



Rattling the cage: Micro- to mesoscopic structure in liquids as simple as argon and as complicated as water

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ABSTRACT

The water molecule has the convenient property that its molecular polarizability tensor is nearly isotropic while its dipole moment is large. As a result, the low-frequency anisotropic Raman spectrum of liquid water is mostly collision-induced and therefore reports primarily translational motions while the far-infrared (terahertz) and dielectric spectrum is dominated by rotational modes. Atomic and globular-molecular liquids have a zero dipole moment as well as an isotropic polarizability tensor. These spectrum-simplifying properties were exploited in a study of a number of liquids and solutions using ultrafast optical Kerr-effect (OKE) spectroscopy combined with dielectric relaxation spectroscopy (DRS), terahertz time-domain spectroscopy (THz-TDS), and terahertz field-induced second-harmonic generation (TFISH) spectroscopy. For room-temperature ionic liquids (RTILs), liquid water, aqueous salt solutions, noble gas liquids, and globular-molecular liquids it was found that, in each case, surprising structure and/or inhomogeneity is observed, ranging from mesoscopic clustering in RTILs to stretched-exponential dynamics in the noble gas liquids. For aqueous electrolyte solutions it is shown that the viscosity, normally described by the Jones–Dole expression, can be explained in terms of a jamming transition, a concept borrowed from soft condensed matter studies of glass transitions in colloidal suspensions.

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1. Introduction

The nanometer scale structuring of liquids is of great importance to an understanding of chemical and biochemical reactions as well as of the thermodynamic properties of liquids. Structure is well known in water as a result of the tetrahedral hydrogen-bond network that is perfect in the crystalline ice Ih phase and perturbed in the liquid phase [1,2]. Changes in the degree and type of local structuring in water [3,4] may give rise to phenomena ranging from multiple crystalline phases to glass formation, and possible liquid–liquid phase transitions [5–11]. Recent studies on room-temperature ionic liquids (RTILs [12,13]) have shown mesoscopic structure that is not liquid crystalline in origin [14–17]. Such RTILs may well form the micelle-like structure that is normally associated with amphiphilic properties. There are hints that such nanoscale aggregation may even occur in molecules as simple as *n*-alcohols [18].

It is widely thought that solutes – in particular charged solutes – can increase or reduce the extent of the structure of the solvent, and are classified in the Hofmeister series as kosmotropes (structure makers) and chaotropes (structure breakers), through their influence on viscosity, and on protein folding and unfolding [19–21]. Mesoscopic structure has been observed in aqueous solutions [22–24] as well as in mixtures [25] by a variety of techniques.

Supercooling and glass formation of liquids has been studied for well over 200 years [26] and is still a very active field. The approach of the glass transition is thought to lead to spatial heterogeneity on increasing length scales and the formation of mesoscopic structure sometimes referred to as Fischer clusters [27,28]. Such behavior can be explained by a locally favored structure that is not the structure corresponding to the global enthalpy minimum [29,30]. For example, in a Lennard–Jones liquid, the locally favored structure is an icosahedron whereas the global minimum enthalpy is achieved for an fcc or hcp lattice [31]. In a few cases, the mesoscopic clustering extends to greater length scales and becomes visible [32,33].

In this short collaborative review, we show that through combining a number of spectroscopic probes and applying these to liquids of varying complexity, a better understanding of the

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macroscopic properties can be achieved. In Section 2, the experimental techniques are introduced. Section 3 gives the methodology of simplifying the spectra, and Section 4 applies this approach to aqueous salt solutions allowing a re-interpretation of viscosity in the context of the jamming transition. In Section 5, the OKE spectra of very simplest liquids are shown to reveal surprisingly complex behavior and in Section 6 this is shown to be remarkably similar to that of water, implying a universality of non-exponential translational relaxation.

2. Experimental

One is typically interested in macroscopic properties of liquids such as the structural relaxation, which is related to the flow of liquid under shear stress as measured by its viscosity. The macroscopic property of viscosity is related to microscopic phenomena through the well-known Stokes–Einstein–Debye (SED) equation, which, for a probe particle immersed in a solvent, expresses the orientational relaxation time t_n as [34–37].

$$t_n = \frac{6}{n(n+1)} \frac{V\eta}{k_B T} \quad (1)$$

where n relates to the type of spectroscopy and is typically 1 or 2, V is the volume of the probe, T the absolute temperature, and η the shear viscosity, which in the simplest cases is given by $\eta \propto \exp(E/k_B T)$. Although originally developed for large probes, the SED equation works surprisingly well for molecular probes to within about an order of magnitude or slightly better. For example, at room-temperature in liquid water, with $n=2$ (appropriate for four-wave mixing spectroscopies), $V=10^{-3}/(55 N_a) \text{ m}^3$ (where N_a is the Avogadro number), $\eta=1$ cP, and $T=300$ K, one obtains $t_2=7.3$ ps, whereas the anisotropy decay time of the OD-stretch in HOD measured using infrared pump-probe experiments is $t_2=2.5\text{--}3$ ps [20]. Thus, the structural relaxation timescale is approximately a picosecond corresponding with a frequency of 1 THz. It is for this reason that the terahertz-frequency region is crucial to an understanding of liquids such as water.

