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Limitations of Kramers-Kronig transform for calculation of the DC conductance magnitude from dielectric measurements

N. M. Chalashkanov[1], S. J. Dodd[1] and J. C. Fothergill[2]
1: Department of Engineering
University of Leicester, UK
2: Pro-Vice-Chancellor
City University, London, UK

Abstract- **The Kramers-Kronig (K-K) transform relates the real and imaginary parts of the complex susceptibility as a consequence of the principle of causality. It is a special case of the Hilbert transform and it is often used for estimation of the DC conductance from dielectric measurements. In this work, the practical limitations of a numerical implementation of the Kramers-Kronig transform was investigated in the case of materials that exhibit both DC conductance and quasi-DC (QDC) charge transport processes such as epoxy resins. The characteristic feature of a QDC process is that the real and imaginary parts of susceptibility (permittivity) follow fractional power law dependences with frequency with the low frequency exponent approaching -1. Dipolar relaxation in solids on the other hand has a lower frequency exponent <1. The computational procedure proposed by Jonscher for calculation of the K-K transform involves extrapolation and truncation of the data to low frequencies so that convergence of the integrals is ensured. The validity of the analysis is demonstrated by performing K-K transformation on real experimental data and on theoretical data generated using the Dissado-Hill function. It has been found that the algorithm works well for dielectric relaxation responses but it is apparent that it does not work in the case of a low frequency power law in which the low frequency exponent approaches -1, i.e. in the case of QDC responses. In this case convergence can only be guaranteed by extrapolating the low frequency power law over many decades towards zero frequency.**

I. INTRODUCTION

When an ac electric field is applied to a dielectric, polarisation occurs inside the material which can be expressed by Eq. 1.

$$P(\omega) = \varepsilon_0 \chi^*(\omega) E(\omega) \qquad (1)$$

where $P(\omega)$ is the frequency-dependent polarisation, ε_0 is the permittivity of free space, $\chi^*(\omega)$ is the frequency-dependent susceptibility, and $E(\omega)$ is the applied ac electric field. $P(\omega)$ and $E(\omega)$ are the Fourier transforms of the corresponding time-dependent polarization and electric field. The frequency-dependent susceptibility is a complex function and it is defined in Eq. 2 as the Fourier transform of the response function, $f(t)$ [1].

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) = \int_0^\infty f(t) \exp(-i\omega t) dt \qquad (2)$$

The response function, $f(t)$, arises because material systems always exhibit a delayed response to an external excitation, unlike for example free space, where the response is instantaneous. The response function is a real function of time, t, and the principle of causality implies that there should be no reaction before action and hence:

$$f(t) \equiv 0 \text{ for } t < 0 \qquad (3)$$

It is also assumed that $f(t)$ obeys the principle of superposition, which states that the total response of the system, occurring due to a series of delta-function excitations, is the sum of the responses due to the individual excitations [1]. Here it is important to emphasize that the response of the dielectric is assumed to be linear.

The amplitude of polarization in phase with the applied ac field is given by the real part, $\chi'(\omega)$, of the complex susceptibility, χ^*. The component in quadrature with the applied field is given by the imaginary part, $\chi''(\omega)$. Hence, the real and imaginary components of χ^* can be defined as the cosine and sine transforms of $f(t)$, respectively:

$$\chi'(\omega) = \int_0^\infty f(t) \cos(\omega t) dt \qquad (4)$$

$$\chi''(\omega) = \int_0^\infty f(t) \sin(\omega t) dt \qquad (5)$$

Another condition is that the above integrals are necessarily finite [3]. The real and imaginary parts of the complex susceptibility obey the Kramer-Kronig relations as a consequence of the principle of causality and can be expressed:

$$\chi''(\omega) = -\frac{2\omega}{\pi} \mathsf{P} \int_0^\infty \frac{\chi'(u)}{u/f - f/u} d(\ln u) \qquad (6)$$

$$\chi'(\omega) = \frac{2}{\pi} \mathsf{P} \int_0^\infty \frac{\chi''(u)}{1 - \omega^2/u^2} d(\ln u) \qquad (7)$$

Where $\mathsf{P}\int$ denotes a Cauchy Principal Value integral. The Kramer-Kronig relations rely on the Hilbert transform of periodic functions, thus $\chi'(\omega)$ and $\chi''(\omega)$ are interrelated. The Hilbert transform of a constant is zero, so the presence in the measured spectrum of a DC conductivity can be recovered from the Kramers-Kronig transformation of the real part of $\varepsilon'(\omega)$ or $\chi'(\omega)$, because a DC conductivity does not contribute to the real part of the permittivity. However, dielectric measurements are performed only over a limited frequency range at discrete values of frequency, hence a numerical procedure is required to calculate the integrals given in Eqs. 6 and 7.

