Introduction to the Distribution of Relaxation Times

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1. Introduction

The distribution of relaxation times (DRT) is a powerful tool for visualizing electrochemical reactions occurring at different rates within an electrochemical system. This is often desired by the engineer or researcher to identify the main sources of performance loss within the system. DRT transforms impedance measurements (often achieved through the use of EIS) into a distribution of resistances at the time constants (relaxation times) of the system. For example, in an electrochemical cell where two dominant reactions are occurring simultaneously, applying the DRT technique will separate the time constant and resistance of each reaction. The shape of a Nyquist or Bode plot is often used to provide a general guidance on the minimum number of processes involved. However, this technique is limited in its ability to distinguish between reactions occurring at similar rates. The DRT technique is better for identifying the exact values of time constants, and distinguishing different processes with time constants which are much closer to each other [1].

In equivalent circuit modeling, one must choose an electrical circuit which describes the system physics, and also provide a reasonable initial guess for the values of the circuit elements to achieve a good fit to the data.This can be a complex process that requires comprehensive understanding of the physical process models and how these processes show up in the system impedance. The advantage of DRT over equivalent circuit modeling is that it requires no initial assumptions about the electrochemical system while revealing useful information about the electrochemical processes in the system [2]. The processes revealed by a DRT can inform the choice of circuit and initial guesses of the parameters for the equivalent circuit model, so calculating the DRT can be a useful first step in equivalent circuit modeling. If good choices can be made, the parameters of the equivalent circuit model can provide more information about physical processes in the electrochemical system than the DRT.

In a DRT, the basic circuit element is the RC element, which is a resistor and capacitor in parallel. For a resistor with resistance R and a capacitor with capacitance C, the impedance $Z(\omega)$ of the RC circuit is [3]

$$Z(\omega) = \frac{R}{1+j\omega RC}$$

The variable ω is the angular frequency, which relates to frequency in hertz by $\omega = 2\pi f$. The impedance can be separated into real and imaginary components:

$$Z(\omega) = Z'(\omega) - jZ''(\omega)$$

$$Z'(\omega) = \frac{R}{1+(\omega RC)^2} \quad \text{and} \quad Z''(\omega) = \frac{\omega R^2 C}{1+(\omega RC)^2}$$

Figure 1 shows the Nyquist plot of an RC element's impedance. At low frequency, the capacitor blocks the current, and the impedance is a simple resistance with value R. At high frequency, the capacitor shorts the resistor, and the impedance approaches 0. In between, the capacitor causes a phase shift between the voltage and current, so the imaginary part of the impedance is nonzero. The imaginary impedance achieves its maximum at $\omega = 1 / (RC)$. The constant RC is called the time constant τ of the RC element.

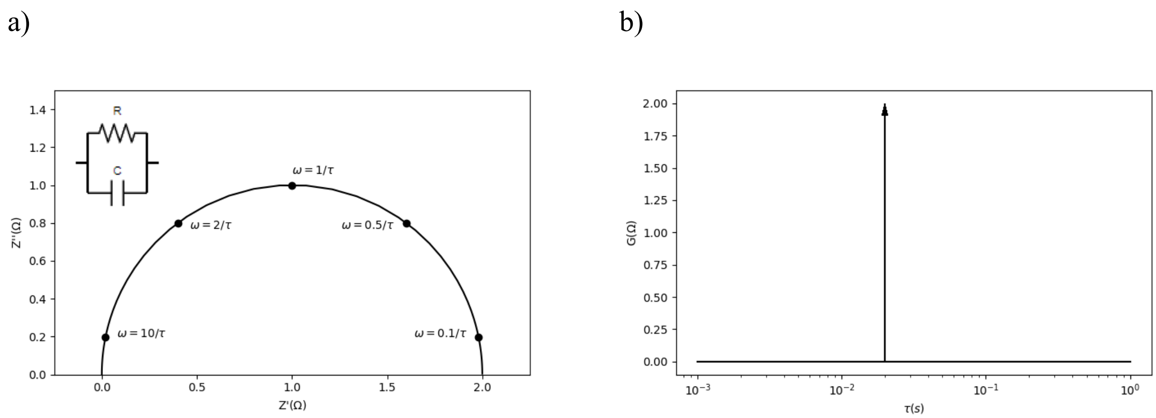

Figure 1: (a) Nyquist plot and (b) Analytic DRT of an RC element. R = 2 Ω and C = 0.01 F

