Battery Computing

An MMSC Case Study on Scientific Computing
Candidate Number: 1072462

Abstract

This work shall attempt to

Our Goal: Numerically obtain the solution $\{a(x,T), b(x,T)\}$ of

$$
\begin{cases}
\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2}, & a : \mathbb{R}^+ \times [0,T] \mapsto [0,1],\ T \in \mathbb{R}^+,\ D_a \in \mathbb{R}^+, \\
\frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2}, & b : \mathbb{R}^+ \times [0,T] \mapsto [0,1],\ D_b \in \mathbb{R}^+, \\
a(\infty,t) = 1,\ b(\infty,t) = 0 & \forall t \in [0,T] \\
a(x,0) = 1,\ b(x,0) = 0 & \forall x \in (0,\infty) \\
a(0,t) = 0,\ \frac{\partial a}{\partial x} + D\frac{\partial b}{\partial x} = 0
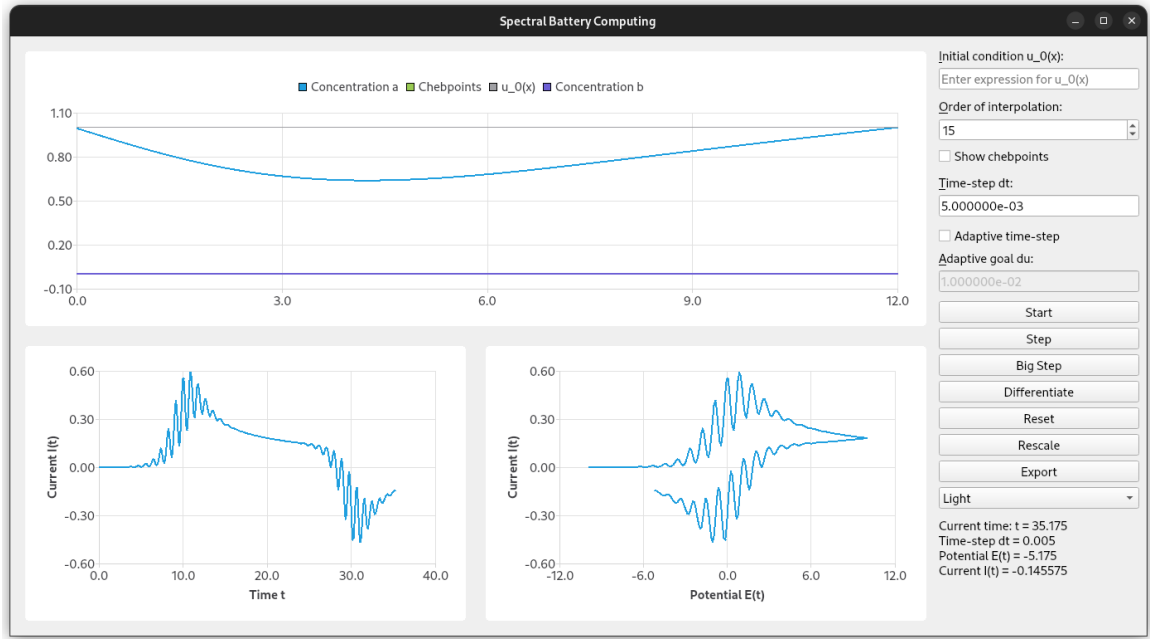\end{cases}
$$

The implementation bla bla

Figure 1: Graphical User Interface

Contents

1   Problem Introduction

Energy storage and its associated challenges are clearly among the most relevant questions, not only for the industrial but also the private sector. Politically, many nations in the world are steering towards greener energy supplies. Renewable energy sources such as wind and sun usually have a fundamental issue however, their availability is subject to an immense amount of fluctuation, which the energy grid must compensate through short- and long-term energy storage.

