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AC and DC conductivity correlation: The coefficient of Barton–Nakajima–Namikawa relation

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ABSTRACT

It has been some time since an empirical relation, which correlates DC with AC conductivity and contains a loosely defined coefficient thought to be of order one, was introduced by Barton, Nakajima and Namikawa. In this work, we derived this relation assuming that the conductive response consists of a superposition of DC conductivity and an AC conductivity term which materialized through a Havriliak–Negami dielectric function. The coefficient was found to depend on the Havriliak–Negami shape parameters as well as on the ratio of two characteristic time scales of ions motion which are related to ionic polarization mechanism and the onset of AC conductivity. The results are discussed in relation to other relevant publications, and they also applied to a polymeric material. Both theoretical predictions and experimental evaluations of the BNN coefficient are in an excellent agreement, while this coefficient shows a gradual reduction as the temperature increases.

1. Introduction

Nearly four decades ago, an empirical relation was introduced by Barton, Nakajima and Namikawa which is known as BNN relation [1–3]. This expression correlates the electrical conductivity to the dielectric strength of the lower frequency polarization mechanism through

$$\sigma_0 = p\varepsilon_0 \Delta\varepsilon \omega_{\max}, \quad (1)$$

where p is a loosely defined parameter, expected to be of order 1, σ_0 is the apparent DC conductivity, $\Delta\varepsilon$ is the dielectric strength, $\omega_{\max}$ is the angular frequency which corresponds to the maximum value of dielectric losses, and ε_0 is the permittivity of vacuum. The loss peak which associated to $\Delta\varepsilon$ is, in general, characterized as broad. $\Delta\varepsilon$ may arise entirely from mobile charge effects and not involve bulk dielectric effects at all. When Eq. (1) is satisfied, both AC and DC conductivity may arise from the same type of charge transport mechanism [4,5].

The BNN relation has played an important role in the analysis and the treatment of frequency response dielectric data [6–11], assuming that $p \sim 1$ with most of the corresponding works dealing with the scaling and universality issues of AC conductivity. In the literature a large number of different conductive disordered materials have been found to satisfy Eq. (1). The BNN relation is valid not only in amorphous solids, ionic glasses, single crystals and polymers but also in a variety of other materials such as microporous systems [12] and proteins in hydrated state [13]. The reported values of the coefficient p vary significantly, about three orders of magnitude from less than one up to a few hundred [1–5]. However, for a variety of materials, the p value falls mostly in the range from 0.5 to 10 [14], while in the majority of the cases the p value is near unity, as is shown as well in Fig. 3 of Ref. [9].

The factors affecting the accurate estimation of p value are discussed in Refs. [14,15]. However, some aspects should be mentioned here which are related to the electrode effects. In the case of fully-blocking electrodes, if the data do not extend to the region where $\sigma'(\omega)$ decreases towards zero in the lower-frequency plateau, the result might not define the DC conductivity accurately. In the case of partial-blocking electrodes behavior two regions of constant $\sigma'(\omega)$ values could possibly appear [16]. In such cases it could be possible that the higher-frequency plateau region would lead to a more plausible p estimate than the lower-frequency one, even though the latter is considered as the DC conductivity [16].

In the various models, which have been proposed for the description of the dielectric response of disordered conductive materials, the BNN relation has been used as a testing equation through the calculation of p coefficient [7,9,17,18]. The value of p is definitive, in order one to classify conductive materials. According to Hunt [19], the role of Coulomb interactions in the derivation of the BNN relation is of great importance, while the non-universality of the high frequency limit of the AC conductivity is incompatible with a universality in the BNN relation [20]. However, various models proposed for a particular kind of materials, such as ionic glasses and disordered conductors, give universal values for the BNN coefficient p. Dyre [7] obtains a value of $p = 0.42$ by using the random energy barrier model. In a subsequent work Dyre and Schrøder [9] reported a value of $p = 1.5 \pm 0.4$

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for the simulation of the symmetric hopping model in the extreme disorder limit. It has been pointed out by Macdonald [6] that the K1 conducting-system model could lead to a quantitative value for p, which depends on the value of β_{1C} of the Kohlrauch–Williams–Watts (KWW) stretched exponential response function. For ion-conducting homogeneous glasses and single crystals with charge motion allowed in all three dimensions, it has been shown that the only possible value is $\beta_{1C}=1/3$, and the resulting high frequency limiting response power law exponent is equal to 2/3 [18]. According to these values, the BNN coefficient has a universal value of $p=1.65$, while in the framework of the K1 model, as $\beta_{1C}\to 1$, p should also approach unity in the limit. In a recent paper Macdonald [15] has provided a detailed analysis and p estimates for the variety of conductive-system models. These models involving a single fractional exponent, for an appreciable range of exponent values, show that the p values are quite near 1.

A modified BNN relation has been suggested by Dygas in Ref. [21]. It proposed that the values of modified p coefficient are related to the spatial extent and time scale of nonrandom local hopping of charge carriers. It also gave an expression of the BNN coefficient in the case of Cole–Cole dielectric behavior of ionic polarization mechanism.

The BNN equation quantifies the relation between short range and long range ions motion of the AC response of conductive materials. To be specific the p coefficient reflects a measure of the correlation between AC and DC conductivity. In the present work, we will attempt to derive the BNN coefficient based on impedance spectroscopy formalism, as well as on widely used phenomenological and empirical relations, and to discuss the results with relevant published works. The exact knowledge of the parameters on which the p coefficient depends is of great importance, not only from the fundamental point of view, but also for applications, because this could lead to design and development of a variety of materials with predetermined dielectric and electrical properties.