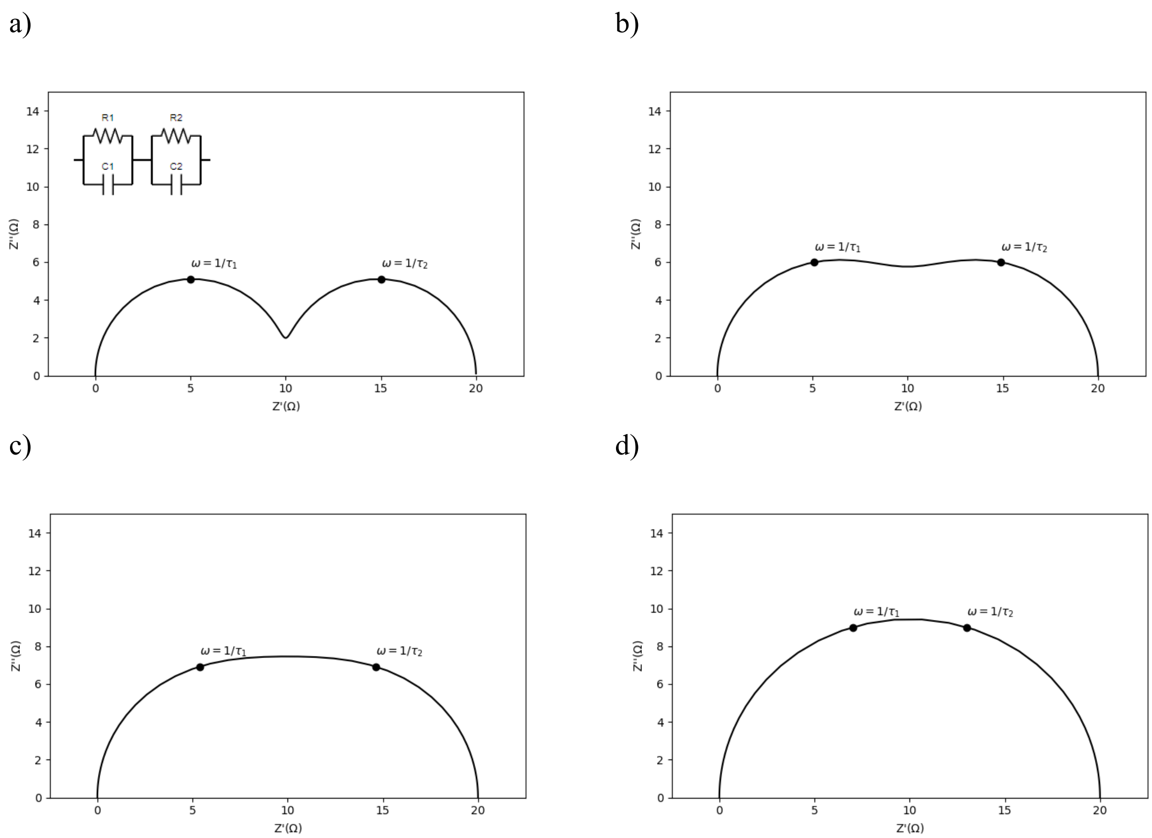

Figure 2: Nyquist plots for a circuit with two time constants. R_1 = 10 Ω, R_2 = 10 Ω, C_1 = 0.001 F. a) C_2 = 0.1 F, b) C_2 = 0.01 F,c) C_2 = 0.005 F, d) C_2 = 0.002 F

Since the RC element has only one time constant (visible on the Nyquist plot as a single semicircle), the DRT is concentrated at a single point, τ. This is a Dirac-δ distribution, centered at τ and scaled by a factor of R. When numerically calculating the DRT, the δ distribution must be approximated as a single, narrow peak (see Section 3).

More complex systems will have multiple time constants. When these time constants are spread out, they can be identified by semi-circles on a Nyquist plot. However, each time constant affects the measured impedance at a range of frequencies around it, so time constants which are close can be hard to distinguish using Nyquist plots. For example, Figure 2 shows the Nyquist plot of two RC elements in series, with time constants getting closer to each other. When the time constants are far apart, as in Figure 2(a), two semicircles are clear, but as the time constants approach each other, the semicircles merge. In this case, the DRT can be used to distinguish between the time constants.

In the following section, the mathematical definition and properties of the distribution of relaxation times are explored. The DRT for several common circuit elements will be included. Section 3 explains the methods for calculating the DRT and how they impact the end result. Section 3 will also explain how to interpret the DRT results.

2. Analytic Distribution of Relaxation Times

As stated in the introduction, the fundamental circuit element for DRT is the RC element, which is a resistor and capacitor in parallel. A Voigt circuit consists of M RC elements in series with a resistor R_∞ (Figure 3). At the limit of high frequencies, the capacitors allow the current through, so the RC elements have 0 impedance. Therefore R_∞ is the resistance at infinite frequency. The Voigt circuit is a very general circuit model for fitting most impedance spectra. Theoretical limitations of the Voigt circuit are described in [4]. Defining the time constant $\tau_i = R_i C_i$, the impedance of this circuit is

$$Z(\omega) = R_\infty + \sum_{i=1}^{M} \frac{R_i}{1 + j\omega\tau_i}$$

Instead of restricting the circuit to a discrete set of time constants, the theoretical DRT model uses a continuous distribution of the time constants, replacing the sum with an integral:

$$Z(\omega) = R_\infty + \int_{0}^{\infty} \frac{g(\tau)}{1 + j\omega\tau} d\tau$$

The distribution $g(\tau)$ (in $\Omega \cdot s^{-1}$) describes the system's resistances at any time constant. Since the time constants are typically considered on a logarithmic scale, the integral will be written in terms of $\ln \tau$. This is accomplished by defining $G(\tau) = \tau\, g(\tau)$ [5]:

$$Z(\omega) = R_\infty + \int_{-\infty}^{\infty} \frac{G(\tau)}{1 + j\omega\tau} d \ln \tau \tag{1}$$

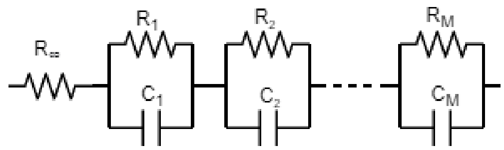

Figure 3: Voigt Circuit

This equation defines the distribution of relaxation times $G(\tau)$, which has units of Ω. For circuits with a single time constant (like the RC element in Figure 1), $G(\tau)$ is concentrated at a single point, which is the δ distribution. The DRT for some other common circuit elements is shown in Section 2.2.

Using the relationship $f = 1/(2\pi\tau)$, G can be plotted against frequencies, which is useful for comparing the DRT and frequency-domain impedance plots. This will be done for the rest of the paper.

2.1 Properties

Given the DRT G of an impedance spectrum Z, the limits of the impedance for high and low frequencies can be determined from Equation (1):

$$Z(0) = R_\infty + \int_{-\infty}^{\infty} G(\tau)\, d \ln \tau \tag{2}$$

$$Z(\infty) = R_\infty \tag{3}$$

The total area under the distribution is the difference between the high and low frequency resistance. As long as this is finite, the impedance will approach a real value at low frequencies, which is the DC resistance. Some impedance spectra will not approach a real value at low or high frequencies. In these cases, some extensions to the DRT model are needed, as described in Section 3.2.

Equation (1) also shows that the relationship between Z and G is linear. This means that, for given impedance spectra Z_1 and Z_2 with their respective DRTs G_1 and G_2, and constants a and b, the DRT of the combined impedance $aZ_1 + bZ_2$ is $aG_1 + bG_2$. It follows that a DRT can be interpreted as a collection of basic circuit elements in series. Separate peaks can be viewed as different circuits and analyzed individually. Solving linear systems gives unique solutions and does not require an initial guess. So DRT has an advantage over non-linear equivalent circuit modeling, which will not find the most optimal solution if the initial guesses are too far from their actual values.

