Higher-Order Mode-Coupling Theory

Description of Dielectric Relaxation in Polymers

introduction

The relaxation patterns observed in dielectric spectra measured on polymers are often quite complicated. Distinctive features, such as loss-free regions (1/f noise), regions linear in frequency as well as horizontal inflection points and double minima are often encountered. Usually, relaxation data are modelled using empirical relations, such as the time-honoured Havriliak-Negami or Kohlrausch-Williams-Watts (KWW) expressions. While these formulae do indeed fit the data well many times, they do usually not apply in the above cases. We will in this article present a method for curve fitting of dielectric data on polymers using the mode-coupling theory (MCT) of the liquid-glass transition [1]. This theory has been quite successful in describing the relaxation behaviour of simple fluids. The application of the theory to, e.g., polymers has in the past been a more controversial subject. One important result of the theory, called the factorization property, does however have as a consequence that close to certain glass transition singularities, the time (or frequency) dependence is separated from the microscopic properties of the material studied. Therefore, a relaxation scenario is predicted that only depends on certain separation parameters. These parameters are in turn dependent upon external physical parameters such as, e.g., temperature and pressure. The MCT therefore provides a universal relaxation scenario that is independent of the microscopic details of the system studied and this justifies the use of the MCT results for complicated systems such as semicrystalline polymers. In order to gain further understanding of the elusive glass transition phenomenon, the analysis presented in this article may be important since it provides a direct connection between experimental data and a theory that has been proven to provide general predictions that in many cases have been verified by experiments.

basics of the mode-coupling theory

The mode-coupling approach is based on the concept of glass transition singularities. In the case of the liquid-glass transition in simple liquids, the A2 scenario, which is the simplest scenario, has been used most successfully. For temperatures above a certain critical temperature, \( T_c \), the imaginary part of the dielectric spectrum \( \varepsilon''(\omega) = \varepsilon''(\omega) - i\varepsilon'(\omega) \) is here modelled around a minimum centred at \( (\nu_{\text{min}}, \varepsilon''_{\text{min}}) \), made up of two power laws with exponents \( a \) and \( b \), according to

\[
\varepsilon'(\omega) = f_1 - \varepsilon_0, \quad f = \left[ \ln \left( \frac{1}{2\nu_{\text{min}}} \right) \right] G_2 G_3 ... G_k
\]

(3a)

\[
\varepsilon''(\omega) = -\frac{\pi}{2} f, \quad f = \left[ \ln \left( \frac{1}{2\nu_{\text{min}}} \right) \right] G_2 G_3 ... G_k
\]

(3b)

where \( f_1 \) and \( \varepsilon_0 \) are fitting parameters, \( f' = df'/dy \), \( y = \ln(2\nu_{\text{min}}) \) and \( t_1 \) is a characteristic microscopic timescale. The function \( f(y;G_2,G_3,...,G_k) \) is determined through

\[
\left( \frac{df'}{dy} \right)^2 = \frac{4}{(k-2)} f'(y) - G_2 f'(y) - G_3 f'(y) - ... - G_k f'(y) - G_k
\]

(4)

This equation cannot be solved analytically. For a sufficiently accurate description of the dielectric function for polymers, the \( A_k (k = 4) \) scenario has been demonstrated to be quite successful [4], and we will therefore focus our attention on this scenario in the present article. We then have

\[
\left( \frac{df'}{dy} \right)^2 = f''(y) - G_2 f''(y) - G_3 f''(y) - G_4 f''(y) - G_4
\]

(5)

The function \( f \) is strongly divergent both in its lower as well as in its higher limit. Automatic curve fitting is therefore very difficult. However, because of eqs. (3) and (5), there is a simple relationship between the real and imaginary parts, according to
For the article to introduce this technique. It is the purpose of this possible to use simple polynomials in the complex polynomial coefficients according to
\[ p = \frac{g_H^2}{12g_L} = \text{constant} \quad (8a) \]

\[ q = \frac{27g_H^3}{4096g_L^3} = \text{constant} \quad (8b) \]

The expression for the master functions in the \( \varepsilon' - \varepsilon'' \) plane is then as follows:

\[ \frac{\varepsilon''}{c_H^4} = \sqrt{\frac{f - \varepsilon'}{c_H^4}} \pm 6\sqrt[3]{\frac{f - \varepsilon'}{c_H^4}} \pm 3 \quad (9) \]

The scaling parameters extracted from such an analysis should then exhibit the following temperature dependences:

\[ \frac{c_H}{c_L} \propto \frac{T_0 - T}{T_0} \quad (10a) \]

\[ \frac{c_H^4}{c_L^4} \propto \left( \frac{T_0 - T}{T_0} \right)^{12} \quad (10b) \]

**examples**

In the figures below, some examples are shown in which the analysis introduced above has been used. Since the expressions introduced above are approximate, it is important to realize that they are only valid in the frequency range around the minimum in \( \varepsilon' \). One therefore expects to find increasingly larger deviations between theoretical and experimental curves as one moves away from the minimum.

