The product form for Debye relaxations

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Abstract
From a phenomenological point of view, the dielectric dispersion function of a
medium can be defined by the location of its zeros and poles in the complex-
frequency plane. This general approach led to the use of a factorized form of the
dielectric function to fit the experimental infrared *reststrahlen* data. Recently,
such an approach has been generalized to the description of relaxation.

At low frequency ranges, the factorized form for relaxation may be
expressed as a product of Debye relaxors. This product form corresponds to the
factorization of the conventional sum model and provides a way to describe the
contribution of the different Debye relaxing units in a poly-dispersive system. It
also allows us to estimate the importance of the interaction between the different
relaxing units.

The present work summarizes the fundamentals of the product model for
relaxation and describes its application to the analysis of the dispersion observed
in the vicinity of the paraelectric to antiferroelectric phase transition in the mixed
crystal (betaine phosphate)$_{0.75}$ (betainearsenate)$_{0.25}$ and at the structural phase
transition of betaine potassium iodide dihydrate.

1. Introduction

It is known, since the pioneering work of Kramers and Kronig [1], that a phenomenological
description of the linear response function of a medium can be obtained by considering the
location of the zeros and poles of a function extended to the complex-frequency plane. In

the particular case of the linear dielectric dispersion function, this general approach led to a factorized form of the dielectric function used to describe infrared *reststrahlen* [2]:

$$\varepsilon(\omega) = \prod_k \frac{\omega^2 + 2iz_k''\omega - (z_k'^2 + z_k''^2)}{\omega^2 + 2ip_k''\omega - (p_k'^2 + p_k''^2)}.$$ (1)

This form, due to Berreman and Unterwald, describes the resonant response resulting from a discrete set of complex poles $p' - ip''$ and zeros $z' - iz''$ that are located in the negative half complex plane near the real frequency axis and distributed symmetrically with respect to the imaginary frequency axis. Physically, such a distribution of complex poles and zeros corresponds to the mapping of the frequencies and damping coefficients of the different transversal and longitudinal polar modes.

As shown by Gervais and Piriou [3], the form (1) provides a description of resonance that is more general than the conventional sum of independent Lorentz oscillators because it incorporates, to some extent, self-energy corrections that result from the perturbative treatment of the interaction of resonant modes. It also provides to the experimentalist a simple method to describe more accurately the resonant dispersion.

In contrast, the analysis of dielectric relaxation is still based on the use of discrete or continuous sums of independent Debye terms (sum model) or on empirical models that are equivalent to the assumption of certain continuous distributions of Debye terms [4]. The limitations of such an approach have been analysed in a recent article aimed at extending the Berreman–Unterwald form to the description of dielectric relaxation [5]. It has been shown that the factorized form not only can be used to describe relaxation but also circumvents basic limitations of the conventional sum model such as the high frequency transparency problem and the absence of coupling between different polar units and between polar and non-polar relaxing units.

At low frequency ranges, the factorized form for relaxation may be expressed as a product of Debye relaxors [5]. This product form, which corresponds to the factorization of the conventional sum model, provides a way to describe the contribution of the different Debye relaxing units in poly-dispersive systems. Here, the description of the experimental data is obtained by adjusting the imaginary poles and zeros of the dielectric function rather than the poles and dielectric strengths, as it is the case in the usual sum form. In spite of the mathematical equivalence of the two procedures, it will be shown that the former method provides a manner to estimate the importance of the interaction between the different relaxing units in the dielectric response of the system.

After a brief review of the fundamentals of the product form, we will analyse the dispersion observed in two betaine compounds chosen as illustrative examples: the mixed crystal (betaine phosphate)$_{0.75}$(betaine arsenate)$_{0.25}$ [(BP)$_{0.75}$(BA)$_{0.25}$] and betaine potassium iodide dihydrate (BKI).