There are numerous techniques for measuring terahertz structural relaxation such as dielectric relaxation spectroscopy (DRS), terahertz time-domain spectroscopy (THz-TDS), Fourier-transform infrared spectroscopy (FTIR), inelastic neutron scattering (INS), Raman scattering, etc. All of these techniques essentially measure a two-point correlation function. The techniques of DRS, THz-TDS, and FTIR measure

$$S_{\text{DR}}(t) \propto \langle \mu(0)\mu(t) \rangle, \quad (2)$$

the two-point correlation function of the (permanent) dipole moment [19,38–44] and will be referred to collectively as dielectric relaxation. Anisotropic Raman scattering and optical Kerr-effect spectroscopy (OKE) measure [40,45–50]

$$S_{\text{OKE}}(t) \propto \langle \alpha_{xy}(0)\alpha_{xy}(t) \rangle, \quad (3)$$

the correlation function of the anisotropic part of the polarizability tensor [40,45–49]. The lesser-known technique of terahertz field-induced second-harmonic generation (TFISH) measures

$$S_{\text{TFISH}}(t) \propto \langle \mu(0)\beta(t) \rangle, \quad (4)$$

the correlation function of the (permanent) dipole moment and the hyperpolarizability tensor [51,52]. Finally, Brillouin light, X-ray, and neutron scattering experiments measure [53]

$$S_{\text{Brillouin}}(r, t) \propto \int dR \langle \delta[R - R_i(0)] \delta[R + r - R_j(t)] \rangle, \quad (5)$$

a two-point correlation function involving position as well as time [53]. Other techniques have been developed that measure higher order correlation functions depending on three or even four time intervals, such as, (infrared) photon echoes and 2D-IR, [54–57] fifth-order spectroscopy, [58–61] and Raman photon echoes [62–64]. Although such higher order techniques can in principle extract more information, generally the depth of analysis is limited by poorer signal-to-noise ratios.

A typical spectrum as measured by one of the two-point correlation function techniques is shown in Fig. 1. In a typical molecular liquid, the spectrum consists of several overlapping broad bands. At the lowest frequency is the structural relaxation or α -relaxation band, which is generally associated with rotational diffusion. At the highest frequencies are librational and vibrational bands, while at intermediate frequencies are bands due to rattling of molecules in the cage of surrounding molecules referred to as β relaxation [38]. In some cases, such as in some room-temperature ionic liquids (RTILs), mesoscopic structure can give rise to an even lower frequency band referred to as sub- α relaxation [16].

The most complete model of relaxation is expected to be provided by mode-coupling theory (MCT) developed and widely applied in studies of glass forming liquids. MCT predicts a critical (singular) temperature T_C typically 15–20% above the glass transition temperature. Above T_C , a low-frequency α relaxation is observed that is diffusive and therefore temperature dependent. This is accompanied by temperature-independent, i.e., non-diffusive or oscillatory fast dynamics. In the supercooled region, the lineshape of the α relaxation is typically stretched (i.e., broadened with respect to a Debye function) but the lineshape and amplitude are temperature-independent above T_C [65–68].

Extending MCT to include the terahertz region is still challenging, and inevitably results in less meaningful fitting models, and we therefore use more conventional but readily interpreted phenomenological models. Even so, the contributions to the low-frequency spectrum are very difficult to disentangle and one of our aims is to identify the individual contributions through simplifying the spectra.

The three experimental techniques used in the work described here are dielectric spectroscopy (DS), optical Kerr-effect spectroscopy (OKE), and terahertz field-induced second-harmonic generation (TFISH).

The experimental setup for the OKE measurements has been described previously [16,69–72] and uses 800-nm 24-fs (FWHM) sech^2 pulses with 8 nJ per pulse at a repetition rate of 76 MHz. The beam is split into pump and probe beams (9:1), which are co-focused by a 10-cm focal length achromat into the sample contained in a 2-mm-pathlength quartz cuvette. The variable pump-probe time delay

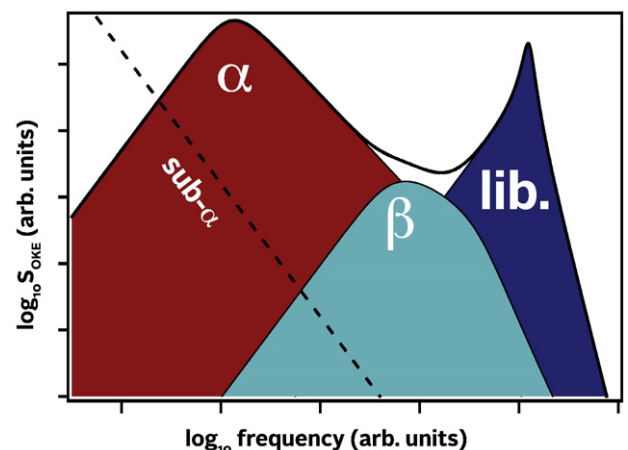


Fig. 1. A typical terahertz-frequency spectrum such as a reduced Raman spectrum or a dielectric relaxation spectroscopy spectrum.

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