Long-term solutions include for example pumped-storage hydroelectricity facilities, but these must be complemented with short-term storage approaches such as Lithium-Ion or Lithium-Iron-Phosphate (LiFePO$_4$) batteries. Most modern batteries exploit electrochemical reactions to relate electrical potentials with chemical potentials and their associated difference ($\rightarrow$ voltage). The oxidation reaction we considere here is

$$A \Rightarrow B + e^- ?$$

where A and B can be any chemicals and e^- is an electron (Gavaghan and Bond 2000).
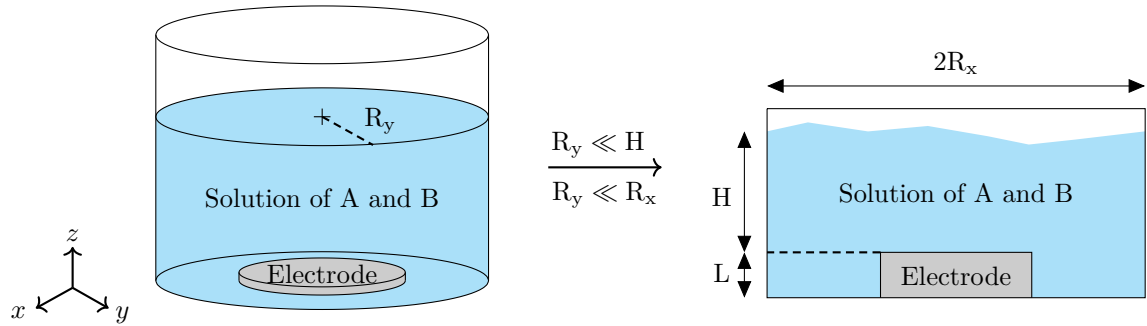
More bla bla later on.

Figure 2: Wohoo.

As stated on Page 1, we consider the following Partial Differential Equation (PDE)s in the concentrations $a, b \in \mathbb{C}^2(\Omega)$

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} \tag{1}$$

$$\frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2} \tag{2}$$

1.1 Chronoamperometry

1.2 Linear Sweep Voltammetry

$$I(t) = \kappa_0 \left(a\mathrm{e}^{(1-\alpha)(E(t)-E_0)} - b\mathrm{e}^{-\alpha(E(t)-E_0)} \right)_{x=0} \tag{3}$$

1.3 Linear Sweep AC Voltammetry

2 Mathematical Background

Let $\mathbb{N}$ denote the nonnegative integers, so $0 \in \mathbb{N}$. Similarly, let $\mathbb{R}^+ = [0, \infty)$ denote the nonnegative real numbers.

2.1 Laplace Integral Transform

What is Laplace?

2.1 Definition: Laplace Integral Transform

Given a function $a : \mathbb{R} \mapsto \mathbb{R}$, its Laplace transform $\hat{a} : \mathbb{C} \mapsto \mathbb{C}$ is given by

$$\hat{a}(s) = \mathcal{L}\{a\}(s) = \int_0^\infty a(t)\mathrm{e}^{-st}\,\mathrm{d}t\,.$$

Laplace transforms are especially valuable for physical systems as many of them expose exponentially decaying and/or periodic behaviours which the Laplace transform is well-suited for due to the form of its kernel. Decaying behaviour is captured by the real component of the argument s, $\mathfrak{Re}(s)$, whereas periodicities are captured by the imaginary part $\mathfrak{Im}(s)$[1].

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[1]Consider for comparision the Fourier transform $\mathcal{F}(a)(\omega) := \int_{-\infty}^\infty a(t)\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t$ which captures periodic frequencies, where the kernel automatically follows multiplication along the unit circle due to the imaginary-valued exponent $\mathrm{i}\omega t$ (the argument $\omega \in \mathbb{R}$ is real-valued). Intuitively, the Laplace transform coincides with the Fourier transform if evaluated at $s = \mathrm{i}\omega$.

2.1 Theorem: Laplace Transform of the Derivative

Given a function $a(t)$ and a corresponding Laplace-transform $\hat{a}(s) = \mathcal{L}\{a\}(s)$, the transform of the derivative $a'(t)$ of the original function is given by

$$\mathcal{L}\{a'\}(s) = \mathcal{L}\left\{t \mapsto \frac{\partial a}{\partial t}\right\}(s) = s\hat{a}(s) - a_0,$$

where $a_0 := a(t = 0)$.

