Systems and EIS quality indicators

I – INTRODUCTION

I – 1 SYSTEM

A system is a physical object with one or more inputs and one or more outputs (Figure 1). An electrochemical interface, an electrochemical system, a battery, a fuel cell for example, are systems. In electrochemistry the input can be a voltage/current and the output a current/voltage.
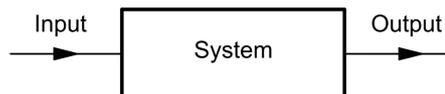

Figure 1: Sketch of a system (single input, single output).

I – 2 DIFFERENT CLASSES OF SYSTEMS

Systems can be of different classes:

- Linear Time-Invariant systems (LTI systems)
- Non-Linear Time-Invariant systems (NLTI systems)
- Linear Time-Variant systems (LTV systems)
- Non-Linear Time-Variant systems (NLTV systems)

Impedance measurements can only be conducted on LTI systems [1]. Electrochemical systems are generally NLTV systems and their dynamic behaviour can be assimilated to the one of the LTI systems only around an operating point of the steady-state characteristic and during a short amount of time [2]. The linear behaviour of the electrochemical system is approached by small amplitude stimulations. Under linear approximation conditions around an operating point, the impedance of the electrochemical system is characteristic of the dynamic behaviour of the system around that point. Experimental conditions should be carefully chosen so that the system varies as little as possible during the investigation.

### I – 3 EIS QUALITY INDICATORS

Quality indicators for Electrochemical Impedance Spectroscopy (EIS) were recently introduced [2, 3, 4]. The Total Harmonic Distortion (THD) and the Non-Stationary Distortion (NSD) are indicators useful to assess the validity of an impedance measurement of a system.

II – LINEAR TIME-INVARIANT SYSTEM (LTI SYSTEMS)

II – 1 DEFINITION

A system is said to be linear when its behaviour can be described by a linear differential equation or a systems of linear differential equations.

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Linear systems satisfy the superposition principle, i.e. the response to several stimuli can be calculated by the sum of the individual responses to each stimulus. For instance, a parallel R/C circuit is a linear system (Figure 2). This system is also time-invariant as long as the values of the R and C elements are constant.
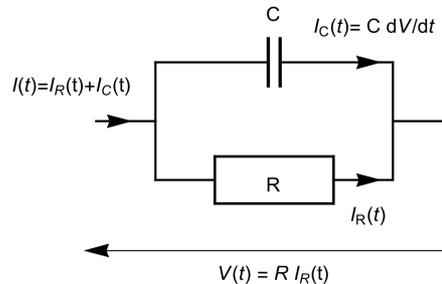

Figure 2: Sketch of a parallel R/C circuit.

II – 2 RESPONSE OF A LTI SYSTEM TO A SINUSOIDAL INPUT

In a steady state regime, the response of a linear time invariant system to a sinus wave stimulation, $x(t) = \delta E \sin(2\pi f t)$ is also a sinus wave of the same frequency (Figure 3). Both frequency spectra of the input and the output, obtained by Fourier[1] transform, show a single line at the frequency f (Figure 4).
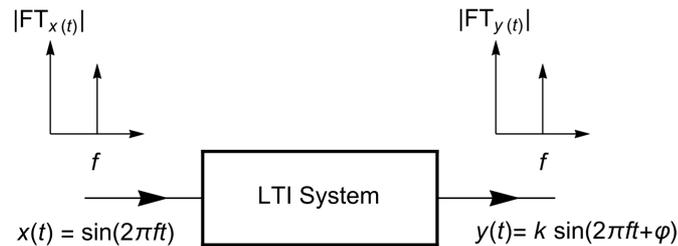
Figure 3: Input and output amplitude spectra of a LTI system in the case of a sinusoidal stimulation.
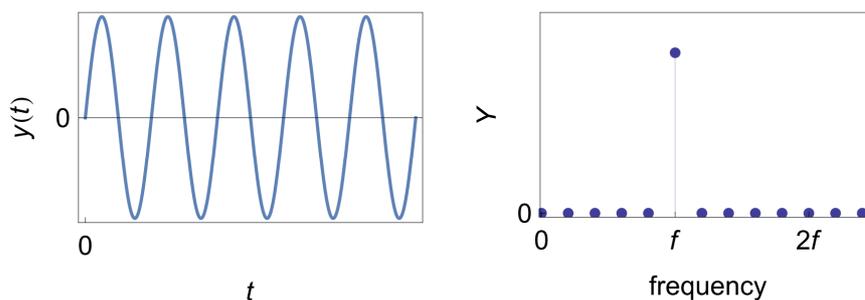
Figure 4: Time and frequency representation of a single sinus wave.