2.2 DRT of Common Circuit Elements

To analyze DRT results from actual systems it is helpful to understand the DRTs of several common circuit elements.

The constant phase element (CPE), often used in equivalent circuit modeling, is a generalized version of a capacitor. These elements can arise from non-idealities in real systems, such as edge effects and uneven surface distributions of impedances [6].

The impedance of a CPE is given by

$$Z_{CPE}(\omega) = \frac{1}{Q(j\omega)^{\alpha}} \text{ where } 0 \leq \alpha \leq 1.$$

The name comes from its constant phase shift of -$\alpha \cdot 90°$. If $\alpha = 1$, the CPE is simply an ideal capacitor. A CPE in parallel with a resistor is called an RQ element (or ZARC element), and has impedance

$$Z_{RQ}(\omega) = \frac{R}{1 + (j\omega\tau_0)^{\alpha}} \text{ where } \tau_0 = (RQ)^{1/\alpha} \tag{4}$$

When $\alpha = 1$ and the CPE is an ideal capacitor, then the RQ element is an RC element, with DRT shown in Figure 1. For $\alpha < 1$, the DRT is given by [7]

$$G_{RQ}(\tau) = \left(\frac{R}{2\pi}\right) \frac{\sin(\alpha\pi)}{\cosh\left(\alpha \ln\left(\frac{\tau_0}{\tau}\right)\right) + \cos(\alpha\pi)}$$

Figure 4 shows the Nyquist and DRT plots for an RQ element. The cosh function has its minimum at 0, therefore $G(\tau)$ has a maximum when $\ln(\tau_0/\tau) = 0$ which occurs at $\tau = \tau_0$. The maximum is given by

$$G_{RQ}(\tau_0) = \left(\frac{R}{2\pi}\right) \frac{\sin(\alpha\pi)}{1 + \cos(\alpha\pi)}$$

As α approaches 1, $\sin(\alpha\pi)$ can be approximated by $-\alpha\pi$ and $\cos(\alpha\pi)$ by $(\alpha\pi)^2 / 2 - 1$. With these approximations,

$$G_{RQ}(\tau_0) = \left(\frac{R}{\pi^2}\right) \frac{1}{1-\alpha}$$

a) b)

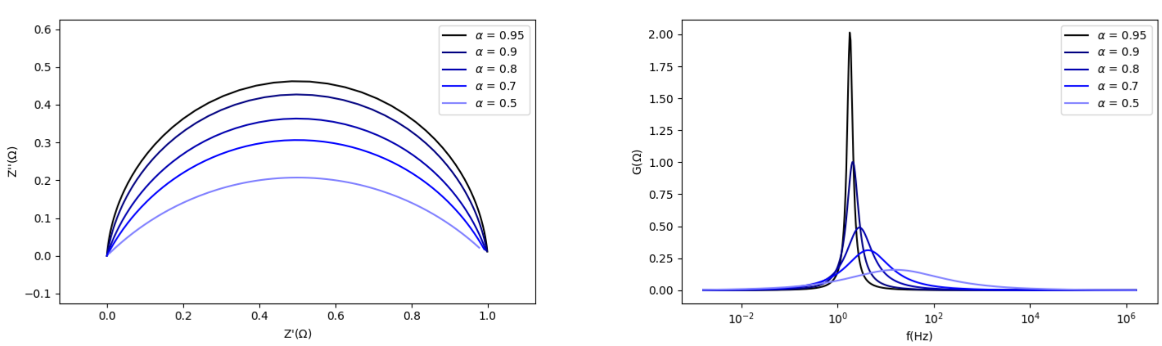

Figure 4: (a) Nyquist plot and (b) DRT of an RQ element. $R = 1\ \Omega$ and $Q = 0.1\ s^{\alpha} \cdot \Omega^{-1}$. On the Nyquist, the plot approaches the real axis at an angle of $\alpha \cdot 90°$

Therefore, the height of the peak of the DRT will increase to infinity as α approaches 1. For $\tau \neq \tau_0$, the cosh function will increase towards infinity as α approaches 1, so the distribution approaches 0. From Equation (4), the limits of the impedance at high and low frequency are $Z(0) = R$ and $Z(\infty) = 0$, respectively. Therefore, with Equations (2) and (3), the total area under the distribution is constant, at R. So the limit of the DRT for an RQ element as α approaches 1 is a δ distribution centered at τ_0 and scaled by a factor R, which is exactly the DRT for an RC element (Figure 1).

An RL element is a resistor R in parallel with an inductor L. The impedance is given by

$$Z_{RL}(\omega) = \frac{j\omega\tau R}{1 + j\omega\tau} \text{ where } \tau = \frac{L}{R}$$

The RL element can be written as an RC element with the same time constant but a negative resistor, in series with another resistor [8]:

$$Z_{RL}(\omega) = \frac{j\omega\tau R}{1 + j\omega\tau} = \frac{R + j\omega\tau R - R}{1 + j\omega\tau} = R + \frac{-R}{1 + j\omega\tau}$$

Like the RC circuit, the RL circuit has only a single time constant and the DRT of an RL circuit is a δ distribution (Figure 5). But, for the RL circuit, the distribution is negative. Therefore, negative peaks in a DRT result indicate inductance in a system. For the RL circuit, $R_\infty = Z(\infty) = R$, and $Z(0) = 0$, so the total area under the distribution is $-R$.