Proof. Proof for Laplace's differentiation theorem.   □

2.2 Theorem: Initial Value

For a function $a \in \mathcal{C}^2(\Omega)$ with corresponding Laplace-transform $\hat{a} = \mathcal{L}\{a\}$,

$$\lim_{s \to \infty} s\hat{a}(s) = \lim_{t \to 0^+} a(t)$$

relates a's *initial value* with the transform evaluated at $s \to \infty$.

2.3 Theorem: Laplace Convolution

For a function $a \in \mathcal{C}^2(\Omega)$ with corresponding Laplace-transform $\hat{a} = \mathcal{L}\{a\}$,

$$\lim_{s \to \infty} s\hat{a}(s) = \lim_{t \to 0^+} a(t)$$

relates a's *initial value* with the transform evaluated at $s \to \infty$.

2.2   Chebyshev Polynomials

2.2 Definition: Chebyshev Polynomial of the First Kind

Chebyshev[2] polynomials $T_k : \mathbb{R} \mapsto \mathbb{R}$ are functions satisfying

$$T_k(x) = T_k(\cos\theta) := \cos(k\theta) = \frac{1}{2}(z^k + z^{-k})$$

$$z := e^{i\theta}, \quad x := \mathfrak{Re}(z) = \cos(\theta) = \frac{1}{2}(z + z^{-1})$$

for degree $k \in \mathbb{N}$. Then, $T_0(x) = 1$, $T_1(x) = x$, $T_2(x) = 2x^2 - 1$, and so on.

> **2.3 Definition: Chebyshev Polynomial of the Second Kind**
>
> Chebyshev polynomials $U_k : \mathbb{R} \mapsto \mathbb{R}$ are functions satisfying
>
> $$U_k(\cos\theta)\sin\theta := \sin\left((k+1)\theta\right)$$
>
> for degree $k \in \mathbb{N}$. Then, $U_0(x) = 1$, $U_1(x) = 2x$, $U_2(x) = 4x^2 - 1$, and so on.

Note that Chebyhsev polynomials of the first and second kind fulfill the same recurrence relationship, $T_{k+1}(x) = 2xT_k(x) - T_{k-1}(x)$ and $U_{k+1}(x) = 2xU_k(x) - U_{k-1}(x)$. The difference between them arises from the second polynomial respectively which is $T_1(x) = x$ for the first kind and $U_1(x) = 2x = 2T_1(x)$ for the second kind.

Proof of $U_k(-1)$'s value.

3   Finite Differences

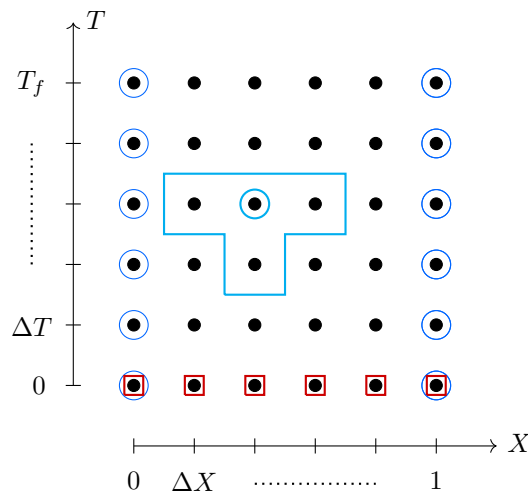Construct $A\boldsymbol{x} = \boldsymbol{b}$.

Figure 3: Schematic of the finite different scheme where ... are the nodes specified by initial conditions, and ... are the nodes specified by boundary conditions.

[2]Named after Pafnuty Lvovich Chebyshev, alternatively transliterated as Tchebycheff, Tchebyshev (French) or TSCHEBYSCHOW (German).

3.1 Results

4 Analytical Approaches

When $D = 1$, $a + b = 1$ because.