This result is the basis of the impedance measurement of a system (or more generally its transfer function) who is defined only for linear and time-invariant systems.

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[1] Joseph Fourier was a French mathematician (1768-1830). In 1810 Fourier sets up the Faculty of Sciences of Grenoble. The frequency spectra of this document are calculated by Discrete Fourier Transform for five signal periods.

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A contrario, the impedance (or the transfer function) is not defined for a non-linear and/or time-variant system. Doing an impedance measurement of such a system, as if it were linear and time-invariant, will give a result but it will not be the impedance of the system.

III – NON-LINEAR TIME-INVARIANT SYSTEMS (NLTI SYSTEMS)

III – 1 DEFINITION

A system is non-linear when its behavior can be described by a non-linear differential equation or a system of non-linear differential equations. A non-linear system does not satisfy the superposition principle. The response $y(t)$ of a NLTI system stimulated by a sinusoidal input $x(t)$ of the frequency f is not a sinusoid like for the linear systems. According to the Fourier theory, the response can be written as a sum of sinusoidal signals of the frequencies $f, 2f, 3f$ etc. (Figure 5 and Figure 6).
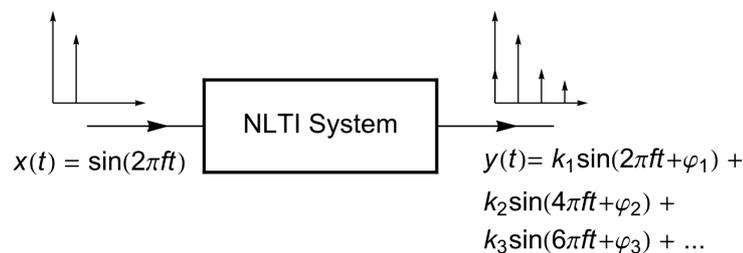

$x(t) = \sin(2\pi ft)$

NLTI System

$y(t) = k_1\sin(2\pi ft + \varphi_1) +$
$k_2\sin(4\pi ft + \varphi_2) +$
$k_3\sin(6\pi ft + \varphi_3) + ...$
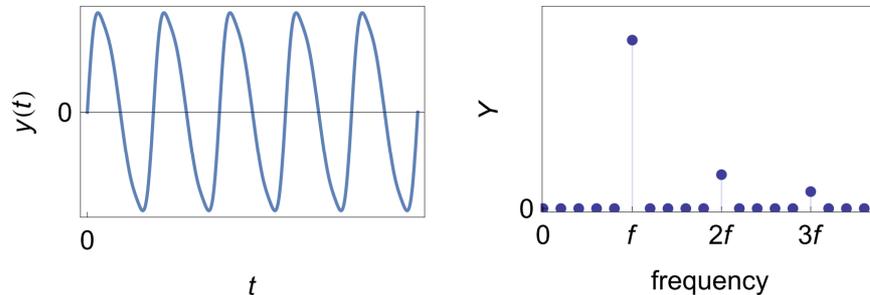
Figure 5: Sketch of a NLTI system.

Figure 6: Time response of a NLTI system and its amplitude spectrum.

III – 2 RESPONSE OF A NLTI SYSTEM TO A SINUSOIDAL INPUT

The frequency spectrum shown in Figure 6 has lines at the frequencies $f, 2f, 3f$ etc. The consequences of an impedance measurement of a NLTI system are detailed in the AN #9 [1]. The impedance magnitude and phase depend then on the stimulation amplitude δE (Figure 7). This property of non-linear systems is advantageously used in the VASP and CASP EC-Lab® techniques [5, 6].

