( t \geq 0 \), the boundary conditions at the charge-neutral, ion-impermeable electrodes read

\[
\begin{align*}
\partial_x \psi(\pm L, t) &= 0 \quad J_i(\pm L, t) = 0 \quad (4a) \\
T(-L, t) &= T_0 \quad T(L, t) = T_0 + \Delta T. \quad (4b)
\end{align*}
\]

We note that Eq. (4) only fixes \( \psi \) up to a constant. Without loss of generality, we therefore moreover impose

\[
\psi(L, t) = 0. \quad (5)
\]

This means that the thermovoltage, \( V_T(t) = \psi(-L, t) - \psi(L, t) \), a key observable of our model system, simply reads \( V_T(t) = \psi(-L, t) \).

As we will show in this article, the transient and steady-state behavior of Eqs. (2), (3), (4), and (5) crucially depends on the two diffusivities, \( a \) and \( D \), and two lengthscales, \( L \) and the Debye length \( \kappa^{-1} = (\varepsilon_0 k_B T_0 / (2 \rho_s e^2))^{1/2} \). First, with these four parameters, one constructs the dimensionless Lewis number \( Le = a/D \) and the dimensionless Debye separation parameter \( n = \kappa L \). At steady state, \( n \) measures to which extent nonzero \( q \)-values penetrate into the bulk: while \( n \gg 1 \) indicates that \( q \) is nonzero only in a small region close to the electrode surface, \( n < 1 \), the ionic charge imbalance permeates the complete cell [cf. Eq. (15)]. Second, by combining either of the two diffusivities with two lengthscales, one can construct time constants. Out of many possible combinations, three of such combination turn out to be fundamental to our cell: the “thermal diffusion time” \( L^2/a \), the “diffusion time” \( L^2/D \), and the “Debye time” \( 1/(D \kappa L^2) \). Depending on \( n \), the four quantities of interest, \( T \), \( \psi \), \( q \), and \( c \), all relax at late times with (combinations of) these three fundamental timescales, often in combination with numerical prefactors.

#### B. Pure thermal relaxation

In absence of ions, or when the source term of the heat equation is negligible, transient thermal response to a boundary value quench is governed by a simplified heat equation, \( \partial_t T = a \partial_x^2 T \), and the same initial and boundary conditions as in Eqs. (3) and (4b). Writing \( K_j = j \pi / 2 \) for \( j = 1, 2, 3, \ldots \), the solution to this textbook problem
The role played by the six dimensionless parameters. However, when we present solutions and results, we prefer to restore conventional units because that makes physical interpretation easier.

### III. Analytical Approximations

As we show next, for \( \epsilon \ll 1 \), we can analytically solve Eqs. (8a) and (8b) both at early times [using Eq. (7)] and at late times [using the steady-state limit of Eq. (6)]. To do so, we expand \( \psi, q \), and the local salt density \( c = \rho_+ + \rho_- \) in the small parameter \( \psi = \psi_0 + \epsilon \psi_1 + O(\epsilon^2) \), \( q = q_0 + \epsilon q_1 + O(\epsilon^2) \), and \( c = c_0 + \epsilon c_1 + O(\epsilon^2) \), respectively, and do the same for the remaining five dimensionless parameters: \( \alpha_i = \alpha_{i,0} + \epsilon \alpha_{i,1} + O(\epsilon^2) \) etc. Inserting those variables and parameters into Eqs. (8a) and (8b) results in \( O(1) \) problems that characterize the initial isothermal situation (clearly, \( \psi_0 = 0, q_0 = 0 \), and \( c_0 = 2 \rho_0 \)), and different \( O(\epsilon) \) problems for \( \psi_1, q_1 \), and \( c_1 \) for the early- and late-time response. With a slight abuse of notation, from hereon, we drop the subscript zeros of all dimensionless parameters, because subscript-one parameters only appear in \( O(\epsilon^2) \) terms. Likewise, if \( \epsilon \) depends on \( T \), Eqs. (9) and (7) apply only if \( \epsilon \ll 1 \). (When we derived these equations for arbitrary \( \epsilon \), we tacitly assumed that \( a(T) = a \).)

We moreover note that the source term in Eq. (2d) is \( O(\epsilon^2) \). This means that the results of Sec. II B, derived by setting \( f = 0 \), are accurate for finite \( f \) as well.

