ORIGINAL PAPER

Electrical conductivity and an approximate mean square displacement

R R Guimarães[1,2]*, D S Vieira[1,2], T Petrucci[1,3], H Mukai[1,3], P R G Fernandes[1,3] and R d S Mendes[1,2]

[1]Departamento de Física, Universidade Estadual de Maringá, Maringá, PR 87020-900, Brazil

[2]National Institute of Science and Technology for Complex Systems, CNPq, Rio de Janeiro 22290-180, Brazil

[3]National Institute of Science and Technology for Complex Fluids, CNPq, São Paulo 05508-090, Brazil

Abstract: Measurements of electrical properties of materials are of interest in diffusion experiments, where the mean square displacement of charge carriers plays a distinctive role. Here, an approximation of the mean square displacement is explored as a route to investigate dynamical aspects of systems from electrical conductivity, independently of the number of types of charge carriers. Within this framework, based on Kubo's linear response theory, we focus on the variance of the center of charges displacement. As an application of this approach, firstly we considered the impedance spectroscopy of a liquid crystal sample at specific experimental conditions. In a second employment of the approach, we discussed the use of the approximate (effective) mean square displacement in relation to an equivalent circuit modeling. Our analysis highlighted the sensitivity of the method in different situations. In addition, these situations are discussed in connection with anomalous diffusion. From a theoretical point of view, the results obtained here offer a basis for making use of effective models that assume the presence of anomalous diffusion.

1. Introduction

Electrical properties and their measurements are significant in several areas of science. In particular, the experimental technique of impedance spectroscopy (IS) plays an important role in the investigation of several materials. With the availability of commercially made impedance bridges covering wide frequency ranges, impedance (conductivity) studies became popular among electrochemists and materials scientists [1]. For instance, one can examine in semiconducting materials how electrically active foreign atoms influence the electrical conductivity. For example, in ion-conducting materials with negligible electronic conduction, one can inspect the conductivity results in connection with the hopping motion of ions. For such materials and many others, the measurement of the electrical conductivity is an indispensable quantity in order to investigate charge carrier diffusion.

Commonly, the diffusive behavior is classified in terms of the mean square displacement (MSD), $\langle r^2(t)\rangle$. The MSD is frequently related to random walks of particles and, in the Brownian (normal or usual) case, Einstein's relation, $\langle r^2(t)\rangle \propto t$, is valid; otherwise, an anomalous diffusion is present. For instance, in the field of solid-state ionics, $\langle r^2(t)\rangle$ refers to the MSD of charge carriers [2–5] and may not be proportional to t. In fact, in ion-conducting materials, if the charge carriers perform simple random walks, the subsequent motion of them are uncorrelated and $\langle r^2(t)\rangle$ increases linearly with t; if there is a correlation, $\langle r^2(t)\rangle$ can be proportional to t only for very small and very large times [6]. When there is only one type of mobile ion, a way to obtain $\langle r^2(t)\rangle$ is through frequency-dependent electrical conductivity, $\sigma(\omega)$, via Kubo's linear response theory [7–9]. Such approach has been successfully employed in the discussion of charge carrier diffusion in a variety of systems [5, 10–19]. Also, note that the MSD can be viewed as a key function to understand the dynamics of ions as it connects experimental spectra with model considerations [20, 21].

---

*Corresponding author, E-mail: renatofisuem@gmail.com

Typically, $\sigma(\omega)$ is obtained directly from impedance spectroscopy (IS) [22–24] measurements. This procedure, which provides the electrical response of a system through the application of a small external voltage $\mathcal{V}$, is largely used to investigate a great diversity of materials, for instance, solids [25–27], liquids [28–32], fuel cells [33–35] and biomaterials [36–38]. In general, to investigate the dynamics of ion transport in materials, where more than one type of charge carrier might be relevant, $\sigma(\omega)$ is a pivotal object to achieve a better understanding of charge carrier behavior [6], including the most diverse experimental conditions that can be imposed on a system. It is also important to mention that in many substances several types of ions may contribute to $\sigma(\omega)$ [39]. For example, a well-documented case is the so-called mixed alkali effect, in which the conductivity dramatically decreases in alkali oxide glasses when some of the alkali ions are replaced by ions of another species [40, 41]. In spite of that, when a relatively simple measurement like IS is applied to different types of materials, one does not have any additional information about each type of ion and their precise relevance or contribution to $\sigma(\omega)$ as well as the specific influence of the experimental conditions in several cases. Therefore, the goal here is to work around this limitation by exploring the possibility of considering a mean square displacement approximation that assumes the presence of several types of charge carriers. As a first application of this approximate MSD, we considered a liquid crystal. After obtaining IS data for the liquid crystal, we used the relationship between the MSD and $\sigma(\omega)$ to identify anomalous and normal diffusion regimes. Lastly, our approximate MSD was employed in connection with well-known equivalent circuits models used for the analysis of impedance spectroscopy data, where we also identified anomalous and normal diffusive regimes.

