

# Translational and localised ionic motion in materials with disordered structures

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Dedicated to Professor Hermann Schmalzried on the occasion of his 75th birthday.

## Abstract

Ionic materials with disordered structures may be crystalline, glassy or polymeric. Broad-band spectra of their ionic conductivities are found to display surprisingly similar features. With the help of linear response theory, time-resolved information on the ion dynamics has been extracted from such spectra. It has thus become evident that three kinds of ionic motion may be distinguished, all of them being collective and cooperative. These are vibrations, strictly localised displacements, and hops along diffusion pathways.

The translational motion along diffusion pathways is well described in terms of a model called the MIGRATION concept, the acronym standing for Mismatch Generated Relaxation for the Accommodation and Transport of IONS. The MIGRATION concept consists of a set of simple rules that are written in the form of rate equations. Model conductivity spectra can be derived from them.

Strictly localised displacive movements may be performed by ions within voids provided by the structure. In our model, this situation requires a modification of one of the rate equations. As a result, we obtain the well-known features of the Nearly Constant Loss (NCL) behaviour.

We present broad-band conductivity spectra of several ionic materials with disordered structures and discuss them in terms of our model treatment.

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## 1. Introduction

One of the basic questions of solid state ionics concerns the mechanisms of ionic motion in materials with high ionic conductivities. In these cases, the ion dynamics are not adequately described in terms of random movements of isolated ionic defects, but rather by highly correlated processes involving interacting ions in disordered structures. The important role played by both interaction and disorder has been known for more than two decades [1,2]. The ionic materials under consideration may be either crystalline such as  $\alpha$ -AgI, with one sublattice displaying structural disorder, or may be molten, polymeric or glassy, lacking long-range order at all. In such ion conductors, valuable information on the mechanisms of ionic motion

is contained in broad-band spectra of the complex ionic conductivity,  $\hat{\sigma}(\omega)$ , which may be taken over more than 17 decades of angular frequency,  $\omega = 2\pi\nu$ , corresponding to more than 17 decades in time [3].

Fig. 1 is a log–log plot of the real part of the frequency-dependent conductivity,  $\sigma(\nu)$ , of a silver thiogermanate glass of composition  $0.5\text{Ag}_2\text{S}\cdot 0.5\text{GeS}_2$  at 273 K [4,5]. When one views such a plot, questions which arise include how one reads such a spectrum properly and how one deduces the essential features contained therein. For example, is it easily possible to identify “fingerprints” of translational or localised movements of the mobile ions?

The following statements can be readily made.

- At low frequencies, there is a constant “DC” value of the conductivity,  $\sigma_{\text{DC}}$ , reflecting macroscopic charge transport. In this regime, the slope of  $\log \sigma$  versus  $\log \nu$  is zero.

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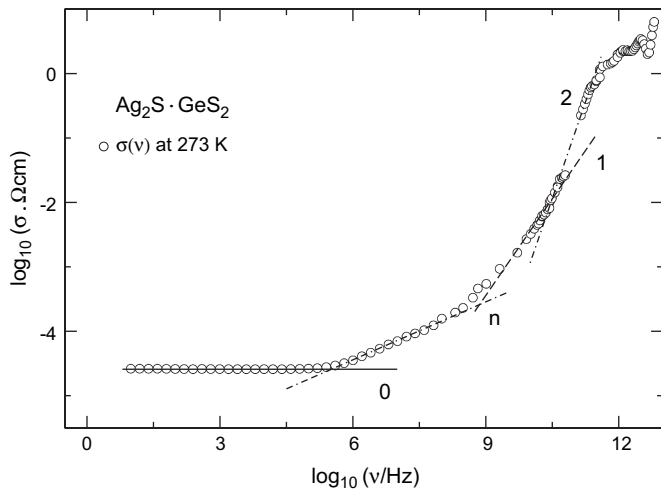


Fig. 1. Broad-band conductivity spectrum of the silver-ion conducting glass  $0.5\text{Ag}_2\text{S}\cdot 0.5\text{GeS}_2$  at 273 K. For the straight lines, see text.

- At high frequencies, there is a conductivity component caused by excitation of vibrational motion. In the log–log representation of Fig. 1, this component has a slope of two on its low-frequency flank, see e.g. [6].
- At intermediate frequencies, there are additional contributions to the conductivity, reflecting the existence of non-vibrational, non-random displacements of the mobile ions. These are the main topics of this paper.

The latter feature is often empirically decomposed into

- an increase of  $\sigma(\nu)$  that follows a power law,  $\nu^n$ , with  $0 < n < 1$ , and
- a further increase which is linear or almost linear as a function of frequency and, therefore, corresponds to a nearly constant loss function,  $\varepsilon''(\nu) = -\text{Im}\hat{\varepsilon}(\nu)$ . The loss function is connected with  $\sigma(\nu)$  via  $\varepsilon''(\nu) = \sigma(\nu)/(\varepsilon_0 2\pi\nu)$ , where  $\varepsilon_0$  is the permittivity of vacuum.

