# Generalized regular singular-point description of low-frequency dielectric responses

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This paper presents a generalized regular singular-point (GRSP) model developed to account for dielectric spectra of the wide range of materials having a frequency response containing more than two power-law regions. In fact, the model is valid for an unlimited number of such regions, and is shown to provide a good description of the entire dielectric spectrum of tablets made of microcrystalline cellulose, including two relaxation peaks and power-law responses at low and high frequencies. This finding puts the GRSP model in a unique position, since no model existing in the literature is able to describe the totality of features present in the spectrum, without resorting to a superposition of more elementary responses.

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Different polarization mechanisms contribute to the dielectric permittivity of a material, each giving rise to dispersion in a certain frequency range, and contributing a constant to the permittivity at lower frequencies.[1,2] For high frequencies, electronic and ionic polarization result in resonance absorption[3,4] at more or less well-defined resonance frequencies, typically in the ultraviolet and infrared ranges, respectively.[1,5] Whereas this high-frequency response nowadays is well understood (see, e.g., Ref. 6, and references therein), the response for lower frequencies remains more elusive.[7] A century ago, Curie and von Schweidler[8,9] reported that the polarization current initially decayed with time as a fractional power-law. Much later Jonsher[10] identified a second power-law at low frequencies, i.e., long times. Since the current response function, according to linear response theory,[11,12] is proportional to the current autocorrelation function, this observation appears to be related to the so-called long-time tails of the autocorrelation function.[13] It is now a well-established experimental fact that the low-frequency response of most solid materials exhibits universal features,[14] being characterized by certain power-laws, both at the high (typically ~MHz) and low frequency (~mHz–Hz) ends of the spectrum, i.e., short and long times.[2,15]

Dissado and Hill (DH) have developed a general cluster model of the dielectric response.[16,17] A macroscopic sample is assumed to contain a large number of microscopic subunits, and a "cluster" is defined as a spatially limited region containing many microscopic subunits over which a microscopic structure is maintained. The DH theory considers two coupled processes each described by a first-order equation, which together give rise to a second-order differential equation for the dielectric response function.[18] In a similar vein, it has been shown that a combination of two fractal processes yields the generalized Davidson–Cole expression,[19] which also predicts a second power-law at low frequencies. Recently a model has been proposed,[20] which is based on the mathematical concept of regular-singular points[21,22] (RSPs) of an ordinary differential equation in time for the current response function. It is well-known[21,22] that a RSP of such an equation gives rise to a power-law behavior in the neighborhood of the singular point.

Many materials exhibit more complicated spectra, which contain more than two power-law regions. Since no theory today is able to account for these "nonideal" cases, the somewhat unsatisfactory solution usually is to use different expressions in different frequency regions, or to use a superposition of expressions. Often the Cole-Cole,[23] Davidson-Cole,[24] or Havriliak-Negami[25] expressions are used for this purpose. Moreover, recent broad-range dielectric measurements on disordered materials have revealed that an additional power-law usually exists for frequencies in the GHz to THz region;[26] thus even the "ideal" spectra most likely are characterized by more than two power-law regions. For these reasons, there is an obvious need to extend existing descriptions of the dielectric response.

Contrary to the other aforementioned models, the RSP model allows an immediate generalization that includes these more complicated cases. This generalization is presented here, and comparisons are made with experimental data for tablets made of microcrystalline cellulose (MCC), whose spectra contain a rather large number of separate power-law regions.[27]

In the time domain, the delayed response of a dielectric material to a time-varying electric field may be described in terms of the dielectric response function $f(t)$ or, equivalently, the current response function $g(t)$ ($t$ is the time). The current response function $g(t)$ is essentially the time derivative of $f(t)$ or, conversely,[20]

$$f(t) = \frac{1}{\varepsilon_0}\int_0^t g(t')\mathrm{d}t' = \frac{1}{\varepsilon_0}\left(\sigma_{\mathrm{dc}} - \int_t^\infty g(t')\mathrm{d}t'\right), \qquad (1)$$

$\varepsilon_0$ being the permittivity of free space. The second equality in Eq. (1) follows from the fact that the integral of the current response function over all times equals the direct-current (dc) conductivity $\sigma_{\mathrm{dc}}$, according to the Kubo formula.[11,12] For a time-harmonic applied electric field, the response is most conveniently described in terms of the complex relative dielectric permittivity $\varepsilon(\omega)=\varepsilon'(\omega)-\mathrm{i}\varepsilon''(\omega)$ as a function of angular frequency $\omega$. The dielectric permittivity is calculated according to[2,11,12]

 

$$\varepsilon(\omega) - 1 = \lim_{\delta \to 0+} \int_0^\infty f(t) e^{-(i\omega + \delta)t} dt, \tag{2}$$

where the free-space contribution has been subtracted from the permittivity, since this contribution is considered to be instantaneous and, hence, is not described by the response function $g(t)$.