In the following section, we present the theoretical aspects concerning the approximate mean square displacement. In Sect. 3, we apply the approximate MSD to a liquid-crystalline sample, and we also employ the approximate MSD in connection with equivalent circuits models. In the last section, we present the conclusions.

2. Methods

Supported by Kubo's linear response theory [7], Roling and co-workers showed how to obtain $\langle r^2(t) \rangle$ of the ionic diffusion directly from $\sigma(\omega)$ if only one type of charge carrier in a bulk sample is present [8, 42, 43]. The resulting expression is

$$\langle r^2(t) \rangle = \frac{12k_{\mathrm{B}}TV}{q^2N\pi} \int_0^t \mathrm{d}t' \int_0^\infty \frac{Re[\sigma(\omega)H_R(\omega)]}{\omega} \sin(\omega t')\mathrm{d}\omega,$$

$$(1)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, V is the volume of the sample, q is the ionic charge, N is the number of charges and $H_R(\omega)$ is the generalized Haven ratio. In several situations, $H_R(\omega)$ can be approximated by a constant, H_R [44]. Essentially, H_R indicates the degree of ionic dissociation [6, 28, 45, 46] and is defined as D/D_σ, where D is the self-diffusion coefficient and D_σ is the diffusion coefficient. Generally, D is acquired via nuclear resonance measurements, while D_σ is obtained from conductivity measurements [47]. Another quantity that can be obtained is proportional to the mean square displacement of the center of charge of mobile ions, $\langle R^2(t) \rangle$ [5, 7, 10, 11], given by

$$\langle R^2(t) \rangle = \frac{12k_{\mathrm{B}}TV}{q^2N\pi} \int_0^t \mathrm{d}t' \int_0^\infty \frac{Re[\sigma(\omega)]}{\omega} \sin(\omega t')\mathrm{d}\omega, \quad (2)$$

where $\mathbf{R}$ is defined as

$$\mathbf{R} = \sqrt{N}\left(\frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \right), \quad (3)$$

with $\mathbf{r}_i$ being the position of the ith charge and N being the number of charge carriers. If $H_R(\omega)$ is constant, a comparison between Eqs. (1) and (2) enables us to write

$$\langle r^2(t) \rangle = H_R \langle R^2(t) \rangle. \quad (4)$$

In general, since H_R is not known for several materials, it is assumed as constant [48], and $\langle R^2(t) \rangle$ is used instead of $\langle r^2(t) \rangle$, given their proportionality. This framework has been successfully employed in discussions of systems involving only one type of charge carriers [5, 10–19]. Here, we are going to consider a generalization of this scheme for when there may be multiple types of charge carriers.

In this generalization, we employ the center of charge displacement,

$$\mathcal{R} = \sqrt{N}\left(\frac{\sum_{i=1}^N q_i\mathbf{r}_i}{\sum_{i=1}^N q_i} \right). \quad (5)$$

Note that if only one type of charge carrier is present, $q_i = q$, Eq. (3) is recovered. From Eq. (5), and adopting the procedure of Roling and co-workers [8], we can obtain the generalized mean square displacement of the mobile ions center of charge as a function of time in a similar way as in Eq. (2). This leads to

$$\langle \mathcal{R}^2(t) \rangle = \frac{12Nk_{\mathrm{B}}T}{\left(\sum_{i=1}^N q_i\right)^2\pi} \int_0^t \int_0^\infty \frac{Re\{\sigma(\omega)\}}{\omega} \sin(\omega t')\mathrm{d}\omega\mathrm{d}t',$$

$$(6)$$

which is the approximate mean square displacement to be employed here.

If there are several types of ions and one of them is the most relevant in a diffusive process, we may think, as a first approximation, that $\langle R^2(t) \rangle$ obtained from Eq. (2) could be seen as the MSD. However, when there are several relevant types of charge carriers, we propose to use $\langle \mathcal{R}^2(t) \rangle$ given in Eq. (6) to investigate the MSD instead of employing Eq. (2). Considering the sample holder as a whole in an IS measurement, $\sigma(\omega)$ captures, in addition to bulk effects, wall effects on electrodes among possible others. Similarly, because of Eq. (6), $\langle \mathcal{R}^2(t) \rangle$ encompasses an analogous amount of aspects. Interestingly, similar effective approaches were considered before [6, 49], although not as directly applicable as $\langle \mathcal{R}^2(t) \rangle$ proposed here. In fact, by putting the experimentally obtained $\sigma(\omega)$ in Eq. (6), we can promptly investigate the behavior of $\langle \mathcal{R}^2(t) \rangle$. Also, note that $\langle \mathcal{R}^2(t) \rangle$ essentially has the same contents as $Re\{\sigma(\omega)\}$ since there is basically an inverse Fourier transform in Eq. (6). These facts and the microscopic interpretation of $\langle \mathcal{R}^2(t) \rangle$ point toward the use of it as a possible framework to investigate systems by using IS data.

