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# On the probability distributions of relaxation times in glasses*

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**Abstract.** The scale of relaxation times in glasses has led to generalizations of the Drude model of the dielectric function in terms of an integral, containing a Drude kernel and a probability distribution. This integral equation is solved by a Mellin or a Stieltjes transform. Beyond known results, we obtain the probability distribution of the Havriliak-Negami dielectric function. Even more general classes of dielectric models can be dealt with, using Mellin's transform. They may serve as checks for numerical procedures applied to the underlying ill-posed problem, if experimental data for the dielectric function are used.

**PACS.** 02.30.Rz Integral equations – 77.22.Ch Permittivity (dielectric function) – 81.05.Kf Glasses (including metallic glasses)

## 1 Introduction

The dielectric properties of an insulator (amber) mark the beginning of electrostatics, most likely discovered by the ancient Greeks. When electromagnetic waves were found and understood, it proved to be necessary to describe the dielectric properties of matter by a dielectric function. In 1900 Drude proposed his model for it [1], which was then extended to describe the dielectric function of metals. The generalization to glasses came later. Glasses are characterized by many relaxation times. Therefore, one of the first ideas was to generalize Drude's model by integrating on the relaxation times with an appropriate weight function. This approach forms the basis of the work by Davidson and Cole [2], who succeeded in in finding the probability weight function of a model for the dielectric function. Later, several other more complicated models were used to fit measured data of the dielectric function of certain glasses, among them the Havriliak-Negami [3] one, and it was tried to obtain the probability weight function by numerical procedures.

In the present paper we show, that the generalized Drude model can be rigorously solved by a Mellin transform or by a Stieltjes transform. The latter has the disadvantage to need the analytically continued dielectric function towards the branch cut along the negative imaginary axis. But it can be shown to be equivalent to the Mellin transform solution. This is dealt with in Section 4 of the present paper.

Section 2 contains the Mellin transform solution, while in Section 3 we rederive the probability weight function of the Cole-Davidson model [2], and derive the one for the Havriliak-Negami [3] model for the first time. We then present a very general model (essentially covering all probability weight functions, containing all known special functions of mathematical physics), from which the corresponding dielectric function can be determined. In the final Section 5 we point out that the general analytic solution may serve as a guideline to numerically solve the underlying ill-posed problem, which always occurs, if numerical data with uncertainties are used in a Fredholm-type integral relation of first kind. We also sketch the present state of the art to come to grips with that difficult problem.

## 2 Phenomenological dielectric function and its Mellin transform

Including the zero and high frequency limits, any dielectric function can be written as

$$\epsilon^{+}(\omega) = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty})E^{+}(\omega). \tag{1}$$

Here the 'plus' indicates that the dielectric function is analytic in the upper $\omega$-half plane. Since in glasses one finds a distribution of relaxation times, one is lead to the following generalization of the Lorentz-Drude model

$$E^{+}(\omega) = \int_0^{\infty} K(\omega\tau)p(\tau)d\tau \tag{2}$$

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with the probability density of the relaxation times $p(\tau)$ and the kernel

$$K(\omega\tau) = \frac{1}{1 - i\omega\tau} \cdot \tag{3}$$

We note in passing, that $E^+(0) = 1$ and $p(\tau)$ is normalized to 1. The structure of the integral equation (2) allows for a Mellin transformation

$$\hat{E}(s) = \int_0^\infty E^+(\omega)\omega^{s-1} d\omega \tag{4}$$

where the Mellin transformed kernel (3) is given by

$$\hat{K}(s) = \frac{(i)^s \pi}{\sin(\pi s)} = (i)^s \Gamma(s)\Gamma(1-s); \quad 0 < \Re\, s < 1. \tag{5}$$

Here $\Gamma(s)$ is the standard Gammafunction.

From the solution of the integral equation in Mellin space

$$\hat{p}(s) = \frac{\hat{E}(1-s)}{\hat{K}(1-s)} \tag{6}$$

one obtains $p(\tau)$ by the inverse Mellin transform

$$p(\tau) = \frac{1}{2\pi i\tau} \int_{c-i\infty}^{c+i\infty} \left(\frac{i}{\tau}\right)^{-s} \frac{\sin(\pi s)}{\pi} \hat{E}(s) ds. \tag{7}$$

So, for any model dielectric function, the probability density $p(\tau)$ can be calculated. This result is more general than the well-known Cole-Davidson one [2], who used a special model for $E^+(\omega)$ to obtain the corresponding $p(\tau)$.

