

MEP Introduction Report

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Abstract

MEP Introduction Report on the master thesis project of Isabel Postmes, supervised by Sonia Conesa Boj. My Master thesis will revolve around the automization of the electron energy loss spectrum (EELS) analysis, documented by the transmission electron microscope (TEM). The focus will be on the low-loss spectrum, where the influence of the zero loss peak (ZLP) is not negligible, and will include an error estimation, which makes it unique. The first step in this was done by Laurien Roest: the detection of the ZLP. I will focuss in my months in generilizing the program Laurien wrote, and I will expand it by including the Kramer-Kronig analysis and peak detection. The final goal is to be able to input an image of spectra, and have an automatic output of what pixels statisfy certain criteria.

Contents

1	Planning	2
1.1	Milestones	3
2	Introduction	3
3	Background info	3
3.1	TEM	3
3.1.1	EELS of the TEM	4
3.1.2	Low loss spectrum	4
3.2	Dielectric function	4
4	Calculations on the spectrum	4
4.1	Approximating continious Fourier transform with dicrete Fourier transform	4
4.1.1	Original definitions	4
4.1.2	Discrete approximation CFT	5
4.1.3	Convolutions	6
4.1.4	Convolution of two gaussians	8
4.1.5	Other calculations on CFTs	8
4.2	Obtaining the single scattering distribution	9
4.2.1	Build-up of measured spectrum	9
4.2.2	Analytical analysis of possible recorded spectra	10
4.3	Kramer-Kronig relations	14
4.3.1	Spectrum analysis	14
4.3.2	Step 1: rescaling intensity	15
4.3.3	Step 2: extrapolating	15
4.3.4	Step 3: normalisation and retrieving $\text{Im} \left[\frac{1}{\varepsilon(E)} \right]$	15
4.3.5	Step 4: retrieving $\text{Re} \left[\frac{1}{\varepsilon(E)} \right]$	16
4.3.6	Step 5: retrieving ε	16

1 Planning

The first couple of weeks will be dedicated to getting acquainted with the subjects at hand, and Lauriens program. Then I will build the program step-by-step: starting by implementing the Fourier Deconvolution, continuing to subtracting the dielectric function with the Kramer-Kronig analysis and than working on the peak detection. For each step I will start by working out a toy model, which is a simplified idealized spectrum. The expected results of such a spectrum can be worked out analytically, which creates the opportunity to validate the functions. Eventually I will implement all this into a program which takes a image of spectra, and gives a visual output and list of pixels depending on what characteristics are selected.

To test the final program, we will measure layered materials.

1.1 Milestones

Even though I find it hard to predict the exact time I will be needing for each step, since with programming problems some expected hurdles can be overcome with relative ease, whereas other smaller tasks can prove an extensive challenge. However, as for now, I would be happy if my time line would be anywhere near:

- End of November: worked out deconvolution part of the program. Have the results in report.
- Christmas holiday: cleaned up/generalized and completely understand Lauriens program. This will form the basis of the second part of my program.
- End of February: have first results
- March/April: difficult for me to oversee, probably working out extra functionals and extending program. Also writing report.
- Beginning of May: finalizing results and program, completing report.
- Half May: first draft report
- End of May: final report and defence.

2 Introduction

The supervisor on my project is Prof. Sonia Conesa Boj. Furthermore, I will be supervised in an unofficial capacity by dr. Juan Rojo of the Nikhef Institute in Amsterdam. The project is a continuation of the thesis project of Laurien Roest, whose paper can be found at

One of the features of the TEM is to obtain electron energy loss spectra of the reviewed sample. This spectrum documents the loss in kinetic energy of electrons travelling through a sample. [1]. Interpretation of these spectra can help in determining the composition and structure of the evaluated sample.

3 Background info

In the sections below, you will find a first overview of some of the critical background information.

3.1 TEM

The transmission electron microscope (TEM) projects a beam of electron through a sample, to record the transmitted electrons on the opposite side of the sample to form an image. Due to the fact that the de Broglie wavelengths of electrons (10^{-2}) are factors smaller than the wavelength of photons (10^2), much higher resolutions can be obtained than with light microscopy. [2] The resolution of a TEM is mostly determined by the focussing power of the electron beam. For TEMs with monochromator, such as the TEM available at the Conesa Boj Laboratory, resolutions of 0.1nm can be obtained, small enough to image single atoms. [1]

3.1.1 EELS of the TEM

The electron energy loss spectrum (EELS) documents the loss in kinetic energy of electrons in their path through a specimen. Due to the quantification of energy levels at elementary level, this energy loss manifests in peaks in the spectrum. The broadness of the observed peaks mainly comes from the inherent imperfect electron source, which transmits electrons in a certain energy distribution focussed around the target energy. The analysis of these peaks gives inside in what energy levels are present in the sample, and with that gives inside in the composition and structure of the specimen. [1]

3.1.2 Low loss spectrum

Much of the interesting information in the EELS is nested in the low loss part ($<50\text{eV}$) of the spectrum. Here, one finds info on bandgaps, plasmons and excitons among others [3]. A significant problem in this part of the spectrum, is that the influence of the zero loss peak (ZLP) is non-negligible. Older tactics to avoid this problem, are centered around fitting the ZLP in each individual spectrum, and subsequently subtracting it. The most prominent problem with this approach is that there is no indication of the error in the estimation of the ZLP. Therefore, it can not be said with how significant the found peaks near the tail of the ZLP are. In her master thesis, Laurien Roest developed a method in which the ZLP is approximated by a neural network, which inherently results in a ZLP with error margins.