The theoretical curves were produced by fitting eq. (6) with \( k = 4 \) to the data. From those fits, the relevant parameters were extracted according to eqs. (7). These parameters were used to calculate the elliptic functions, eqs. (3), which were then used in the frequency-domain plots. Figure 1 shows data from dielectric measurements on PET with a varying degree of crystallinity [2]. The dielectric measurements were performed using a Schumielner Solartron 1260 Impedance Gain/Phase Analyzer together with a Chelsea Dielectric Interface and a Hewlett-Packard HP4284A Precision LCR Meter. The

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**Figure 1.** Dielectric spectra for PET. a) Complex plane fit, b) real part of dielectric function, c) imaginary part of dielectric function. Circles: 9% crystallinity at 90°C, diamonds: 26% crystallinity at 110°C, squares: 31% crystallinity at 115°C.
temperature was controlled with a Novocontrol Quatro cryosystem. As can be clearly seen, there is excellent agreement between theoretical and experimental curves.

Figure 2. Dielectric spectra for PCTFE. a) Complex plane fit, b) real part of dielectric function, c) imaginary part of dielectric function.

Figure 3. Scaling plots for the same PCTFE data as presented in Figure 2. The variable $u$ is a rescaled frequency, see [4] for details. The variables $a$ and $b$ are defined as: $a = (f_c c')^{-1} c'^4$ and $b = \varepsilon'' c'^4$.

Figure 4 presents dielectric data for PCTFE. These data were taken from the literature [3]. There is also in this case very good agreement between theory and experiment [4].

One difficulty with performing a complete MCT $A_4$ analysis of dielectric spectra is due to the fact that it is not easy to find data that fall on scaling lines according to eq. (8). Nevertheless, the PCTFE data do follow such a scaling line and the result of the scaling analysis is presented in figures 3 and 4.

In figure 3, a master curve is plotted and presented in the complex plane as well as in the frequency domain. Figure 3a shows the rescaled data together with the master function given by eq. (9). The scaling expressions in the frequency domain have been omitted in this article, but the results from such an analysis are nevertheless shown in figures 3b and c. The details regarding the frequency domain scaling expressions can be found in [4]. As expected, the data found along the scaling line do indeed collapse on this master curve. Figure 4, finally, shows the temperature dependence of the scaling parameters.

While there is clearly agreement between theory and experiment, the temperature range is not wide enough to provide conclusive evidence as to whether the scaling laws are valid or not. As may be understood, a complete $A_4$ analysis of dielectric data is cumbersome and difficult as well as time-consuming. Nevertheless, we do hope that this brief presentation may inspire other workers to take on the challenge and try to confirm or disprove the theory by using the procedure put forward in this article.

References

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**New Presentation of the Dielectric Data**

R. R. Nigmatullin and S. I. Osokin

**introduction**

There are several problems that complicate the analysis of dielectric spectra. One of them is that the restriction to the low frequency limit of the experimental frequency window invariably leads to the situation when one can observe only part of a low frequency response and cannot determine whether it is a "tail" of an inaccessible relaxation process (with the peak located at frequencies below the experimental frequency window) or a true low frequency dispersion (LFD) [1].

Another problem is ambiguity in determination of the 'true' number of processes within a complex dielectric spectrum, especially if there are several processes that are very close to each other and are differentiated in amplitude by a factor of 10, or even 100.

The situation becomes more complicated when a large contribution from a low frequency dispersion is observed. In this case it is impossible using conventional presentations (normal presentation, where the real or imaginary parts of complex permittivity are plotted vs. the logarithm of frequency and the Cole-Cole presentation, where the imaginary part of the complex permittivity is plotted with respect to its real part) to reveal even the number of the processes involved.

To overcome these difficulties we suggest a new format. This data presentation defined as the *ratio presentation* (RP) format is turned out to be very effective in solving the problems mentioned above.