2. The fundamentals of the product form

The factorized form of the dielectric function is based on the assumption that the analytic continuation of the dielectric function in the complex frequency plane $\tilde{\omega} = \omega + i\phi$, $\varepsilon(\tilde{\omega})$, is squared integrable on the real frequency axis [6], regular on the positive imaginary half complex plane (requirement of causality) [2, 6], and does not possess essential singularities[6] and continuous domains of singularities in the negative imaginary half plane [2, 5]. From the

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[6] The function $f(z)$ has an essential singularity at $z = a$ if the Laurent series of $f(z)$ in the vicinity of $z = a$ contains an infinite number of non-zero coefficients a_i with $i < 0$.

first condition, it follows that the contribution of dc conductivity to the dielectric loss, which originates from a pole at $\omega = 0$, cannot be directly accounted for and must be considered separately[7]. From the latter simplifying assumption (absence of essential singularities and continuous domains of singularities) it follows that $\varepsilon(\tilde{\omega})$ can be written as [5]

$$\varepsilon(\tilde{\omega}) = \frac{\prod_{m=1}^{M} (\tilde{\omega} - \tilde{z}_m)}{\prod_{n=1}^{N} (\tilde{\omega} - \tilde{p}_n)} \varphi(\tilde{\omega}), \tag{2}$$

where M and N represent the number of complex zeros ($\tilde{z}$) and poles ($\tilde{p}$) on the negative imaginary half plane, respectively, and $\varphi(\tilde{\omega})$ is any bounded analytic function with non-zero modulus.

Because the linear susceptibility must vanish for any complex frequency $\tilde{\omega}$ of infinite modulus, the generalized dielectric function $\varepsilon(\tilde{\omega}) \to 1$ as $|\tilde{\omega}| \to \infty$. It is therefore a simple consequence of the theorem of Liouville [7] that $\varphi(\tilde{\omega})$ must be a constant. From the limiting condition $\varepsilon(\tilde{\omega}) \to 1$, such a constant must be $\varphi(\tilde{\omega}) = 1$ and the number of poles equal to the number of zeros ($M = N$). The simplest form of the dielectric function is therefore the projection on the real frequency axis of $\varepsilon(\tilde{\omega})$ (see the theorem of Titchmarsh in [6, 8]), i.e.:

$$\varepsilon(\omega) = \prod_{n=1}^{N} \frac{\omega - \tilde{z}_n}{\omega - \tilde{p}_n} \qquad \omega \in \Re. \tag{3}$$

The product model of Debye relaxors results from the particular contribution of the purely imaginary poles and zeros that can occur in the negative half of the imaginary axis ($\tilde{p}_k = -\mathrm{i}p_k$; $\tilde{z}_k = -\mathrm{i}z_k$; $z_k, p_k \in \Re^+$). The contribution of N such pairs to the dielectric function is expressed as

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{k=1}^{N} \frac{\omega + \mathrm{i}z_k}{\omega + \mathrm{i}p_k}, \tag{4}$$

where ε_∞ is the contribution (real) to $\varepsilon(\omega)$ resulting from the set of all pairs of poles and zeros with real frequencies $\upsilon \gg \omega$. As can be easily seen, a single pair corresponds to a Debye unit:

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\omega + \mathrm{i}z}{\omega + \mathrm{i}p} = \varepsilon_\infty \left[\frac{\omega + \mathrm{i}z}{\omega + \mathrm{i}p} - 1 + 1 \right] = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \frac{\omega}{\mathrm{i}p}}, \tag{5}$$

with a dielectric strength $\Delta\varepsilon = \varepsilon_\infty(\frac{z}{p} - 1)$.

In multi-dispersive systems, the contribution of each polar relaxing unit (i.e., a pair of one imaginary zero and one imaginary pole) to the static dielectric constant depends on the global distribution of poles and zeros. In fact, if $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty = \varepsilon_\infty(-1 + \prod_{i=1}^{N} \frac{z_i}{p_i})$ is to be expressed as a sum of the contributions of different relaxing units, i.e. $\Delta\varepsilon = \sum_{i=1}^{N} \Delta\varepsilon_i$, then, similar to the case of *reststrahlen* [2], the dielectric strength of each unit must be defined as [5]

$$\Delta\varepsilon_i = \varepsilon_\infty \frac{1}{p_i} \frac{\prod_{k=1}^{N} (z_k - p_i)}{\prod_{k \neq i} (p_k - p_i)}. \tag{6}$$

This fact is generally overlooked because the conventional sum model suggests that the dielectric response of a poly-dispersive system results from the superposition of independent contributions. However, it is well known that the presence of other polar degrees of freedom contributes to generating a reaction field that alters the local field acting on a given relaxing unit. The dielectric strength of one Debye pair remains approximately unaffected ($\Delta\varepsilon_i = \varepsilon_\infty(\frac{z_i}{p_i} - 1)$) only if the reaction field due to the other relaxing units can be ignored.