Since the ZLP is an indication of the distribution of the energies of the electrons produced by the electron source [1], the errors around the ZLP track through in all the rest of the spectrum. Therefore, in my project I will use the program developed by Laurien to estimate the ZLP, and use this in the detection and quantification of the peaks in the spectrum and the other variables to be extracted from the spectrum.

3.2 Dielectric function

The dielectric function, also called permittivity, is a measure for the polarisability of a material. From the dielectric function, a multitude of other characteristics can be calculated. Since the dielectric function can be extracted from the electron energy loss spectrum through Kramer-Kronig analysis, for an image of spectra, the dielectric function can be calculated for each pixel. [3]

4 Calculations on the spectrum

4.1 Approximating continuous Fourier transform with discrete Fourier transform

Let's start with a small refresher on Fourier transforms, and evaluate how to approximate the continuous Fourier transform with the discrete Fourier transform.

4.1.1 Original definitions

The continuous Fourier transform (CFT) of function $f(x)$ is defined as:

$$\mathcal{F}\{f(x)\} = F(\nu) = \int_{-\infty}^{\infty} e^{-i2\pi\nu x} f(x) dx. \quad (4.1)$$

The inverse of the CFT is given by:

$$\mathcal{F}^{-1}\{F(\nu)\} = f(x) = \int_{-\infty}^{\infty} e^{i2\pi\nu x} F(\nu) d\nu. \quad (4.2)$$

The discrete Fourier transform (DFT) of discrete function $f[n]$ defined on $n \in \{0, \dots, N-1\}$ is given by:

$$\text{DFT}\{f[n]\} = F[k] = \sum_{n=0}^{N-1} e^{-i2\pi kn} f[n], \forall k \in \{0, \dots, N-1\}. \quad (4.3)$$

The inverse of the CFT is given by:

$$\text{DFT}^{-1}\{F[k]\} = f[n] = \sum_{k=0}^{N-1} e^{i2\pi kn} F[k], \forall n \in \{0, \dots, N-1\}. \quad (4.4)$$

4.1.2 Discrete approximation CFT

If one approximates function $f(x)$ by $f[x_0 + n\Delta x]$, $\forall n \in \{0, \dots, N-1\}$, and ν by $k\Delta\nu$, $\forall k \in \{0, \dots, N-1\}$, where:

$$\Delta x \Delta \nu = \frac{1}{N}, \quad (4.5)$$

starting from eq. (4.1), one can obtain:

$$\begin{aligned} F(\nu) \approx F[k\Delta\nu] &= \sum_{n=0}^{N-1} \Delta x f[x_0 + n\Delta x] \exp[-i2\pi k\Delta\nu(x_0 + n\Delta x)], \\ &= \Delta x \exp[-i2\pi k\Delta\nu x_0] \sum_{n=0}^{N-1} \exp[-i2\pi nk/N] f[x_0 + n\Delta x], \\ &= \Delta x \exp[-i2\pi k\Delta\nu x_0] \text{DFT}\{f[n]\}. \end{aligned} \quad (4.6)$$

Similary, we can reobtain the original function $f(x) \approx f[n\Delta x + x_0]$ from the approximation of $F(\nu) \approx F[k\Delta\nu]$, using eq. (4.2):

$$\begin{aligned} f(x) \approx f[n\Delta x + x_0] &= \sum_{k=0}^{N-1} \Delta\nu F[k\Delta\nu] \exp[i2\pi k\Delta\nu(n\Delta x + x_0)] \\ &= \Delta\nu \sum_{k=0}^{N-1} F[k\Delta\nu] \exp[i2\pi k\Delta\nu x_0] \exp[i2\pi kn/N]. \end{aligned} \quad (4.7)$$

Defining:

$$G[k\Delta\nu] = \exp[i2\pi k\Delta\nu x_0] F[k\Delta\nu], \quad (4.8)$$

we find:

$$\begin{aligned} f(x) \approx f[n\Delta x + x_0] &= \Delta\nu \sum_{k=0}^{N-1} G[k\Delta\nu] \exp[i2\pi kn/N] \\ &= \Delta\nu \text{DFT}^{-1}\{G[k\Delta\nu]\} \end{aligned} \quad (4.9)$$

4.1.3 Convolutions

Definition of concolution The concolution of two functions $f(x)$ and $g(x)$ is defined as the integral:

$$h(x) = \int_{-\infty}^{\infty} f(\bar{x})g(x - \bar{x})d\bar{x}. \quad (4.10)$$

Assuming $f(x)$ and $g(x)$ have a limited domain, $h(n)$ will also have a limited domain, given by:

$$\begin{aligned} f(x) &= \begin{cases} f(x), & x_{0,f} \leq x \leq x_{1,f} \\ 0, & x < x_{0,f} \vee x > x_{1,f} \end{cases}, \\ g(x) &= \begin{cases} g(x), & x_{0,g} \leq x \leq x_{1,g} \\ 0, & x < x_{0,g} \vee x > x_{1,g} \end{cases}, \\ h(x) &= \begin{cases} h(x), & x_{0,f} + x_{0,g} \leq x \leq x_{1,f} + x_{1,g} \\ 0, & x < x_{0,f} + x_{0,g} \vee x > x_{1,f} + x_{1,g} \end{cases}. \end{aligned} \quad (4.11)$$

This simplifies eq. (4.10) to:

$$h(x) = \int_{x_{0,f}}^{x_{1,f}} f(\bar{x})g(x - \bar{x})d\bar{x}. \quad (4.12)$$