In this work, we have investigated a numerical algorithm previously proposed in the literature for calculation of the K-K transform on experimental data [2]. The aim was to assess the validity and the accuracy of the approach in the case of dielectric spectra containing QDC response.

II. NUMERICAL PROCEDURE

We have followed the numerical procedure described in [2]. The code of the computer program used for the calculations is given in [1]. Here is presented only a brief outline of the method. The procedure involved interpolation and extrapolation of the measurement data. In Fig. 1 are defined the parameters involved in the numerical procedure for a K-K transform. The dielectric data are measured (simulated) over the frequency range from f_1 to f_N. In order to calculate χ'' using the K-K transform near the extremes of the range, it is necessary to extrapolate χ' outside the range of measured frequencies to $0.1f_1$ and $10f_N$. The value of $\chi'(f)$ is considered constant outside this frequency range, which results in the truncation region indicated in Fig. 1. In order to handle numerically the singularity that occurs at $f = u$, a low and a high frequency limit are defined around f, $u_1 = 0.8f$ and $u_2 = 1.25f$, respectively. Dielectric data are usually acquired at logarithmically spaced frequency intervals. To apply simple methods of integrations it is therefore necessary to interpolate between the points, which involves fitting exact parabolae to sets of three consecutive data points (see Eq. 8) [2].

$$\ln \chi(f) = A(\ln f)^2 + B\ln f + C \qquad (8)$$

A least squares straight line is used to fit to the first (or last) few data points on a $\ln \chi$ versus $\ln \omega$ plot using Eq. 9.

$$\ln \chi(f) = B\ln f + C \qquad (9)$$

In the above expressions A, B, and C are constants determined from the data.
The evaluation of the integral (6) near the singularity is handled using the following expression:

$$-\int_{u_1}^{u_2} \frac{f\chi'(u)}{u^2 - f^2} = -\frac{af}{2}\ln\left|\frac{f^2 - u_2^2}{f^2 - u_1^2}\right| - \frac{b}{2}\ln\left|\frac{f - u_2 f + u_1}{f - u_1 f + u_2}\right| \qquad (10)$$

Simpson's rule was used to evaluate the integrals with equal increments of $\ln(u)$. The number of increments was 50 per decade. An interpolating interval is the region in which a single interpolation equation is used. The following order was kept to perform the numerical integration over one interval (or part of an interval) at a time [2]:
1. The remainder of the interval below u_1 (=0.8f)
2. The remainder of the interval above u_2 (=1.25f)
3. The rest of the intervals above f, stopping if an interval gives a negligible contribution
4. The rest of the intervals below f, stopping if an interval gives a negligible contribution

$\chi'(f)$ is assumed to take the end of range values outside the extrapolated frequency range. An extra contribution to the integral, which takes into account that $\chi'(f)$ is constant outside the frequency range, is calculated using the following expression:

$$-\frac{2f}{\pi}\left[\chi'(0.1f_1)\int_0^{0.1f_1}\frac{du}{u^2 - f^2} + \chi'(10f_N)\int_{10f_N}^{\infty}\frac{du}{u^2 - f^2}\right]$$
$$= -\frac{1}{\pi}\left[\chi'(0.1f_1)\ln\left(\frac{f - 0.1f_1}{f + 0.1f}\right) - \chi'(10f_N)\ln\left(\frac{10f_N - f}{10f_N + f}\right)\right]$$
$$(11)$$