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[7] For dc-loss dielectrics, a Drude term must be added to the product form to describe the contribution of conductivity.

As can be seen from equation (6), this situation corresponds to the limiting case where the frequencies of the different relaxing entities are well apart (i.e. $\frac{z_k - p_i}{p_k - p_i} \approx 1$; $k \neq i$).

The product model of Debye relaxing units, expressed by equation (4), includes as a particular case a generalization of the Lyddane–Sach–Teller (LST) relation [9] to relaxation phenomena ($\frac{\varepsilon(0)}{\varepsilon_\infty} = \prod_{i=1}^{N} \frac{z_i}{p_i}$). The LST relation was originally derived for resonance [9–12] by using more or less detailed arguments which involved the introduction of a microscopic charge in each unit cell, the consideration of the difference between the macroscopic and the local field, and the use of a Lorentz cavity. However, Barker [13] has shown that such type of relation could be directly obtained from the Kramers–Kronig theorem by assuming that the dielectric loss falls off at high frequencies, is zero at zero frequency, and has a peak located at a finite frequency. These general requirements indicate that the LST has a validity that goes beyond resonance. This led Barker to deduce, for the first time, the above LST relation for relaxation and to call attention to the fact that the pole and zero frequencies enter the LST relation linearly and not quadratically as in the case of resonance [13]. The reason for such a difference can be understood by the relationship between the product form of Debye units and the factorized form for relaxation proposed in [5].

3. Experimental details

Let us now consider two simple examples of dielectric relaxation data that have been chosen to illustrate cases where the interactions between the relaxing units are important or can be neglected. As referred to above, these examples are the dispersion observed in the vicinity of the paraelectric to antiferroelectric phase transition in (betaine phosphate)$_{0.75}$(betaine arsenate)$_{0.25}$ and the structural phase transition of betaine potassium iodide.

### 3.1. Betaine phosphate–betaine arsenate mixed crystals

Ferroelectric betaine arsenate (BA) and antiferroelectric betaine phosphate (BP) have similar structures [14, 15], and mixed crystalline solid solutions (BP)$_{1-x}$(BA)$_x$ can be grown over the full concentration range [16, 17]. In the pure end-members, the nature of the atom (X = As, P) occupying the centre of the inorganic XO_4 tetrahedra (which, in the crystal structure, are ordered in quasi-one dimensional chains) determines the nature of the cooperative phase stabilized at low temperatures. In a mixed solid solution, the competition between ferro and antiferro interactions gives rise to the complex and not fully elucidated dielectric behaviour observed at low temperatures.

Figure 1 shows the temperature dependence of the real (ε_b') and the imaginary (ε_b'') components of the dielectric function, measured at 100 kHz on cooling. The insets in the figure illustrate the type of hysteresis loops observed in different temperature ranges.