4.1 Similarity Solution

4.2 Voltammetry Integral Equation

4.2.1 Derivation using the Laplace Transform

As mentioned above, the Laplace Integral Transform is especially useful in the context of differential equations, mostly due to Theorem 2.1. Applying it to our *partial* differential diffusion equation Equation (1) transforms the problem into one of solving an *ordinary* differential equation. Similarly, ODEs could be turned into algebraic equations using a similar approach.

Starting from Equation (1), we Laplace-transform both sides and then apply Theorem 2.1 in time t to arrive at

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} \qquad \text{Laplace-transform w.r.t. } t$$

$$\mathcal{L}\left\{t \mapsto \frac{\partial a}{\partial t}\right\} = D_a \mathcal{L}\left\{t \mapsto \frac{\partial^2 a}{\partial x^2}\right\} \qquad \text{Use Theorem 2.1}$$

$$s\hat{a}(s) - a_0(x) = D_a \frac{\partial^2 \hat{a}}{\partial x^2} \qquad \text{Rearrange}$$

$$\frac{\partial^2 \hat{a}}{\partial x^2} - \frac{s}{D_a}\hat{a} = -\frac{a_0(x)}{D_a}$$

where $\hat{a} := \mathcal{L}\{a\}$ and $a_0(x) := a(x, t = 0)$, which is a second-order constant-coefficient Ordinary Differential Equation in space x. Its characteristic polynomial is $\lambda^2 + \frac{s}{D_a} = 0$ which, together with the initial condition $a_0 = 1$ and resulting particular solution $\hat{a}_p(x, s) = \mathcal{L}\{-1\}(s) = \frac{1}{s}^3$, leads us to the general solution

$$\hat{a}(x, s) = c_1 e^{\sqrt{\frac{s}{D_a}}x} + c_2 e^{-\sqrt{\frac{s}{D_a}}x} + \frac{1}{sD_a}, \quad c_1, c_2 \in \mathbb{R}. \tag{4}$$

The constant c_1 then vanishes when applying the initial value theorem (Theorem 2.2)

$$\lim_{s \to \infty} s\hat{a}(s) = \lim_{s \to \infty} \underbrace{c_1 s e^{\sqrt{\frac{s}{D_a}}x}}_{\to \infty} + \underbrace{c_2 s e^{-\sqrt{\frac{s}{D_a}}x}}_{\to 0} + 1 \overset{!}{=} \lim_{t \to 0^+} a(t) = 1$$

---

[3] $\mathcal{L}\{1\} = \int_0^\infty e^{-st}\, dt = \frac{1}{s}\left[e^{-st}\right]_0^\infty = \frac{-1}{s}$.

because $c_1 \neq 0$ would cause its corresponding term to explode. Considering the other boundary condition of linear sweep voltammetry

$$\left.\frac{\partial a}{\partial x}\right|_{x=0} = I(t) \quad \Leftrightarrow \quad \frac{\partial \hat{a}}{\partial x} \overset{!}{=} \hat{I}(s) \quad \Leftrightarrow \quad c_2 \sqrt{\frac{s}{D_a}}e^0 = \hat{I}(s),$$

where $\hat{I}(s) := \mathcal{L}\{I\}(s)$ and we obtain $c_2(s) = \frac{-\hat{I}(s)}{\sqrt{s}}$. So Equation (4) becomes

$$\hat{a}(x,s) = \frac{-\hat{I}(s)}{\sqrt{s}}e^{-\sqrt{\frac{s}{D_a}}x} + \frac{1}{sD_a}, \tag{5}$$

which, evaluated at $x = 0$, becomes $\hat{a}(s,0) = \frac{-\hat{I}(s)}{\sqrt{s}} + \frac{1}{sD_a}$, depending on the Laplace transform of the current $I(t)$.

In principle, this is already a complete result in and of itself, as it provides the full solution on the entire domain in frequency-space [4]. If one obtains the Laplace-transform of the current expression Equation (3) and performs the inverse transform of $\hat{a}$, even just numerically, the linear sweep voltammetry problem is solved in full as a similar procedure leads to the solution of the other concentration b.