Diffusion elements like the Gerischer and Warburg elements have more complex DRTs, which are also more difficult to calculate numerically. The Gerischer element's impedance is given by the equation

$$Z_G(\omega) = \frac{R}{\sqrt{1 + j\omega\tau_0}}$$

a) b)

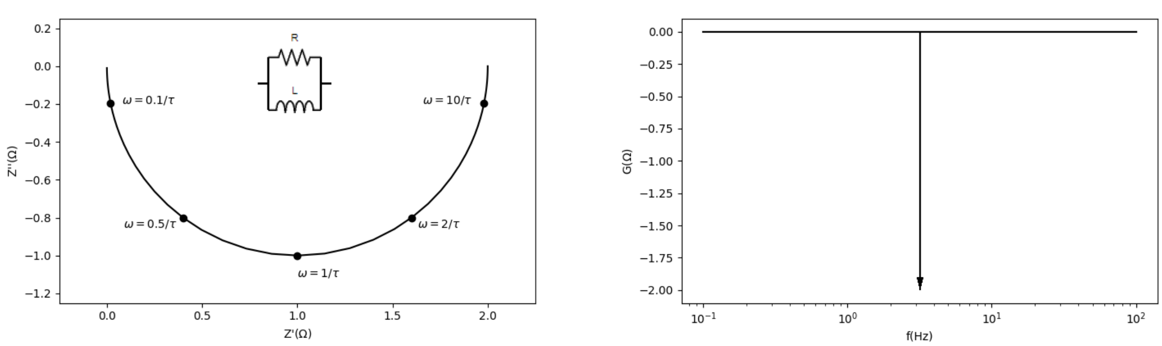

Figure 5: (a) Nyquist plot and (b) DRT of an RL element. R = 2 Ω and L = 0.1 H

The DRT for the Gerischer element is [7]

$$G_G(\tau) = \frac{R}{\pi}\sqrt{\frac{\tau}{\tau_0 - \tau}}$$

For $\tau > \tau_0$, $G_G(\tau) = 0$. The infinite discontinuity at $\tau = \tau_0$ makes the DRT of a Gerischer impedance harder to compute numerically.

The impedance of a finite length Warburg element looks similar to the Gerischer. On a Nyquist plot (Figure 6), both have a 45° angle at high frequencies, but the Warburg element will go above the 45° line as the frequency decreases, before the imaginary impedance drops to 0.

$$Z_W(\omega) = \frac{R}{\sqrt{j\omega\tau_0}}\tanh\left(\sqrt{j\omega\tau_0}\right)$$

The DRT for the finite length Warburg element is a series of δ distributions, at locations τ_k [7]:

$$\tau_k = \frac{\tau_0}{\pi^2(k-0.5)^2},\ k = 1,\ 2,\ 3,\ \ldots \tag{5}$$

The scale of each δ distribution is $2R(\tau_k/\tau_0)$. When numerically computing the DRT of a finite length Warburg, often only the first δ distribution (at $\tau = \tau_0 / (\pi/4)^2$) is visible, and the rest of the distribution is lumped together in a single peak.

While the complexity of the DRT of diffusion elements makes them harder to identify, diffusion is more easily identified by the 45° angle on the Nyquist plot (Figure 6). See Section 3.4 for more details on numerical calculations for diffusion elements.

a) b)

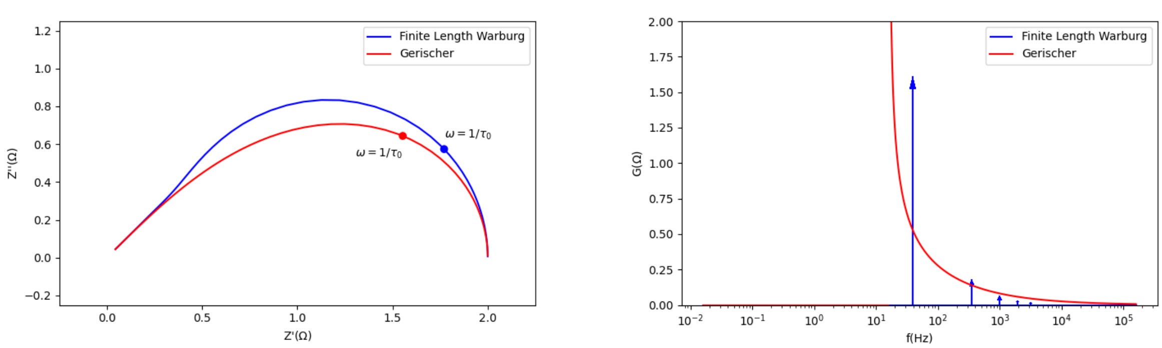

Figure 6: (a) Nyquist plot and (b) DRT of Finite Length Warburg and Gerischer elements. R = 2 Ω and τ_0 = 0.01 s

3. Numerical Calculation

Recall the definition of DRT in Equation (1):

$$Z(\omega) = R_\infty + \int_{-\infty}^{\infty} \frac{G(\tau)}{1+j\omega\tau} d \ln \tau$$

The impedance Z is measured at a set of angular frequencies ω_i, for $1 \le i \le M$. A set of N time constants at which to calculate the DRT must be chosen. Let τ_k be the time constants, for $1 \le k \le N$. The impedance at the angular frequency ω_i is affected by the resistance at the time constants around $1/\omega_i$. To account for the entire frequency range, the smallest time constant τ_1 should be at most $1/\omega_M$ (for example, $0.1/\omega_M$), where ω_M is the largest angular frequency. Similarly, the largest time constant τ_N should be chosen to be at least $1/\omega_1$, (for example, $10/\omega_1$) where ω_1 is the smallest angular frequency [2]. While the system may have important time constants outside of this range, their effects would likely not be detectable on the measured impedance. The other time constants are distributed logarithmically in between τ_1 and τ_N. A larger number of time constants N can produce a higher precision DRT, but the precision is also limited by the number of measured frequencies. In general, $N = 5M$ is a good choice.

By splitting the impedance Z into real and imaginary parts and approximating the integral by a sum, Equation (1) becomes a system of equations which is linear in G_k and R_∞:

$$Re(Z_i) = R_\infty + \sum_{k=1}^{N} \frac{G_k}{1+(\omega_i\tau_k)^2} \Delta \ln \tau \quad \text{for } 0 < i < M$$

$$Im(Z_i) = \sum_{k=1}^{N} \frac{-\omega_i\tau_k G_k}{1+(\omega_i\tau_k)^2} \Delta \ln \tau \quad \text{for } 0 < i < M$$

The term $\Delta \ln \tau$ is the difference between the natural logarithm of adjacent time constants, which is constant if τ_k are logarithmically spaced. The system can be written as $Z = AX$ where Z is a vector with length $2M$ containing the real and imaginary values for Z_i, X is a vector length $N + 1$ containing the values of G_k and R_∞, and A is a matrix of size $(2M) \times (N + 1)$ which contains the above equations. In this equation, AX is the impedance calculated from the DRT, which should be equal to the measured impedance Z.