## 3 Models for the dielectric function and their probability densities

Studying the dielectric behavior of some silicate and borate glasses, Cole and Davidson [2] suggested the following form of the dielectric function:

$$E^+(\omega) = (1 - i\tau_0\omega)^{-\beta}; \qquad \tau_0 > 0 \quad , \Re\,\beta < 1. \tag{8}$$

The Mellin transform of $E^+(\omega)$ is given by [5]:

$$\hat{E}(s) = (\tau_0)^{-s} e^{i\frac{\pi}{2}s} B(s, \beta - s) \tag{9}$$

with Euler's Beta function $B(x,y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}$. Expressing also the $\sin(\dots)$ in (8) by Gamma functions (see (5)), we obtain

$$p(\tau) = \frac{1}{\tau_0}\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} ds \left(\frac{\tau_0}{\tau}\right)^s \frac{\Gamma(\beta+s-1)}{\Gamma(s)\Gamma(\beta)} \cdot \tag{10}$$

Mellin transforms of Gamma functions can be found in [5]. The final result is

$$p(\tau) = \begin{cases} \frac{\sin(\pi\beta)}{\pi}\frac{1}{\tau}\left(\frac{\tau}{\tau_0 - \tau}\right)^\beta & \text{if } 0 < \frac{\tau}{\tau_0} < 1 \\ 0 & \text{otherwise.} \end{cases} \tag{11}$$

One easily verifies, that $p(\tau)$ is properly normalized. In the limit $\beta \to 1$ one obtains a delta function for $p(\tau)$, *i.e.* the model goes over into the simple Drude model with one relaxation time $\tau_0$.

Another model to fit the experimental results for certain glasses in terms of a phenomenological dielectric function is the Havriliak-Negami one [3].

$$\begin{aligned} &E^+(\omega) = (1 - (i\tau_{HN}\omega)^\alpha)^{-\gamma}; \\ &\tau_{HN} > 0 \quad , 0 < \gamma, \quad 0 < \alpha \le 1 \end{aligned} \tag{12}$$

(if $\alpha = 1$, then $\gamma < 1$ is required). For this model $p(\tau)$ is unknown, according to our knowledge. We will show in the following, that it can be obtained by Mellin's transform. We start from [4,5]

$$\hat{E}(s) = \alpha^{-1}\tau_{HN}^{-s} e^{i\frac{\pi}{2}s} B\left(\frac{s}{\alpha}, \gamma - \frac{s}{\alpha}\right) \cdot \tag{13}$$

Expressing Euler's Beta function in terms of Gamma functions as before, we have as an intermediate result a Mellin-Barnes integral:

$$\begin{aligned} p(\tau) = &\frac{1}{\alpha\tau_{HN}}\frac{1}{\Gamma(\gamma)}\frac{1}{2\pi i} \\ &\times \int_{c-i\infty}^{c+i\infty} ds \left(\frac{\tau_{HN}}{\tau}\right)^s \frac{\Gamma(\frac{1-s}{\alpha})\Gamma(\gamma - \frac{1-s}{\alpha})}{\Gamma(s)\Gamma(1-s)} \cdot \end{aligned} \tag{14}$$

Quite generally, Mellin-Barnes integrals are related to Fox's $H$-function [7], for which series expansions are available. In the present case the result reads:

$$\begin{aligned} p(\tau) = &(\alpha\tau_{HN}\Gamma(\gamma))^{-1} H_{2,2}^{1,1}\left(\frac{\tau}{\tau_{HN}}\right) \\ = &\frac{1}{\tau}\left(\frac{\tau}{\tau_{HN}}\right)^{\alpha\gamma} \sum_0^\infty \frac{(-1)^n}{n!}\frac{\sin(\pi\alpha(n+\gamma))}{\pi}(\gamma)_n \left(\frac{\tau}{\tau_{HN}}\right)^{\alpha n} \\ &\text{if } 0 < \left|\frac{\tau}{\tau_{HN}}\right| < 1 \end{aligned} \tag{15}$$

$$\begin{aligned} = &\frac{1}{\tau}\sum_0^\infty \frac{(-1)^n}{n!}\frac{\sin(\pi(1+\alpha n))}{\pi}(\gamma)_n \left(\frac{\tau}{\tau_{HN}}\right)^{-\alpha n} \\ &\text{if } \left|\frac{\tau}{\tau_{HN}}\right| > 1. \end{aligned} \tag{16}$$

Here $(\gamma)_n = \gamma(\gamma+1)\dots(\gamma+n-1)$ denotes Pochhammer's symbol, and besides the earlier conditions for $\alpha$ and $\gamma$ one also must have $\alpha\gamma < 1$.