**ratio presentation format**

In practice, it is necessary to differentiate between an LFD process and a relaxation process of the Cole-Cole type, and to find a criterion that helps to detect a mixture of these (and other) processes from their separate contributions. One can solve this problem with the use of RP format. It is defined as:

\[
\text{RP} = \frac{\text{Re}[\varepsilon(j\omega)]}{\text{Im}[\varepsilon(j\omega)]} = \frac{1}{\text{Im}[\varepsilon(j\omega)]} - j \frac{\text{Re}[\varepsilon(j\omega)]}{\text{Im}[\varepsilon(j\omega)]} = \cot(q) + \frac{\varepsilon_e}{\Delta \varepsilon} \sin(q) \tag{1}
\]

Here

\[\varepsilon(j\omega) = \text{Re}[\varepsilon(j\omega)] - j \text{Im}[\varepsilon(j\omega)]\]

Complex function \(D(j\omega)\) is determined from the relationship

\[D(j\omega) = \frac{\varepsilon_e + \Delta \varepsilon}{D(j\omega)} \exp(j\varphi)\]

In RP format the LFD function appears as a straight sloping line when \(\varepsilon=1\) or as a broken straight line when \(\varepsilon<1\), with formulae is expressed by equation:

\[-\frac{\text{Re}[\varepsilon(j\omega)]}{\text{Im}[\varepsilon(j\omega)]]} = A + Bj\omega\] \tag{2}

Fig. 1 shows the frequency dependence of function (2) for some concrete values of the fitting parameters \(\varepsilon_e, \sigma\) (where \(\sigma = 1/(\varepsilon_\text{LF}^{\alpha})\)) and \(\alpha\). The relationship between the parameters \(A(\varepsilon_e, \sigma, \alpha)\) and \(B(\varepsilon_e, \sigma, \alpha)\), and the conventional parameters \(\varepsilon_e, \sigma\) and \(\alpha\) are given in Table 1. The use of expression (2) for recognition of the existence of an LFD process becomes very simple. Moreover, the application of expression (2) effectively involves the simultaneous fitting of both the real and imaginary parts that makes the fitting function more reliable.

In the case of Cole-Cole function RP format has the form

\[-\frac{\text{Re}[\varepsilon(j\omega)]}{\text{Im}[\varepsilon(j\omega)]} = A + Bj\omega + Cj^{\alpha}\] \tag{3}

Fig. 2 shows the presentation (3) of the Cole-Cole function, for certain values of the fitting parameters in double-log scale. The relationship of the fitting parameters \(A, B, C\) to the initial parameters of the Cole-Cole
function (i.e. $\varepsilon_{\infty}$, $\Delta \varepsilon$, $\tau=1/(\omega \tau)$) are given in Table 1. The shape of Cole-Cole function in this presentation looks like profile resembling the letter ‘V’. We wish to stress here, that the function appears in the V-shaped form, even in cases, when the normal presentation exhibits only the tail of this process. It can be explained by the fact that the frequency minimum of this function is found from the relationship

$$f = \frac{B}{C} \sqrt{\frac{\varepsilon_{\infty}}{\varepsilon_s}} \frac{1}{2\pi} \frac{1}{\sqrt{\varepsilon_s}} \frac{1}{\sqrt{\varepsilon_{\infty}}}$$

and always is shifted to the high-frequency region because of the ratio $\varepsilon_s/\varepsilon_{\infty} >> 1$.

Open circles in Fig. 3 represent the linear combination of an LFD and Cole-Cole function. On the same figure one can see the LFD and Cole-Cole functions separately. The visual presentation of this case in RP format allows one to notice a peak created by the combination of these two processes that provides evidence of the coexistence of two processes.

Fig. 4 shows RP format for the series combination of two recap elements with one resistance in parallel. The definition of recap or constant phase angle elements is given in [2]. This picture demonstrates asymmetric behavior (which is characterized by the downward displacement of the high-frequency branch), obtained for a model spectrum. Here the asymmetry always appears on the right side of V-shaped function. Dashed line shows the position of the high frequency branch in the case of the negligible influence of the second process (provided by the second recap element). Arrow shows the movement of the high-frequency branch due to influence of the second process. Hence we have an ‘dropping’ asymmetry due to the falling down of the high-frequency branch. This asymmetry therefore differentiates between a model defined by two recap elements combined in series and a model defined by a single Cole-Cole function, which is characterized by mirror-like symmetry with respect to the minimum frequency.