In practice, Z will not be exactly equal to AX because of errors in measurement and the discrete approximation of Z and G. Instead, the goal is to find X which minimizes $\|Z - AX\|_2$, the distance between the measured impedance and the impedance calculated from the DRT. The subscript 2 indicates the ℓ^2 norm, also called the Euclidean norm, defined for a vector $W = (w_1, \ldots, w_N)$ by:

$$\|W\|_2 = \sqrt{\sum_{i=1}^{N} w_i^2} \qquad (6)$$

Differences between the DRT fit AX and the original impedance Z mean that the measured impedance cannot be modeled by a Voigt circuit. This could indicate that the DRT model needs to be extended (Section 3.2), or that there is a problem with the measurements.

In the absence of inductive effects, the DRT will be nonnegative. A neater DRT result can sometimes be obtained by constraining the solution to nonnegative values.

3.1 Regularization

If $N + 1$ is greater than $2M$ (for example, if $N = 5M$ as suggested above), then there will be more free parameters than constraints, and the above least squares problem is underdetermined. This means there will be many values of X which minimize $\|Z - AX\|_2$. Choosing a smaller value of N means that precision is lost in determining the location of the time constants. Instead, the problem can be regularized. While there are an infinite number of possible values for X, most of them are extremely chaotic and therefore provide very little information. The problem can be further constrained by assuming some regularity about X.

Elastic net regularization [5] changes the function to be minimized by adding the ℓ^1 (taxicab) and ℓ^2 (Euclidean) norms of X:

$$\|Z - AX\|_2^2 + \lambda_1\|X\|_1 + \lambda_2\|X\|_2^2$$

For a vector $W = (w_1, \ldots, w_N)$, the ℓ^1 norm is defined by

$$\|W\|_1 = \sum_{i=1}^{N} |w_i| \qquad (7)$$

Because of the power of 2 in its definition (6), the ℓ^2 norm places a large penalty on high values of the DRT, bringing them down and creating a smoother solution. The ℓ^1 norm has a higher penalty on low values of the DRT than the ℓ^2 norm, so it tends to bring low values of the DRT down to 0 and groups wide distributions into narrow peaks. The values λ_1 and λ_2 are called the regularization parameters. Often, it is more convenient to express the regularization parameters in terms of the total weight $\alpha = \lambda_1 + \lambda_2$ and relative weight of the ℓ^1 norm $r = \lambda_1/(\lambda_1 + \lambda_2)$. The parameter α should be positive and $0 \le r \le 1$. Figure 7 illustrates the effects of different parameters for elastic net regularization. It is useful to attempt a range of values to see which one produces the best results. There are open source libraries for solving elastic net problems, including scikit-learn in Python [9].

The special case $r = 0$ is called ridge regression (which is also a special case of Tikhonov regularization), while $r = 1$ is called lasso regression. Ridge regression has a closed form solution, but for $r > 0$, iterative methods are required to find a solution which can increase computation time. Formally, for any value of r, the minimization function is convex, which simplifies solving the problem since the only local minimum is the global minimum.