In agreement with previous results [18], the complex dielectric constant of $BA_{0.25}BP_{0.75}$ displays anomalies at $T_{AF} = 83$ K and $T^* = 75$ K. The anomaly at 83 K appears as a rather diffuse shoulder and marks the onset of the antiferroelectric (AF) phase. This phase exhibits some peculiar characteristics. The critical field of the hysteresis loops decreases with decreasing temperatures, which is uncommon for a typical antiferroelectric phase. The origin of the sharp anomaly observed at $T^* = 75$ K is not clear, and it has been tentatively related either to an additional structural transition [18] or to an internal bias field induced by the inclusion of arsenate [19]. The transition into a low temperature phase is marked by the broad anomalies observed in $\varepsilon'(T)$ and $\varepsilon''(T)$ at $T \sim 50$ K [19]. From the analysis of hysteresis loop measurements, this phase was identified as a slightly polar phase (see figure 1).
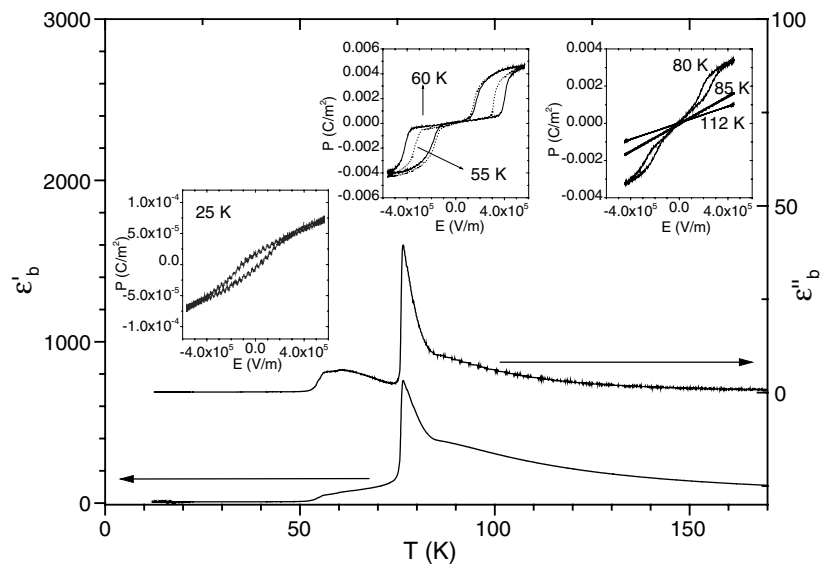
Figure 1. The temperature dependence of the real and imaginary parts of the dielectric function of $(BP)_{0.75}(BA)_{0.25}$ mixed crystal measured along the polar axis **b**. The insets show examples of the hysteresis loops observed in different temperature ranges.
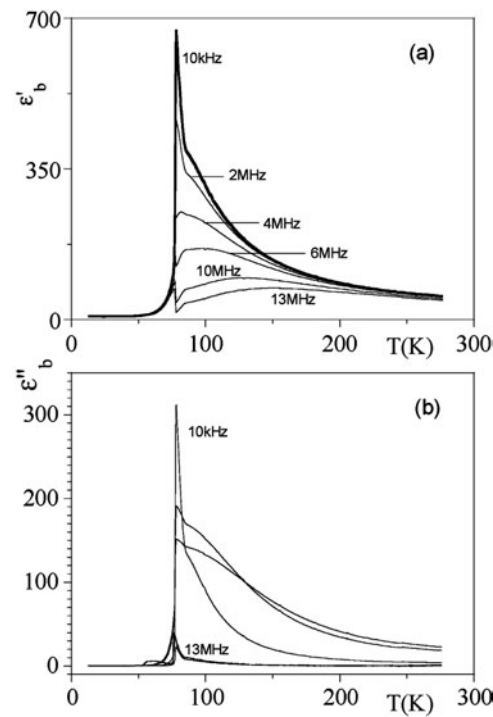
Figure 2. The dielectric dispersion observed in $(BP)_{0.75}(BA)_{0.25}$ in the vicinity of the transition between the paraelectric and the antiferroelectric phase ($T_{c1} = 85$ K).
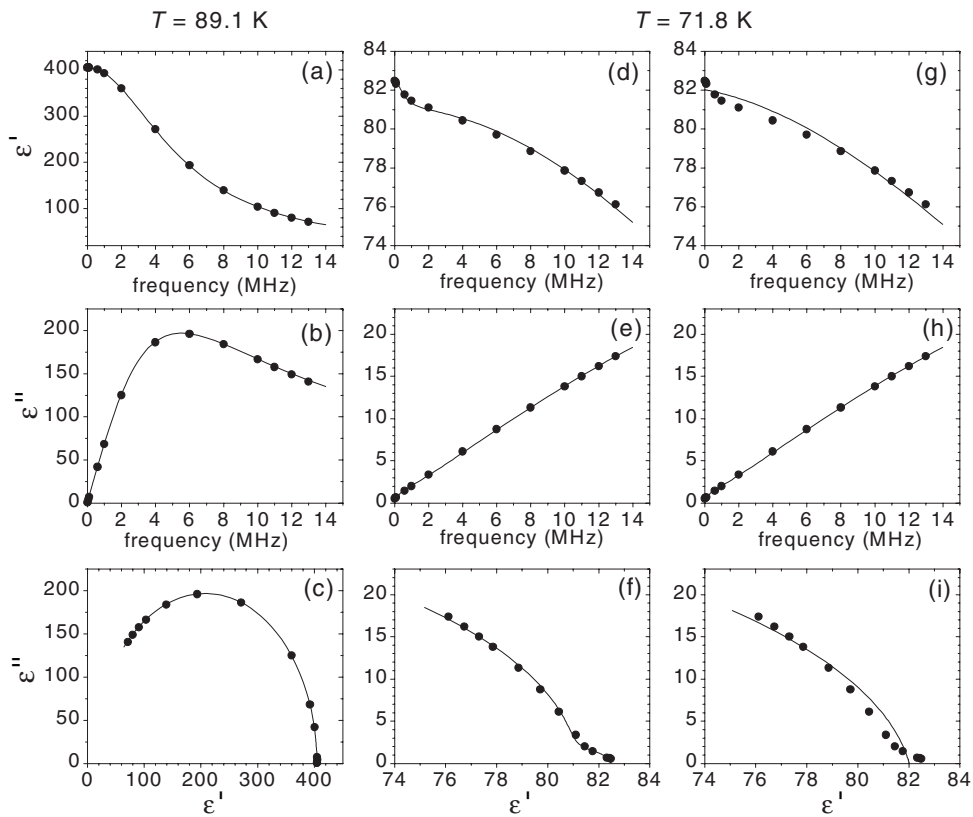
Figure 3. The frequency dependence of ε'_b and ε''_b and Cole–Cole plots observed above ($T = 89.1$ K; (a)–(c)) and below T_{c2} ($T = 71.8$ K; (d)–(i)) in $(BP)_{0.75}(BA)_{0.25}$. The fittings of the data to the product form and to the empirical Cole–Cole formula are shown for comparison in (d)–(f) and (g)–(i), respectively.