Futhermore, the Fourier transform of the convolution has the beautiful property that, for the limited domain functions, but this can be extended into infinity:

$$\begin{aligned} H(\nu) &= \int_{x_{0,1}+x_{0,g}}^{x_{1,f}+x_{1,g}} h(x) \exp[-i2\pi] dx, \\ &= \int_{x_{0,1}+x_{0,g}}^{x_{1,f}+x_{1,g}} \int_{x_{0,1}}^{x_{1,f}} f(\bar{x})g(x - \bar{x})d\bar{x} \exp[-i2\pi\nu x] dx, \\ &= \int_{x_{0,1}}^{x_{1,f}} \int_{x_{0,1}+x_{0,g}}^{x_{1,f}+x_{1,g}} g(x - \bar{x}) \exp[-i2\pi\nu x] dx f(\bar{x})d\bar{x}. \end{aligned} \quad (4.13)$$

Defining $\hat{x} = x - \bar{x}$, evaluation the limits on the integrals and realising $d\hat{x} = dx$, you obtain:

$$\begin{aligned} H(\nu) &= \int_{x_{0,f}}^{x_{1,f}} \int_{x_{0,g}}^{x_{1,g}} g(\hat{x}) \exp[-i2\pi\nu(\hat{x} + \bar{x})] d\hat{x} f(\bar{x})d\bar{x}, \\ &= \int_{x_{0,g}}^{x_{1,g}} g(\hat{x}) \exp[-i2\pi\nu\hat{x}] d\hat{x} \int_{x_{0,f}}^{x_{1,f}} f(\bar{x}) \exp[-i2\pi\nu\bar{x}] d\bar{x}, \\ &= F(\nu)G(\nu). \end{aligned} \quad (4.14)$$

Discretisation of the convolution and its CFT Again, we can approximate $f(x)$, $g(x)$ and $h(n)$ by:

$$\begin{aligned} f(x) &\approx f[n_f(\Delta x)_f + x_{0,f}], \forall n_f \in \{0, N_f - 1\}, (\Delta x)_f = (x_{1,f} - x_{0,f})/N_f, \\ g(x) &\approx g[n_g(\Delta x)_g + x_{0,g}], \forall n_g \in \{0, N_g - 1\}, (\Delta x)_g = (x_{1,g} - x_{0,g})/N_g. \end{aligned} \quad (4.15)$$

If we ensure that $(\Delta x)_f = (\Delta x)_g \equiv \Delta x$, we can approximate $h(n)$:

$$h(x) \approx h[n_h \Delta x + x_{0,f} + x_{0,g}], \forall n_h \in \{0, N_f + N_g - 1\}, \quad (4.16)$$

where

$$h[n_h \Delta x + x_{0,f} + x_{0,g}] = \sum_{k=0}^{N_f-1} f[k \Delta x + x_{0,f}] g[n \Delta x + x_{0,g} - k \Delta x] \Delta x. \quad (4.17)$$

To discretize the continuous Fourier transform, we once again need to define $\Delta\nu$, but mind the difference for $\Delta\nu$ for the discretizations of $f(x)$ or $g(x)$ and $h(x)$:

$$\begin{aligned} (\Delta\nu)_f &= \frac{1}{N_f \Delta x} \\ (\Delta\nu)_g &= \frac{1}{N_g \Delta x} \\ (\Delta\nu)_h &= \frac{1}{(N_f + N_g) \Delta x} \\ &= ((\Delta\nu)_f^{-1} + (\Delta\nu)_g^{-1})^{-1} \end{aligned} \quad (4.18)$$

Now the discrete approximation of the CFT of the convolution (given by eq. (4.13)) is given by:

$$\begin{aligned} H(\nu) &\approx H[k(\Delta\nu)_h] = \sum_{n=0}^{N_f+N_g-1} h[n \Delta x + x_{0,f} + x_{0,g}] \exp[-i2\pi k(\Delta\nu)_h(n \Delta x + x_{0,f} + x_{0,g}) \Delta x], \\ &= \sum_{n=0}^{N_f+N_g-1} \sum_{l=0}^{N_f-1} f[l \Delta x + x_{0,f}] g[(n-l) \Delta x + x_{0,g}] \exp[-i2\pi k(\Delta\nu)_h(n \Delta x + x_{0,f} + x_{0,g})] (\Delta x)^2. \end{aligned} \quad (4.19)$$

Defining $m = n - l$, and swapping summation order, you obtain:

$$\begin{aligned} H[k(\Delta\nu)_h] &= (\Delta x)^2 \exp[-2\pi i k(\Delta\nu)_h x_{0,f}] \sum_{l=0}^{N_f-1} f[l(\Delta\nu)_h + x_{0,f}] \\ &\quad \exp[-2\pi i k(\Delta\nu)_h x_{0,g}] \sum_{m=-l}^{N_f+N_g-l-1} g[m \Delta x + x_{0,g}] \exp[-2\pi i k(\Delta\nu)_h(m+l) \Delta x], \end{aligned} \quad (4.20)$$

reevaluating the boundaries on the second summation, inputting eq. (4.18) and shuffling above result leads to:

$$\begin{aligned} H[k(\Delta\nu)_h] &= \exp[-2\pi i k(\Delta\nu)_h x_{0,f}] \sum_{l=0}^{N_f-1} f[l(\Delta\nu)_h + x_{0,f}] \exp[-2\pi i k l / (N_f + N_g)] \\ &\quad \exp[-2\pi i k(\Delta\nu)_h x_{0,g}] \sum_{m=0}^{N_g-1} g[m \Delta x + x_{0,g}] \exp[-2\pi i k h m / (N_f + N_g)]. \end{aligned} \quad (4.21)$$