Observe that if there is only one type of charge carrier in Eq. (6), $q_i = q \; \forall \; i$, Eq. (2) is recovered. Similarly, if $\sigma(\omega) = \sigma$ (constant), it is verified that

$$\langle \mathcal{R}^2(t) \rangle = \left(\frac{6Vk_\mathrm{B}TRe\{\sigma\}}{\left(\sum_{i=1}^{N} q_i\right)^2 N} \right) t, \tag{7}$$

i.e., the usual Brownian regime for $\langle \mathcal{R}^2(t) \rangle$ is obtained.

The way σ depends on ω is of considerable interest for different materials [22, 50]. One of the first works on this issue was the one published by Jonscher [51], who showed that different kinds of conductors exhibit a threshold frequency (approximate) from which $\sigma(\omega)$ is not constant anymore. Nowadays, the presence of interactions and, consequently, correlations in the ions diffusion have been used to explain such type of frequency dependence on conductivity [22].

In view of this, the ionic conductivity has been commonly expressed as [2, 3, 22, 52]

$$\sigma(\omega) = \sigma_0 \left[1 + \left(\frac{\omega}{\omega_0} \right)^p \right], \quad \text{with} \quad 0 < p < 1, \tag{8}$$

in which σ_0 is the portion frequency—independent of $\sigma(\omega)$ and ω_0 is a dispersion frequency. From Eq. (8), when $\omega \lesssim \omega_0$, $Re\{\sigma(\omega)\} \approx \sigma_0 = $ constant; therefore, the diffusion is usual (Eq. 7). On the other hand, if $\omega \gtrsim \omega_0$, the diffusion is anomalous. In order to further understand this aspect, we consider the integrals in Eq. (6) with $Re\{\sigma(\omega)\} \propto \omega^p$. In this way, we have

$$\langle \mathcal{R}^2(t) \rangle \propto \int_0^t \int_0^\infty \frac{\omega^p}{\omega} \sin(\omega t') \mathrm{d}\omega \mathrm{d}t' \propto t^{1-p}. \tag{9}$$

This last proportionality can also be visualized via dimensional analysis. Indeed, as $\sin(\omega t)$ is dimensionless, we have $\omega \sim t^{-1}$ and consequently the integrals (9) in terms of t. As high (low) frequencies are related to short (long) times, by using the full Eq. (8), we obtain normal diffusion at long times and anomalous diffusion at short times as indicated by Eq. (9).

Particularly in anomalous diffusion, one usually has the power law

$$\langle r^2(t) \rangle = A\,t^\alpha, \tag{10}$$

with A constant. If $\alpha > 1$, the process is superdiffusive; if $\alpha < 1$, the process is subdiffusive; and $\alpha = 1$ refers to normal diffusion [53–55]. As pointed out before, in many cases $\langle r^2(t) \rangle = H_R \langle R^2(t) \rangle$ and Eq. (2) has been successfully used to investigate diffusion in solid materials when there is only one type of charge carrier. In particular, it was found that the dynamics of mobile ions is subdiffusive in short timescales, approaching normal diffusion in long timescales [5, 8, 11–18, 42, 48, 56–58].

After the theoretical extension conducted along this section, we are considering the possibility of using Eq. (6) and, consequently, Eq. (2) as special case, as an effective mean square displacement to investigate situations related to electrical conductivity. In the next section, we discuss the application of the approximate mean square displacement $\langle \mathcal{R}^2(t) \rangle$ to a liquid-crystalline sample and we also employ the approximate MSD in connection with equivalent circuits models.

3. Results and discussion

3.1. Application of $\langle \mathcal{R}^2(t) \rangle$ to a liquid crystal

When analyzing the liquid crystal sample studied here, it was observed that a bit modified Jonscher's expression seems to be more suitable for $\sigma(\omega)$ data, namely

$$\sigma(\omega) = \sigma_0 \left[1 + \left(\frac{\omega}{\omega_0} \right)^q \right]^{p/q}, \quad \text{with } 0 < p < 1 \text{ and } q = 2. \tag{11}$$

This equation has the same asymptotic behavior observed in Jonscher's formula (Eq. 8) and, when $p = 0$, one has normal diffusion, since $\sigma(\omega) = \sigma_0$. In comparison with Eq. (8), one advantage of Eq. (11) is it fits better to data that present a more pronounced increase in $\sigma(\omega)$ after the dispersion frequency.