As can be seen in figure 2, in the vicinity of T_{AF} and T^* both ε'_b and ε''_b display strong frequency dispersion. This dispersion was analysed by fitting the data to the Cole–Cole empirical law [20]. It has been found that above $T^* = 75$ K the relaxation is mono-dispersive (Cole–Cole parameter $\beta = 1$). Below this temperature the value of β decreases continuously down to 0.85, indicating that the system becomes poly-dispersive at low temperatures.

Alternatively, the data were fitted to the product model of Debye relaxors (equation (5)). Figure 3 shows typical examples of the frequency dependence of $\varepsilon'(T)$ and $\varepsilon''(T)$, observed above and below T_{c2}, as well as the corresponding Cole–Cole plots. As can be seen, while for $T > T^*$ the data can be fitted by adjusting a single pole–zero pair (Debye behaviour, figures 3(a)–(c)), for $T < T^*$ one observes the appearance of one additional low frequency mode that is responsible for the deformation of the Cole–Cole plot (figures 3(d)–(f), $T = 71.8$ K). For comparison, the best fittings of the same data to the empirical Cole–Cole formula $\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1-(i\omega\tau)^\beta}$ (with $\Delta\varepsilon = 70.8$, $\tau = 1.94 \times 10^{-8}$ s and $\beta = 0.943$) are shown in figures 3(g)–(i). It is clear that these fittings fail to provide a description of the dispersion as accurate as the analysis based on the product model and do not clarify the poly-dispersive nature of the response of the system for $T < T^*$.

As illustrated in figure 4, the parameters of the fit to equation (4) reflect the onset of the AF phase at $T_{AF} = 85$ K: different slopes are observed above and below T_{AF} in $\varepsilon_\infty(T)$ (see the inset
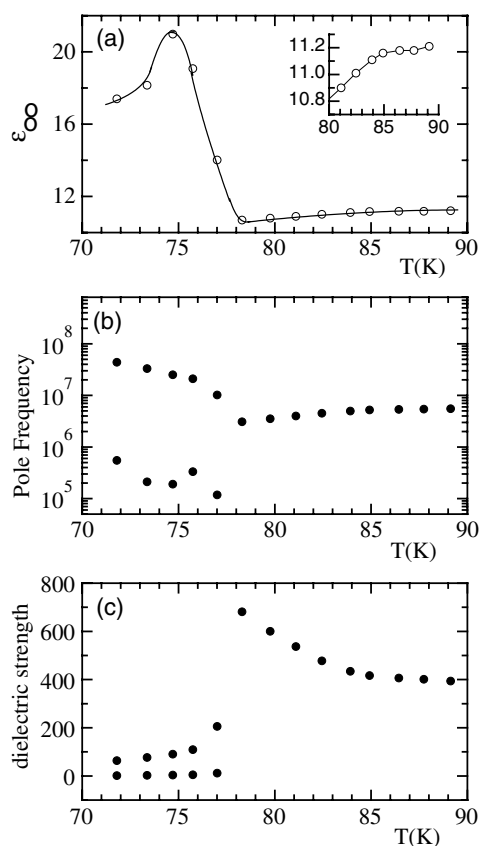
Figure 4. The temperature dependence of (a) ε_∞; (b) pole frequency and (c) dielectric strength. The parameters of the model show anomalies at $T_{AF} = 85$ K and $T^* = 75$ K. The appearance of an additional relaxational mode is observed at T^*.