Looking at the above equation, one almost recognizes a multiplication of two approximate CFT's (see eq. (4.6)). However, there is a significant difference, which means it is not a simple multiplication of the two CFT's: where in the CFT of the singular function, you see that $\Delta\nu = 1/N_f$ or $\Delta\nu = 1/N_g$ respectively, whereas in eq. (4.21), $\Delta\nu = 1/(N_f + N_g)$, as given by eq. (4.18). Nor is it a simple factor with which the CFT's could be multiplied: the factor is present in the exponential within the summations. Each single exponential term in the summations need to be raised to the power $(N_f + N_g)/N_f$ and $(N_f + N_g)/N_g$ respectively.

4.1.4 Convolution of two gaussians

Defining:

$$f(x) = \frac{A_f}{\sqrt{2\pi}\sigma_f} \exp \left[-\frac{(x - \mu_f)^2}{2\sigma_f^2} \right], \quad (4.22)$$

we can find the Fourier transform of $f(x)$ as:

$$\mathcal{F}\{f(x)\} \equiv F(\nu) = A_f \exp[-2\pi i \nu \mu_f] \exp[-2\pi^2 \sigma_f^2 \nu^2], \quad (4.23)$$

which is in itself a gaussian again. We can do the same for a function $g(x)$:

$$g(x) = \frac{A_g}{\sqrt{2\pi}\sigma_g} \exp \left[-\frac{(x - \mu_g)^2}{2\sigma_g^2} \right], \quad (4.24)$$

giving:

$$\mathcal{F}\{g(x)\} \equiv G(\nu) = A_g \exp[-2\pi i \nu \mu_g] \exp[-2\pi^2 \sigma_g^2 \nu^2]. \quad (4.25)$$

Then the Fourier transform of $f(x)$ and $g(x)$ is given by:

$$\begin{aligned} \mathcal{F}\{f(x)^* g(x)\} &= F(\nu) G(\nu), \\ &= A_f A_g \exp[-2\pi i \nu (\mu_f + \mu_g)] \exp[-2\pi^2 (\sigma_f^2 + \sigma_g^2) \nu^2]. \end{aligned} \quad (4.26)$$

In the equation above, a gaussian can be recognised. This means you can write it as: which you can write as:

$$F(\nu) G(\nu) = \frac{A_C}{\sqrt{2\pi}\sigma_C} \exp \left[-\frac{(x - \mu_C)^2}{2\sigma_C^2} \right], \quad (4.27)$$

with:

$$\begin{aligned} A_C &= A_f A_g \sqrt{2\pi} \sigma_C \exp[-2\pi i \nu (\mu_f + \mu_g)], \\ \mu_C &= 0, \\ \sigma_C &= \frac{1}{2\pi(\sigma_f^2 + \sigma_g^2)^{1/2}}. \end{aligned} \quad (4.28)$$

The inverse of this Fourier transform now gives the convolution of the two signals, which you can see is again a gaussian.

$$\begin{aligned} f(x)^* g(x) &= \mathcal{F}^{-1}\{F(\nu) G(\nu)\} \\ &= \frac{A_f A_g}{\sqrt{2\pi} (\sigma_f^2 + \sigma_g^2)} \exp \left[-\frac{(x - \mu_f - \mu_g)^2}{2 (\sigma_f^2 + \sigma_g^2)} \right], \end{aligned} \quad (4.29)$$

which you can write as:

$$\begin{aligned} f(x)^* g(x) &= \frac{A_c}{\sqrt{2\pi}\sigma_c} \exp \left[-\frac{(x - \mu_c)^2}{2\sigma_c^2} \right], \\ A_c &= A_f A_g, \\ \mu_c &= \mu_f + \mu_g, \\ \sigma_c &= (\sigma_f^2 + \sigma_g^2)^{1/2}. \end{aligned} \quad (4.30)$$

4.1.5 Other calculations on CFTs

For the deconvolution of the spectra, we will need the division and logarithmic values of two CFT's.

4.2 Obtaining the single scattering distribution

4.2.1 Build-up of measured spectrum

When electrons go through the sample, the intensity of electrons that has no inelastic scattering is given by the zero-loss peak: $I_{ZLP}(E)$. The intensity of the electrons that do scatter, $I_{EEL}(E)$, is than dividable in the single scatter intensity, $I_1(E)$, the double scatter intensity, $I_2(E)$, the triple scatter intensity, $I_3(E)$, etc:

$$I(E) = I_{ZLP}(E) + I_{EEL}(E) = I_{ZLP}(E) + \sum_{n=0}^{\infty} I_n(E). \quad (4.31)$$

MAYBE DISREGARD? The integrated intensity of each n-scattering spectrum N_n is this a logical choice of letter? depends on the total integrated intensity N , assuming independed scattering events, through the bionomal distribution:

$$N_n = \frac{N}{n!} \left(\frac{t}{\lambda} \right)^n \exp[-t/\lambda]. \quad (4.32)$$

Here t is the thickness of the sample, and λ is the mean free path of electrons in the sample. END DISREGARD

Since we know the zero-loss-peak due to Lau [4], the response function of the instrument, $R(E)$, is easily deducted by:

$$R(E) = I_{ZLP}(E)/N_{ZLP}, \quad (4.33)$$

where N_{ZLP} is the integrated intensity of $I_{ZLP}(E)$.