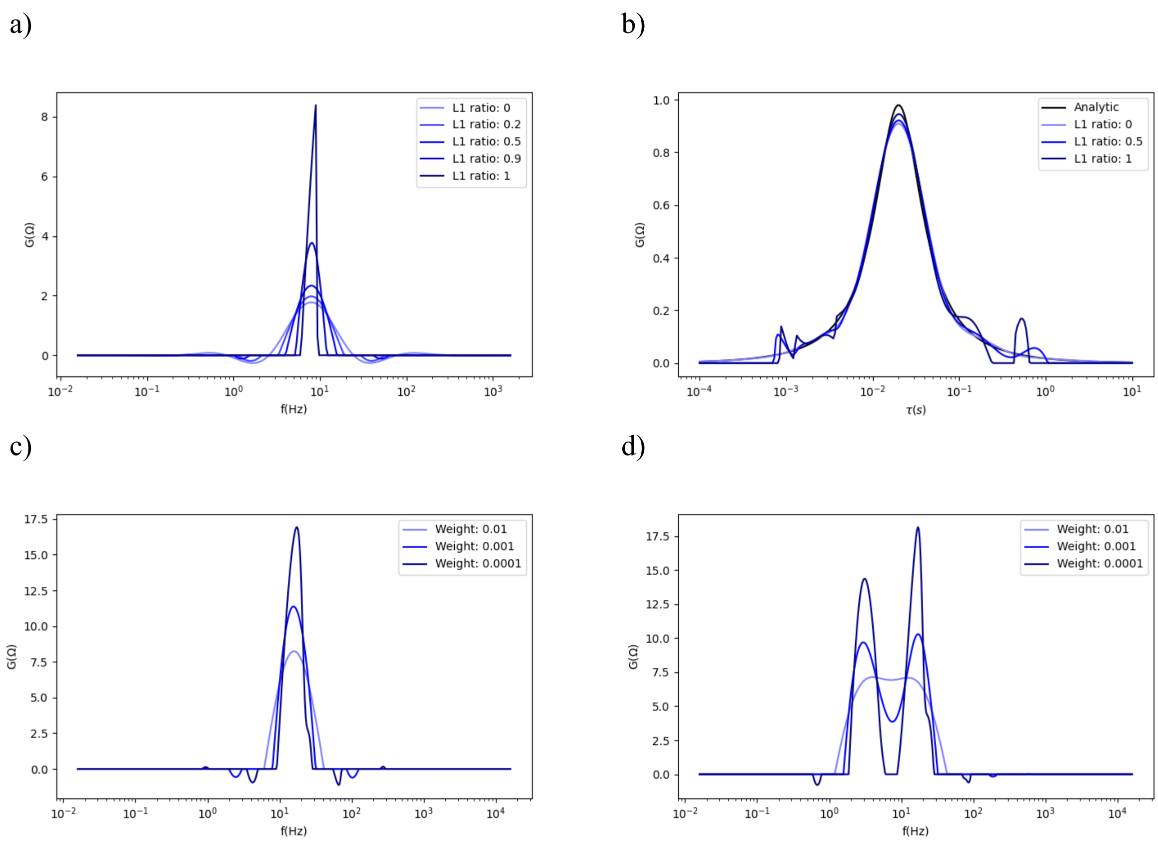

Figure 7: Effect of regularization. DRT of an RC element (a) and RQ element (b) with different values of the L1 ratio r*, and weight* α *= 0.001. DRT of (a) one RC element and (b) two RC elements with close time constants with different regularization weights* α*, and L1 ratio* r *= 0.5*

Figure 7 shows the effects of different regularization parameters. A higher value of r (L1 ratio) tends to produce narrower distributions, which is better for the δ distribution of Figure 7(a), but bad for the tails of the distribution in Figure 7(b). A higher weight tends to flatten peaks (Figure 7(c)) and merge them together (Figure 7(d)), but it also does a better job of eliminating noise. Figure 7 also shows "pseudo-peaks" when bad parameters are chosen. If regularization distorts the distribution too much, the pseudo-peaks often arise to provide a correction. They can also come from measurement noise. Higher regularization tends to flatten the pseudo-peaks.

Two common heuristic methods for choosing a regularization weight are the L-curve method [10] and generalized cross validation (GCV) [11].The general idea behind both of these methods is to balance the error on DRT calculation with the strength of the regularization. If the impedance data is very noisy, greater regularization is needed to suppress pseudo-peaks resulting from the noise. These methods cannot factor in background knowledge of the system, expected results, or which models are easier to interpret, so manual selection of parameters by trial and error can sometimes produce better results.

A brief overview of generalized cross validation will be presented here, while the full details can be found in [11]. While it only works for ridge regression, it can inform the selection of the value of α for the elastic net. The matrix A is written in terms of its singular value decomposition (SVD)

$$A = U\Sigma V^T$$

In the SVD, *U* and *V* are orthonormal matrices with columns called the left singular vectors for *U* and right singular vectors for *V*. The diagonal matrix *Σ* has values σ_i which describe the weight of the singular vectors. Ridge regression filters out the singular vectors according to filter factors

$$f_i = \frac{\sigma_i^2}{\sigma_i^2 + \alpha}$$

When $\alpha \ll \sigma_i^2$, the filter factor has a value near 1, and the corresponding singular vector remains important, but when $\alpha \gg \sigma_i^2$, the filter factor has a value near 0, and the singular vector is ignored. The GCV chooses α to minimize the function

$$GCV(\alpha) = \frac{\|Z - AX^*\|_2^2}{T(\alpha)^2}$$

The numerator is the error on the solution X^* found using α as the regularization parameter. In the denominator, *T* is a function which quantifies the amount of regularization, defined by

$$T(\alpha) = m - \sum_{k=1}^{m} f_i$$

In this equation, *m* is the length of *Z* (which is 2*M* in the DRT example). A high value of *T* means the filter factors are small, so regularization is high. The minimum of the GCV will balance the numerator (accuracy of the DRT) with the denominator (amount of regularization). While this method requires calculating the DRT multiple times, the SVD only needs to be calculated once and greatly improves the DRT calculation time.

3.2 Extending the DRT Model

While the Voigt circuit which forms the basis of DRT is a very general circuit, it is unable to fit some common circuit elements, like series inductors and series capacitors. In theory, it can fit a semi-infinite Warburg element, but it requires an infinite range of time constants. In order to fit these elements, they can be added in series to the DRT model [2]. The updated DRT equation becomes

$$Z(\omega) = R_\infty + j\omega L_0 + \frac{1}{j\omega C_0} + \frac{W_0}{\sqrt{j\omega}} + \int_{-\infty}^{\infty} \frac{G(\tau)}{1 + j\omega\tau} d\ln\tau$$

The second term is the impedance of an inductor, the third term is the impedance of a capacitor, and the fourth term is the impedance of a semi-infinite Warburg element. Choosing which of these terms to include can be decided by looking at the Nyquist plot, as shown in the following examples.

Consider Figure 8, where the impedance of an inductor in series with an RQ element is shown. There is one clearly visible time constant for the RQ element. Rather than approaching 0, Z'' goes towards negative infinity at high frequencies because of the inductor. Including the L_0 term in the DRT greatly improves the quality of the fit. It also makes the DRT result more readable by eliminating the large pseudo-peaks which attempt to fit the inductor.

In Figure 9, the inductor is replaced by a capacitor. This time, Z'' goes towards positive infinity at low frequencies. The DRT attempts to fit this with a large positive peak at low frequencies. Adding the C_0 term to the DRT model eliminates the peak and produces a much better fit.

Figure 10 replaces the capacitor with a semi-infinite Warburg element. On the Nyquist plot, the Warburg makes the impedance increase at a 45° angle at low frequencies. The Warburg tends to produce multiple peaks at low frequencies, which can obscure other system time constants. Adding the W_0 term both increases the quality of the fit, and makes the system's time constants more visible.

a) b)