Within the scope of this report, we will consider an integral equation relating current $I(t)$ and the potential $E(t)$ to verify our numerical results. Inverse-transforming Equation (5) at $x = 0$ where our boundary condition is given and using the convolution theorem (Theorem 2.3), we arrive at

$$a(x,t) = -\mathcal{L}^{-1}\left\{s \mapsto \hat{I}(s) \cdot \hat{g}(s)\right\}(t) + \mathcal{L}^{-1}\left\{s \mapsto \frac{1}{sD_a}\right\}(t) = -(I * g)(t) + \frac{1}{D_a},$$

where we introduced $\hat{g}(s) := \frac{1}{\sqrt{s}} = \mathcal{L}\{g\}(s)$ the Laplace transfrom of $g(t) = \frac{1}{\sqrt{\pi t}}$.

Proof. $\mathcal{L}\{t \mapsto \frac{1}{\sqrt{\pi t}}\}(s) = \frac{1}{\sqrt{\pi}}\int_0^\infty t^{-\frac{1}{2}}e^{-st}\,dt = \frac{1}{\sqrt{\pi}}\int_0^\infty \cancel{t}^{\frac{1}{2}}e^{-su^2}\cancel{t^{\frac{1}{2}}}\,du = [\mathrm{erf}(\sqrt{s}u)/\sqrt{s}]_0^\infty$ where we used a substitution $u = \sqrt{t}$ to resolve the product in the integrand, resulting in the Gaussian integral and subsequently, the error function $\mathrm{erf}(\sqrt{s}u)$ which satisfies $\mathrm{erf}(0) = 0$ and $\mathrm{erf}(\infty) = 1$ so the full transformation pair is $\frac{1}{\sqrt{\pi t}} \circ\!\!-\!\!\bullet \frac{1}{\sqrt{s}}$. $\quad\square$

When $D = 1$, this results in the following expressions for $a(x = 0, t)$ and $b(x = 0, t)$,

$$a(x = 0, t) = 1 - (I * g)(t) = 1 - \int_0^t \frac{I(\tau)}{\sqrt{\pi(t-\tau)}}\,d\tau,$$

$$b(x = 0, t) = 1 - a(x = 0, t) = \int_0^t \frac{I(\tau)}{\sqrt{\pi(t-\tau)}}\,d\tau,$$

which we will verify numerically.

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[4]Frequency space is a term borrowed from Fourier analysis, where we say that the transformed functions reside in "frequency space". The usage is the same for Laplace's transformation.

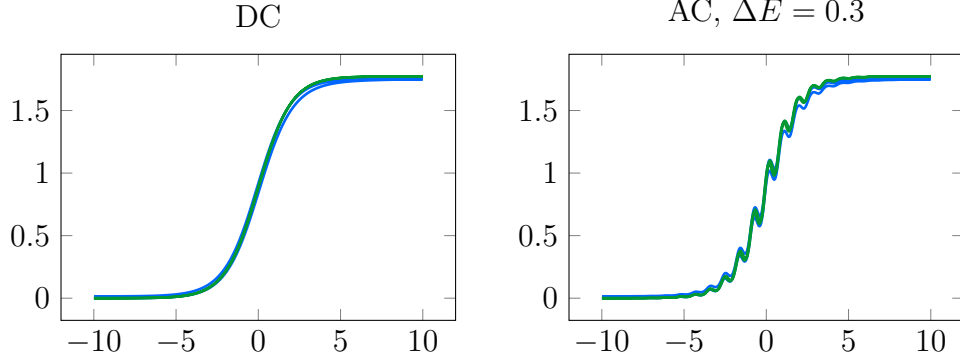### 4.2.2   Numerical Solution

Figure 4: Convolution Integrals

5   Spectral Method

From the definition of Chebyshev polynomials $T_k(x) = \cos(k\theta)$ (Definition 2.3), we can derive that