This result is plotted in Figure 1. As for the Cole-Davidson distribution, at small $\tau$ one here has a weak divergence

$$p(\tau) = O(\tau^{\alpha\gamma - 1}) \tag{17}$$

while for large $\tau$ on has $p(\tau) = O(\tau^{-1})$.
We note in passing that also the case $\gamma = 1$, $\alpha < 1$, the Cole-Cole model [6], is solved by (15) and (16), see Figure 2.

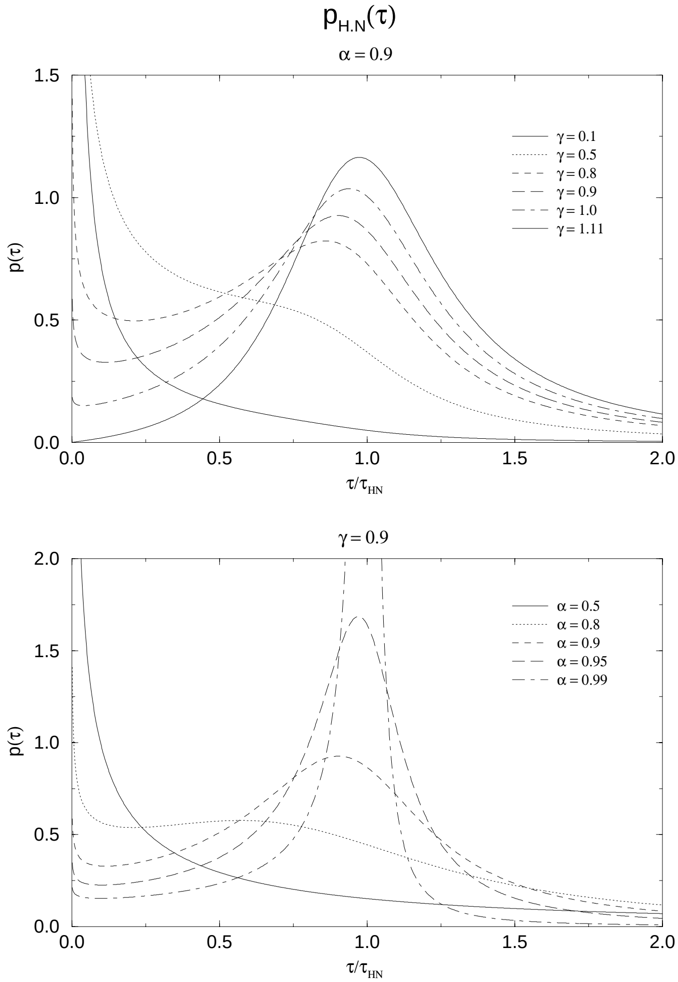


**Fig. 1.** The probability density for the Havriliak-Negami model, plotted for different $\gamma$ (upper part) and $\alpha$ (lower part).

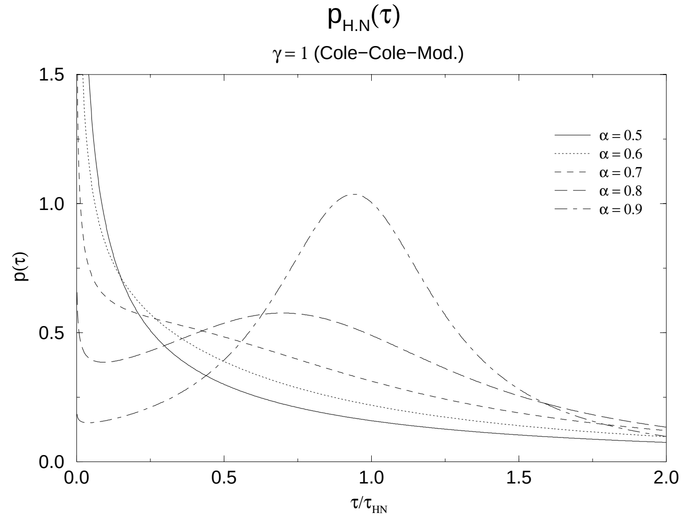


**Fig. 2.** The probability density for the Cole-Cole model for different $\alpha$.

The models can be further generalized in the following way: With the Fox-function [7]