in figure 4(a)), in the pole frequency $\omega_p(T)$ (figure 4(b)) and in the pole strength (figure 4(c)). However, below T^*, the frequency of the high temperature relaxational mode starts to increase on cooling and an additional low frequency mode appears. Similar to the bifurcations of some lattice modes [19], observed by infrared or Raman spectroscopy, this *bifurcation* of the relaxational mode may point out the occurrence of some structural transformation at T^*.

3.2. Betaine potassium iodide dihydrate (BKI)

At room temperature, paraelectric betaine potassium iodide dihydrate $[(CH_3)_3NCH_2COO]_2\cdot$KI$\cdot$2H$_2$O is triclinic (space group $P\bar{1}$ (No. 2); $a = 5.653(2)$ Å, $b = 5.894(2)$ Å, $c = 14.02(1)$ Å, $\alpha = 82.23(4)°$, $\beta = 82.16(4)°$, $\gamma = 73.22(2)°$; $Z = 1$) [21]. At about $T_c = 100$ K a structural phase transition to a non-polar phase occurs, which is marked by a strongly dispersive anomaly in the dielectric constant [22, 23]. This anomaly can be detected along different crystallographic directions but it is more intense along the $[\bar{1}10]$ axis (see figure 5, from [19]).

The nature of the phase transition in BKI is not fully elucidated, and the determination of the symmetry of the low temperature phase is presently in progress. Detailed Raman studies disclosed several aspects of the lattice dynamics [24] that can be summarized as follows:
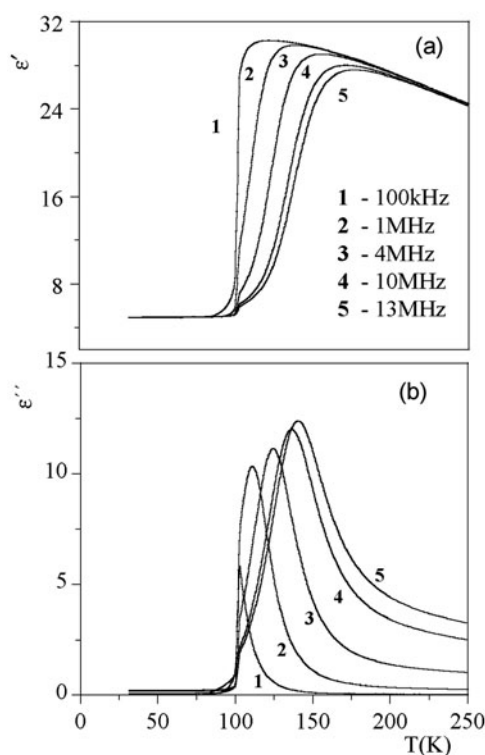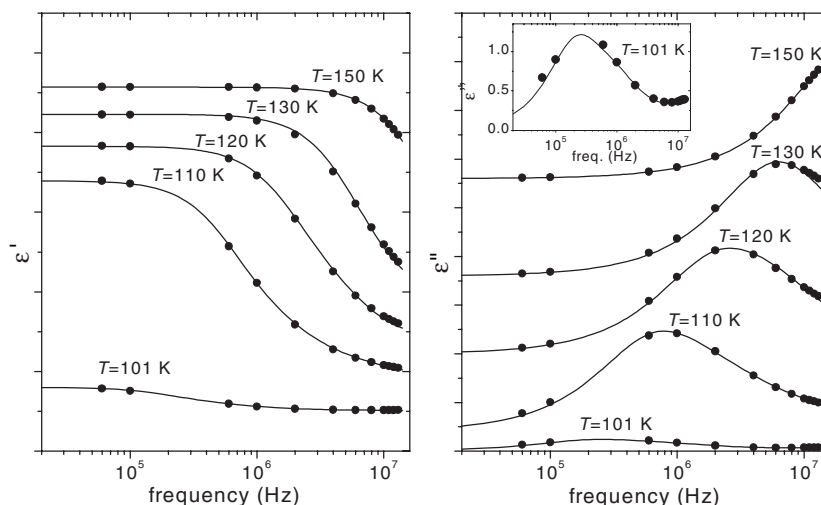
Figure 5. The temperature dependence of the real (a) and imaginary (b) parts of the dielectric constant of BKI, measured along the direction (frequency range 100 kHz–13 MHz; see [22]).