It is evident from Fig. 1 that this decomposition into two components will, indeed, reproduce a typical conductivity spectrum. The first of these components is the famous “Jonscher power law”, which has also been termed “Universal Dynamic Response (UDR)” [7,8]. The other is regarded as a “Nearly Constant Loss (NCL)” phenomenon [9]. Most authors implicitly assume that the Jonscher term results from hops of mobile ions along interconnected sites and passageways, eventually contributing to translational transport [10]. On the other hand, the NCL term has been associated with a localised motion of charge carriers [11,12].

At this point, a number of questions arise. Is the Jonscher power law a law of nature? Does it properly describe displacements of ions via interconnected sites? Is it possible to explain the NCL term by ionic displacements that remain localised?

These questions will be addressed in this paper, and examples will be discussed. In particular, it will be shown that the interpretation sketched above is too simplified and must be replaced by a more refined modelling.

## 2. High-frequency plateau

An important observation is illustrated in Fig. 2. In the spectrum of Fig. 1, the vibrational component, which varies as frequency squared on its low-frequency flank, can be carefully removed from the experimental data points. In spite of the scatter of the data thus obtained, a short plateau is seen to emerge at the high-frequency end of the resulting “non-vibrational” spectrum,  $\sigma_{\text{non-vib}}(\nu)$  [13]. As this conductivity component is caused by the hopping motion of the ions, it will sometimes be denoted by  $\sigma_{\text{hop}}(\nu)$ . The same procedure has also been successfully applied to a conductivity spectrum taken from the low-temperature  $\gamma$ -phase of the famous silver ion conductor rubidium silver iodide,  $\gamma\text{-RbAg}_4\text{I}_5$ , at 113 K [14]. Again, see Fig. 3, the non-vibrational conductivity spectrum,  $\sigma_{\text{hop}}(\nu) = \sigma_{\text{non-vib}}(\nu)$ , shows a saturation at high frequencies, converging to a high-frequency limiting value,  $\sigma_{\text{HF}}$ . Strom and Ngai were the first to detect such a limiting value,  $\sigma_{\text{HF}}$ , as early as 1981, in Na- $\beta$ -alumina [15].

In the so-called high-frequency plateau, every hop of an ion is recorded in the spectrum [16]. A simple reason can be given for this statement, even without employing linear response theory. In the regime where  $\sigma_{\text{HF}}$  is observed, half a period of the electric field is so short that more than one hop of a given ion would not fit in. At this frequency, a hop is, therefore, recorded even if it is followed by a correlated backward hop, which nullifies the first on a longer time scale. Indeed, the latter process causes  $\sigma_{\text{hop}}(\nu) = \sigma_{\text{non-vib}}(\nu)$  to decrease as frequency is reduced. As early as 1991, the corresponding “sublinear” time dependence of the mean square displacement of the hopping ions was reproduced in Monte Carlo simulations [17,18].

We may thus formulate a clear conceptual distinction between the “non-vibrational” conductivities observed in the limits of low and high frequencies,  $\sigma_{\text{DC}}$  and  $\sigma_{\text{HF}}$ . While all hops are recorded in  $\sigma_{\text{HF}}$ , only the “successful” ones, i.e., those that are not nullified by correlated backward hops, contribute to  $\sigma_{\text{DC}}$  [16].

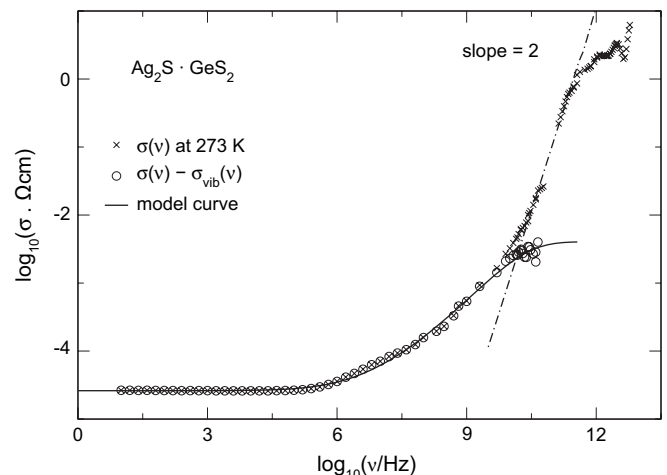


Fig. 2. Broad-band conductivity spectrum of  $0.5\text{Ag}_2\text{S}\cdot 0.5\text{GeS}_2$  glass at 273 K (crosses), along with its non-vibrational component (open circles) as obtained by removing the contribution of the low-frequency flank of the vibrational component (dash-dotted line with slope 2). The solid curve is a MIGRATION-type model spectrum, see Section 8.

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