$$H^{m,n}_{p,q}(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds\, x^{-s} \times \frac{\prod_{i=1}^{m} \Gamma(b_i+\beta_i s)\prod_{j=1}^{n}\Gamma(1-a_j-\alpha_j s)}{\prod_{i=m+1}^{q}\Gamma(1-b_i-\beta_i s)\prod_{j=n+1}^{p}\Gamma(a_j+\alpha_j s)} \tag{18}$$

where the coefficients $a_i$ and $b_j$ may be complex quantities, while $\alpha_i$ and $\beta_j$ are real, and with

$$\lambda = \sum_{i=1}^{q}\beta_i - \sum_{j=1}^{p}\alpha_j$$
$$\mu = \prod_{j=1}^{p}\alpha_j^{\alpha_j}\prod_{i=1}^{q}\beta_i^{-\beta_i} \tag{19}$$

one may define [7]

$$p(\tau) = \frac{\exp(-d\tau)\tau^{\lambda-1}}{c(1+b\tau^k)^{\mu-1}} H^{m,n}_{p,q}\left(\left(\frac{a\tau^k}{1+b\tau^k}\right)^s\right) \quad \text{if} \quad \tau > 0 \tag{20}$$

$p(\tau) = 0$ otherwise. The parameters $a$, $b$, $d$, $s$ are real and positive, $k$ is a positive integer, and the normalization constant $c$ is given by

$$c = \sum_{r=0}^{\infty}\frac{(-d)^r b^{\frac{\lambda+r}{k}}}{r!k}\frac{\Gamma(\mu-1-\frac{\lambda+r}{k})\Gamma(2-\mu+s^2)}{\Gamma(1-\frac{\lambda+r}{k}+s^2)\Gamma(\mu-1-s^2)} \times H^{m,n}_{p,q}\left(\left(\frac{a}{b}\right)^s\right). \tag{21}$$

According to Mathay and Saxena [7] the parameters can be chosen in such a way, that $p(\tau)$ is nonnegative and properly normalized, and that a large number of probability functions used in statistics are special cases of this distribution. We consider (20) simply as a very general solution of the basic integral relation (2), from which we obtain the corresponding dielectric function $E^+(\omega)$, because Fox's function includes practically all known special functions of mathematical physics. Correspondingly $p(\tau)$ at small $\tau$ can be zero or finite or weakly singular. This behavior of $p(\tau)$ contributes to a long standing discussion among glass-physicists and -chemists about the shape of the function $p(\tau)$ at small $\tau$. The models show, that $p(\tau)$ may be zero, or adopt a finite value, or may even slightly diverge at $\tau \to 0$.

## 4 Stieltjes' integral relation and the connection to the Mellin transform

Rewriting the original integral relation (2) with the kernel (3) as

$$\frac{1}{\omega}E^+\left(\frac{i}{\omega}\right) = \int_0^\infty \frac{1}{\omega+\tau}p(\tau)d\tau \tag{22}$$

one arrives at an integral relation of the Stieltjes type [8]. This can be solved by Fourier transform. Indeed, the solution of (22) is given by

$$p(\tau) = \frac{i}{2\pi\tau}\left[E^+\left(\frac{i}{\tau}e^{i\pi}\right) - E^+\left(\frac{i}{\tau}e^{-i\pi}\right)\right] \tag{23}$$

*i.e.* as a jump across the branch cut of the dielectric function along the negative imaginary axis. While this is appealing from a physical point of view ('singularities determine the physics'), from a mathematical point of view, an analytic continuation of $E^+(z)$ into the lower $z$-half-plane is required.

$$E^+(z) = \frac{1}{2\pi i}\int_C \frac{E^+(\omega')}{\omega'-z}d\omega'. \tag{24}$$

The contour $C$ surrounds the negative imaginary $\omega'$-axis in the counterclockwise direction and is closed by a circle at very large $|\omega'|$. In view of measurements of $\epsilon^+(\omega)$ or $E^+(\omega)$ on the positive real $\omega$-axis at discrete points with experimental uncertainties, such an analytic continuation is practically impossible. So the Stieltjes solution (23) of the integral relation is less useful than the one with the Mellin transform. It is nevertheless interesting to map the two solutions on each other.