#### A. Early-time \( (t \ll \tau_T) \) response

Inserting Eq. (7) into Eq. (8b) yields

\[
\partial_t \tilde{q}_1 = \partial^2_{\tilde{x}} \tilde{q}_1 - n^2 \tilde{q}_1 + \frac{\alpha_d(1 - \tilde{x})}{\sqrt{\pi(\alpha D) \tilde{t}}} \exp \left[ \frac{-D(1 - \tilde{x})^2}{4\alpha \tilde{t}} \right] \quad (10a)
\]

\[
\partial_t \tilde{c}_1 = \partial^2_{\tilde{x}} \tilde{c}_1 + \frac{\alpha_s(1 - \tilde{x})}{\sqrt{\pi(\alpha D) \tilde{t}}} \exp \left[ \frac{-D(1 - \tilde{x})^2}{4\alpha \tilde{t}} \right] \quad (10b)
\]

with \( \alpha_d = \alpha_+ - \alpha_- \) and \( \alpha_s = \alpha_+ + \alpha_- \). The \( n^2 \tilde{q}_1 \)-term in Eq. (10a) stems from the electromotive term \( 2 \partial^2_{\tilde{x}} \tilde{q}_1 \) in \( \tilde{J}_q \), together with Eq. (8a). The corresponding electromotive term in the salt flow \( \partial^2_{\tilde{x}} \tilde{q}_1 \partial_{\tilde{x}} \tilde{q}_1 \) is \( O(\epsilon^2) \) thus neglected in Eq. (10a).

At time \( t = 0 \), the system is still charge neutral \( [q(x, t) = 0] \) and the nonzero ionic charge current is caused solely by thermodiffusion. There will be early (but finite) times at which thermodiffusion still dominates electromigration: times, thus, at which the electromotive term \( n^2 \tilde{q}_1 \) in Eq. (10a) can be neglected. Clearly, (1) we cannot expect to find a self-consistent nonzero solution for \( q(x, t) \) in this way and (2) the temporal range of validity of this approximation will decrease with increasing \( n \). With the omission of the \( n^2 \tilde{q}_1 \)-term in Eq. (10a), the equations governing the early-time response of \( \tilde{q}_1/\alpha_d \) and \( \tilde{c}_1/\alpha_s \) are the same. Since the same
equations have the same solutions, our forthcoming results for \( q_1 \) are trivially transferable to \( c_1 \). Substituting \( p = D(\tilde{x} - 1)^2/(4a\tilde{t}) \) in Eq. (10a) yields an inhomogeneous ordinary differential equation:

\[
p\frac{d^2q_1}{dp^2} + \left( \frac{1}{2} + \frac{a}{D} \right) \frac{dq_1}{dp} = -\frac{2\alpha_d}{\sqrt{\pi}} \sqrt{p} \exp[-p] \quad \text{(11a)}
\]

\[
\frac{d^2q_1}{dp^2}\bigg|_{p=0} = -\frac{2\alpha_d}{\sqrt{\pi}}, \quad \text{(11b)}
\]

where Eq. (11b) follows from \( \tilde{J}_q(1, \tilde{t}) = 0 \) [cf. Eq. (9b)]. While Eq. (11b) fixes one of the two integration constants of the general solution of Eq. (11a), it turns out that the other integration constant cannot be fixed by \( \tilde{J}_q(\tilde{x} = -1, t) = 0 \); we simplify do not have the freedom to impose \( dq/dp \) in two positions. This must be because Eq. (11a) resulted from a procedure that ignores the electrode at \( \tilde{x} = -1 \). To fix this second integration constant nevertheless, we enforce charge neutrality

\[
\int_{-1}^{1} d\tilde{x} \tilde{q}_1(\tilde{x}, \tilde{t}) = 0 \Rightarrow \int_{0}^{D/(4\alpha_d)} d\tilde{p} \tilde{q}_1(p)/\sqrt{p} = 0, \quad \text{which arrises naturally from Eqs. (2b) and (4a).}
\]

We find

\[
\frac{q_1(x,t)}{2\rho_a\alpha_d} = \frac{2D}{D - a} \left[ \sqrt{\frac{at}{L}} \left( \exp \left[ \frac{L^2}{D t} \right] - \exp \left[ \frac{L^2}{at} \right] \right) \right. \\
- \sqrt{\frac{a}{D}} \text{Erf} \left( \frac{L - x}{2\sqrt{D}t} \right) + \text{Erf} \left( \frac{L - x}{2\sqrt{at}} \right) \\
\left. + \sqrt{\frac{a}{D}} \text{Erf} \left( \frac{L}{\sqrt{at}} \right) - \text{Erf} \left( \frac{L}{\sqrt{at}} \right) \right], \quad \text{(12)}
\]

and the same for \( c_1/(2\rho_a\alpha_s) \).