2. Theoretical considerations

The complex conductivity $\sigma^*(\omega)=\sigma'(\omega)+j\sigma''(\omega)$ is connected to the total complex dielectric constant $\varepsilon^*(\omega)=\varepsilon'(\omega)-j\varepsilon''(\omega)$ via the following relation

$$\sigma^*(\omega)=j\omega\varepsilon_0\varepsilon^*(\omega). \tag{2}$$

In the above relation, if the contribution of the DC conductivity, σ_0, is subtracted from $\varepsilon^*(\omega)$, then

$$\sigma^*(\omega)=\sigma_0+j\omega\varepsilon_0\varepsilon_d^*(\omega), \tag{3}$$

where $\varepsilon_d^*(\omega)$ represents the complex dielectric constant caused only from the dynamic conductivity.

In ionic materials, the description of the real part of complex conductivity spectra in the low frequency regime, below 100 MHz, and in the absence of electrode polarization effects, is given by the equation [22–26]

$$\sigma'(\omega)=\sigma_0\left[1+\left(\frac{\omega}{\omega_0}\right)^n\right], \tag{4}$$

where n (with $0<n<1$) is a constant. The characteristic frequency ω_0 corresponds to the onset of AC conductivity. At this frequency, the real part of complex conductivity becomes twice to that of the DC conductivity, $\sigma'(\omega_0)=2\sigma_0$. This last equation has been introduced in Ref. [27], in order to describe crystals with defects and an activated number of charge carriers. Eq. (4) cannot be taken as a model relation, because it is not able to reproduce the individual AC response characteristics which are derived from other functions of impedance spectroscopy (i.e. the peak and the dielectric strength, in $\varepsilon^*(\omega)$ formalism when ionic dispersions take place). Eq. (4) is considered as a relation which approximates well only the frequency dependence of the real part σ', since at low frequencies, σ' describes the DC conductivity plateau of AC response, while at high frequencies, σ' describes the well-known Jonscher power law behavior [28]. In general, depending on the individual characteristics of $\varepsilon''_d(\omega)$ responses, Eq. (4) can or cannot describe satisfactorily the function $\sigma'(\omega)$ at the onset region.

If we assume that the real parts of Eqs. (2), (3) and (4) are equal not only at the high frequency limit but also at $\omega=\omega_0$, then in these cases, from Eqs. (2), (3) and (4) with $\omega=\omega_0$ we find

$$\sigma_0=\varepsilon_0\omega_0\varepsilon''(\omega_0)/2 \tag{5}$$

and

$$\sigma_0=\varepsilon_0\omega_0\varepsilon''_d(\omega_0). \tag{6}$$

So, in these cases the characteristic frequency, ω_0, should be defined also as the frequency at which the losses from the DC conductivity are equal to the respective ones of the dynamic conductivity, since $\varepsilon''(\omega_0)=2\varepsilon''_d(\omega_0)$.

3. The BNN relation

In what follows, let us consider that the conductive response of a disordered material in the frequency spectrum under study is characterized only by the existence of DC conductivity and an AC conductivity term. The latter is considered that includes entirely contribution due to mobile ions effects. These effects should lead to the appearance of a polarization mechanism in ε^* formalism, which should take place around the onset frequency ω_0, with loss peak frequency, ω_{max}, and strength $\Delta\varepsilon$. The real part of complex conductivity should be given by using Eq. (3), as follows:

$$\sigma'(\omega)=\sigma_0+\varepsilon_0\omega\varepsilon''_d(\omega). \tag{7}$$

The $\varepsilon''_d(\omega)$ should be considered as $\varepsilon''(\omega)$ conductive-system values, while for its description the well known and widely used Havrilak–Negami(H–N) empirical dielectric function is used here as well [29],

$$\varepsilon''_d(\omega)=\frac{\Delta\varepsilon\sin(\beta\phi)}{\left[1+2(\omega/\omega_{HN})^\alpha\cos(\alpha\pi/2)+(\omega/\omega_{HN})^{2\alpha}\right]^{\beta/2}} \tag{8}$$

where

$$\phi=\arctan\left(\frac{(\omega/\omega_{HN})^\alpha\sin(\alpha\pi/2)}{1+(\omega/\omega_{HN})^\alpha\cos(\alpha\pi/2)}\right). \tag{9}$$

The shape parameters take values in the range $0<\alpha,\beta\le 1$ and are closely related to the slopes in $\log\varepsilon''_d$ vs. $\log\omega$ plots ($\varepsilon''_d\sim\omega^\alpha$ at $\omega\ll\omega_{max}$ and $\varepsilon''_d\sim\omega^{-\alpha\beta}$ at $\omega\gg\omega_{max}$). It should be mentioned here that there exist models which have been proposed for the interpretation of the limiting behavior of the H–N relaxation function, a behavior that is related to the slopes α and $-\alpha\beta$ [30,31]. The limiting case of $\alpha=\beta=1$ corresponds to Debye behavior with a single relaxation time $\tau=1/\omega_{HN}$. The frequency ω_{HN} is related to ω_{max} through

$$\omega_{max}=A\omega_{HN}, \tag{10}$$

where

$$A=\left(\frac{\sin(\alpha\pi/(2\beta+2))}{\sin(\alpha\beta\pi/(2\beta+2))}\right)^{1/\alpha}. \tag{11}$$

The total dielectric losses should be written as

$$\varepsilon''(\omega)=\varepsilon''_d(\omega)+\varepsilon''_c(\omega), \tag{12}$$