

Broadband Dielectric Spectroscopy

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Foreword

The interaction of electromagnetic (EM) radiation with molecular systems gives rise to quantized transitions between the electronic, vibrational and rotational molecular energy states which may be observed by UV/visible and infra-red absorption spectroscopies at frequencies above about 1 THz (10^{12} Hz). These quantum spectroscopies for molecules in the gaseous, liquid and solid states form a large part of physical chemistry and chemical physics. However, if one asks a fellow scientist “what happens when EM radiation in the range 10^{-6} to 10^{12} Hz is applied to those systems” the answer is usually tentative and incomplete, which shows that a majority of scientists are unfamiliar with the dielectric dispersion and absorption phenomena that occur in this vast frequency range due to (i) dipole relaxation arising from the reorientational motions of molecular dipoles and (ii) electrical conduction arising from the translational motions of electric charges (ions, electrons). This is the domain of *Broadband Dielectric Spectroscopy* (BDS).

At frequencies below about 10^8 Hz a dielectric sample is regarded as a complex electrical impedance $Z^*(\omega)$, expressed in terms of the resistance $R(\omega)$ and capacitance $C(\omega)$, which are frequency-dependent *extensive* properties (here $\omega = 2\pi f/\text{Hz}$ where f is the measuring frequency). The *intensive* complex dielectric quantities of dielectric permittivity $\epsilon^*(\omega)$, electrical modulus $M^*(\omega)$, electrical conductivity $\sigma^*(\omega)$ and resistivity $\rho^*(\omega)$ are immediately derivable from $Z^*(\omega)$. Researchers traditionally use these different quantities to express BDS data for materials, which is a source of confusion when assessing the dielectric/electrical properties of a given material reported in the literature. Dipole relaxation behaviour is normally represented in terms of ϵ^* and electric conduction behaviour in terms of σ^* , Z^* , M^* or ρ^* .

Starting in the late nineteenth century, dielectric measurement techniques were developed for materials such as molecular liquids and solids and moderately-conducting materials such as electrolytes and semiconductors. Transient current methods were used for very low frequencies ($f < 1$ Hz) and a.c. bridges for power, audio, UHF and VHF frequencies (1 to 10^7 Hz). In the 1940s distributed circuit methods were introduced for microwave frequencies (10^8 to 10^{11} Hz) and in the 1970s novel spectroscopic methods were developed for far infrared frequencies (3×10^{11} to 3×10^{12} Hz). In the main, measurements were made point-by-point at each frequency in the range of interest, which was difficult, and time-consuming. This held back the use of dielectric spectroscopy as an investigative physical technique at times when rapid advances were being made in the related techniques of NMR, quasi-elastic light scattering and photon-correlation spectroscopy. Nevertheless extensive dielectric data for a host of organic and inor-

ganic materials were obtained prior to the early 1980s using these methods. Subsequently modern commercial impedance measuring devices for low frequencies and commercial network analysers, time-domain reflectometers and laser spectroscopies for high frequencies became available and were developed for broadband dielectric studies of materials. Automatic measurement and processing methods, made possible by on-line computers used in combination with the new instruments, transformed dielectric measurements of materials. Now it is possible to obtain accurate dielectric data quickly and efficiently over the entire frequency range 10^{-6} to 10^{12} Hz and means that BDS has now taken its rightful place alongside other modern investigative techniques for studying the structure and molecular dynamics of materials.

Debye (1927) established that *dielectric relaxation*, which is the dispersion of the real permittivity (ϵ') and the occurrence of dielectric absorption (ϵ'') in the f -domain for dipolar liquids and solids, was due to the reorientational motions of the molecular dipoles. Many dielectric studies followed, especially those by Smyth (Princeton) and Cole (Brown) that were started in the 1930s. Early areas of study included dipolar liquids (e.g. chlorobenzene, polar solutes in non-polar solvents), rotator-phase crystals (e.g. cyclohexanol, the polymorphs of ice), non-polar polymers (e.g. polyethylene, polypropylene), polar polymers (e.g. polyacrylates, nylons, polyamides). Knowledge of the low frequency permittivity allowed molecular dipole moments to be determined, which was useful for the elucidation of molecular structures prior to the use of modern spectroscopic techniques. The dielectric loss spectra characterized the reorientational dynamics of molecules in the different materials. Also dielectric studies were made for inorganic solids that have ferroelectric properties (e.g. barium titanate) or are semi-conducting (e.g. doped silicon, organic photoconductors and semi-conductors) which have important applications in solid state devices. In parallel, extensive BDS data were obtained for electrolytes, polyelectrolytes, organic and inorganic semi-conductors, giving information on electrical conductivity and hence the mobilities of the effective charge carriers. More recently many BDS studies have been made for novel polymers, glass-forming liquids, liquid crystals (e.g. alkylcyanobiphenyls), polymeric liquid crystals (e.g. polysiloxanes with mesogenic side chains), ferroelectric organic materials (e.g. chiral alkylcyanobiphenyls and their polymeric derivatives), electrolytes (e.g. KCl/H₂O), molten salts (e.g. Ca-K/NO₃) and polyelectrolytes (e.g. polyethylene oxide/salt solutions). Such researches were often motivated by the applications of these materials in devices for modern technology. For example (i) the dielectric anisotropy of the liquid crystal is the source of the optical switching process in liquid crystal displays while (ii) new thin-film solid-state electrolytes are sought for battery applications.