(i) the stretching vibration bands of water, located around 3500 cm^{-1}, are very broad and weak at ambient temperature, and become intense and narrow on cooling towards T_c;

(ii) several Raman lines (such as the one detected at 175 cm^{-1} assigned to a betaine libration mode) exhibit gradual hardening and narrowing on cooling;

(iii) on crossing the phase transition several additional modes appear, particularly below 200 cm^{-1} (external modes), indicating a discontinuous symmetry reduction;

(iv) above T_c some additional modes are detected, indicating a pre-transitional short range ordering occurring in small regions of the sample.

The analysis of the Raman spectra suggests that the motion of the water exhibits a considerable slowing down and a gradual freezing, which is likely to be related to the reinforcement of the H-bonds linking the crystal water to the carboxylic group of betaine. This effect may originate the driving mechanism of the phase transition.

The dispersion observed in the dielectric constant measured along $[\bar{1}10]$ is shown in figure 5 (spectral range 100 kHz–13 MHz). The data have been previously analysed by considering a superposition of Cole–Cole functions [23], it being concluded that the system becomes progressively poly-dispersive on cooling towards T_c (the Cole–Cole parameter decreases from $\beta = 1$ above 150 K to $\beta = 0.8$ near 100 K).

Consider, alternatively, the analysis based on the product model of Debye relaxors. Figure 6 displays the frequency dependence of the real (ε') and the imaginary (ε'') parts of the dielectric function. As can be seen, the relaxational mode can only be partially detected at $T = 150$ K in the frequency range available. Moreover, below the phase transition the

Figure 6. The frequency dependence of the real and imaginary dielectric constant of BKI measured at different temperatures above $T_c = 100$ K. The curves correspond to the best fits of the data to the product model (equation (4)).

intensities of the relaxational modes are strongly reduced. Therefore, the dispersion data can only be reliably analysed in the narrow temperature range 150–100 K, only providing information on the pre-transitional critical behaviour.

The continuous lines in figure 6 represent the best fits of the data to the product model. Above $T = 130$ K the system shows a Debye behaviour characterized by a single relaxation frequency showing a critical slowing down. On cooling, additional weak modes are detected in the vicinity of T_c, with characteristic frequencies higher than that of the main mode. Similar to the case found in the Raman spectra, the detection of additional modes just above the phase transition may testify to either the onset of short-range order, anticipating the structural transformation, or the presence of other weak modes that cannot be disclosed at higher temperatures due to their higher frequencies or to the much higher intensity of the main mode.
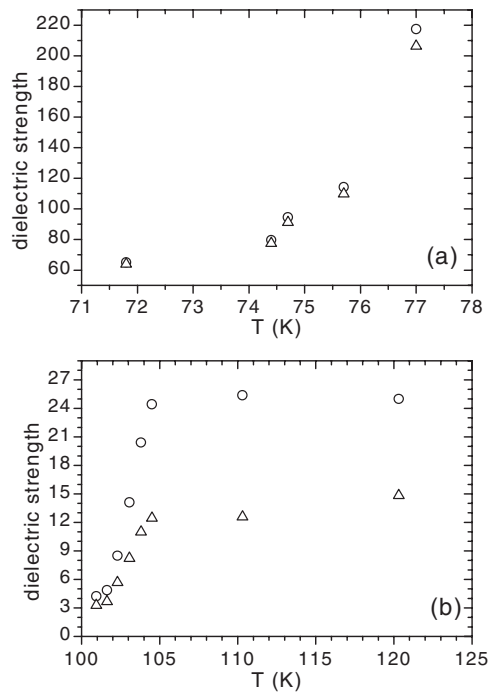
The temperature dependence of the pole frequencies and the pole strengths (see equation (5)) of the different modes is depicted in figure 7. The softening of the main relaxational mode is evident, as well as the progressive decrease of its dielectric strength. This behaviour is consistent with the hypothesis of the progressive freezing of the water molecules, which may represent the most important mechanism that triggers the phase transition in BKI.