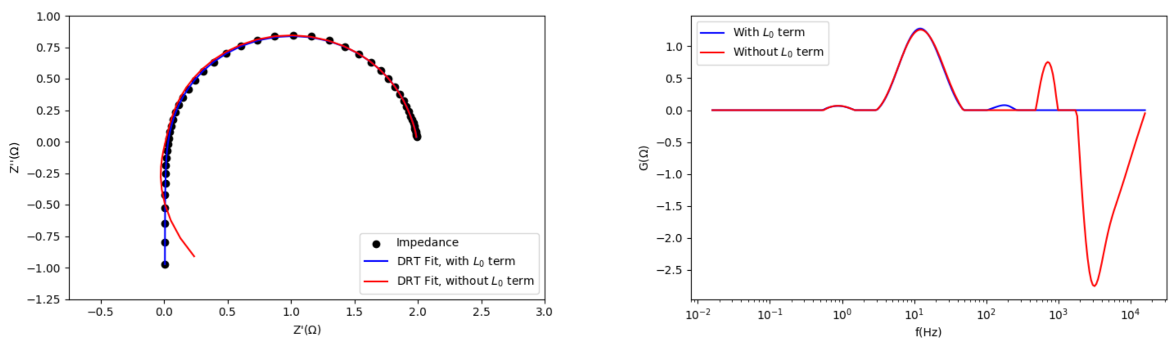

Figure 8. (a) Nyquist plot for an inductor in series with an RQ element. Adding the L_0 term greatly improves the fit. (b) DRT with and without L_0 term. The L_0 term eliminates large pseudo-peaks.

a) b)

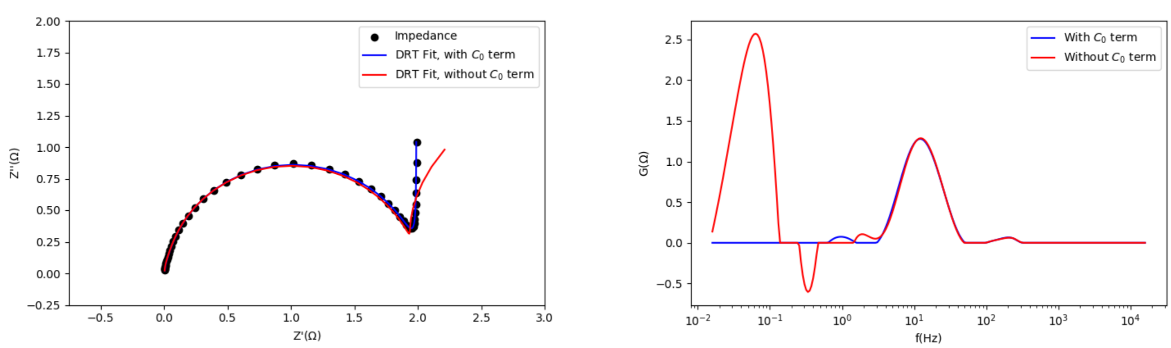

Figure 9. (a) Nyquist plot for a capacitor in series with an RQ element. Adding the C_0 term greatly improves the fit. (b) DRT with and without C_0 term. The C_0 term eliminates large pseudo-peaks.

a) b)

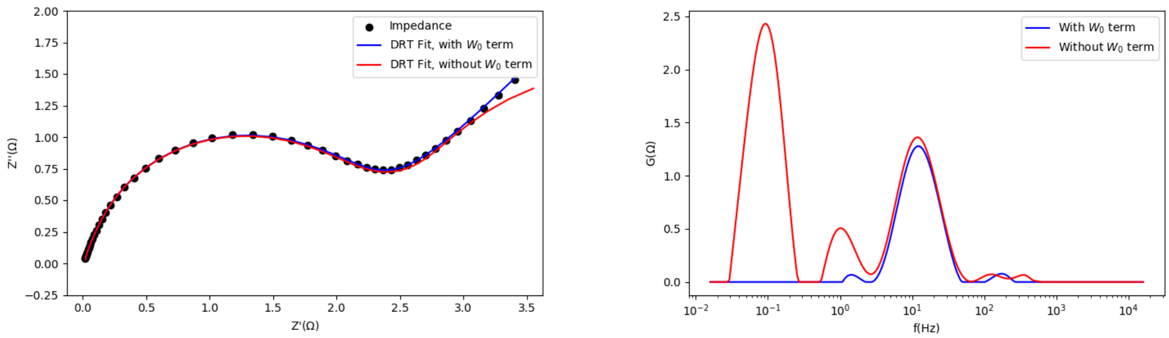

Figure 10. (a) Nyquist plot for a semi-infinite Warburg in series with an RQ element. Adding the W_0 term greatly improves the fit. (b) DRT with and without W_0 term. The W_0 term eliminates large pseudo-peaks.

To determine which of the terms should be included in the DRT model, look at the high and low frequency limits of the Nyquist plots. If Z'' goes towards negative infinity at high frequencies, an inductor should be added in series to the DRT model. If Z'' goes towards positive infinity at low frequencies, a capacitor should be added. If the plot forms a 45° angle at low frequencies, add a semi-infinite Warburg element. This will improve the quality of the fit and make the system time constants more visible. The values of L_0, C_0, and W_0 found from the DRT calculation can also be useful in choosing initial conditions for an equivalent circuit.

3.3 Interpreting DRT Results

Consider the example in Figure 11. The impedance is of an RC element and RL element in series. The RC circuit has a much larger resistance and a smaller time constant. At low frequencies, the inductor's impedance is near 0, while the capacitor has a large impedance. Therefore, the current must flow through the resistor in the RC circuit (R1), but will pass through the inductor instead of the RL element's resistor (R2). As the frequency increases, the inductor's impedance increases, so that the current must flow through both resistors. For very high frequencies, the capacitor allows current to flow, and therefore the current can avoid R1.

a) b)

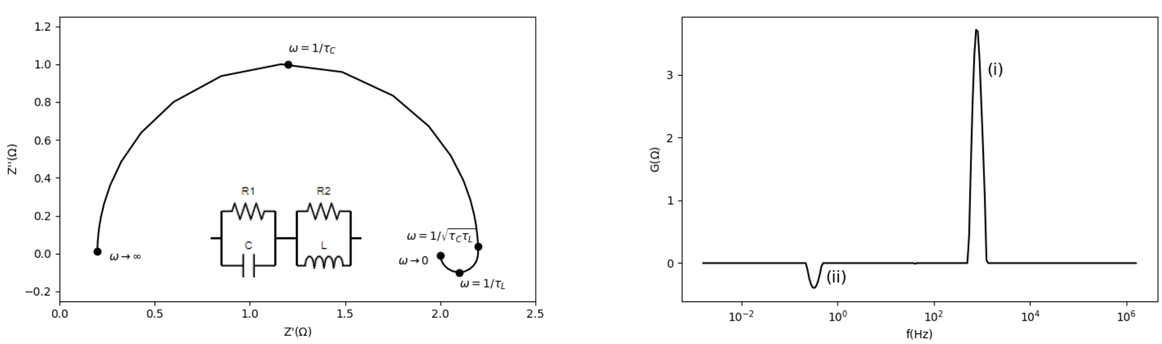

Figure 11. (a) Nyquist and (b) DRT of an RC element and RL element in series.
$R_1 = 2\ \Omega,\ C = 10^{-4}\ F,\ R_2 = 2\ \Omega,\ L = 10^{-4}\ H$