As the data-base for the broadband dielectric behaviour of different materials increased, phenomenological and molecular theories for dipole relaxation and charge conduction were developed. The molecular theories required the deduction of $\epsilon^*(\omega)$ or $\sigma^*(\omega)$ from the field-induced perturbation of the field-free reorientational and translational motions of molecular species. Such theories become extremely difficult for complex motions, e.g. as for multi-site motions of dipoles or ions in crystals or structured liquids. The situation changed completely when Kubo (1957), using linear response theory and time-dependent sta-

tistical mechanics, showed that $\sigma^*(\omega)$ was related, via Fourier transformation, to the field-free mean-squared displacement of charges with time $\langle \Delta R^2(t) \rangle$ or to their velocity correlation function $\langle v(0)v(t) \rangle$. For dielectric relaxation Glarum (1961) and Cole (1965) related $\varepsilon^*(\omega)$, via Fourier transformation, to the field-free dipole moment correlation function $\langle \mu(0)\mu(t) \rangle$ with time. Thus Fourier inversion of $\sigma^*(\omega)$ or $\varepsilon^*(\omega)$ gave direct determinations of these t -dependent molecular properties, which could in turn be fitted by chosen models for motions of molecules or charges. Research texts dealing with dielectric data (mainly for molecular liquids and solids) were published by Smyth (1955), Fröhlich (1958), Hill, Vaughan, Price and Davies (1969) and Böttcher and Bordewijk (1978) and for polymers by McCrum, Read and Williams (1967) and Runt and Fitzgerald (eds) (1997). Obviously the wide range of materials studied in different frequency bands for their dipole relaxation and conduction behaviour, the differing backgrounds of the researchers (physicists, chemists, materials scientists, electrical engineers, chemical engineers, theorists) and the publication of the researches in different journals of physics, physical chemistry/chemical physics, electrical engineering, polymer science and materials science made it increasingly difficult for scientists to monitor overall activities in dielectric spectroscopy. A great help to this effect have been the *International Discussion Meetings on Relaxations in Complex Systems* organized by K. L. Ngai and his associates held in Crete (1990), Alicante (1993) and Vigo (1997), published as special issues of *J Non-Crystalline Solids*, and that held in Crete (2001) where researchers in different areas of dielectrics science have been brought together along with a host of researchers that use related relaxation, scattering and spectroscopic techniques for the study of the dynamics of materials.

The stage has been reached where the foundations of broadband dielectric spectroscopy are well-established in terms of the large body of literature for the dielectric behaviour of dipolar materials and moderately-conducting electrolyte systems, phenomenological and molecular theories that relate $\varepsilon^*(\omega)$ and $\sigma^*(\omega)$ to empirical relaxation functions and to time-dependent molecular properties that give information on the reorientational and translational motions of molecules and charges in molecular liquids and solids. In this book the editors Friedrich Kremer and Andreas Schönhals have built on these foundations, through their own contributions and those of other leading scientists, taking the subject forward into those areas where BDS is making vital and new contributions to our understanding of the dynamics of complex systems. After a summary of the essentials of modern experimental techniques and dielectric theories (Chaps. 1–3) experimental data are shown over the entire frequency range for glasses, supercooled liquids, amorphous polymers (Chaps. 4, 5, 7), (polymeric) liquid crystals (Chap. 10) and semi-conducting disordered materials (Chap. 12) where multiple dipole relaxations are observed and are analysed in terms of particular motional processes. BDS provides a powerful method for studying the dynamics of molecules in confined spaces down to the mesoscopic and molecular levels (Chap. 6). Since the capacitance of a dielectric sample is inversely proportional to its thickness, BDS is highly suitable for studies of ultra-thin films, in contrast to NMR, light scattering and other spectroscopic techniques. The effects of film thickness on molecular dynamics in ultra-thin poly-