We can now find \( \psi(x,t) \) by integrating \( q_1 \) twice and enforcing \( \psi(L,t) = 0 \) and \( \partial_\tilde{t}\psi(L,t) = 0 \). The solution, which is too lengthy to be reproduced here, turns out to satisfy the boundary condition \( \partial_\tilde{t}\psi(-L,t) = 0 \) as well. This means that the electromotive term drops out of \( \tilde{J}_q(-1, \tilde{t}) \). We determined the importance of the two remaining terms in \( \tilde{J}_q(-1, \tilde{t}) = -\partial_\tilde{t}q_1(-1, \tilde{t}) - 2\alpha_d\tilde{J}_1 \tilde{t} \) in Eq. (7) and (12) and found for \( a/D = 100 \) that \( \tilde{J}_q(-1, \tilde{t}) = \{10^{-15}, 1.8 \times 10^{-4}\} \) at \( ta/L^2 = \{10^{-1}, 1\} \), respectively. Hence, as long as Eq. (7) approximates \( T(x,t) \) decently, the boundary condition \( \tilde{J}_q(-1, \tilde{t}) = 0 \) that we could not strictly impose is satisfied approximately nevertheless.

### B. Late-time \((t \gg \tau_q)\) response

Upon inserting the steady-state temperature profile \( \tilde{T} = 1 + \epsilon(1 + \tilde{x})/2 \), at \( \mathcal{O}(\epsilon) \), Eq. (8b) simplifies to

\[
\partial_\tilde{t}\tilde{q}_1 = \partial_\tilde{x}^2 \tilde{q}_1 - n^2 \tilde{q}_1 \quad \partial_\tilde{t}\tilde{c}_1 = \partial_\tilde{x}^2 \tilde{c}_1. \quad \text{(13)}
\]

Here, the thermodiffusion terms in the ionic fluxes amount to constants \( J_i \sim \alpha_i \); hence, their spatial derivatives are absent in Eq. (13). As pointed out by Refs. [3, 15], \( \alpha_q \) and \( \alpha_d \) then only appear in the boundary conditions,

\[
\tilde{q}_1(\tilde{x}, \tilde{t} < 0) = 0 \quad \tilde{c}_1(\tilde{x}, \tilde{t} < 0) = 0 \quad \text{(14a)}
\]

\[
\partial_\tilde{t}\tilde{q}_1(\pm 1, \tilde{t}) = -\alpha_d \quad \partial_\tilde{t}\tilde{c}_1(\pm 1, \tilde{t}) = -\alpha_s \quad \text{(14b)}
\]

hence do not affect the relaxation rates. Only few of the original six dimensionless numbers controlling Eq. (8) and Eq. (9) now remain. We have effectively set \( a/D \to \infty \), which has transferred \( \alpha_d \) from the PDEs to the BCs. Moreover, as long as \( f \ll 1 \), the source term of the heat equation (8c) is \( \mathcal{O}(\epsilon^2) \) hence irrelevant. With \( \epsilon \) only appearing in the small-\( \epsilon \) expansions, \( n \) is the only remaining parameter that can influence the relaxation rates of our system. In Appendix A we solve Eqs. (8a) and (13) subject to Eq. (14). Writing \( N_j = (j - 1/2)\pi \), the solutions read

\[
\psi_1(x,t) = -n^2 \frac{1}{2} \sum_{j=1}^{\infty} \frac{(-1)^j \sin[N_j x/L]}{N_j^2 [n^2 + N_j^2]} \exp \left[ -t/\tau_q^j \right] + \frac{1}{2n} \sinh(nx/L) - \sinh n + \frac{1}{2} \frac{x}{2L} \quad \text{(15a)}
\]

\[
\frac{q_1(x,t)}{2\rho_a\alpha_d} = -2 \frac{1}{n} \sum_{j=1}^{\infty} \frac{(-1)^j \sin[N_j x/L]}{n^2 + N_j^2} \exp \left[ -t/\tau_q^j \right] - \frac{1}{n} \sinh(nx/L) \cosh n \quad \text{(15b)}
\]

\[
\frac{c_1(x,t)}{2\rho_a\alpha_s} = -2 \frac{1}{n} \sum_{j=1}^{\infty} \frac{(-1)^j \sin[N_j x/L]}{N_j^2} \exp \left[ -\frac{N_j^2 D t}{L^2} \right] - \frac{x}{L} \quad \text{(15c)}
\]

where \( \tau_q^j = L^2/[D(n^2 + N_j^2)] \) and where Eq. (15c) appeared previously in Ref. [14]. We see that, indeed, the relaxation of \( \psi \) and \( q \) (in units of \( L^2/D \)) depends only on \( n \), while the relaxation of \( c \) (in units of \( L^2/D \)) has no parametric dependence whatsoever. At late times, the relaxation of the functions in Eq. (15) is dominated by the \( j = 1 \) terms of the sums: while \( c \) decays with approximately \( 4L^2/(\pi^2 D) \), \( \psi \) and \( q \) relax with \( \tau_q \approx L^2/[D(n^2 + \pi^2/4)] \), as anticipated in the introduction. Hence, for \( n \ll 1 \) we find a universal decay time \( 4L^2/(\pi^2 D) \) proportional to the diffusion time, whereas for \( n \gg 1 \), \( \psi \) and \( q \) relax with the Debye time \( 1/(\kappa D) \).