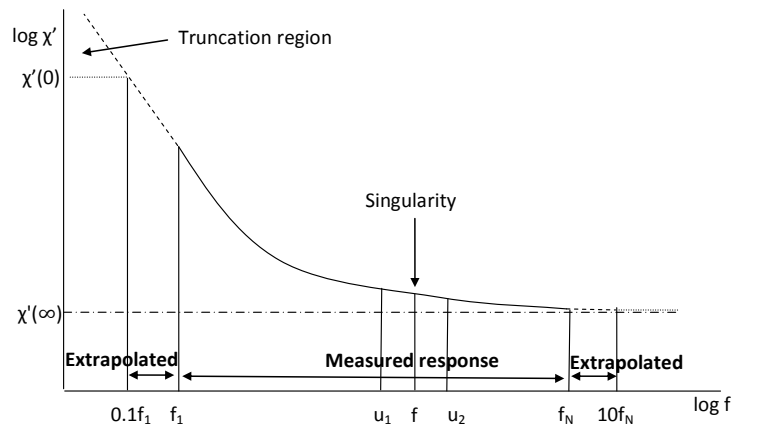Adding this to 2/π times the sum of all the other contributions gives $\chi''(f)$ [2].

Fig. 1. A schematic diagram of the measured and extrapolated data (not to scale)

III. EXPERIMENTAL DATA

A typical dielectric spectrum of a DGEBA epoxy resin above the glass transition temperature is shown in Fig. 2. Such spectra were analyzed in [3, 4] using an equivalent circuit model. The model comprised four processes in parallel, namely a frequency independent capacitance C_∞, a DC conductance G, a QDC process and a dispersion D. The equivalent circuit model allows the individual contribution of each process to be determined and the two main contributions have been found to be due to a QDC process and a mid-frequency dispersion D. Hence a K-K transform was performed on each of them individually and on the entire dielectric spectrum in order to assess the applicability of the numerical procedure described above in the case of materials exhibiting QDC behavior (also known as low frequency dispersion [1]).
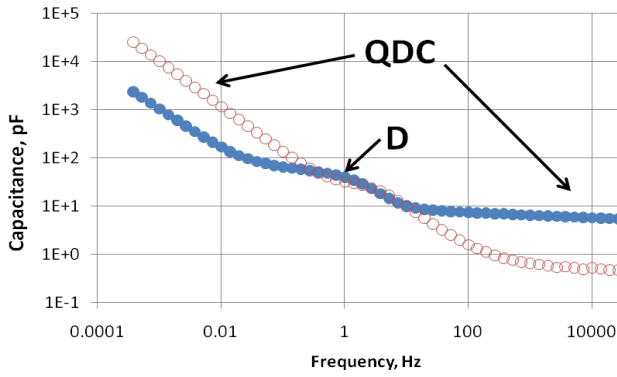
Fig. 2. A typical dielectric response of DGEBA epoxy resin above T_g. Real part (solid markers) and imaginary part (open markers)

IV. RESULTS AND DISCUSSION

A. K-K transform in the case of a loss peak, D

Theoretical data were generated using the expression for a loss peak according to the Dissado-Hill theory [5]. The loss peak parameters were: magnitude 798 pF, low frequency parameter m=1, high frequency parameter n=0.146 and characteristic frequency f_c=39 Hz. These values were chosen as typical values representing the dispersion process D shown in Fig. 2. The K-K transformation was performed on the theoretical data using the numerical procedure described above. The result is shown in Fig. 3. In this case, the overall accuracy of the method is satisfactory with most data points being transformed with accuracy better than 5%. The only exception was the points on the lowest frequency end of the spectrum, which were estimated with a significantly higher error.
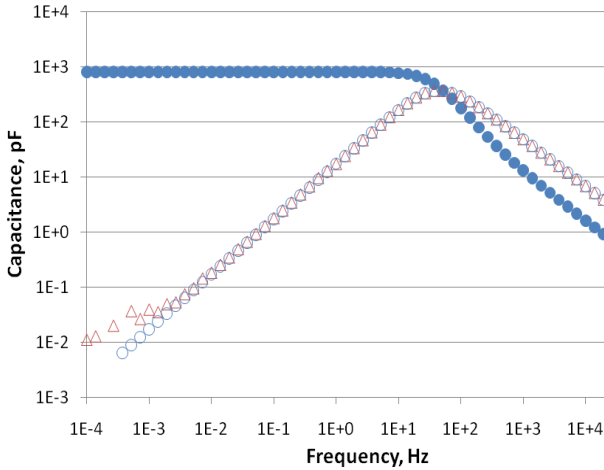

