

Dielectric Relaxation Spectroscopy

Dielectric Relaxation Spectroscopy (DRS) probes the interaction of a macroscopic sample with a time-dependent electric field [1]. The resulting polarization, either expressed by the frequency-dependent complex permittivity and conductivity or as an impedance spectrum, characterizes amplitude and timescale (via the relaxation time) of the charge-density fluctuations within the sample. Such fluctuations generally arise from the reorientation of the permanent dipole moments of individual molecules or from the rotation of dipolar moieties in flexible molecules, like polymers. Other possible mechanisms include intermolecular vibrations, the transport of ions or the accumulation of interfacial charges in heterogeneous systems. The timescales of these fluctuations depend on the sample and on the relevant relaxation mechanisms. Relaxation times range from a few hundred femtoseconds for molecular librations in low-viscosity liquids to hours for structural relaxation in glasses, probably marking DRS as the technique with the most extensive coverage of dynamical processes. The corresponding measurement frequencies range from 10^{-4} Hz to 10^{15} Hz, which requires a series instruments for complete coverage. However, it is generally sufficient to focus on a smaller frequency range adapted to the sample properties.

In contrast to conventional spectroscopic methods, like NMR or vibrational spectroscopy, DRS is especially sensitive to intermolecular interactions. DRS is able to monitor cooperative processes and thus provides a link between molecular spectroscopy, which monitors the properties of the individual constituents, and techniques characterizing the bulk properties of the sample, especially the viscoelastic and rheological behaviour. The decomposition of the dielectric spectrum into its individual relaxation processes informs on the relative amplitudes and characteristic times of the underlying molecular motions.

DRS is widely applied in the characterization of ion-conducting solids, polymers and mesophases [1-4]. But it is also of large potential interest for the investigations of liquid [5-13] and colloidal systems [14-17]. Additionally, the effects studied by DRS are of increasing importance for technical applications, like moisture-content determination in materials, dielectric heating or remote sensing [6, 14, 17-21]. Possible applications include:

- *Static permittivity* [6, 7]

The static permittivity, ϵ , is a central solvent property which determines and reflects the magnitude of solute-solvent interactions. It influences the solubility of solutes, the formation of micelles or the osmotic coefficients of electrolytes. *Vice versa* ϵ strongly depends on the composition of the solution (e.g. the static permittivity of pure N-methylformamide at 25°C is 184, but for a 0.5 M NaCl solution in this solvent $\epsilon = 111$ is observed). Note that DRS is the only technique which allows the determination of the static permittivity of electrically conducting liquids, like electrolyte solutions.

- *Dielectric heating* [19, 20]

DRS routinely determines the dielectric loss, ϵ'' , or - for samples of conductivity κ - the total loss, $\eta'' = \epsilon'' + \kappa/(2\pi\nu\epsilon_0)$, as a function of the frequency, ν , ϵ_0 is the electric field constant (vacuum permittivity). These quantities characterize the absorption of electromagnetic energy by the sample and therefore determine the efficiency of dielectric heating (e.g. in microwave ovens). Recently, dielectric heating has become a popular tool in chemical synthesis because it is not only very efficient but for several classes of reactions otherwise inaccessible product pathways are followed.

- *Liquid-state Dynamics* [8-12]

When extended into the far-infrared region DRS provides the full dynamics of liquids from molecular librations to large-scale cooperative motions. Since DRS probes the fluctuations of induced (in the far infrared) and permanent dipole moments, *i.e.* of vectors, its information is highly complementary to information from computer simulations [9] and other spectroscopies yielding information on dynamical processes, like time-resolved optical Kerr-effect (OKE) [10], low-frequency Raman [11] or time-resolved infrared spectroscopy [12].

· *Solvation* [8, 10-13]

Ion-solvent interactions are of prime importance in a wide field of physical chemistry, ranging from the physical (and thus implicit the physiological) properties of seawater or body fluids via hydrometallurgy to protein stability. DRS allows the determination of effective ion solvation numbers from the analysis of the solvent relaxation processes. These solvation numbers generally differ from coordination numbers obtained with scattering techniques or computer simulation because they do not only reflect packing effects but essentially monitor the relative strength of ion-solvent *vs.* solvent-solvent interactions.

· *Speciation in Electrolyte Solutions* [8,13]

In electrolyte solutions ion-ion interactions may lead to the formation of aggregates, like ion-pairs or ion-triples. The identification and quantitative determination of such species is of crucial importance for the understanding of electrolyte properties and the modeling of geological and industrial processes. DRS is specific to species with a permanent dipole moment, like ion-pairs. In contrast to other spectroscopic techniques, which monitor only contact ion-pairs, DRS is also able to detect solvent-separated ion-pairs.

· *Dynamics of complex liquid mixtures - microheterogeneities, hydrophobic hydration* [8-12]

DRS is especially sensitive to cooperative processes. For instance in the case of alcohol-water mixtures of increasing alcohol content DRS indicates the transition of hydrated alcohol monomers to dimers to hydrated alcohol chains with pockets of frustrated water molecules. Around hydrophobic ions a shell of water molecules with strongly reduced mobility can be distinguished from bulk water. DRS thus allows to monitor the influence of solute-solvent interactions on structure and dynamics of the *solvent* as well as of the *solute*. Such information is important for the understanding of solubilization phenomena.

· *Emulsions and microemulsions* [7,14-17]

DRS yields information on the type of emulsion (o/w or w/o), emulsion stability and aggregation behaviour (including percolation phenomena), droplet size and distribution. The dynamics of stabilizers and additives, as well as their interaction with water can be investigated.

· *Colloids* [7,14-17]

DRS monitors counterion diffusion on the surface of colloidal particles. From the observed relaxation time information on particle size and shape can be inferred.

· *Micelles and liposomes* [7,14-17]

DRS yields information on the particle size and the surface diffusion coefficient of bound

counter ions. It allows the determination of the phase diagram. From the individual spectral contributions specific information on the headgroup dynamics of the surfactant molecules as well as on the structure of the hydration shell can be obtained. Additionally, the interactions of polar probe molecules with the different environments present in such systems can be investigated. Due to its high sensitivity towards conducting contaminants, DRS is very effective in the purity control of liposomes.

The timescales covered by these solution processes range from milli- to femtoseconds, so that experiments must be conducted in the range of radio- and microwaves, possibly extended into the far-infrared region. Due to now available impedance analyzers dielectric relaxation studies up to 3 GHz are becoming increasingly popular for the investigation of complex liquids, see ref. [7]. However, a perusal of the literature reveals that generally the interpretation of the data is not as unambiguous as one would wish. This essentially arises from the large bandwidths of the spectral components, so that precise spectra over a broad frequency range are necessary for a meaningful decomposition. In many studies, especially of colloidal or surfactant systems, the generally dominating solvent response in the 1-100 GHz region is not appropriately covered and questionable approximations are often used to separate solute-specific relaxations. Only recently commercial instruments reaching 50 GHz have become available.

Coming from the investigation of "simple" liquids and solutions with experience in the development of DRS instrumentation for highly conducting electrolyte solutions, our laboratory is now able to perform DRS experiments in the frequency range $0.01 \leq \nu / \text{GHz} \leq 89$ with 2% accuracy relative to ϵ . We are unique in being able to cover both *solute* and *solvent* response with high accuracy for temperatures between -45°C and 75°C [5,11].

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