Regarding the experimental procedures, a Solartron SI 1296 A impedance–gain phase analyzer was used to carry out impedance spectroscopy measurements. The frequency range employed was 10^3 Hz to 5 MHz, with the external voltage amplitude fixed at $\mathcal{V} = 10$ mV. The sample was placed between two stainless steel circular electrodes with an area of 3.14 cm^2, separated by a distance $d = 1.0$ mm, with the total volume of $v = 0.314$ ml. In advance of starting the measurements, the surface of the electrodes was decontaminated in two steps: first, by washing with detergent and deionized water and second, by an ultrasonic bath in acetone (C$_3$H$_6$O, molar mass = 58.08 g mol^{-1}) for 10 min.

The first step is to perform the fit of $\sigma(\omega)$ obtained via IS by using Eq. (11). Figure 1 shows $\sigma(\omega)$ as a function of ω for the investigated sample, a thermotropic liquid crystal E7, with temperature fixed at 52 °C. This figure also shows the fit with Eq. (11).

The values of the parameters from the best fit (adjusted $R^2 = 0.99$) are $\sigma_0 = 0.0948\,\Omega^{-1}$ cm^{-1} [0.0947; 0.0949]$_{95\%}$, $\omega_0 = 1.0241 \times 10^6$ Hz [0.9855×10^6; 1.0628×10^6]$_{95\%}$ and $p = 0.1747$ [0.1698; 0.1796]$_{95\%}$, where the values between brackets are the 95% confidence interval. By using $\langle \mathcal{R}^2(t) \rangle$ as an effective (approximate) mean square displacement, its calculation and comparison with Eq. (10) show a subdiffusion for $\omega \gtrsim \omega_0$ (or short times) with the proportionality constant $A = 0.0060$ [0.0059; 0.0061]$_{95\%}$ and exponent $\alpha = 0.827$ [0.826; 0.829]$_{95\%}$, as shown in Fig. 2 (green dotted line). This behavior is probably because the charge carriers in the E7 sample find large molecular clusters [59] as they move through the material. For large times ($\omega \lesssim \omega_0$), the $\langle \mathcal{R}^2(t) \rangle$ behavior approaches the usual regime, in which the fit parameters are $A = 0.047$ [0.045; 0.050]$_{95\%}$ and $\alpha = 0.978$ [0.974; 0.983]$_{95\%}$ (Fig. 2, red dashed line).
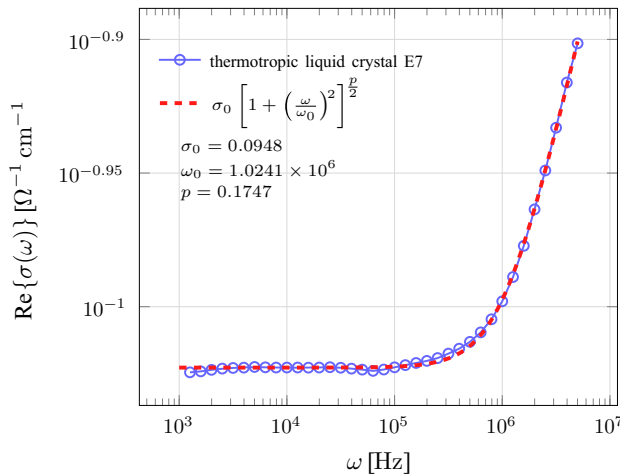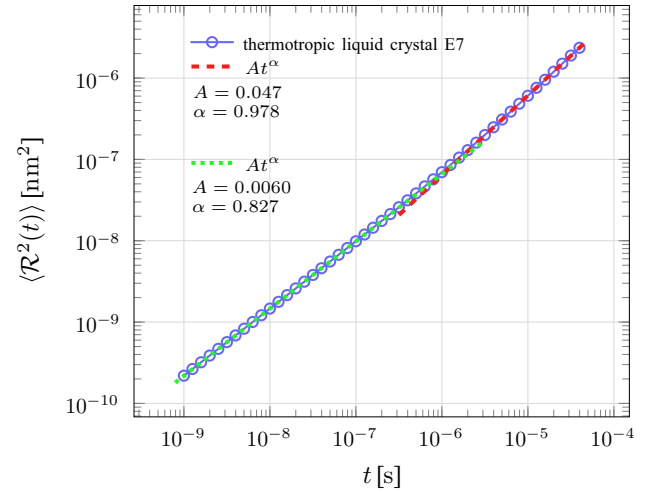

Fig. 2 Diffusive behavior of the charge carriers in the thermotropic liquid crystal E7 sample

This type of diffusive behavior has also been found when Eq. (2) is applied to solid samples. For example, for silver phosphate glasses, the silver ion migration presents $\langle R^2(t) \rangle \propto t^{1-p}$ at short times, where the exponent p varies between 0.65 and 0.68 for different temperatures and compositions, while at large times $\langle R^2(t) \rangle$ approaches the normal diffusive regime [12] ($\propto t$). Also, for silver ion dynamics in molybdophosphate glasses, $\langle R^2(t) \rangle \propto t^{0.40}$ at short times, approaching the normal diffusive regime at large times [13]. For ions in lithium phosphate, bismuth borate and borotellurite glasses, a similar behavior was observed, as $\langle R^2(t) \rangle \propto t^{1-p}$, with $p = 0.64 - 0.70$ depending on the composition of the glasses [15–18].