First we note, that interchanging integrations in Mellin transforms very often is impossible. *E.g.* if one inserts (4) into (7) integrates first on $s$, the inverse Mellin transform of the inverse kernel would not exist. Similarly, for showing the equivalence of the two solution of the integral relations, one first has to express $E^+(z)$ by its values along the branch cut at the negative imaginary axis. Since the contributions of the infinite circle in the contour $C$ vanish, we have finite contributions from left to the branch cut with $\omega' = y\ e^{i\frac{3\pi}{2}}$ and from right to it with $\omega' = y\ e^{-i\frac{\pi}{2}}$. This leads to

$$E^+(\omega) = \frac{1}{2\pi}\int_\infty^0 dy \frac{E^+(y\ e^{i\frac{3\pi}{2}}) - E^+(y\ e^{-i\frac{\pi}{2}})}{iy+\omega} \tag{25}$$

with $z=\omega$ on the real axis. Inserting this result into (4), we may then interchange the integrations, perform the integral on $\omega$ and insert the result into (7). The resulting inverse Mellin transform is given by

$$\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds(\tau y)^{s-1} = (\tau y)^{c-1}\delta(\ln(\tau y)) = \frac{1}{\tau}\delta(y-\frac{1}{\tau}) \tag{26}$$

exploiting the delta-function, we arrive at the result (23). So the Stieltjes form follows from the Mellin one and vice versa, provided that the analytic continuation of the dielectric function towards the branch cut at the negative imaginary axis is possible.

## 5 Further comments, discussion and summary

In the mathematical literature [8], a linear problem

$$A\phi = f \tag{27}$$

is said to be well-posed, if two metric spaces $\Phi$ and $F$ exist such that $A\phi$ is defined on $\Phi$ and adopts its values in $F$. Furthermore, the solution of (27) exists for any $f \in F$, is unique in $\Phi$ and depends *continuously* on $f$. If one of the three conditions is violated, the problem is said to be ill-posed.

In many cases the 3rd condition is violated. Fredholm integral equations of first kind are well known examples [9], including the integral relations of the convolution type like (2). This is unfortunate, because the function $E^+(\omega)$ in (2), which corresponds to $f$ in (27), is experimentally known only at discrete values on the positive real axis with uncertainties. One possibility, which can be followed in such a case [10], is to take the data seriously, and exploit the normalization and the positivity of $p(\tau)$ for obtaining rigorous upper and lower bounds for the *integrated* probability function

$$I(\tau_0) = \int_{\tau_0}^\infty p(\tau)d\tau. \tag{28}$$

From (28) one may draw tentative conclusions on the behavior of $p(\tau)$.

One of the reasons to study the ill-posed problem in more detail [11], was to investigate, whether the procedure used in [10] was of any help in numerical procedures, applied to that problem. Another reason was to investigate, whether so called stabilization factors could be used in the inverse Mellin transform to obtain a regularized solution depending on the regularization parameter $\alpha$.

$$p(\tau,\alpha) = \frac{1}{2\pi i\tau}\int_{c-i\infty}^{c+i\infty} ds\left(\frac{i}{\tau}\right)^{-s}\frac{\sin(\pi s)}{\pi}\hat{E}(s)F(s,\alpha). \tag{29}$$

A frequently used stabilization factor is [12]

$$F(s,\alpha) = \exp(-\alpha^2(i\pi s)^2) \tag{30}$$

but we think that the inverse Mellin transform requires a special tretment. For the inverse Fourier transform the conditions for the stabilizing factor, which generates a regularized solution, are known [8]. For the inverse Mellin transform or the inverse (two-side) Laplace transform to our knowledge only the principal application of a stabilizing function is known, but explicit conditions for it do not seem to exist in the mathematical literature. We tried to close this gap by finding the conditions for the existence of the stabilizing factor, using the theory of the Mellin transform as well as the theory of distributions. We also found recipes for explicitely constructing the stabilizing factor, using so called regularized sequences which go beyond (30). This will be published in a separate paper.

In summary, we think that for testing of numerical procedures for the ill-posed problem, arising from experimental data for $E^+(\omega)$ in (2), it is useful to have as many analytical models for $E^+(\omega)$ and $p(\tau)$ as possible. The models solved in Section 3 seem to fulfill these requirements. Work is in progress to apply the numerical procedures with stabilization factors to these models and compare them with rigorous solutions.

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