Now we will show how the total recorded spectrum is build up from single-scattering distribution $S(E)$, and the above defined response function $R(E)$.

The spectrum recorded due to the single scattering events, $J^1(E)$, is these two distributions convoluted:

$$I_1(E) = R(E) * S(E) \equiv \int_{-\infty}^{\infty} R(E - E') S(E') dE'. \quad (4.34)$$

It can be easily seen, that as a double-scattering event, is a series of two single-scattering event, the double-scattering intensity is given by the self convolution of the single-scattering intensity, normalised to match eq. (4.32), and once again convoluted with the response function:

$$I_2(E) = R(E) * S(E) * S(E) / (2!N_{ZLP}). \quad (4.35)$$

For higher order scattering spectra, this generalises to HOW TO WRITE DOWN A SUCCESSION OF CONVOLUTIONS?:

$$I_n(E) = R(E) [^* S(E)]^n / (n!N_{ZLP}^{n-1}). \quad (4.36)$$

The complete recorded spectrum, neglecting any surface plasmons, is than given by (analogous to eq. (4.31)):

$$\begin{aligned} I(E) &= I_{ZLP}(E) + I^1(E) + I^2(E) + I^3(E) + \dots \\ &= I_{ZLP}(E) * [\delta(E) + S(E)/N_{ZLP} + S(E) * S(E) / (2!N_{ZLP}^2) \\ &\quad + S(E) * S(E) * S(E) / (3!N_{ZLP}^3) + \dots] \\ &= I_{ZLP}(E) * \left[\delta(E) + \sum_{n=1}^{\infty} \delta(E) [^* S(E)]^n / (n!N_{ZLP}^n) \right]. \end{aligned} \quad (4.37)$$

Since a convolution in energy domain translates to a multiplication in the frequency domain, it makes sense to take the Fourier transform (FT) of the above equation. Eq. (4.37) then becomes, using the Taylor expansion of the exponential function:

$$\begin{aligned}
i(\nu) &= z(\nu) \left\{ 1 + s(\nu)/N_{ZLP} + [s(\nu)]^2 / (2!N_{ZLP}^2) + [s(\nu)]^3 / (3!N_{ZLP}^3) + \dots \right\} \\
&= z(\nu) \sum_{n=0}^{\infty} \frac{s(\nu)^n}{n!N_{ZLP}^n} \\
&= z(\nu) \exp [s(\nu)/N_{ZLP}],
\end{aligned} \tag{4.38}$$

where $i(\nu)$ is the FT of the intensity spectrum, $z(\nu)$ is the FT of the zero-loss peak, and $s(\nu)$ is the FT of the single-scattering distribution.

The single scattering distribution can then be retrieved by rewriting eq. (4.38), and taking the inverse Fourier transform:

$$s(\nu) = N_{ZLP} \ln \left(\frac{i(\nu)}{z(\nu)} \right), \tag{4.39}$$

$$\begin{aligned}
S(E) &= \mathcal{F}^{-1} \{s(\nu)\} \\
&= \mathcal{F}^{-1} \left\{ N_{ZLP} \ln \left[\frac{i(\nu)}{z(\nu)} \right] \right\} \\
&= \mathcal{F}^{-1} \left\{ N_{ZLP} \ln \left[\frac{\mathcal{F} \{I(E)\}}{\mathcal{F} \{I_{ZLP}(E)\}} \right] \right\}
\end{aligned} \tag{4.40}$$

However, eq. (4.60) only works for an “ideal” spectrum. Any noise on the spectrum will blow up, as noise normally reveals itself at higher frequencies, and $i(\nu)$ tends towards zero for high frequencies. Therefore, it is advised to calculate not $S(E)$, but $I_1(E)$, by convoluting once more with $I_{ZLP}(E)$, see eq. (4.34). [3]

Discussion points What is the most official way to calculate the errors in $R(E)$, from the errors in the ZLP? Just calculate for each ZLP and take the std of those, or can you use the error of the ZLP to calculate it at once? Because it comes back in the N_{ZLP} as well.

There are NaN values in the $s(\nu)$ calculation in the python file, how best to handle those, just set them to 0?

Looking at the $S(E)$ vs I_{ZLP} etc plot, there are some things that don't make sense

4.2.2 Analytical analysis of possible recorded spectra

To be able to analyse a deconvolution program, it is useful to create some toy models which represent different possible $I(E)$, of which we know what the expected outcome is, so we can validate the program written.

Single scattering distribution as Gaussian One of the interesting approximations of a spectrum to review as toy model, is a spectrum in which the zero loss peak is a gaussian such that:

$$I_{ZLP}(E) = N_{ZLP} \exp [-(x - \mu_{ZLP})/(2\sigma_{ZLP}^2)], \tag{4.41}$$

and the single scattering distribution is a gaussian, given by:

$$S(E) = A_S \exp [-(x - \mu_S)/(2\sigma_S^2)]. \tag{4.42}$$

By combining eq. (4.31), (4.30), and eq. (4.36) you obtain for complete recorded spectrum $I(E)$:

$$\begin{aligned}
I(E) &= \sum_{n=0}^{\infty} \frac{A_n}{\sqrt{2\pi}\sigma_n} \exp \left[-\frac{(x - \mu_n)^2}{2\sigma_n^2} \right], \\
A_n &= \frac{1}{n!N_{ZLP}^n} N_{ZLP} A_S^n, \\
&= \frac{A_S^n}{n!N_{ZLP}^{n-1}}, \\
\mu_n &= \mu_{ZLP} + n\mu_S, \\
\sigma_n &= (\sigma_{ZLP}^2 + n\sigma_S^2)^{1/2}.
\end{aligned} \tag{4.43}$$

This means that for an $I(E)$ constructed as the equation above, with our program, we hope to retrieve $S(E)$ as given by (4.42).