4. Discussion and conclusion

The two examples analysed in the previous section show that the product form allows reliable fits of relaxational data that provide more information than those obtained from the use of empirical formulae such as the Cole–Cole equation. Because of their mathematical equivalence, a similar analysis by using the conventional sum form would disclose the same information in what concerns the number and location of the poles (i.e. the distribution of relaxation times) and the dielectric strengths. However, we note that the zeros of the dielectric function are not directly fitted when the sum form is used. For a single Debye unit, the zero can be calculated from the dielectric strength and pole as $z = [\frac{\Delta\varepsilon + \varepsilon_\infty}{\varepsilon_\infty}]p$. For a poly-dispersive material, the values calculated in this manner, $\tilde{z}_i = [\frac{\Delta\varepsilon_i + \varepsilon_\infty}{\varepsilon_\infty}]p_i$, do not correspond to actual
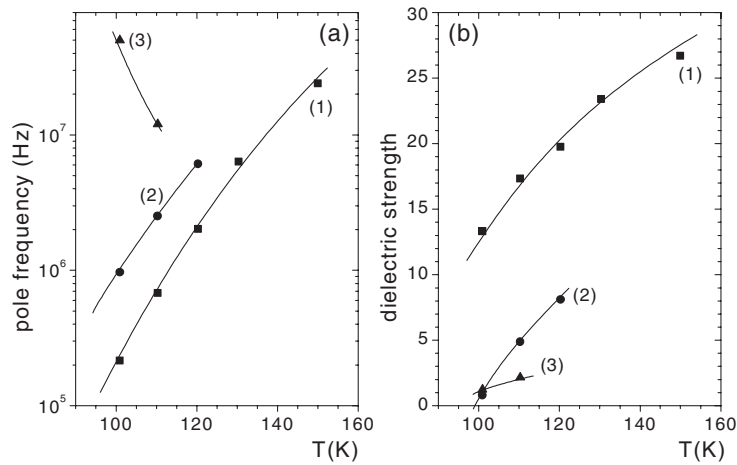
Figure 7. The temperature dependence of the pole frequencies (a) and dielectric strength (b) according to the fit of dispersion data of BKI to equation (4).

Figure 8. The temperature dependence of Δ_{TOTAL} (circles) and Δ_{IND} (triangles) calculated for BA–BP (a) and BKI (b).

zeros of the dielectric function and may not verify the condition of alternate with each pole in the negative imaginary axis [13].

The importance of coupling between the different relaxing units for the building up of the dielectric response of a given system can be estimated from the knowledge of the values of the imaginary zeros and poles directly provided by the fit of the data to the product form. In fact, it is clear that the total dielectric strength resulting from relaxational mechanisms (Δ_{TOTAL}) must be

obtained by summing up the individual dielectric strengths given by equation (6). On the other hand, if the different relaxing units were completely independent, the total dielectric strength (Δ_{IND}) could be expressed as the sum of contributions that would depend only on the local values of zeros and poles, i.e. $\Delta_{\text{IND}} = \sum \varepsilon_{\infty}(\frac{z_i}{p_i} - 1)$. In general, the quantities Δ_{TOTAL} and Δ_{IND} may be substantially different depending on the importance of the cooperative response resulting from the interaction of the different units.

Figure 8 shows the temperature dependence of Δ_{TOTAL} and Δ_{IND} calculated for BA–BP (a) and BKI (b). As can be seen, while the two values nearly coincide for BA-BP, they are remarkably different for BKI, particularly for $T \geqslant 105$ K. This indicates that the interaction between the relaxing units can be ignored for the first compound (the frequencies of the modes are well separated, so they do not influence each other) but it is essential for the dielectric response of BKI. In this latter case, the local field acting on each unit is modified by the presence of other relaxing permanent dipoles, particularly at a close vicinity of the structural phase transition.

In conclusion, the product form of Debye relaxors is founded on very general grounds and represents a simple alternative to the use of the conventional sum model. It allows accurate descriptions of relaxational data that may help in clarifying not only the physical mechanisms underlying the relaxation phenomena but also the relative importance of cooperative effects on the dielectric response observed on a given compound.

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