Whereas the above discussion was completely general, let us now restrict our attention to the specific response functions that may be obtained by using the RSP concept. We will primarily work with the current response function $g(t)$, since this response function [contrary to $f(t)$] exhibits power-law behaviors for both short and long times, regardless of the value of the dc conductivity.

As linear response theory shows,[11,12] the current response function is proportional to the current autocorrelation function evaluated at equilibrium. The time-dependence of this autocorrelation function is determined by that of the current operator, which is known to satisfy the Heisenberg equation of motion in the quantum case or the corresponding equation formulated in terms of Poisson brackets in the classical regime,[11,12] both of which are first order in time. From the above considerations it follows that $g(t)$ fulfills a first order homogenous differential equation in time, which we write as

$$\frac{dg(t)}{dt} + Q(t)g(t) = 0, \tag{3}$$

where $Q(t)$ is an, as yet, unspecified function of time. We note that de la Fuente *et al.*[28] have shown that the memory effect in the dielectric response can be described by an equation of the form of Eq. (3), and that the function $Q(t)$ in fact contains the same information as the memory function introduced in nonequilibrium statistical mechanics to describe non-Markovian processes (see, e.g., Ref. 29).

Since our objective is to describe the power-law processes that occur at relatively low frequencies (i.e., large times) we now restrict our attention to times $t \geqslant \xi$, where $\xi$ represents a time sufficiently large that resonance absorption is unimportant. We replace the function $Q(t)$ in Eq. (3) by another function $Q_1(t)$, and require that $Q_1(t)$ and $Q(t)$ be identical for times $t \geqslant \xi$. The response function $g(t)$ is analogously replaced by $g_1(t)$, which is identical to $g(t)$ for times $t \geqslant \xi$.

Two finite singularities were used in Ref. 20 to obtain a unified description of two coupled power-laws. Now we instead use $n$ finite singularities in order to couple $n$ power-laws ($n \geqslant 2$). If Eq. (3) has $n$ finite singularities located at $t = -t_k$ ($k = 1, \ldots, n$), the function $Q_1(t)$ may be written[21]

$$Q_1(t) = -\sum_{k=1}^{n} \frac{m_k}{t + t_k}, \tag{4}$$

where $m_k$ ($k = 1, \ldots, n$) is the exponent of the RSP $t = -t_k$. Furthermore, the "point at infinity" is a RSP if[21]

$$m_\infty = -\sum_{k=1}^{n} m_k \neq 0. \tag{5}$$

Since experiments show that a power-law exists for long times, we expect $m_\infty$ to be nonzero, and the "point at infinity" to be a RSP. Inserting Eq. (4) in Eq. (3), and solving the resulting equation by the method of integrating factor, we obtain

$$g_1(t) = -A \frac{\varepsilon_0}{t_2^2} \prod_{k=1}^{n} \left( \frac{t}{t_2} + \frac{t_k}{t_2} \right)^{m_k}, \tag{6}$$

where the normalization constant (which is negative) has been written $-A\varepsilon_0/t_2^2$ for dimensional reasons. When deriving Eq. (6) we have assumed that the finite singularities fulfil $0 \leqslant t_1 < t_2 < \cdots < t_n$; hence $t_2$ has been used to nondimensionalize the time variable. It is evident from Eq. (6) that the times $t_k$ may be identified with the crossover times between the different power-laws. In order to describe the power-laws themselves, it is more convenient to introduce a second set of exponents $\gamma_k$ ($k = 1, \ldots, n$), defined by

$$\sum_{l \leqslant k} m_l = -(\gamma_k + 1). \tag{7}$$

As a result, the current response function decays as $g(t) \propto t^{-(\gamma_k + 1)}$ between the appropriate crossover times.