### IV. RESULTS

We numerically solved Eq. (8) with 

\[
\text{COMSOL MULTIPHYSICS 5.4 for } a/D = 100, \alpha_+ = 0.5, \alpha_- = 0.1, f = 2 \times 10^{-3}, \epsilon = 10^{-3}, \text{ and } n = 1 \text{ and } n = 100.
\]

These parameters correspond roughly to an aqueous 1:1 electrolyte \( \varphi \approx 10^6 \text{ g m}^{-3}, \sigma_0 \approx 4 \text{ J g}^{-1}, a/D \) and \( \alpha_\pm \) from Ref. [15] subject to a thermal quench of 0.3 K around room temperature. For a 0.1 M salt solution, \( n = 100 \) corresponds to an 0.2 \( \mu \text{m} \)-wide device. Conversely, at 1 M, \( n = 1 \) requires \( 2L = 6.6 \text{ nm} \). Clearly,
the latter case might be difficult to reach experimentally. Moreover, either going to even higher salt concentrations or further device miniaturization, the validity of our continuum framework [Eq. (2)] becomes questionable. Notwithstanding these reservations, we discuss the $n = 1$ case because, judging from Eq. (1), if anywhere, this is the parameter setting for which the instantaneous temperature ansatz [and Eq. (15)] should work best.

We show analytical (lines) and numerical (symbols) solutions to Eq. (8) for $n = 1$ in Fig. 2 where we plot the position dependence of $T$, $\psi$, $q$, and $c$ for logarithmically separated times between $tD/L^2 = 10^{-6}$ and $tD/L^2 = 10^{-4}$. In Fig. 2 (a) we show the temperature. As a sanity check, we also compared numerical solutions for $(T(x,t)−T_0)/\Delta T$ at $f = 0$ to the exact result Eq. (6) [in this section we truncate the sums in Eqs. (6) and (15) after 2000 terms]; the difference between either predictions was at most 0.02 (at $tD/L^2 = 10^{-6}$), dropping to $10^{-12}$ at late times. The difference between $T$ calculated with either $f = 2 \times 10^{-3}$ or $f = 0$ (and other parameters as before) was too small to detect within this numerical error margin. In any case, with our choice $f = 2\epsilon$, the source term of the heat equation (8c) is $O(\epsilon^2)$. Therefore, its effects are beyond the range of validity of our theory.

As anticipated in Sec. III B, Fig. 2 (a) moreover shows that Eq. (7) accurately describes $T(x,t)$ at $ta/L^2 = 0.1$ (plusses) as well as at earlier times (not shown). For the stated parameter set, Fig. 2 shows that $T(x,t)$ relaxes almost completely before $\psi$, $q$, and $c$ deviate from their initial values. Consequently, the ionic relaxation falls predominantly in the late-time regime ($t \gg \tau_\rho$) discussed in Sec. III B. From $ta/L^2 = 10$ onwards, the assumption of a thermal steady state that we used to derive Eq. (15) is justified. Consequently, at late times, we observe a decent correspondence between numerics and the analytical predictions for $\psi_1, q_1$, and $c_1$ [Eqs. (15a), (15b), and (15c), respectively]. Conversely, at early times ($t \ll \tau_\rho$), when Eq. (7) accurately describes $T(x,t)$, one expects the predictions of Eq. (12) for $q_1$ and $c_1$ to be accurate. Indeed, the inset of Fig. 2 (c) (a zoom-in of the main panel to the region $x \lesssim L$) shows an excellent agreement between Eq. (12) (dashed lines) and the same numerical data until $tD/L^2 = 10^{-3}$, while at that same time, Eq. (15b) gives erroneous predictions (the line does not pierce the open squares). Interestingly, this inset exhibits a tiny ionic charge density wave that moves with the front of thermal perturbation and that breaks the antisymmetry (present at late times) of $q$ and $c$ around the midplane at early times. The given equivalence at early times of $q_1/\alpha_d$ to $c_1/\alpha_\psi$ as discussed in Sec. III A, the inset of Fig. 2 (d) shows that the same analytical expression Eq. (12) also describes the evolution of $c_1$ at early times well.