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III – 3 TOTAL HARMONIC DISTORTION (THD) A NON-LINEARITY INDICATOR

The Total Harmonic Distortion is defined as the ratio of the sum of the amplitude of all harmonic frequencies to that of the fundamental frequency [7]:

$$\text{THD}(f) = \frac{1}{Y_f} \sqrt{\sum_{k=2}^{\infty} Y_{kf}^2} \qquad (1)$$

where Y_{kf} is the amplitude of the kth harmonic number. Practically only a number N of harmonics are necessary:

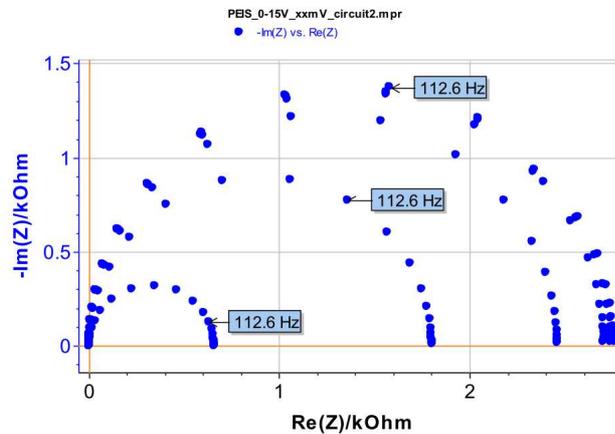$$\text{THD}(f) = \frac{1}{Y_f} \sqrt{\sum_{k=2}^{N} Y_{kf}^2} \qquad (2)$$

Figure 7: Nyquist diagram of impedance measured on the Test Box #3-2, with different values of amplitudes δE. This figure is taken from [1].

Simulation results of THD variation over frequency obtained on a circuit that corresponds to the one of the Test Box #3-2 [3] are given in Figure 8. The Nyquist plot suggests an R/C behavior and the THD shows that the circuit is linear at high frequencies and non-linear at the low frequencies.
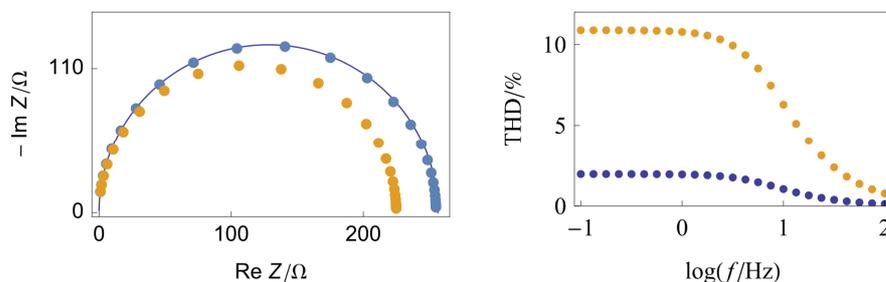

Figure 8: Example of impedance and THD variation with amplitude. Blue line - theoretical impedance, blue dots - low amplitude, yellow dots - high amplitude.

THD has been used in electrochemistry for example for the study of fuel cells [8, 9, 10, 11, 12] and electrolyzers [13].

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IV – TRANSIENT RESPONSE OF SYSTEMS

IV – 1 TRANSIENT OR NON-STEADY STATE RESPONSE OF LTI SYSTEMS

Figure 9 shows an example of a transient current response of a R1 + R2/C1 circuit to an input voltage step $\Delta E\, u(t)$, where $u(t)$ is the unit step function (Heaviside function). The current tends asymptotically to a constant value equal to $\Delta E/(\text{R1} + \text{R2})$ corresponding to a new steady state.
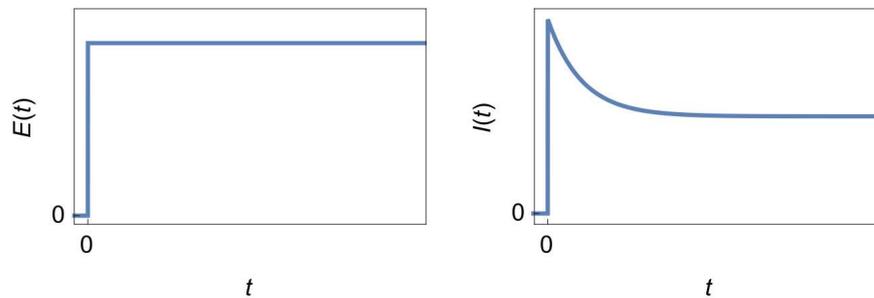

Figure 9: Current response of a R1 + R2/C1 to a voltage step.