Whereas Eq. (6), thus, provides the functional form of $g(t)$ for times $t \geqslant \xi$, we have no knowledge of the behavior of $g(t)$ for smaller times. When evaluating the dielectric response function, this ignorance amounts to the introduction of an arbitrary integration constant, which, in fact, may be identified as the dc conductivity, as Eq. (1) shows. As explained in Ref. 20, the integration in Eq. (2) yields, provided $\omega \ll 1/\xi$, another constant, which may be identified as $\varepsilon_\infty - 1$, $\varepsilon_\infty$ being the high-frequency permittivity. In fact, provided $\omega \ll 1/\xi$, we find by combining Eqs. (1) and (2) that[20]

$$\chi(\omega) = -\frac{1}{\varepsilon_0} \int_0^\infty e^{-i\omega t} \left( \int_t^\infty g_1(t') dt' \right) dt, \tag{8}$$

where

$$\chi(\omega) \equiv \varepsilon(\omega) - \varepsilon_\infty - \frac{\sigma_{dc}}{i\omega\varepsilon_0} \tag{9}$$

is the dielectric susceptibility.

The short and long time behaviors of $g_1(t)$ are determined by the values of the short and long time exponents $\alpha \equiv \gamma_1$ and $\beta \equiv \gamma_n$. We note that $\alpha$ and $\beta$ are the exponents seen in the conductivity spectra at high and low frequencies, respectively. For Jonscher's "universal" response, the exponents are constrained by the inequalities $0 < \alpha < 1$ and $0 < \beta < 2$.[2,15] For $0 < \beta < 1$, low-frequency dispersion (LFD) is obtained, while for $1 < \beta < 2$ a relaxation peak is described. Even though $t_1$, strictly speaking, always should be positive, to ensure that the current response function is finite for all times, we may for $\alpha < 1$ let $t_1 \to 0$ in order to simplify the calculations, as was done in Ref. 20. This procedure changes the value of $g_1(t)$ for very small times only, for which other processes than those considered here, neverthe-

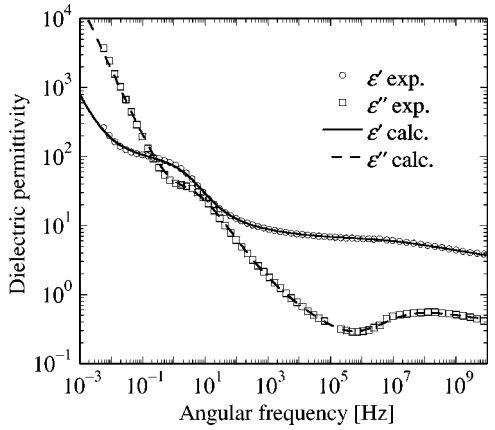


FIG. 1. Comparison between the experimental and calculated dielectric permittivity for MCC tablets.

less, dominate. If, however, we use the model to describe the superlinear power-law in the GHz to THz region, discovered by Lunkenheimer and Loidl,[26] we will find that $1<\alpha<2$. In order to ensure that the integrals in Eq. (8) converge, we then need a cutoff at short times, which means that we must demand that $t_1>0$.

For $n=2$, the transform in Eq. (8) may be calculated analytically, and the result expressed in terms of a confluent hypergeometric function.[20,30] For $n>2$ this is not possible, and one has to resort to numerical methods. In this work, the following strategy was employed: First a function $g_2(t)$ was introduced, with known analytic transform, which had the same asymptotic behavior as $g_1(t)$ for short and long times. The function $g_2(t)$ was constructed as a combination of a number of power-type functions. Then the difference $\Delta g(t)\equiv g_1(t)-g_2(t)$, for which the numerical transform was needed, was everywhere finite and exhibited an asymptotic decay at least as fast as $t^{-2}$ for large times. By using the analyticity of $\Delta g(t)$, the oscillatory integral along the positive real $t$ axis was transformed into a virtually nonoscillatory integral along the negative imaginary $t$ axis. This integral was finally transformed into an integral with finite limits, and decomposed into real and imaginary parts. Thus two real, virtually nonoscillatory integrals with well-behaved integrands over finite intervals resulted, which were evaluated by using the QUADPACK FORTRAN routine DGAG.