Recorded inelastic scattering spectrum as Gaussian Starting the other way around, with again an $I_{ZLP}(E)$ as given as eq. (4.41), but now $I_{EEL}(E)$ is also given itself a gaussian, instead of a summation over convolutions of gaussians. Now, we need to follow the route given in the section above to obtain the single scattering distribution $S(E)$:

$$\begin{aligned}
I(E) &= I_{ZLP}(E) + I_{EEL}(E), \\
&= \frac{N_{ZLP}}{\sqrt{2\pi}\sigma_{ZLP}} \exp [-(x - \mu_{ZLP})/(2\sigma_{ZLP}^2)] + \frac{A_{EEL}}{\sqrt{2\pi}\sigma_{EEL}} \exp [-(x - \mu_{EEL})^2/(2\sigma_{EEL}^2)].
\end{aligned} \tag{4.44}$$

Following eq. (4.60), we need the Fourier transforms of both the $I_{ZLP}(E)$, and $I(E)$, for which we can use eq. (4.23):

$$\mathcal{F}\{I_{ZLP}(E)\} \equiv z(\nu) = N_{ZLP} \exp [-2\pi i\nu\mu_{ZLP}] \exp [-2\pi^2\sigma_{ZLP}^2\nu^2], \tag{4.45}$$

$$\mathcal{F}\{I_{EEL}\} \equiv i_{EEL}(\nu) = A_{EEL} \exp [-2\pi i\nu\mu_{EEL}] \exp [-2\pi^2\sigma_{EEL}^2\nu^2], \tag{4.46}$$

$$\begin{aligned}
\mathcal{F}\{I(E)\} \equiv i(\nu) &= z(\nu) + i_{EEL}(\nu) \\
&= N_{ZLP}\sqrt{\pi}\sigma_{ZLP} \exp [-2\pi i\nu\mu_{ZLP}] \exp [-2\pi^2\sigma_{ZLP}^2\nu^2] + \\
&\quad A_{EEL}\sqrt{\pi}\sigma_{EEL} \exp [-2\pi i\nu\mu_{EEL}] \exp [-2\pi^2\sigma_{EEL}^2\nu^2].
\end{aligned} \tag{4.47}$$

Now eq. (4.60) becomes:

$$\begin{aligned}
S(E) &= \mathcal{F}^{-1} \left\{ N_{ZLP} \log \left[\frac{i(\nu)}{z(\nu)} \right] \right\} \\
&= \mathcal{F}^{-1} \{ N_{ZLP} \log [1 + i_{EEL}/z_\nu] \}.
\end{aligned} \tag{4.48}$$

Since both $i_{EEL}(\nu)$ and $z(\nu)$ are gaussians with mean $\mu = 0$, the devision of the two is also an gaussian given by:

$$\begin{aligned}
i_{EEL}/z_\nu &= \frac{A_{EEL} \exp [-2\pi i\nu\mu_{EEL}] \exp [-2\pi^2\sigma_{EEL}^2\nu^2]}{N_{ZLP} \exp [-2\pi i\nu\mu_{ZLP}] \exp [-2\pi^2\sigma_{ZLP}^2\nu^2]}, \\
&= \frac{A_{EEL}}{N_{ZLP}} \exp [-2\pi i\nu(\mu_{EEL} - \mu_{ZLP})] \exp [-2\pi^2(\sigma_{EEL}^2 - \sigma_{ZLP}^2)\nu^2],
\end{aligned} \tag{4.49}$$

which can be written as, analogous to eq. (4.23):

$$\begin{aligned}
i_{EEL}(\nu)/z(\nu) &= A_d \exp[-2\pi i \nu \mu_d] \exp[-2\pi^2 \sigma_f^2 \nu^2], \\
A_d &= \frac{A_{EEL}}{N_{ZLP}}, \\
\mu_d &= \mu_{EEL} - \mu_{ZLP}, \\
\sigma_d &= \sqrt{\sigma_{EEL}^2 - \sigma_{ZLP}^2}.
\end{aligned} \tag{4.50}$$

Now realising that $z(\nu)$ is always exponentially bigger than $i_{EEL}(\nu)$, we can use a Taylor expansion to approximate $\text{Log}(z + 1)$ (with $\text{Log}(z)$ the primitive value of the complex logarithm):

$$\text{Log}(z + 1) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} z^n. \tag{4.51}$$

With the equations above, we can rewrite eq. (4.48):

$$\begin{aligned}
S(E) &= \mathcal{F}^{-1} \left\{ N_{ZLP} \log \left[1 + \frac{i_{EEL}}{z(\nu)} \right] \right\}, \\
&= \mathcal{F}^{-1} \left\{ N_{ZLP} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} (A_d \exp[-2\pi i \nu \mu_d] \exp[-2\pi^2 \sigma_f^2 \nu^2])^n \right\}, \\
&= \mathcal{F}^{-1} \left\{ N_{ZLP} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} A_d^n \exp[-2\pi i \nu n \mu_d] \exp[-2\pi^2 n \sigma_f^2 \nu^2] \right\}, \\
&= \mathcal{F}^{-1} \{F_1(\nu)\} + \mathcal{F}^{-1} \{F_2(\nu)\} + \mathcal{F}^{-1} \{F_3(\nu)\} + \dots, \\
&= \sum_{n=1}^{\infty} \mathcal{F}^{-1} \{F_n(\nu)\},
\end{aligned} \tag{4.52}$$