The signal given by:

$$E(t) = \Delta E\, u(t) + \delta E\, \sin(2\pi f t) \qquad \textbf{(3)}$$

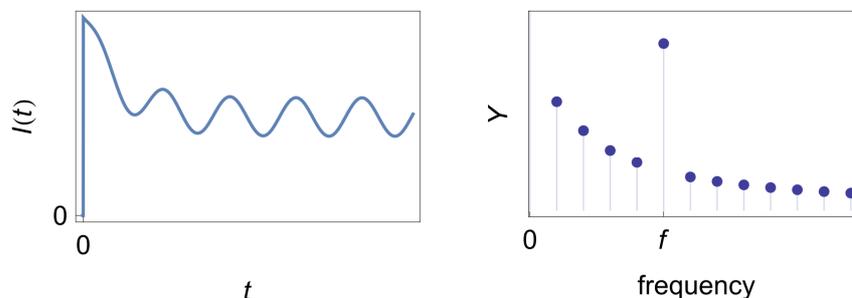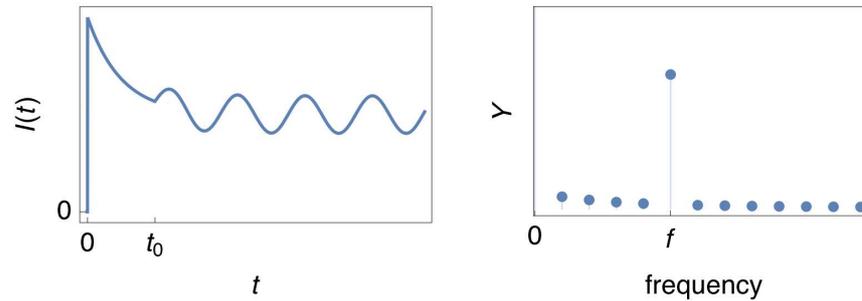will be used to measure the impedance of an R1 + R2/C1 circuit.

Figure 10: Response of a R1 + R2/C1 circuit to a combination of a voltage step and a sinus stimulation (Eq. (3)). The measurement starts at $t = 0$. The DC line in the spectrum was intentionally removed.

The response of a LTI system in a transient regime is not a periodic signal, therefore its amplitude spectrum contains more lines than just one line at the stimulation frequency (Figure 10). These lines form a baseline with an exponential decay shape which raises the line at the frequency of interest and thus generating measurement errors.

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The error decreases if the measurement is delayed which obviously increases the measurement duration (Figure 11).

Figure 11: Response of a $R1 + R2/C1$ circuit to a combination of a voltage step and a sinus stimulation (Eq. (3)). The measurement starts at $t = t_0$. The DC line in the spectrum was intentionally removed.

1.1.1 Consequences of the non-steady state on impedance measurements

An example of impedance measurement errors of a LTI system in a non-steady state is shown in Figure 12. The plot obtained by an impedance measurement starting at the beginning of a voltage step shows a loop in the middle frequency range that can lead to erroneous interpretations.
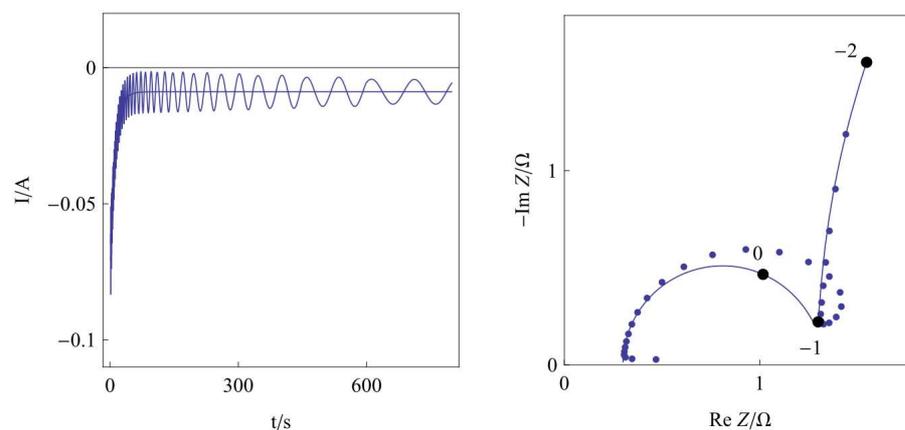
Figure 12: Simulation of an impedance measurement of a $R1 + R2/C2 + R3/C3$ circuit. Scanning from high to low frequencies, measurement starts at $t = 0$. Thin line: theoretical impedance, dots: measurement simulation during the transient.