Fig. 5 shows RP format for the parallel combination of two recaps with resistance. This picture demonstrates asymmetric behavior (which is characterized by the downward displacement of the low-frequency branch), obtained for a model spectrum. Here the asymmetry always appears on the left side of V-shaped function. Dashed line shows the position of the low frequency branch in the case of the negligible influence of the second process (provided by the second recap element). Arrow shows the movement of the low-frequency branch due to influence of the second process. Hence we have an ‘dropping’ asymmetry due to the falling down of the low-frequency branch. This asymmetry therefore differentiates between a model defined by two recap elements combined in parallel from a model defined by a Cole-Cole function, which is characterized by mirror-like symmetry relatively the minimum frequency and a model defined by two recap elements in series, which is characterized by right-hand asymmetry.

**Table 1.** The relationship between the parameters of the low-frequency dispersion (LFD) and the Cole-Cole functions, and the parameters $A$, $B$, $C$ from expressions (2) and (3).

<table>
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<th>LFD</th>
<th>Cole-Cole</th>
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<tbody>
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<td>$\varepsilon(j\omega) = \varepsilon_{\infty} + \frac{1}{(j\omega)^2}$</td>
<td>$\varepsilon(j\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{\infty} - \varepsilon_s}{1 + (j\omega)^2}$</td>
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<tr>
<td>$A = \coth \left( \frac{\pi \alpha}{2} \right)$</td>
<td>$B = \frac{\varepsilon_{\infty} (2\pi)^2}{\sin \left( \frac{\pi \alpha}{2} \right)}$</td>
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<tr>
<td>$B = \frac{\varepsilon_{\infty} (2\pi)^2}{\sin \left( \frac{\pi \alpha}{2} \right)}$</td>
<td>$C = \frac{\varepsilon_{\infty} (2\pi)^2}{(\varepsilon_{\infty} - \varepsilon_s) \sin \left( \frac{\pi \alpha}{2} \right)}$</td>
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The RP format helps to differentiate, at least qualitatively, between various functions (including LFD, Cole-Cole and more complex functions) and their linear combinations.

The frequency minimum of the Cole-Cole type function in RP format always is shifted to the high-frequency region in comparison.
with frequency maximum of the imaginary part of this function in normal presentation.

In the RP format for all chosen fitting functions, one can obtain all fitting parameters simultaneously for both parts of complex permittivity, except \( \varepsilon_n \) and \( \varepsilon_e \). For these limiting values only the reliable ratio \( \varepsilon_e/\varepsilon_n \) can be obtained.

**conclusions**

In this note we have attempted to outline the advantages of the presenting dielectric data in the ratio presentation (RP) format for \( \text{Re}[\varepsilon(j\omega)]/\text{Im}[\varepsilon(j\omega)] \). In spite of the fact that the inverse value of the RP format coincides with tangent of the phase angle all peculiarities of new presentation are opened in double-log scale.

They are:

- RP format gives us an evidence of possible equivalent circuit that can provide true fit of the real data.
- Any fit in RP format is realized not only for the real or imaginary parts of complex susceptibility but simultaneously for the both parts that makes the fitting procedure more reliable and justified.

Alongside with conventional presentation of DS data in Cole-Cole and normal formats we suggest new presentation, which is more informative especially in the cases, where usual formats are non-informative and ambiguous.

**Fig.4.** RP format spectrum formed from two recap elements combined in series, and described by the function

\[
\varepsilon(j\omega) = \varepsilon_n + \frac{\Delta\varepsilon}{1 + (j\omega\tau_1)^\nu + (j\omega\tau_2)^\nu}
\]

with parameters: \( \nu_1 = 0.98, \tau_1 = 0.005, \nu_2 = 0.6, \tau_2 = 0.05, \varepsilon_n = 200, \varepsilon_e = 1.5 \). Dashed line shows the position of the high frequency branch in the case of the negligible influence of the second process (provided by the second recap element).

**Fig.5.** RP format spectrum formed from two recap elements combined in parallel, and described by the function

\[
\varepsilon(j\omega) = \varepsilon_n + \frac{\Delta\varepsilon}{1 + (j\omega\tau_1)^\nu + (j\omega\tau_2)^\nu}
\]

with parameters: \( \nu_1 = 0.98, \tau_1 = 0.001, \nu_2 = 0.6, \tau_2 = 0.05, \varepsilon_n = 1000, \varepsilon_e = 2 \). Dashed line shows the position of the low frequency branch when the influence of the second process (provided by the second recap element) is negligibly small.

**References**


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- [ ] Economical dielectric spectrometers (3 μHz - 300 kHz or 3 μHz - 3 MHz)
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- [ ] ALPHA high voltage extension (+-150 Vp ac and / or dc, 3 μHz - 1 MHz or +-500 Vp ac and / or dc, 3 μHz - 10 kHz)
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