mer films are clearly demonstrated (Chap. 11) and provide severe tests of results for glass-forming materials obtained from other physical techniques. Inhomogeneous media (Chap. 13) give rise to interfacial polarization in addition to dipole relaxation and charge-conduction and this is particularly important in multi-phase liquids and polymers, emulsions and biological systems. The component structures of relaxation processes and the questions of dynamic heterogeneity in organic materials are further elucidated by the new, sophisticated techniques of pulsed and non-resonant dielectric hole-burning (Chap. 14). BDS studies provide evidence for the structure and molecular dynamics in all these systems, evidence is obtained on the molecular dynamics which complements that obtained using the related techniques of solvation dynamics (Chap. 15), dynamical mechanical spectroscopy (Chap. 16), multi-dimensional multi-nuclear NMR (Chap. 17) and neutron scattering (Chap. 18). While dielectric relaxation behaviour is usually studied over wide ranges of frequency and sample temperature, the relaxation strength, relaxation time and its distribution are all affected significantly by applied pressure. This 'forgotten variable' (G. Floudas, Chap. 8) can be used to separate overlapping relaxations or induce crystallization – which transforms the relaxation behaviour in crystallizable polymers. Modern techniques allow broadband dielectric measurements to be made in real time for polymerizing systems where a liquid mixture transforms to a glass or an elastomer during reaction (Chap. 9). These studies monitor changes in molecular dynamics during the polymerization reaction and demonstrate the role of diffusion-control on reaction rate when a glass is formed.

Thus the editors and contributors show in this remarkable book that modern BDS techniques, as applied to a wide range of amorphous, crystalline and liquid crystalline systems, can give new and vital information on the reorientational and translational motions of dipolar molecules or electric charges and how the characteristics of these motions vary with temperature and pressure and with the physical condition of the material (bulk or thin film, confined geometries, macroscopic orientation (e.g. for liquid crystals)). They show how the wide frequency range of BDS may be utilised to obtain a detailed knowledge of individual motional processes whose time-scale may be in a range from picoseconds to kiloseconds and show further how this information complements that obtained for the same materials using related relaxation, scattering and spectroscopic techniques. A new researcher, or one from a related field of study, will find this 'state-of-the-art' account of broadband dielectric spectroscopy to be invaluable since *inter alia* it provides clear examples of the power of the technique to elucidate the dynamics of condensed systems, many of which have applied interest. Most important of all, the information provided by the BDS researches described here will stimulate new lines of research, not only into the applications of modern dielectric techniques to new materials and to time-varying systems but also to the development of further novel techniques that will test and extend the conclusions reached presently from BDS, NMR, mechanical relaxation, light scattering, neutron scattering, optical relaxation and related techniques concerning the detailed nature of molecular dynamics in organic and inorganic materials.

Preface

The interaction of electromagnetic waves with matter in the frequency regime between 10^{-6} and 10^{12} Hz is the domain of broadband dielectric spectroscopy. In this extraordinarily extended dynamic range, molecular and collective dipolar fluctuations, charge transport and polarization effects at inner and outer boundaries take place, and determine the dielectric properties of the material under study. Hence broadband dielectric spectroscopy enables us to gain a wealth of information on the dynamics of bound (dipoles) and mobile charge carriers depending on the details of the molecular system. In recent years novel dielectric instrumentation has been developed which allows for automatic measurements in nearly the entire range from ultra low frequencies up to the Far Infra Red.

It is intended that this book be more than a monograph at the leading edge of research. Therefore in three introductory chapters written in the style of a textbook, broadband dielectric spectroscopy is described in its theoretical foundation, its experimental techniques, and in the way dielectric spectra have to be analyzed. In the chapters 4–13, examples are described where the dielectric method has made important contributions to modern scientific topics. This is, of course, far from being a comprehensive overview and corresponds to the research interests of the editors. In chapters 14 and 15, two novel experimental techniques are introduced which are closely related to dielectric spectroscopy. Special attention is given in chapters 16–18 to the comparison between dielectric and other spectroscopic techniques such as mechanical, NMR, and neutron scattering.

The editors would like to thank all the contributors to this volume for their efficient collaboration. Many chapters of the book were read by G. Williams who made numerous suggestions from which the book benefited a great deal. The patient help of Mrs. I. Grünwald in typing some of the manuscripts and managing the correspondence is thankfully acknowledged. The editors would also like to thank Dr. M. Hertel and Springer Verlag for the competent cooperation.

July 2002

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