1.1.2 Non-steady state indicators

Several methods, most of them qualitative, can be used to check the presence of a transient regime. One can follow the mean value of the response during an impedance measurement, sequentially measure two or more impedance spectra [14], plot the voltage vs. current Lissajous[2] figure or do the Kramers-Kronig[3] transform [15]. A more detailed comparison of this methods are given in [16].

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[2] Jules Lissajous was a French physicist and mathematician (1822-1880).
[3] Mathematical relation named in honour of Hendrick A. Kramers (1894-1952) a Dutch physicist and Ralph Kronig (1904-1995) a German American physicist.

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a. *Non-Stationary Distortion coefficient (NSD coefficient)*

A new indicator called non-stationary distortion (NSD) coefficient was recently introduced [3, 4]. The NSD can quantitatively characterize the influence of the spectrum base line (Figure 10) on the amplitude at the frequency of interest.

$$\text{NSD}(f) = \frac{1}{Y_f} \sqrt{Y_{f-\Delta f}^2 + Y_{f+\Delta f}^2} \tag{4}$$

where Y_f is the amplitude at the stimulation or fundamental frequency, $Y_{f-\Delta f}$ and $Y_{f+\Delta f}$ are the amplitudes at the adjacent frequencies to the fundamental and Δf is the spectral frequency resolution. The values of the NSD are about 35 % and 5 % for the data shown in Figure 10 and Figure 11, respectively, in agreement with the height of the spectral base line.

Examples of NSD variation with frequency are given in Figure 13. The simulation corresponds to an impedance measurement obtained with an input signal given by Eq. (3), like the SPEIS technique.
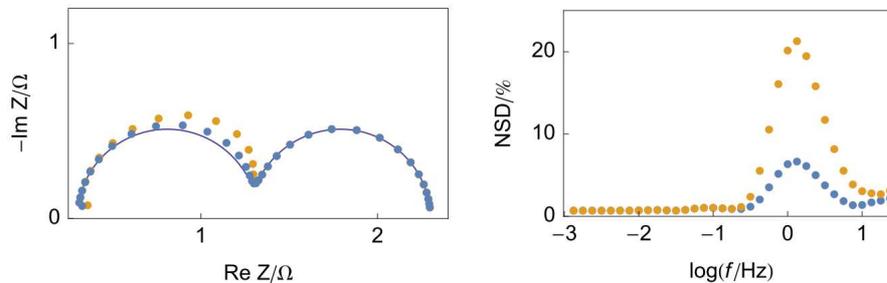
Figure 13: Circuit $R1 + R2/C2 + R3/C3$. Steady state Nyquist diagram: thin line ($\Delta E = 0$), low transient: blue dots (low ΔE), high transient: yellow dots (high ΔE). Right: change of NSD with frequency.

b. *Non-steady state correction*

The EC-Lab drift correction is a patented correction method for impedance measurements done on a LTI system in a non-steady state [17, 18, 19]. The principle of correction is based on the measurement of the spectrum lines $Y_{f-\Delta f}$ and $Y_{f+\Delta f}$ adjacent to the fundamental.

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IV – 2 TRANSIENT RESPONSE OF A NLTI SYSTEM

The transient and spectral response of a NLTI system in a non-steady state are shown in Figure 14. The spectrum is a combination of non-linearities (harmonics) and a transient regime (baseline with an exponential decay). The spectrum can be characterized by THD and NSD coefficients.
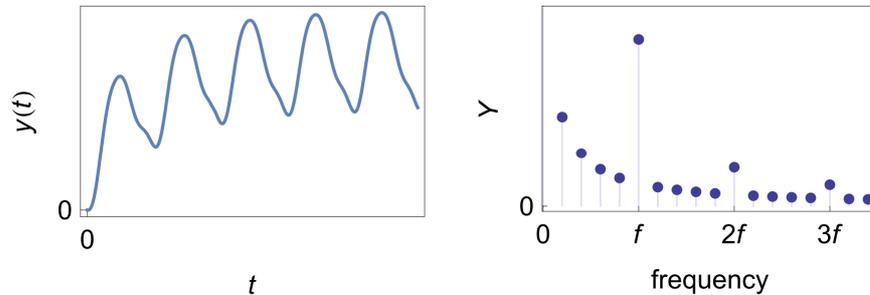

Figure 14: Transient response of a NLTI system and its amplitude spectrum. THD = 27 %, NSD = 20 %.