Where $F_n(\nu)$ can be written as, analogous to eq. (4.23):

$$\begin{aligned}
F_n(\nu) &= A_n \exp[-2\pi i \nu \mu_n] \exp[-2\pi^2 i \nu^2 \sigma_n^2], \\
A_n &= \frac{(-1)^{n+1}}{n} N_{ZLP} A_d^n, \\
&= (-1)^{n+1} \frac{A_{EEL}^n}{n N_{ZLP}^{n-1}}, \\
\mu_n &= n \mu_d, \\
&= n(\mu_{EEL} - \mu_{ZLP}), \\
\sigma_n &= \sqrt{n} \sigma_d, \\
&= \sqrt{n(\sigma_{EEL}^2 - \sigma_{ZLP}^2)}.
\end{aligned} \tag{4.53}$$

Using this, and the inverse relation between eq. (4.22) and eq. (4.23), one can find the inverses of the Gaussians that build $S(E)$:

All these inverse Fourier transform of gaussians return gaussians on their part, resulting in a single scattering distribution which is a summation of gaussians, with alternating positive and negative amplitude. These gaussians are given by:

$$\mathcal{F}^{-1} \{F_n(\nu)\} = \frac{A_n}{\sqrt{2\pi} \sigma_n} \exp \left[-\frac{(x - \mu_n)^2}{2\sigma_n^2} \right]. \tag{4.54}$$

Combining all the above, we find single scattering distribution given by:

$$S(E) = \sum_{n=1}^{\infty} \frac{(-1)^n A_{EEL}^n}{n N_{ZLP}^{n-1} \sqrt{2\pi n(\sigma_{EEL}^2 - \sigma_{ZLP}^2)}} \exp \left[-\frac{(x - n(\mu_{EEL} - \mu_{ZLP}))^2}{2n(\sigma_{EEL}^2 - \sigma_{ZLP}^2)} \right] \quad (4.55)$$

4.3 Kramer-Kronig relations

The Kramer-Kronig relations are two functions that relate the imaginary part of a complex function to the real part and vice versa. The relations hold as long as the complex function is analytic in the upper half-plane. The relations for function $\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega)$, with ω a complex variable are given by [5]:

$$\chi_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} d\omega', \quad (4.56)$$

and:

$$\chi_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} d\omega'. \quad (4.57)$$

Here \mathcal{P} denotes the Cauchy principal value of the integral. For causal functions, due to (anti)symmetries arising from its causality, these can be rewritten to [5]:

$$\chi_1(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' \chi_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (4.58)$$

and:

$$\chi_2(\omega) = -\frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega \chi_1(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (4.59)$$

Since the single scattering spectrum of a medium can be related to the imaginary part of the complex permittivity, the Kramer-Kronig relations can be used to retrieve energy dependence of the real permittivity [3].

4.3.1 Spectrum analysis

If one ignores the instrumental broadening, surface-mode scattering and the retardation effects, the single scattering spectrum is approached by the single scattering distribution, which in place can be obtained from the recorded energy loss spectrum by the Fourier log method. [3]

$$\begin{aligned} I_1(E) \approx S(E) &= \frac{2N_{ZLP}t}{\pi a_0 m_0 v^2} \text{Im} \left[\frac{-1}{\varepsilon(E)} \right] \int_0^{\beta} \frac{\theta d\theta}{\theta^2 + \theta_E^2} \\ &= \frac{N_{ZLP}t}{\pi a_0 m_0 v^2} \text{Im} \left[\frac{-1}{\varepsilon(E)} \right] \ln \left[1 + \left(\frac{\beta}{\theta_E} \right)^2 \right] \end{aligned} \quad (4.60)$$

In this equation is $J^1(E)$ the single scattering distribution, $S(E)$ the single scattering spectrum, N_{ZLP} the zero-loss intensity, t the sample thickness, v the velocity of the incoming electron, β the collection semi angle, α the angular divergence of the incoming beam, and θ_E the characteristic scattering angle for energy loss E . In this equation α is assumed small in comparison with β . If this is not the case, additional angular corrections are needed. Furthermore, θ_E is given by:

$$\theta_E = E/(\gamma m_0 v^2). \quad (4.61)$$

Furthermore, it should be noted that to retrieve $\text{Re} [1/\varepsilon(E)]$ from $\text{Im} [-1/\varepsilon(E)]$, equation (4.58) should be rewritten to [6]:

$$\text{Re} \left[\frac{1}{\varepsilon(E)} \right] = 1 - \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \text{Im} \left[\frac{-1}{\varepsilon(E')} \right] \frac{E' dE'}{E'^2 - E^2}. \quad (4.62)$$

QUESTIONS on my end Will we be working with $J(E)$, and is there the need for a Fourier method, or is $J^1(E)$ provided? Are additional angular corrections needed? Where does the 1 come from in eq (4.62), is it due to the minus sign in the $\text{Im}[-1/\varepsilon]$?