Fig. 3 shows numerical solutions to Eq. (8) and the same analytical approximations as before, now for $n = 100$. Since $T$ and $c_1$ are essentially $n$-independent [cf. Eqs. (6), (7), (12) and (15)], we only show $\psi_1$ in Fig. 3 (a) and $q_1$ in Fig. 3 (b). We see in Fig. 3 (b) that

![Figure 2](image-url)
Eq. (12) is now accurate only until $tD/L^2 = 10^{-5}$ [as this equation is $n$-independent, the dashed lines in Fig. 3(b) are the same as in the inset of Fig. 2(c)]. This difference with the $n = 1$ case (accurate until $tD/L^2 = 10^{-3}$) is understood in terms of the larger error made for higher $n$ in neglecting the term $n^2\hat{q}_1$ in Eq. (10a). Equation (15b) is accurate after $tD/L^2 = 10^{-2}$, comparable to $tD/L^2 = 10^{-1}$ for the $n = 1$ case. The key difference with the $n = 1$ case, however, is that at $tD/L^2 = 10^{-1}$, $q_1(x,t)$ has already reached its steady-state profile [cf. Eq. (1): with increasing $n$, the early-time ($t \ll \tau_T$) regime of the transient response of $q$ and $\psi$ gains in importance]. Hence, Eq. (15b) is irrelevant for the description of the transient behavior of $q(x,t)$ for $n = 100$ and solely captures its steady state. Yet, out of curiosity, we plot the corresponding late-time expression for $\psi_1$ [Eq. (15a)] in Fig. 3(a): while this expression gets the shape of $\psi_1$ completely wrong (except at steady state), it surprisingly accurately estimates the thermovoltage $V_T(t) = \epsilon \psi_1(-L,t)$ at all times considered. Apparently, for the development of $V_T(t)$, it is not necessary that the thermal perturbation has spanned the system: The local charge separation as observed in Fig. 3(b) leads to the same voltage drop, but now already over the small region coincident with the thermal perturbation. Meanwhile, it comes as somewhat of a surprise that the analytical prediction for $\psi_1$ calculated with Eqs. (12) provides fair approximations to our numerical results only for very early times ($tD/L^2 = 10^{-6}, 10^{-5}$), thereafter overestimating $\psi_1$ greatly. Since this method to approximate $\psi_1$ already goes awry at $t \ll \tau_T$, this discrepancy cannot be attributed to usage of the approximate early-time temperature [Eq. (7) instead of Eq. (6)] in the derivation of Eq. (12). Apparently, $\psi_1$ is very sensitive to the errors in $q_1$ (observable in Fig. 3(b)) from $tD/L^2 = 10^{-4}$ onwards resulting from the omission of the electromotive term $\epsilon \partial_x^2 \psi_1$ in Eq. (10).

In Fig. 4, we show numerics (symbols) and analytical predictions from Eq. (15) (lines) for the relaxation of $V_T(t) = \psi_1(-L,t)$ and the absolute boundary values of the ionic charge and salt densities, $|q_1(\pm L,t)|$ and $|c_1(\pm L,t)|$ respectively. Concerning $V_T(t)$, we see that analytical predictions agree well with numerics for $n = 1$ [unsurprising, given the agreement observed in Fig. 2(b)] and $n = 100$, where a minor discrepancy is observed at very early times. Again, since the steady-state temperature ansatz is only justifiable after $tD/L^2 = 0.1$, the good agreement observed in Fig. 4(b) between numerics and Eq. (15a) up to $tD/L^2 = 10^{-2}$ [pushing that equation five orders of magnitude into temporal terra incognita] is remarkable. The small-$t$ scaling of $\beta_0 e^{\psi_1/(\alpha_d)} = k^2Dt$ (black dashed lines) is derived in Appendix B.

We see in Fig. 4 that, at early times ($t \ll \tau_T$), $|c_1(\pm L,t)|$ and $|q_1(\pm L,t)|$ are perturbed at the quenched ($x = L$) electrode (down triangles and circles), and unperturbed at the other side (up triangles and squares). With Eq. (12) we find that the early-time plateaus observed in Fig. 4 lie at $\lim_{t \to 0^+} |q_1(L,t)|/(2\rho_s \alpha_d) = 2/(1 + \sqrt{a/D}) \approx 0.18$, independent of $n$. Interestingly, at $n = 100$ this prediction for $c_1$ is still accurate around $t \approx \tau_T$, when Eq. (12) inaccurately describes $q_1$ [Fig. 3(b)]. At $n = 1$ the omission of the $n^2 q_1$-term in Eq. (10a) is justifiable and the prediction $\lim_{t \to 0^+} |q_1(L,t)|/(2\rho_s \alpha_d) \approx 0.18$ holds up to $t \approx \tau_T$ as well. From $tD/L^2 = 0.01 \approx \tau_T$ onwards, we see, for $n = 1$, that numerics and analytical predictions from Eq. (15) converge, in line with our observations in Fig. 2. Once converged, they scale as $|q_1(\pm L)| = |c_1(\pm L)| = 2\sqrt{D t/L^2 \pi}$ (red dashed lines) as derived in Appendix B finally relaxing to their steady-state values around $tD/L^2 = 1$. Figure 4(b) shows a separation of timescales over four orders of magni-
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{The relaxation of $V_T(t) = \epsilon \psi_1(-L, t), q_1(\pm L, t)$, and $c_1(\pm L, t)$ (black, red, blue) from numerics (symbols) and Eq. (15) (lines) ($j \leq 10$), for $n = 1$ (a) and $n = 100$ (b). Plotted as well are $\kappa^2Dt$ (black dashed) and $2\sqrt{Dt/(L^2\pi)}$ (red dashed).}
\end{figure}