V – LINEAR TIME-VARIANT SYSTEMS (LTV SYSTEMS)

V – 1 DEFINITION

The systems change with time either because their structure changes, which leads to a modification of the system of equations describing their behaviour, or because the values of one or more parameters of the system of equation vary with time. Only the latter, sometimes called system with variable parameters [20], is considered in this document.

V – 2 RESPONSE OF A LTV SYSTEM TO A SINUSOIDAL INPUT

A spectrum of a system response signal containing more than just the line of the fundamental frequency is representative of a deviation from a pure sinusoidal response. Lines on each side of the fundamental forming a "skirt" are typical for a LTV system. An example of LTV response is shown Figure 15.
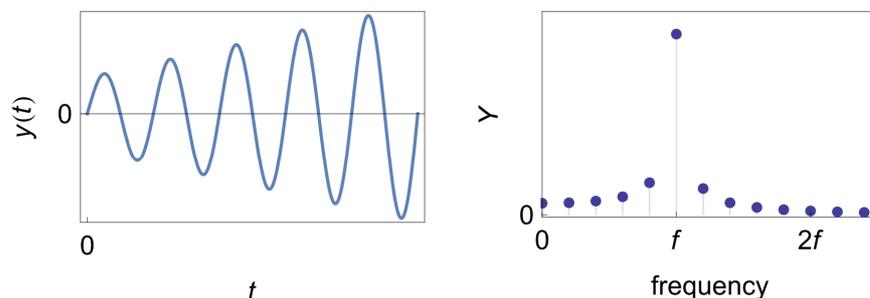

Figure 15: Time response of a LTV system and its amplitude spectrum, NSD = 23 %.

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V – 3 INDICATOR OF VARIATION

The NSD coefficient (Eq. (4)) can also be used to characterize the variation of a system (Figure 17). Note that the shape of the NSD curves is different than the one observed in Figure 13.
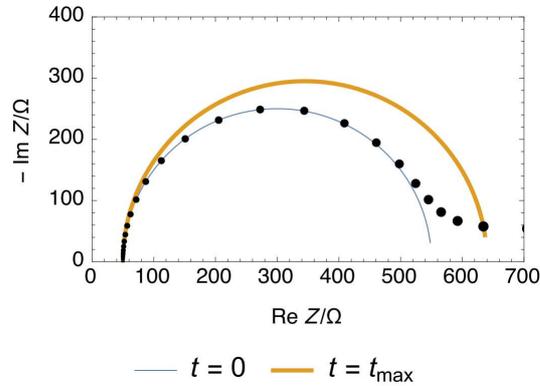

Figure 16: Instantaneous Nyquist impedance diagrams ($t = 0$ and $t = t_{max}$) of the circuit $R1 + R2(t)/C1$ and simulation of the measured diagram (dots). The dot size increases with increasing time. The figure is taken from [12].
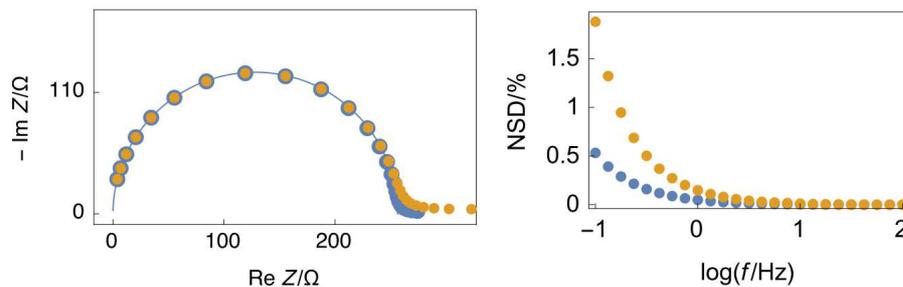

Figure 17: Circuit $R1(t)/C1$, instantaneous Nyquist diagram (thin line, t = 0), simulation of the measured diagram (blue dots small R1 variation, orange dots higher R1 variation) and change of NSD with frequency.

V – 4 TRANSIENT RESPONSE OF A LTV SYSTEM

An example of non-steady state response of a LTV system and its amplitude spectrum are shown Figure 18. The spectrum combines the skirt characteristic of a LTV system and the base line of the non-steady state.