Thereof, our results reveal that an anomalous diffusion of the charge carriers, at least when one considers $\langle \mathcal{R}^2(t) \rangle$, may be present in the liquid crystal investigated here. Specifically, the exponent found for the anomalous case is smaller than one, which represents subdiffusive processes. This is an indication that the employment of $\langle \mathcal{R}^2(t) \rangle$ can be useful in the study of liquid materials.

Although not explored here, another application of $\langle \mathcal{R}^2(t) \rangle$ could be in the study of phase transitions. Conductivity as a function of frequency is constant for a frequency range, such as the initial plateau in Fig. 1. In general, the value of σ corresponding to this plateau is called σ_{dc} (dc conductivity) [22]. In Eq. (7), we saw that, in a general way, $\langle \mathcal{R}^2(t) \rangle = \mathcal{D}t$ when $\sigma(\omega) = \sigma_{dc} = $ constant. Along with the temperature dependence T in $\mathcal{D}$, σ_{dc} also has a temperature dependence given by the Arrhenius relation [15]. In a first-order phase transition, for instance, σ_{dc} may present a jump in its value as the temperature varies, which will directly correspond to a jump in the diffusion constant value $\mathcal{D}$. In this way, phase transitions

Fig. 1 Conductivity as a function of frequency for the thermotropic liquid crystal E7 sample

could also be investigated by employing the scenario of the approximate mean square displacement $\langle \mathcal{R}^2(t) \rangle$.

In the next subsection, we theoretically discuss the usage of the effective mean square displacement in equivalent circuits models used in impedance spectroscopy analysis.

3.2. Approximate mean square displacement in connection with equivalent circuits

Another approach widely used in connection with IS measurements is to fit the data by using equivalent circuits. These circuits are commonly composed by resistors and capacitors [22]. The simplest RC (resistor–capacitor) circuit is shown in Fig. 3.

This circuit provides a fairly simplified approximation of an electrolytic cell. Typically, the resistance represents the sample, and the capacitance corresponds to the electrodes. The connection with $\langle \mathcal{R}^2(t) \rangle$ is made by obtaining the equivalent impedance Z_{eq}. For the RC circuit in Fig. 3, the association between the resistor with resistance R and the capacitor with capacitance C leads to

$$\frac{1}{Z_{\text{eq}}} = \frac{1}{Z_R} + \frac{1}{Z_C} = \frac{1}{R} + i\omega C, \tag{12}$$

in which was used that the resistive and capacitive impedance are $Z_R = R$ and $Z_C = 1/(i\omega C)$, respectively. In turn, the conductivity is given by

$$\sigma(\omega) \propto \frac{1}{Z_{\text{eq}}}; \tag{13}$$

therefore, $Re\{\sigma(\omega)\} \propto Re\{1/Z_{\text{eq}}\} = 1/R = $ constant. Thus, by means of Eq. (6), a system that is well represented by the RC circuit presents only the normal diffusion (see Eq. (7)).

Generally, the modeling of experimental data requires more elaborate equivalent circuits. An example is a Randles circuit, which is one of the simplest and most common models used for many aqueous, conductive and ionic solutions [60]. It includes only a solution resistance R_{SOL}, a parallel combination of a double-layer capacitor C_{DL} and a charge transfer or polarization resistance R_{CT} (Fig. 4).
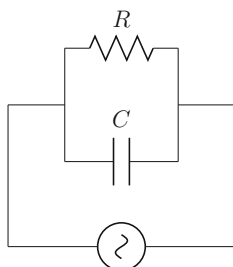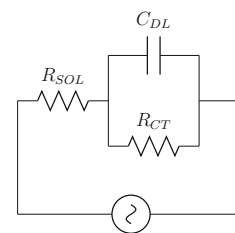

Fig. 3 Resistor–capacitor (RC) circuit

Fig. 4 Randles circuit

The details of current distribution in the Randles circuit are largely similar to those in the RC circuit, with the necessary correction for the presence of the additional series resistor R_{SOL}. The simplified Randles model is often the starting point for other more complex models, mainly for charge-transfer kinetic analysis in highly conductive solution systems not impeded by migration and diffusion mass-transport effects [60]. The circuit analysis results in the expression for total impedance of the circuit as

$$Z_{\text{eq}} = R_{\text{SOL}} + \frac{R_{\text{CT}}}{1 + (\omega R_{\text{CT}} C_{\text{DL}})^2} - i \frac{\omega R_{\text{CT}}^2 C_{\text{DL}}}{1 + (\omega R_{\text{CT}} C_{\text{DL}})^2}. \tag{14}$$