...tude for the three observables $\psi_1(-L, t), q_1(\pm L, t)$, and $c_1(\pm L, t)$. The separation of time scales of boundary observables $V_T(t)$ and $q(\pm L, t)$ seems to contradict the intuition that ionic charge and electrostatic potential are instantaneously related via the Poisson equation, and should thus relax in lockstep. As is clear from Fig. 3(a), however, the thermovoltage $V_T$ settles much faster than the overall electrostatic potential; at $tL^2/2 = 1$ (diamonds), $\psi(x, t)$ has not reached its steady state yet.

V. DISCUSSION

We note that our finding $V_T(t) \sim \exp[-Dk^2t]$ of Eq. (12) is at odds with Ref. [13]. They studied the relaxation of an ionic liquid-filled cell ($L = 3$ mm) and found that their experimental data could be fitted by $V_T(t) \sim \exp[-\pi^2D^*t/(4L^2)]$, with $D^*$ an effective (fitted) diffusion constant, a factor 3 off from literature values. A direct comparison between our results is difficult, however, as their setup: (1) used an ionic liquid, which invalidates our continuum Nernst-Planck description of the ionic currents (reasonable for dilute electrolytes) and to which it is difficult to assign a the Debye length; (2) had comparable lateral and in-plane dimensions, which invalidates usage of a one-dimensional model, and; (3) was exposed to a thermal quench two orders of magnitude larger. Exploratory numerical simulations of Eq. (15) with $\epsilon = 0.1$ (and $T$-independent dimensionless parameters) that we performed showed that point (3) cannot explain the discrepancy to our work: in that case, the qualitative behavior (including the separation of relaxation times scales) of our setup remains the same, with the notable exception that the anti-symmetry of the steady-state profiles $c$ and $q$ around $x = 0$ is broken.

VI. CONCLUSION

We have studied the response of a model electrolytic cell subject to a quench in the temperature at one of its two confining electrode surfaces. The system is modeled by four coupled differential equations [8] in which six dimensionless numbers appear: the size of the quench $\epsilon$, the Debye separation parameter $\kappa L$, the ratio of thermal to ionic relaxation $a/D$, the reduced ionic Soret coefficients $\alpha_+$ and $\alpha_-$, and the combination $k_B\rho_s/\varphi c_p$ for ionic heat production, respectively. We found analytical approximations to the ionic charge density $q$, neutral salt concentration $c$, and electrostatic potential $\psi$ for early and late times compared to the thermal relaxation. These expressions were shown to correspond well to numerical simulations of the same quantities in their respective temporal regimes of validity [we performed the numerical simulations of Eq. (8) using a parameter set typical for an aqueous 1:1 electrolyte]. This leaves behind an intermediate time window for which we only have numerical data. Notably, the size of this window depends on $\kappa L$ because the early-time expression for $q$ was derived with the...
omission of the thermodiffusion term \((\kappa L)^2 q\) in the ionic charge current. This means that the early-time expressions approximate \(q\) over a longer time period at \(\kappa L = 1\) (valid until \(tD = 10^{-1}\)) than at \(\kappa L = 100\) (valid until \(tD = 10^{-3}\)). The importance of either regimes (early- and late-time) was shown to depend on \(\kappa L\). For \(\kappa L = 1\), the system behaves mainly as explained in Ref. [15]: the quenched temperature relaxes quickly, after which the electrostatic potential and ionic charge and salt densities relax slowly. Conversely, for \(\kappa L = 100\), the rearrangement of ions in thermal gradients is sufficiently fast that the ionic charge density can track the thermal relaxation. For all parameters considered, an ionic charge density wave is observed that spreads as the thermal perturbation travels through the system. While the ionic relaxation becomes enslaved to the slow thermal relaxation, the thermovoltage develops on the Debye timescale, in this case, the fastest timescale of the system.

The main conclusions of this article are twofold. Depending on the Debye separation parameter: (1) the thermovoltage of a dilute 1:1 electrolyte can settle much faster than the diffusion time scale \(L^2/D\), namely, on the Debye time scale \(1/(D\kappa^2)\), and; (2) assuming an instantaneous steady-state temperature profile gives satisfactory predictions for the transient ionic density profiles, but wrong predictions for the transient ionic charge density, and electrostatic potential profiles.