$$\frac{\mathrm{d}T_k}{\mathrm{d}x} = \frac{\mathrm{d}T_k}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}x} = ... = kU_{k-1}(x),$$

where $U_k : [-1, 1] \mapsto \mathbb{R}$ denote the Chebyshev polynomials of the second kind, which in turn are defined by

$$U_k(\cos\theta)\sin(\theta) = \sin\left((n+1)\theta\right).$$

In order to enforce a von-Neumann boundary condition on the left and a Dirichlet boundary condition on the right, we are interested in explicitly setting coefficients a_k such that

$$a_x(-1, t) = \frac{\mathrm{d}a}{\mathrm{d}x}\bigg|_{x=-1} = \tilde{l} \quad \text{and} \quad a(1) = r, \quad \text{where} \quad \tilde{l}, r \in \mathbb{R}.$$

Using the Chebyshev series ansatz

$$a(x, t) = \sum_{k=0}^{N-1} a_k^{(t)} T_k(x)$$

we have that

$$\frac{\mathrm{d}a}{\mathrm{d}x} = \sum_{k=0}^{N-1} a_k^{(t)} \frac{\mathrm{d}T_k}{\mathrm{d}x}(x),$$

so we are interested in

$$a_x(-1, t) = \frac{\mathrm{d}a}{\mathrm{d}x}\bigg|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} \frac{\mathrm{d}T_k}{\mathrm{d}x}\bigg|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} kU_{k-1}(-1).$$

Following from TODO (explained on Wikipedia), we know that

$$U_k(-1) = (-1)^k(k+1) \quad \text{and} \quad T_k(1) = 1 \quad \forall k \in \mathbb{N}\,,$$

which turns our conditions into algebraic conditions w.r.t. the coefficients $a_k^{(t)}$,

$$a_x(-1,t) = \left.\frac{\mathrm{d}a}{\mathrm{d}x}\right|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} k^2 (-1)^{k-1} \overset{!}{=} \tilde{l} \quad \text{and} \quad a|_{x=1} = \sum_{k=0}^{N-1} a_k^{(t)} \overset{!}{=} r\,.$$

Knowing that the heat equation Forward Euler numerical scheme modifies all but the two highest-degree coefficients in the series, we expand:

$$a_x(-1,t) = \sum_{k=0}^{N-1} a_k^{(t)} T_k'(-1) = -\overbrace{\sum_{k=0}^{N-3} a_k^{(t)} k^2 (-1)^k}^{:=\Sigma_3} -(N-2)^2(-1)^{N-2} a_{N-2}$$

$$- (N-1)^2(-1)^{N-1} a_{N-1} = l\,,$$

$$a(1,t) = \sum_{k=0}^{N-1} a_k^{(t)} T_k(1) = \underbrace{\sum_{k=0}^{N-3} a_k^{(t)}}_{:=\Sigma_2} + a_{N-2} + a_{N-1} = r\,,$$

5.1   Enforcing Boundary Conditions

Von Neumann on the left

5.2   Implicit Euler

5.3   Implementation

The solver was implemented in C++, using TschebFun and is based on the HeatFun numerical integrator.
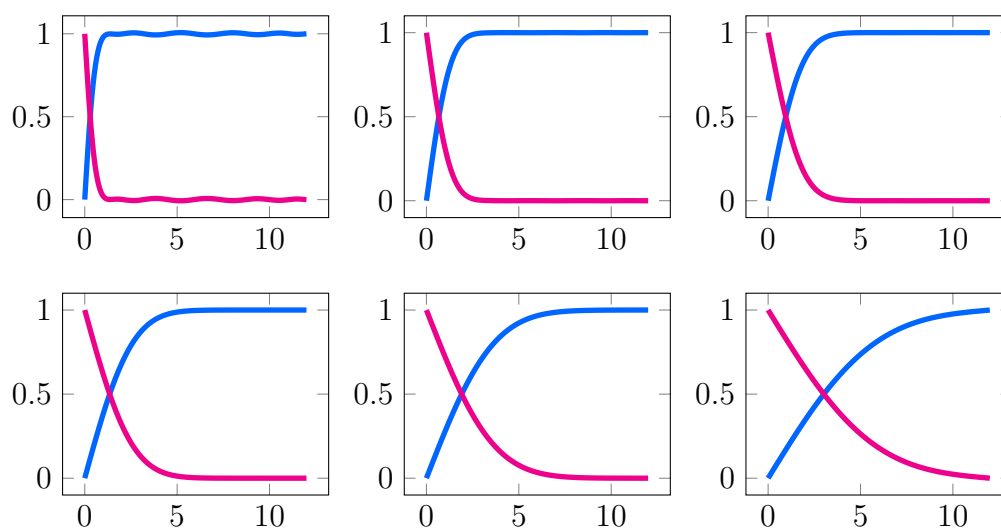
5.4   Results