4.3.2 Step 1: rescaling intensity

The first step of the K-K analysis is now to rewrite Eq. (4.60) to:

$$I_{1,ac}(E) = \frac{I_1(E)}{\ln \left[1 + \left(\frac{\beta}{\theta_E} \right)^2 \right]} = \frac{N_{ZLP} t}{\pi a_0 m_0 v^2} \text{Im} \left[\frac{-1}{\varepsilon(E)} \right]. \quad (4.63)$$

As θ_E scales linearly with E , see eq. (4.61), the intensity in on the left side of the equation above now relatively increases for high energy loss with respect to low energy loss. **SOMETHING about aperture correction, is that relevant?**

QUESTIONS on my end I assume β and v are known, and that we do not take a distribution for v ?

4.3.3 Step 2: extrapolating

Since the upcoming integrals all extend to infinity, but the data acquisition is inherently up to a finite energy, the spectra need to be extrapolated. An often used form is AE^{-r} , where $r = 3$ if you follow the Drude-model, or r can be deducted from experimental data.

4.3.4 Step 3: normalisation and retrieving $\text{Im} \left[\frac{1}{\varepsilon(E)} \right]$

Taking $E' = 0$ in (4.62), one obtains:

$$1 - \text{Re} \left[\frac{1}{\varepsilon(0)} \right] = \frac{2}{\pi} \int_0^\infty \text{Im} \left[\frac{-1}{\varepsilon(E)} \right] \frac{dE}{E}. \quad (4.64)$$

Now dividing both sides of Eq. (4.65) by the energy, and subsequently integrating them over energy results in a comparable integral:

$$\int_0^\infty I_{1,ac}(E) \frac{dE}{E} = \frac{N_{ZLP} t}{\pi a_0 m_0 v^2} \int_0^\infty \text{Im} \left[\frac{-1}{\varepsilon(E)} \right] \frac{dE}{E}. \quad (4.65)$$

Combining the two leads to:

$$\frac{\int_0^\infty I_{1,ac}(E) \frac{dE}{E}}{\frac{\pi}{2} (1 - \text{Re} \left[\frac{1}{\varepsilon(0)} \right])} = \frac{N_{ZLP} t}{\pi a_0 m_0 v^2} \equiv K, \quad (4.66)$$

in which K is the proportionality constant, used to estimate the absolute thickness if the zero-loss integral and the incident energy are known. This formula requires $\text{Re} \left[\frac{1}{\varepsilon(0)} \right]$ to be known, as is the case in for example metals ($\text{Re} \left[\frac{1}{\varepsilon_{\text{metal}}(0)} \right] \approx 0$). If this is not the case, other options to estimate K will be discussed later on.

This value of K , which is constant over E , can than in turn be used to retrieve the function of $\text{Im} \left[-\frac{1}{\varepsilon(E)} \right]$ from the observed single scattering energy distribution $J^1(E)$ with eq. (4.65).

need to add other estimations of K ?

4.3.5 Step 4: retrieving $\text{Re} \left[\frac{1}{\varepsilon(E)} \right]$

Having retrieved $\text{Im} \left[-\frac{1}{\varepsilon(E)} \right]$ from the steps above, one can now use eq. (4.62) to obtain $\text{Re} \left[\frac{1}{\varepsilon(E)} \right]$, where one must pay attention to avoid including $E = E'$ in the discrete integral over the spectrum, as this is a singularity. To avoid this singularity in a discrete signal, a couple of approaches are possible:

- In the integral (for discrete signals: summation) in eq. (4.62), simply exclude the $E = E'$ values.
- Shift the values of $\text{Re} \left[\frac{1}{\varepsilon(E)} \right]$ to values at $E''_i = (E_i + E_{i+1})$, to make sure to avoid $E'' = E'$ in the summation.
- The dielectric function in the energy domain relate to the dielectric response function $1/\varepsilon(t) - \delta(t)$ through:

$$\text{Re} \left[\frac{1}{\varepsilon(E)} \right] = \mathcal{C} \left\{ \frac{1}{\varepsilon(t)} - \delta(t) \right\} = \mathcal{F}\{p(t)\}, \quad (4.67)$$

and

$$\text{Im} \left[\frac{-1}{\varepsilon(E)} \right] = \mathcal{S} \left\{ \frac{1}{\varepsilon(t)} - \delta(t) \right\} = i\mathcal{F}\{q(t)\}, \quad (4.68)$$

where $p(t)$ and $q(t)$ are the even and odd parts respectively of the dielectric response function, and \mathcal{C} and \mathcal{S} are the cosine and sine Fourier transforms respectively. Since the dielectric response function is a response function and therefor causal, it is 0 for $t < 0$. This results in:

$$p(t) = \text{sgn}[q(t)]. \quad (4.69)$$

Combining all this means that one can also obtain $\text{Re} \left[\frac{1}{\varepsilon(E)} \right]$ from $\text{Im} \left[-\frac{1}{\varepsilon(E)} \right]$ by:

$$\text{Re} \left[\frac{1}{\varepsilon(E)} \right] = \mathcal{C} \left\{ \text{sgn} \left[\mathcal{S}^{-1} \left\{ \text{Im} \left[\frac{-1}{\varepsilon(E)} \right] \right\} \right] \right\}. \quad (4.70)$$

4.3.6 Step 5: retrieving ε

The dielectric function can subsequently be obtained from:

$$\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E) = \frac{\text{Re}[1/\varepsilon(E)] + i \text{Im}[-1/\varepsilon(E)]}{\{\text{Re}[1/\varepsilon(E)]\}^2 + \{\text{Im}[-1/\varepsilon(E)]\}^2}. \quad (4.71)$$

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