In this example, the time constants are greatly separated, so it is easy to read this information off the Nyquist plot. A DRT can provide the same information, even if the time constants are closer together. The properties in Section 2.1 will be applied here.

Because of the linearity of the DRT, the two peaks of the DRT can be considered separately. At high frequencies, the resistance of the system is given by the value of R_∞, from Equation (3). In this case, it is 0.2 **Ω**. Moving from right to left on the DRT plot, the first feature encountered is a large positive peak, labelled (i). This indicates an RC element. From Equation (2), the area under the peak (2 **Ω**) is the change in resistance from passing this peak. For an RC circuit, the area under the peak is the value of the resistor. Reading the exact value of this resistor can be easier on the Nyquist plot when time constants are far apart, but if the system's time constants were closer together, the overlap in each time constant's effects would make that impossible. The time constant of this RC element is given by the position of the peak. The peak is located around $f = 800$ Hz, so the time constant is $\tau = 1 / (2\pi f) \cong 2\times10^{-4}$ s. After passing this peak, the total resistance in the system is 2.2 **Ω**. Continuing to lower frequencies on the DRT plot, there is a much smaller, negative peak (ii), which indicates an RL element. The area between this peak and the frequency axis is 0.2 **Ω**, which is subtracted from the total resistance, so that the low frequency resistance is 2 **Ω**. Since the frequency of the peak is 0.31 Hz, the time constant is 0.5 s.

Identifying which physical processes cause these two features requires background knowledge about the system. But, based only on the DRT, it can be concluded that most of the system's resistance comes from a single dominant reaction, while a much smaller process exists with inductive effects.

3.4 Diffusion elements

As noted in Section 2.2, the DRT of diffusion elements is quite complex, and therefore they can often be easier to identify based on the Nyquist plot instead of the DRT. But the DRT can still be helpful in separating the diffusion element from other elements in the system. See Figure 6 for the theoretical DRT of diffusion elements.

If semi-infinite Warburg diffusion exists in the system, it is best handled by adding a semi-infinite Warburg element to the DRT model (Section 3.2). For finite length Warburg diffusion, there are in theory an infinite number of peaks in the DRT, becoming smaller and closer at higher frequencies. Figure 12(a) is an attempt to model these peaks with a numerically calculated DRT. Since the ℓ^1 norm tends to group peaks together, ridge regression (only ℓ^2 norm) is used. A non-negative constraint removes negative correction peaks. The first peak is large and easy to identify, even with higher regularization weights. However, only extremely small regularization weights can separate out the second peak, and the remaining peaks are all lumped together. From Equation (5), the ratio between the time constants of each peak is given by

$$\frac{\tau_k}{\tau_{k+1}} = \frac{(k+0.5)^2}{(k-0.5)^2}$$

The first few values of this sequence are {9, 2.78, 1.96, 1.65, 1.49, …}. While it is easy to separate time constants with a ratio of 9, it is nearly impossible for ratios less than 2, especially since the size of the peaks is also decreasing.

Gerischer diffusion is also difficult to model. In Figure 12(b), ridge regression and a nonnegative constraint are used to model Gerischer diffusion numerically. The infinite peak cannot be modeled exactly, and therefore correction peaks are added to the tail. A nonnegative constraint cannot remove these peaks because the tail is larger than 0. While smaller regularization weights can produce a higher peak, more regularization will create a smoother distribution.

In general, diffusion tends to produce non-symmetric DRTs with a tail extending into the high frequencies. This tail can consist of several individual peaks, as in the finite length Warburg case. For diffusion, as for any other application, it is useful to compare the DRT to the impedance spectrum, since both plots can provide complementary information about the system's response.

a) b)

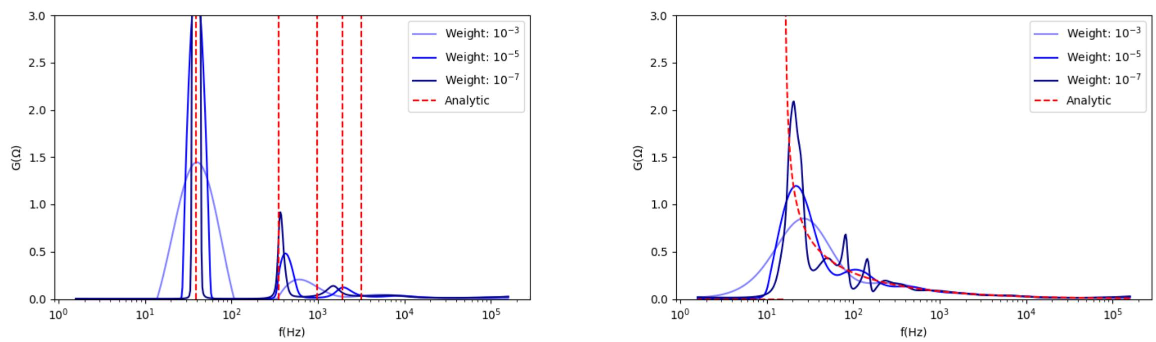

Figure 12. DRT of (a) Finite Length Warburg and (b) Gerischer elements, with different regularization weights. For the FLW, red dashed lines indicate the locations of the δ distributions. It is difficult to separate peaks beyond the first one. For the Gerischer, the difficulty lies in modeling an infinite peak with a large tail. Ridge regression is used for both examples.

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