Chronoamperometry (step potential),

Figure 5: Chronoamperometry
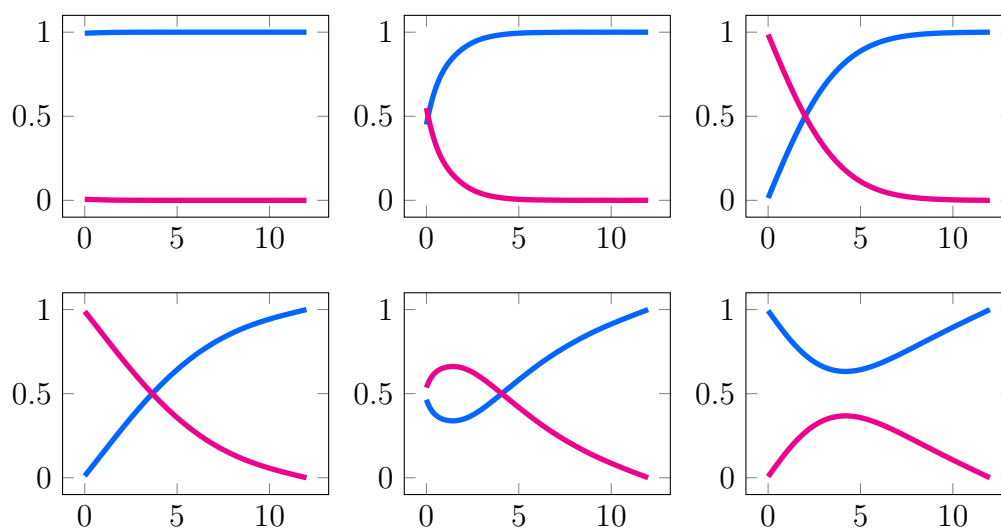
DC Linear Sweep Voltammetry, AC Linear Sweep Voltammetry
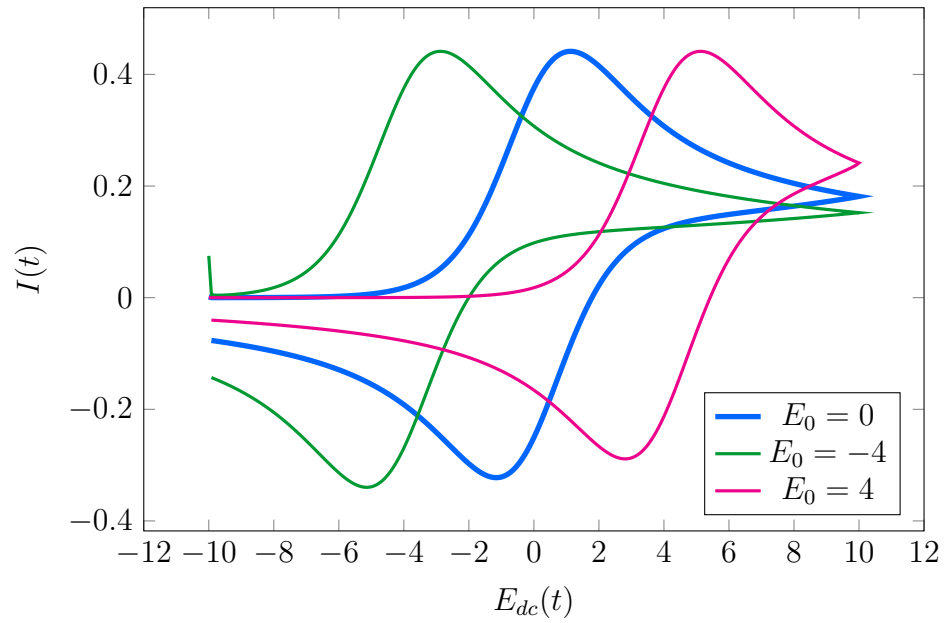