From this, the real part of conductivity can be evaluated as

$$Re\{\sigma(\omega)\} \propto Re\left\{\frac{1}{Z_{\text{eq}}}\right\} = \frac{R_{\text{SOL}} + B}{[R_{\text{SOL}} + B]^2 + D^2}, \tag{15}$$

where $B = R_{\text{CT}}/[1 + (\omega R_{\text{CT}} C_{\text{DL}})^2]$ and $D = \omega R_{\text{CT}} C_{\text{DL}} B$. From this result, the first analysis that can be conducted is to consider the limit case of $R_{\text{SOL}} \to 0$, which corresponds to the RC circuit case. At this limit, one obtains $Re\{\sigma(\omega)\} \propto 1/R_{\text{CT}} = $ constant; therefore, the diffusion is normal as expected. In a second analysis, the full Eq. (15) is considered and the integral in Eq. (6) can be numerically performed in order to obtain $\langle \mathcal{R}^2(t) \rangle$. The result is illustrated in Fig. 5 with $R_{\text{SOL}} = 20\,\Omega$, $R_{\text{CT}} = 350\,\Omega$ and $C_{\text{DL}} = 30\,\mu\text{F}$.

The system presents two separated normal diffusive regimes, which are mainly caused by the values of the resistances. For example, the inset in Fig. 5 shows $\langle \mathcal{R}^2(t) \rangle$ calculated with $R_{\text{SOL}} = 350\,\Omega$, $R_{\text{CT}} = 20\,\Omega$ and $C_{\text{DL}} = 30\,\mu\text{F}$. For this set of values, it is difficult to visualize another diffusive regime than the normal one. In general, equivalent circuits with more resistive and capacitive elements present a richer scenario for $\langle \mathcal{R}^2(t) \rangle$.

Another common equivalent circuit that has been used is the one with R_{SOL} replaced by a constant phase element (CPE), as shown in Fig. 6. In this type of circuit, the RC part represents the bulk of the sample, and the CPE represents the effects on the electrodes surfaces [22, 61].

The impedance of the CPE element is [60]

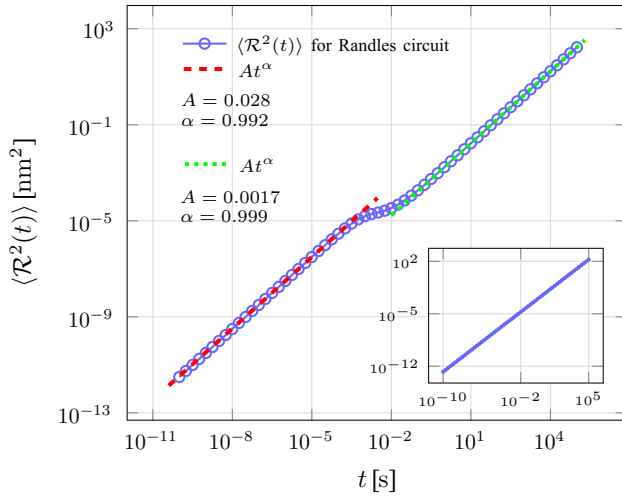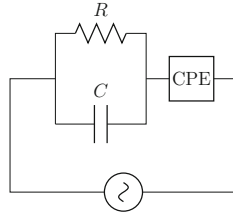$$Z_{\text{CPE}} = \tilde{T}(i\omega)^{-\nu}, \quad \text{with} \quad 0 < \nu < 1, \tag{16}$$

Fig. 5 Diffusive behavior of the charge carriers for a system described by a Randles circuit with typical values: $R_{SOL} = 20\,\Omega$, $R_{CT} = 350\,\Omega$ and $C_{DL} = 30\,\mu F$. The inset shows $\langle \mathcal{R}^2(t) \rangle$ calculated assuming $R_{SOL} = 350\,\Omega$, $R_{CT} = 20\,\Omega$ and $C_{DL} = 30\,\mu F$

Fig. 6 RC circuit connected in series with a constant phase element (CPE)

where $\tilde{T}$ and v are real phenomenological parameters that depend on the electrodes type and the solution, for the case of liquid samples. It can be noted that, when $v \to 0$ ($v \to 1$), Z_{CPE} is reduced to a resistance (capacitance). In general, the CPE element interpolates resistive and capacitive behaviors.

Instead of analyzing $\sigma(\omega)$ for this full circuit, for simplicity's sake, suppose that it comes down to just the CPE element. In this simplified scenario,

$$Re\{\sigma(\omega)\} \propto Re\left\{\frac{1}{Z_{CPE}}\right\} = \frac{\cos\left(\frac{v\pi}{2}\right)}{\tilde{T}}\,\omega^v. \quad (17)$$

Therefore, as done in Eq. (9), the CPE element corresponds to a subdiffusion of the charge carriers with a time exponent $1 - v$. This result indicates that systems which are best described by equivalent circuits with CPE elements present, to some degree, a subdiffusive aspect.

