20 Ionic Transport in Disordered Materials

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20.1 Introduction

The low-frequency dynamic response of many non-metallic materials is governed by the transport of mobile ions or other charged mobile defects. The classes of such materials include traditional ionic glasses, polymeric and glassy superionic conductors, highly defective crystals or even highly viscous liquids such as glassforming melts. To get an understanding of the microscopic transport mechanism in these materials, a large number of experimental techniques has been applied, among them are tracer experiments (Chap. 1 and [1]), conductivity measurements including impedance spectroscopy (Chap. 21, [2–5]), nuclear magnetic resonance (NMR) relaxation (Chap. 9, [6–10]), quasielastic neutron scattering (Chaps. 2, 3 and 13, [11,12]), internal friction and ultrasonic absorption measurements (Brillouin scattering) (Chap. 11, [13,14]). In all these experiments the measured quantities show characteristic deviations from the standard behavior that one would expect for a purely random motion of the mobile ions.

For example, the dynamic conductivity $\hat{\sigma}(\omega)$ in disordered crystalline and glassy ionic conductors exhibits, for fixed temperature $T$, a dc-plateau at low frequencies (below some crossover frequency $1/\tau_\sigma$), and follows an approximate power law behavior at larger frequencies [15],

$$\hat{\sigma}(\omega) \sim \begin{cases} \sigma_{dc}, & \omega \tau_\sigma \ll 1, \\ (i\omega)^n, & \omega \tau_\sigma \gg 1. \end{cases} \quad (20.1)$$

The dc conductivity $\sigma_{dc}$ usually shows an Arrhenius behavior below the glass transition temperature,

$$\sigma_{dc}T = A_\sigma \exp(-E_\sigma/k_BT), \quad (20.2)$$

and also the crossover frequency $\tau_\sigma^{-1}$ is thermally activated with the same activation energy $E_\sigma$. The exponent $n_\sigma > 0$ tends to increase, if the temperature is lowered or if the frequency is increased by several orders of magnitude. From standard random walk theory on a lattice with equivalent sites one would expect no dispersion to occur, i.e. $n_\sigma = 0$ (see Sect. 20.2.2). The overall behaviour (20.1) is not restricted to ionically conducting solids but
occurs also in disordered electronic conductors such as amorphous semiconductors, electronic conducting polymers and disordered polaronic conductors. The widespread occurrence of such similar low-frequency dielectric behavior in all disordered solids was first pointed out by Jonscher [16] and is known as the “universal dielectric response”.

A second, “universal” type of response in disordered ionic systems occurs at even higher frequencies, \( \omega > \omega_{\text{NCL}} \gg \tau_{\sigma}^{-1} \). Going at ambient temperatures to the Gigahertz regime, the real part of the conductivity increases nearly linearly with frequency,

\[
\text{Re} \sigma(\omega) \sim \omega; \quad \omega > \omega_{\text{NCL}}.
\]  

This is equivalent with a frequency-independent dielectric loss, \( \chi''(\omega) \simeq \text{const} \), and is thus known as “nearly constant loss” (NCL) response [17–19]. Its temperature dependence is much weaker than implied by (20.2) and (20.1) with the consequence that at low temperatures the NCL response dominates the spectrum in the experimentally accessible frequency-range.

In some glassy fast ion conductors it was found that the dc-conductivity shows strong deviations from a simple Arrhenius law even below the glass transition temperature [20, 21]: The values of \( \sigma_{\text{dc}} \) at ambient temperatures are significantly smaller than expected when extrapolating the Arrhenius law valid at low temperatures \( T \). We note that a non-Arrhenius behaviour was found earlier in ion conducting glasses but disappeared after annealing [22].

Strongly non-Arrhenius diffusion of a different type occurs in yet another class of amorphous materials, namely ion conducting polymers above their glass transition temperature [23]. Certain chain polymers carry polar groups in their repeat unit and are therefore capable of dissolving salts. When temperature is lowered, the polymer chains tend to freeze. In contrast to (20.2), the strong coupling of ions to the network degrees of freedom generally leads to Vogel-Fulcher-Tammann (VFT)-type behavior [24] of the conductivity,

\[
\sigma_{\text{dc}} T \propto \exp(-E/k_B(T - T_{\text{VFT}}))
\]

Here \( E \) is an energy parameter and \( T_{\text{VFT}} \) the VFT-temperature, commonly referred to as “ideal glass transition temperature”. Much effort is being spent to explore transport mechanisms in these complex materials, and to optimize their electrical conduction properties with respect to their use in electrochemical devices.

Apart from conduction and dielectric measurements, the perhaps most common experimental technique to probe ionic motion in disordered media is nuclear magnetic resonance (see Chap. 9). The behavior of the diffusion-induced spin-lattice relaxation (SLR) rate \( 1/T_1(\omega_L, T) \), as a function of temperature \( T \) and Larmor frequency \( \omega_L \), can be summarized as follows:

\[
\frac{1}{T_1}(\omega_L, T) \sim \begin{cases} 
\exp(E_{\text{SLR}}^{1}/k_B T), & T \gg T_{\text{max}}(\omega_L), \\
\omega_L^{n_{\text{SLR}}-2} \exp(-E_{\text{SLR}}^{2}/k_B T), & T \ll T_{\text{max}}(\omega_L),
\end{cases}
\]  

(20.5)