Figure 6: AC Voltammetry

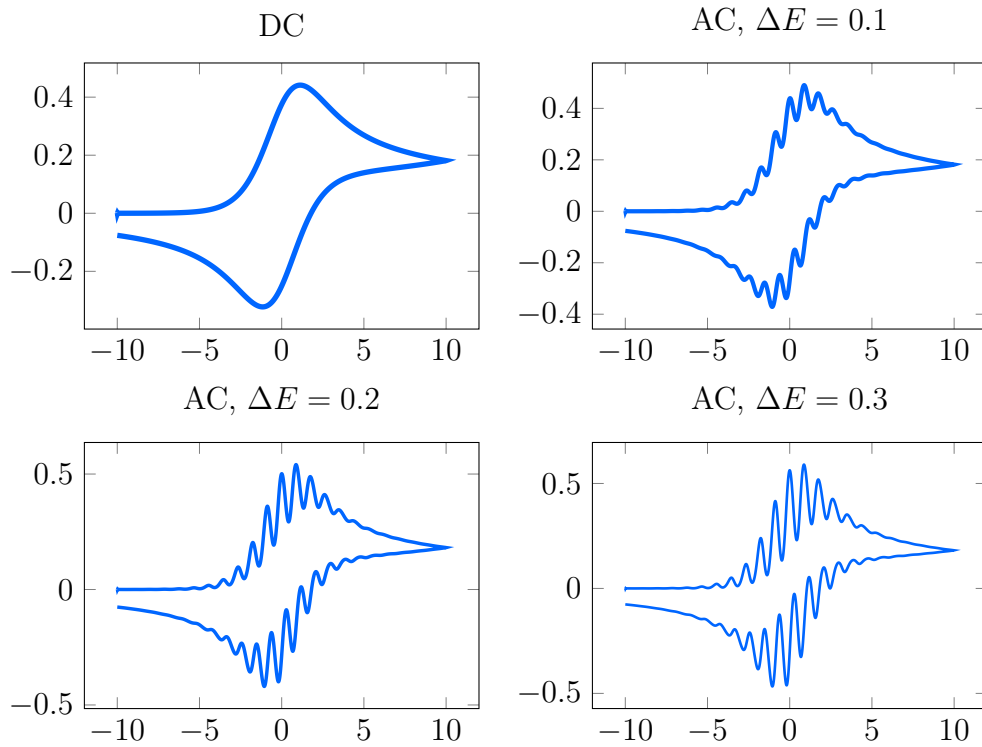**Figure 7:** Voltammetry Current $I(t)$ vs the DC Potential $E_{dc}(t)$

Figure 8: Voltammetry Current $I(t)$ vs the DC Potential $E_{dc}(t)$

6 Conclusion

Table 1: Runtime Comparison

References

Gavaghan, D. J. and A. M. Bond (Jan. 2000). 'A complete numerical simulation of the techniques of alternating current linear sweep and cyclic voltammetry: analysis of a reversible process by conventional and fast Fourier transform methods'. In: *J. Electroanal. Chem.* 480.1, pp. 133–149. ISSN: 1572-6657. DOI: 10.1016/S0022-0728(99)00476-3.

Acronyms

ODE   Ordinary Differential Equation   7
PDE   Partial Differential Equation   3