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Appendix A: Derivation of Eq. [15]

We apply Laplace transformations on Eqs. (8a) and (13) to transform the PDEs for \(\psi\), \(\tilde{q}\), and \(\tilde{c}\) into ODEs for their Laplace transformed counterparts \(\tilde{\psi}\), \(\tilde{\tilde{q}}\), and \(\tilde{\tilde{c}}\) [we denote the Laplace transform of a function \(f(x, t)\) by \(\hat{f}(\hat{x}, \hat{t}) = \int_0^\infty dt \exp(-st)f(x, t)\)]. Stout and Khair [14] already found solutions to these ODEs [see their Eq. (20)], which in our notation read

\[
\begin{align*}
\tilde{c}_1(\hat{x}, s) &= -\frac{1}{\alpha_s} \frac{\sinh(r\hat{x})}{rs \cosh r} \quad (A1a) \\
\tilde{\tilde{q}}_1(\hat{x}, s) &= -\frac{1}{\alpha_d} \frac{\sinh(m\hat{x})}{ms \cosh m} \quad (A1b) \\
\tilde{\psi}_1(\hat{x}, s) &= \frac{n^2}{2m^2 s} \left[ \frac{\sinh(m\hat{x}) - \sinh m}{m \cosh m} + 1 - \hat{x} \right] \quad (A1c)
\end{align*}
\]

with \(r^2 = s\) and \(m^2 = n^2 + s\). To determine \(\tilde{\psi}, \tilde{\tilde{q}},\) and \(\tilde{\tilde{c}}\), we need to perform inverse Laplace transformations on Eq. (A1). For instance, determining \(\psi(\hat{x}, \hat{t})\) comes down to

\[
\hat{\psi}_1(\hat{x}, \hat{t}) = \sum_{s \in \sigma} \text{Res} \left( \hat{\psi}_1 \exp(s\hat{t}), s \right), \quad (A2)
\]

where the poles \(s_i = \{s_0, s_n, s_j^\ast\}\) of \(\hat{\psi}(\hat{x}, s)\) are located at \(s_0 = 0, s_n = -n^2\), and \(s_j^\ast = (m^2)^{1/2} - n^2\) where \(m^2 = \pm (j - 1/2)^2\pi \equiv \pm i\ell_j\) with \(j \in \mathbb{N}\). The pole \(s_0 = 0\) gives the steady-state solution,

\[
\text{Res} \left( \hat{\psi}_1 \exp(s\hat{t}), 0 \right) = \frac{\sinh(n\hat{x}) - \sinh n}{2n \cosh n} + \frac{1 - \hat{x}}{2} \quad (A3)
\]

To find the residue of the pole at \(s_n = -n^2\), we expand \(\hat{\psi}_1\) around \(s = -n^2\),

\[
\hat{\psi}_1 \mathop{\longrightarrow}^{s = -n^2} \frac{1}{2m^2} \left[ \frac{x}{L} + \mathcal{O}(m^3) \right] = \mathcal{O}(m) \quad (A4)
\]

This implies

\[
\text{Res} \left( \hat{\psi}_1 \exp(s\hat{t}), s = -n^2 \right) = 0, \quad (A5)
\]

because \(m = 0\) at \(s = -n^2\). For the poles at \(s_j^\ast\) we expand

\[
\cosh(m) \mathop{\longrightarrow}^{s = s_j^\ast} 2\left((\pm 1)^j m^* / s - s_j^\ast\right) = \left((\pm 1)^j m^* / s - s_j^\ast\right) \quad (A6)
\]

where, going to the second line we used \(m(s_j^\ast) = \pm m_j^\ast\), and \(\sinh m_j^\ast = i(\pm 1)^{j+1}\). We find

\[
\sum_{j = 1} \text{Res} \left( \hat{\psi}_1 \exp(s\hat{t}), s_j^\ast \right) = \sum_{j = 1} \text{Res} \left( \frac{\exp(s\hat{t})}{(m^*)^j s - s_j^\ast}, s_j^\ast \right) = \sum_{j = 1} \frac{1}{N_j^2 \left[ 1 + N_j^2 / n^2 \right]} \exp \left( -\left( n^2 + N_j^2 \right)^j \hat{t}\right). \quad (A7)
\]

Combining Eqs. (A3), (A4), and (A7) yields Eq. (15a).

We now easily find \(\tilde{q}_1, \tilde{c}_1\) [Eq. (15b)] by inserting Eq. (15a) into the Poisson equation (2a). Likewise, noting the equations governing \(\tilde{q}_1/\alpha_d\) and \(\tilde{c}_1/\alpha_d\) are the same for \(n \to 0\) [cf. Eq. (13)], \(\tilde{c}_1\) [Eq. (15c)] is found from Eq. (15b) by taking \(n \to 0\) therein. We have checked Eq. (15) against numerical Laplace inversions of Eq. (A1), using the ’t Hoog algorithm [28]. The results coincided perfectly for all times and parameters considered.