In general, following the line of reasoning shown above, we can connect $\sigma(\omega)$ to $\langle \mathcal{R}^2(t) \rangle$ for any equivalent circuit. However, a difficulty in using these circuits is the lack of a more detailed interpretation of the relation between the circuit elements and the physical system elements under consideration [22]. Note that, despite this difficulty, the use

of $Re\{\sigma(\omega)\} \propto Re\{1/Z_{eq}\}$ enables us to write the MSD for the system via Eq. (6).

4. Conclusions

To put the subject matter in its proper perspective, and to make clear the nature of our study about the dynamics of charge carriers, we have highlighted some aspects. From Eq. (6), the impedance spectroscopy data can be directly translated into an approximate (effective) mean square displacement for charge carriers. Also, the electrical conductivity, $\sigma(\omega)$, is basically connected with $\langle \mathcal{R}^2(t) \rangle$ via a Fourier transform. Furthermore, after using a general equation as in Eq. (10), the α exponent may quantitatively inform, at least approximately, the diffusive behavior of the full system. Thus, as an alternative of using only information from $\sigma(\omega)$ to investigate materials, we also indicate the employment of $\langle \mathcal{R}^2(t) \rangle$, mainly motivated by two attributes: $\langle \mathcal{R}^2(t) \rangle$ is interpreted as a microscopic feature of the random walk of the charge carriers and, when the use of an Eq. (10) like is suitable, the properties of $\sigma(\omega)$ are mapped into only two parameters, A and α. It must also be pointed out that the adequacy of $\langle \mathcal{R}^2(t) \rangle$ to investigate the dynamics of charge carriers is supported by several experimental results on solids and glasses [5, 8, 10–19, 42, 48, 56–58], where it was possible to assume one type of charge carrier, and by our present investigation on a liquid crystal, considering the possibility of many types of charge carriers and several experimental effects on the sample holder. Concerning equivalent circuits, and the sometimes complex interpretation of their elements, we verified that the $\langle \mathcal{R}^2(t) \rangle$ approach gives a very direct information regarding the diffusion, i.e., if it is normal or anomalous. From a theoretical point of view, these achievements give rise to the possibility of employing simple effective models assuming that anomalous diffusion is present or not. These facts enable us to claim that the effective anomalous diffusion approach explored here may be a simple, direct and concise route to investigate charge carrier dynamics in general, together with electrical properties of matter, from impedance spectroscopy data.

References

[1] H Mehrer *Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes* . Springer Series in Solid-State Sciences (Berlin: Springer, 2007)

[2] B Roling, C Martiny and S Murugavel *Phys. Rev. Lett.* **87** 085901 (2001)

[3] R Nigmatullin, A A Arbuzov, F Salehli, A Giz, I Bayrak and H Catalgil-Giz *Physica B* **388** 418 (2007)

[4] D L Sidebottom *Rev. Mod. Phys.* **81** 999 (2009)

[5] S Kabi and A Ghosh *EPL (Europhysics Letters)* **108** 36002 (2014)

[6] P Maass, M Meyer and A Bunde *Phys. Rev. B* **51** 8164 (1995)

[7] R Kubo *J. Phys. Soc. Jpn.* **12** 570 (1957)

[8] B Roling, C Martiny and S Brückner *Phys. Rev. B* **63** 214203 (2001)

[9] J C Dyre, P Maass, B Roling and D L Sidebottom *Rep. Prog. Phys.* **72** 046501 (2009)

[10] D Zielniok, H Eckert and C Cramer *Phys. Rev. Lett.* **100** 035901 (2008)

[11] M Micoulaut and M Malki *Phys. Rev. Lett.* **105** 235504 (2010)

[12] S Kabi and A Ghosh *EPL (Europhysics Letters)* **100** 26007 (2012)

[13] B Deb and A Ghosh *EPL (Europhysics Letters)* **97** 16001 (2012)

[14] B Deb and A Ghosh *J. Appl. Phys.* **112** 094110 (2012)

[15] A Shaw and A Ghosh *J. Phys. Chem. C* **116** 24255 (2012)

[16] A Shaw and A Ghosh *EPL (Europhysics Letters)* **100** 66003 (2013)

[17] A Shaw and A Ghosh *J. Chem. Phys.* **139** 114503 (2013)

[18] A Shaw and A Ghosh *J. Chem. Phys.* **141** 164504 (2014)

[19] M Bauchy, A Kachmar and M Micoulaut *J. Chem. Phys.* **141** 194506 (2014)

[20] K Funke *Prog. Solid State Chem.* **22** 111 (1993)

[21] K Funke and D Wilmer *Solid State Ionics* **136** 1329 (2000)