The MCC tablets investigated in this study were compressed from MCC powder (Avicel PH 101, FMC, Ireland) in a single punch tablet machine (Korch, EK0, Germany) equipped with circular punches having a diameter of 11.3 mm. The maximum compression pressure used was 150 MPa, and the powder mass was adjusted so as to produce tablets of ~2.0 mm height. Prior to compression the powder was stored for at least one week over a saturated salt solution of NaI corresponding to a relative humidity (RH) of 37% or a moisture content of ~4 wt.% in the powder.[27] After compression the tablets were again stored over a NaI solution for approximately one month to ensure equilibrium.

Two different sets of dielectric spectroscopy measurements were performed; one for circular frequencies between $10^{-4}$ and $10^{6}$ Hz and the other between $10^{6}$ and $10^{9}$ Hz. The low-frequency dielectric measurements used a Solartron 1260 Frequency Response Analyzer together with a Novocontrol Broadband Dielectric Converter, while a Novocool Quatro Cryosystem with an Agilent 4291B was used for the high-frequency measurements. In both measurements the amplitude of the applied voltage was 1.00 V. The electrodes and the tablet were situated in an enclosed and electrically screened encasement containing the NaI solution, thus ensuring a constant RH of 37% during the measurements. The measurement procedure is described more thoroughly in Ref. 27.

TABLE I. Parameters used to calculate the dielectric permittivity displayed in Fig. 1

| $k$ | $t_k(s)$ | $\gamma_k(-)$ |
|---|---|---|
| 1 | 0.00 | 0.926 |
| 2 | $1.41\times10^{-7}$ | 1.69 |
| 3 | $1.47\times10^{-6}$ | 0.690 |
| 4 | 0.0109 | 0.00 |
| 5 | 0.945 | 3.47 |
| 6 | 4.78 | 0.0242 |

Figure 1 displays the experimental dielectric permittivity for MCC tablets compacted at 150 MPa, measured over more than 12 orders of magnitude in frequency. This figure is analogous to Fig. 1 of Ref. 27, which displays the permittivity for tablets compacted at 50 MPa. It is evident that the dielectric permittivity exhibits a rather complex behavior. At low frequencies, both the real and imaginary parts appear to obey a power-law, which is indicative of LFD.[17] At higher frequencies, two relaxation peaks, centered at ~5 and $\sim10^{8}$ Hz are clearly seen. Moreover, an additional power-low region in between the two relaxation peaks may be discerned.

The low-frequency relaxation process appears as a consequence of the presence of water in the material,[31] but its molecular origin is not entirely clear. It has been suggested that this process takes place in a micro-gel-like water-cellulose mixed phase and that it represents a collective but local motion of water-linked chain segments.[32] The high-frequency relaxation peak is, on the other hand, known to be related to the segmental motion of the polymer chain.[32] This peak may be observed not only for cellulose but for other polysaccharides as well, and is only weakly influenced by the particular substructure of the polymer chain.[32]

In order to describe this spectrum quantitatively by using the GRSP model we, thus, need 6 exponents $\gamma_k$ (one for each power-law, and two for each relaxation peak). Consequently, we use Eq. (6), with $n=6$ finite singularities, located at $t=-t_k$. Since the short time exponent $\alpha$ is smaller than unity, we keep $t_1$ fixed at zero. At both ends of the spectrum, the real and imaginary parts appear to follow power-laws, with the same low- and high-frequency exponents. The experimental data, thus, indicate that the contributions from $\varepsilon_\infty$ and $\sigma_{dc}$ are negligible. These parameters were, consequently, kept fixed at zero. The lines in Fig. 1 show the best least-

squares fit of the calculated permittivity to the displayed experimental data. The least-squares fitting was performed on a logarithmic scale for both the real and imaginary parts at the same time, and employed the MINPACK FORTRAN routine LMDIF1. The parameters obtained are given in Table I. It is evident from the figure that the GRSP expression is able to describe the experimental spectrum well. Even though the comparison presented here is restricted to one material, we conclude that the GRSP model provides an interesting and potentially very useful tool for the interpretation of dielectric data in general. If the RSP concept is correct, it also has interesting theoretical implications, since the reason why the ordinary differential equation for the current response function [Eq. (3)] is characterized by a number of RSPs remains an open question.

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