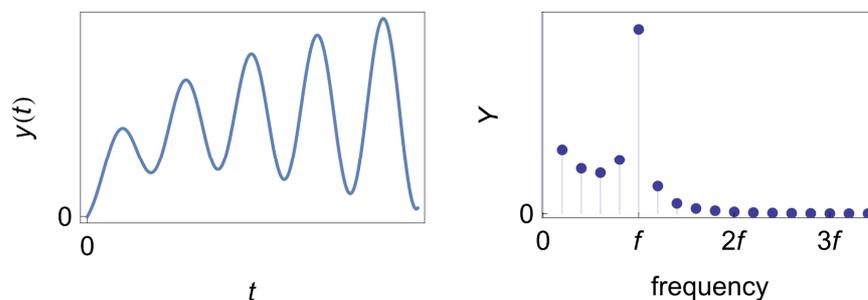**Figure 18: Transient response of a LTV system and amplitude spectrum of the response. NSD = 33 %.**

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VI – NON-LINEAR TIME-VARIANT SYSTEMS (NLTV SYSTEMS)

VI – 1 DEFINITION

Non-linear time-variant systems are non-linear systems whose parameters vary with time.

VI – 2 RESPONSE OF A NLTV SYSTEM TO A SINUSOIDAL INPUT

The response of a NLTV system and its amplitude spectrum are shown Figure 19. The spectrum combines the characteristic of a NLTI system (harmonics at 2f, 3f, etc.) and the characteristic of a time-variant system (skirt). The spectrum can be characterized by the THD and the NSD coefficients.
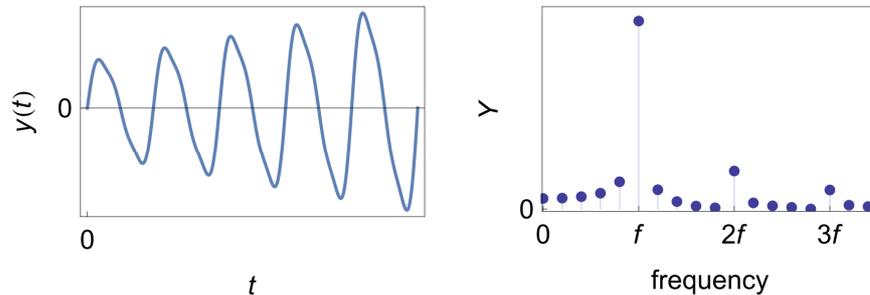

Figure 19: Response of a NLTV system and its amplitude spectrum. THD = 22 %, NSD = 18 %.

VI – 3 TRANSIENT RESPONSE OF NLTV SYSTEMS

The time response of a NLTV system in a non-steady state and the amplitude spectrum of the response are shown Figure 20. The spectrum combines the characteristics of the NLTI systems (harmonics at 2f, 3f, etc.), time-variant systems (skirt) and non-steady state (base line). This response can be characterized by the THD and NSD coefficients.
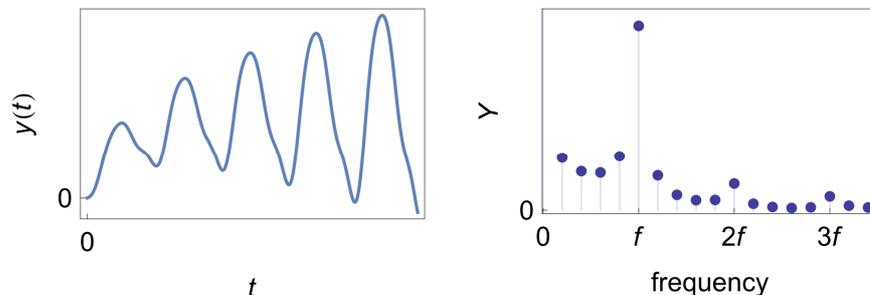

Figure 20: Transient response of a NLTV system and its amplitude spectrum. THD = 16 %, NSD = 35 %.

VII – CONCLUSION

The spectrum response of a system depends of the nature of the system. The indicators such as the THD and NSD can be used to quantitatively characterize the spectrum and provides information about the nature of the system. They are quantitative indicators for the quality of impedance measurements.

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VIII – REFERENCES

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