[22] J R Macdonald and E Barsoukov *Impedance Spectroscopy Theory, Experiment, and Applications*, 2nd ed. (New Jersey: Wiley, 2005)

[23] A Lasia *Electrochemical Impedance Spectroscopy and its Applications* (New York: Springer, 2014)

[24] O Kanoun *Lecture Notes on Impedance Spectroscopy* vol. 5 (Boca Raton: CRC Press, 2015)

[25] D C Sinclair, T B Adams, F D Morrison and A R West *Appl. Phys. Lett.* **80** 2153 (2002)

[26] Z Bao *et al. Nature* **446** 172 (2007)

[27] E C Shin *et al. Solid State Ionics* **232** 80 (2013)

[28] K Funke, R D Banhatti, D Laughman, M Mutke and M D Ingram *Eur. Phys. J. Special Top.* **161** 65 (2008)

[29] E K Lenzi, P R G Fernandes, T Petrucci, H Mukai and H V Ribeiro *Phys. Rev. E* **84** 041128 (2011)

[30] F Ciuchi, A Mazzulla, N Scaramuzza, E K Lenzi and L R Evangelista *J. Phys. Chem. C* **116** 8773 (2012)

[31] A R Duarte, F Batalioto, G Barbero and A M F Neto *J. Phys. Chem. B* **117** 2985 (2013)

[32] D S Vieira, M Menezes, G. Gonçalves, H Mukai, E K Lenzi, N C Pereira and P R G Fernandes *Grasas Aceites* **66** e083 (2015)

[33] D Eder and R Kramer *Phys. Chem. Chem. Phys.* **8** 4476 (2006)

[34] B Liu, H Muroyama, T Matsui, K Tomida, T Kabata and K Eguchi *J. Electrochem. Soc.* **158** B215 (2011)

[35] M Fleckenstein, S Fischer, O Bohlen and B Baker *J. Power Sources* **223** 259 (2013)

[36] S Grimnes *Bioimpedance and Bioelectricity Basics* (Cambridge: Academic Press, 2000)

[37] J Wtorek and A Polinski *IEEE Trans. Biomed. Eng.* **52** 41 (2005)

[38] A Schröter, A Walther, K Fritzsche, J Kothe, A Rosen-Wolff and G Gerlach *Procedia Chem.* **6** 175 (2012)

[39] A W Imre, F Berkemeier, H Mehrer, Y Gao, C Cramer and M D Ingram *J. Non-Cryst. Solids* **354** 328 (2008)

[40] P Maass, A Bunde and M D Ingram *Phys. Rev. Lett.* **68** 3064 (1992)

[41] A Bunde, K Funke and M D Ingram *Solid State Ionics* **86** 1311 (1996)

[42] B Roling, C Martiny and K Funke *J. Non-Cryst. Solids* **249** 201 (1999)

[43] D L Sidebottom, B Roling and K Funke *Phys. Rev. B* **63** 024301 (2001)

[44] P Heitjans and J Kärger *Diffusion in Condensed Matter: Methods, Materials, Models* (Berlin: Springer, 2006)

[45] P Maass, M Meyer, A Bunde and W Dieterich *Phys. Rev. Lett.* **77** 1528 (1996)

[46] F Endres, D MacFarlane and A Abbott *Electrodeposition from Ionic Liquids* (New Jersey: Wiley, 2008)

[47] H Ohno *Electrochemical Aspects of Ionic Liquids* (New Jersey: Wiley, 2011)

[48] T Frömling, M Kunze, M Schönhoff, J Sundermeyer and B Roling *J. Phys. Chem. B* **112** 12985 (2008)

[49] P Maass, B Rinn and W Schirmacher *Philos. Mag. B* **79** 1915 (1999)

[50] A Tabib, N Sdiri, H Elhouichet and M Férid *J. Alloys Compd.* **622** 687 (2015)

[51] A Jonscher *Nature (London)* **267** 673 (1977)

[52] C Cramer *Z. Naturforsch. A* **50** 613 (1995)

[53] J P Bouchaud and A Georges *Phys. Rep.* **195** 127 (1990)

[54] R Metzler and J Klafter *Phys. Rep.* **339** 1 (2000)

[55] R Klages, G Radons and I Sokolov *Anomalous Transport: Foundations and Applications* (New Jersey: Wiley, 2008)

[56] S Murugavel and B Roling *J. Phys. Chem. B* **108** 2564 (2004)

[57] K Funke and R D Banhatti *Solid State Ionics* **169** 1 (2004)

[58] E Sunyer, P Jund and R Jullien *J. Phys. Condens. Matter* **15** L431 (2003)

[59] S Chandrasekhar *Liquid Crystals* (Cambridge: Cambridge University Press, 1992)

[60] V Lvovich *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena* (New Jersey: Wiley, 2015)

[61] F Batalioto, A R Duarte, G Barbero, A M F Neto *J. Phys. Chem. B* **114** 3467 (2010)