Before performing the inverse Laplace transforms on Eq. (A1), Ref. [13] first applied Padé approximations to those expressions. Approximations to \(\tilde{\psi}_1, \tilde{q}_1, \tilde{c}_1\) are then easily read off. Notably, the timescales \(\tau_q^{\text{app}}\) and \(\tau_q^{\ast\ast}\) with which the approximated \(\tilde{q}_1\) and \(\tilde{\psi}_1\) relaxed were unequal, \(\tau_q^{\text{app}} \neq \tau_q^{\ast\ast}\). However, \(q\) and \(\psi\) are related via the Poisson equation (2a). Because any ionic
motion is much slower than the speed of light, the potential readjusts itself instantaneously hence any difference \( \tau^a \) and \( \tau^b \) must stem from the Padé approximation scheme employed. This suspicion is confirmed by Eq. [15], where \( \tilde{v}_1 \) and \( \tilde{q}_1 \) contain identical decaying exponentials. Other than fixing this glitch, the merits of Eq. [15] over the approximate expressions of Ref. [15] are limited. As discussed in Ref. [29], Padé approximations around \( s_0 = 0 \) lead to decent predictions for the late-time response of the respective functions. Indeed, we have seen that Eq. [15] (that also captures all fast-decaying \( s_j^\alpha \) modes) deviates strongly from the Padé approximations only at early times \( \tilde{t} < 0.1 \). But as discussed in the main text, at those early times, Eq. [15] does not describe the physics of interest, because the steady-state temperature ansatz is erroneous there.

**Appendix B: Early-time boundary value scaling of Eq. [15]**

From Eq. [15a] follows a prediction for \( V_T(t) \):

\[
\beta_0 e V_T(\tilde{t}) = 1 - \frac{n \tanh n}{n} - \frac{2}{N_j} \exp \left[ - \frac{n^2 + N_j^2}{N_j^2} \tilde{t} \right].
\]

Expanding this expression around \( t = 0 \), for the first two terms of the expansion, the infinite sum can be performed. Hence, at short times, \( V_T \) increases as

\[
\lim_{\tilde{t} \to 0} \frac{\beta_0 e V_T(\tilde{t})}{\alpha d e} = n^2 \tilde{t}. \tag{B1}
\]

To determine \( \lim_{\tilde{t} \to 0} \tilde{q}_1(-L, \tilde{t}) \), we rewrite Eq. [15c] to

\[
\hat{c}_1(-1, \tilde{t}) = 2 \sqrt{\sum_{j \geq 1} \tilde{t} \left( 1 - \exp \left[ -\frac{p^2}{p^2} \right] \right)}.
\]

With \( p = N_j \sqrt{\tilde{t}} \). Now consider the following integral

\[
\int_{N_j \sqrt{\tilde{t}}}^{N_j \sqrt{\tilde{t}}} dp \frac{1 - \exp \left[ -\frac{p^2}{p^2} \right]}{p^2} = \int_{N_j \sqrt{\tilde{t}}}^{N_j \sqrt{\tilde{t}}} dp \left( p - N_j \sqrt{\tilde{t}} \right) \frac{1 - \exp \left[ -\frac{p^2}{p^2} \right]}{N_j^2 \sqrt{\tilde{t}}} = 0
\]

where we used integration by parts and \( (d/dp)(p - j \pi \sqrt{\tilde{t}}) = 1 \). With \( N_j - N_{j+1} = -\pi \) we conclude that

\[
\frac{1 - \exp \left[ -\frac{N_j^2 \tilde{t}}{N_j^2 \sqrt{\tilde{t}}} \right]}{N_j^2 \sqrt{\tilde{t}}} = \int_{N_j \sqrt{\tilde{t}}}^{N_j \sqrt{\tilde{t}}} dp \frac{1 - \exp \left[ -\frac{p^2}{p^2} \right]}{\pi p^2} + O(\tilde{t}),
\]

because the integral on the right hand side of Eq. [B4] is \( O(\tilde{t}) \). Inserting the above result into Eq. [B3] gives

\[
\frac{\hat{c}_1(-1, \tilde{t})}{\alpha_s} = \frac{1}{\alpha_s} \frac{2 \sqrt{\tilde{t} \sum_{j \geq 1} \tilde{t} \left( 1 - \exp \left[ -\frac{p^2}{p^2} \right] \right)}}{\pi} + O(\tilde{t}^{3/2})
\]

\[
= 2 \sqrt{\tilde{t}} \int_{\pi \sqrt{\tilde{t}}/2}^{\pi \sqrt{\tilde{t}}} \frac{1 - \exp \left[ -\frac{p^2}{p^2} \right]}{\pi p^2} + O(\tilde{t})
\]

\[
= 2 \frac{\sqrt{\tilde{t}}}{\pi} + O(\tilde{t}). \tag{B6}
\]

With a similar calculation one finds

\[
\lim_{\tilde{t} \to 0} \tilde{q}_1(-1, \tilde{t}) / \alpha_d = 2 \sqrt{\tilde{t}} / \pi + O(\tilde{t})
\]

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