Fig. 3. K-K transform from real to imaginary part of complex capacitance in the case of a loss peak. Model real (solid circle markers) and imaginary (open circle markers), K-K calculated imaginary part (open triangle markers)

B. K-K transform in the case of QDC

Model data were generated using the theoretical expression for a QDC response according to the Dissado-Hill theory [6]. The characteristic parameters of the QDC process were: magnitude 326pF, low frequency parameter p=-0.952, high frequency parameter n=0.905, and characteristic frequency f_c=1560Hz. These values were chosen as typical values

representing the QDC process in flexible epoxy resins. The K-K transformation was performed on these data using the same numerical procedure as before. The result is shown in Fig. 4. In this case, the result of the transform was quite poor because the values of the imaginary part of the capacitance were significantly underestimated. The only points that were evaluated with a reasonable accuracy were in the last decade on the high frequency end of the spectrum.
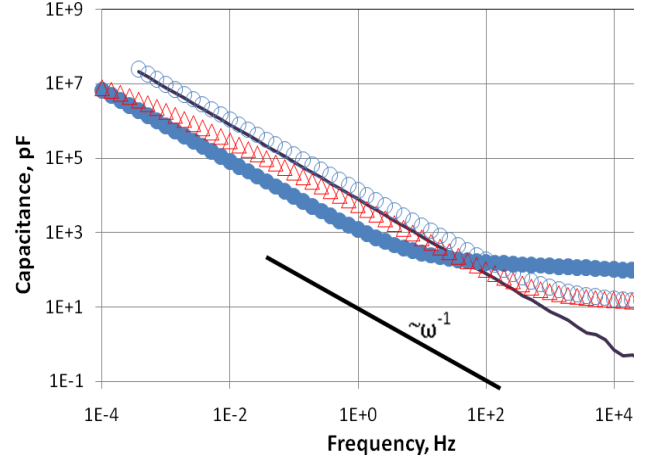

Fig. 4. K-K transform from real to imaginary part of complex capacitance in the case of QDC response. Model real (solid circle markers) and imaginary (open circle markers), K-K calculated imaginary part (open triangle markers)

The solid line in Fig. 4 shows the differences (residuals) between the theoretical values of the imaginary capacitance (C'') due to the QDC process and the values of C'' calculated using the numerical K-K transform. This line approximately follows ω^{-1} dependence with frequency (with a slope $\approx$-1 on a log-log scale.) In the literature such dependence of the residuals from the transform is often attributed to be due to a contribution from DC conductance [2, 7]. However in the present case it is important to emphasize that the model data shown in Fig. 4 and used for the K-K transform contain only one process, namely QDC, and no DC conductance was included in the model data. Hence, the ω^{-1} dependence of the residuals is solely due to a truncation error occurring as a result of the numerical procedure used. This error occurs as a consequence of the extrapolation procedure used and was because χ' was assumed to be a constant outside the extrapolated frequency range. The influence of the extrapolation range was further investigated and an improvement in the procedure was sought by changing the value in Eq. 11 from only one decade below and above the lowest and highest frequency respectively, to many decades of frequency. The influence of the low frequency parameter p of the QDC process was also investigated. The results are summarized in Table 1. An extrapolation of 1 decade was not enough to obtain a sufficient accuracy in any of the cases. In the cases where the absolute value of the low frequency was smaller than 0.9, an extrapolation of 10 decades was sufficient to decrease the relative value of the computational error below 2%. However, in the cases p was in the range -0.9 to -0.99 (typical values for epoxy resin data) this had to be done over many more decades. In the extreme case where p=-0.99, even

an extrapolation of 30 decades is not sufficient to provide accuracy better than 51%.

TABLE I
MAXIMUM VALUE OF THE RELATIVE ERROR AS A FUNCTION OF P
AND EXTRAPOLATED FREQUENCY RANGE

	Relative error, %						
	p -0.5	p -0.6	p -0.7	p -0.8	p -0.9	p -0.95	p -0.99
1 decade	21%	28%	38%	52%	72%	85%	97%
10 decades	<2%	<1%	<1%	<2%	9%	33%	80%
15 decades	<2%	<1%	<1%	<1%	2%	19%	71%
20 decades	<2%	<1%	<1%	<1%	<2%	11%	64%
25 decades	<2%	<1%	<1%	<1%	<2%	6%	57%
30 decades	<2%	<1%	<1%	<2%	<2%	3%	51%

a) 1 decade extrapolation (solid line), 10 decades (dashed), 15 decades (dotted), 20 decades (markers)

b) From top to bottom: 1 decade extrapolation, 10 decades, 15 decades, 20 decades, 25 decades and 30 decades
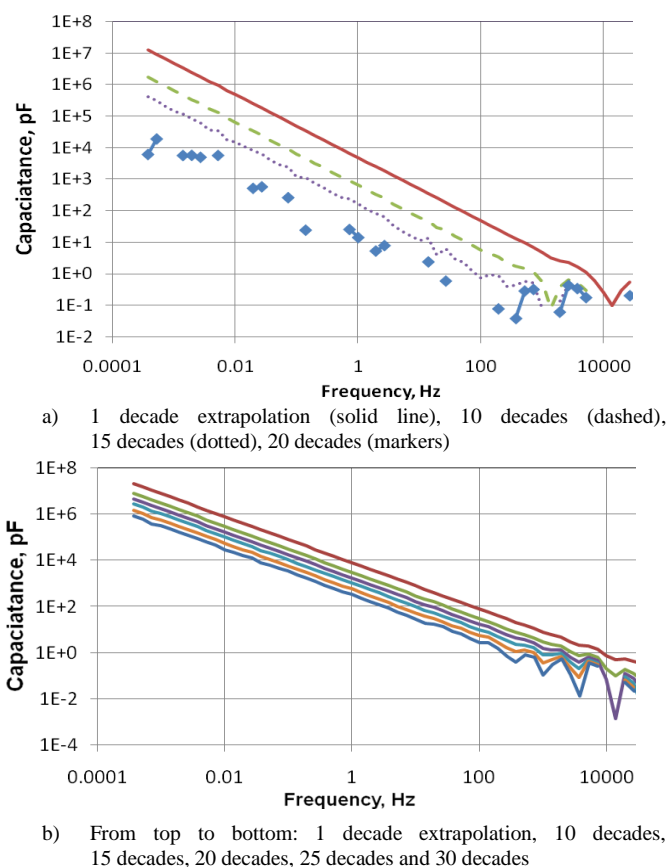
Fig. 5: Residuals between the 'true' value of C'' and the K-K transform as a function of frequency on a log-log plot; a) p=-0.9, b) p=-0.95

In Fig 5 a) and b) are shown the residuals as a function of frequency on a log-log plot in the case of p=-0.9 and p=-0.95, respectively. In Fig. 5a the residuals form approximately straight lines with a slope ~ -1 in the case of extrapolation intervals of 1, 10 and 15 decades below 10kHz, which might be mistaken for DC conduction as explained before. The corresponding maximum relative errors from Table 1 are 72%, 9% and 2%. The value of the relative error drops below 2%

when the extrapolated interval is over 20 decades and the residuals (C''-C''_{KK}) are no longer always positive but obtain negative (overestimated) values as well. This is indicated by the missing data markers in Fig.5a, since a logarithm of a negative value is not defined. In this case, the influence of the truncation error is greatly reduced and the small values of the residuals (positive and negative) can be explained by round off errors.

For p=-0.95, however, the relative error is more than 3% in all cases, which results in a family of approximately straight lines parallel to each other for the various extrapolation intervals, respectively. Again the slopes of the lines are ~ -1 and can be mistaken for contributions to C'' due to DC conduction.

CONCLUSIONS

The applicability of a numerical Kramers-Kronig transform was investigated in two theoretical cases, namely a loss peak and a QDC process so that the mathematical procedure can be verified. In the former case, the shape of the loss peak was correctly reproduced by the K-K transformation with a small calculation error affecting only a few data points in the low frequency range. The error occurs as a consequence of the extrapolation procedure used and due to the fact that $\chi'(0)$ was assumed to be a constant over the extrapolated frequency range. However, in the case of a QDC process, a major truncation error was identified. The error was due to the limited frequency range originally used for data extrapolation. It has been found that the extrapolation must be performed over at least 10 decades of frequency, with the exact value being dependent on the low frequency parameter (p) of the QDC process. The study presented here outlines the computational difficulties of performing a numerical K-K transform over dielectric data containing QDC (low frequency dispersion) response and the limited use of this transform for calculating the DC conductivity in such materials.

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