Dynamics of supercooled aqueous systems at low temperature and high pressure

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Abstract

Aqueous mixtures are excellent systems to deepen the understanding of the relaxation dynamics of supercooled water in the temperature region usually unaccessible without crystallization. The first part of this thesis provides an investigation, by means of dielectric spectroscopy, of the molecular dynamics of water mixed with propylene glycol oligomers ($n$-PG, $n = 1, 3, 7$) at ambient and extremely high pressure (up to 1.8 GPa). By changing in a systematic way the relative concentration of water (starting from small amount of water, 2.0 wt.%) added to polypropylene glycol, PPG400, three relaxation processes show up: a) the slowest process, whose dynamic properties indicate that it is the structural $\alpha$-relaxation of the aqueous mixture leading to glass transition at $T$ equal to the calorimetric $T_g$; b) a faster process ($\nu$-relaxation process), which appears close to $\beta$- (secondary) process of PPG400 in dielectric spectra even for the lowest water concentration mixture (similarly as in the case of many other water mixtures) and has the characteristics of an intermolecular Johari-Goldstein secondary relaxation; c) the fastest process ($\gamma$-relaxation process), originating from hydroxyl group rotation, which is prominent for anhydrous PPG400, but this process is weak and becomes hidden by the much stronger $\nu$-relaxation for high water concentration mixture.

In addition, a change of the dynamics of the water related ($\nu$-) process occurs in all isobaric measurements: the temperature dependence of $\nu$- relaxation time, $\tau_\nu$, that has an Arrhenius behaviour in the glassy state, becomes stronger on increasing temperature in the liquid state. Such a crossover is in a way significantly different from similar phenomenon observed in literature for confined water. Moreover, our studies under pressure revealed that the secondary relaxation process for aqueous mixtures of PPG400 with low (4 wt.%) and high (26 wt.%) amount of water behaves in a different way. Our results show that the secondary relaxation in the mixtures with low content of water is mainly influenced by the dynamics of the solute molecules and has the characteristics of the Johari-Goldstein $\beta$-relaxation occurring in van der Waals and polymeric glassformers. In the case of high water content, where each molecule of water is mainly surrounded by other water molecules, the $\nu$- (secondary) relaxation has very specific characteristics, quite different from those of conventional glassformers in its ability to rotate and translate after breaking two hydrogen bonds.
Finally, mixing water with \( n \)-PG oligomers (increasing the number of repeating units, \( n \)) with similar weight concentration of water allowed us to study how the dynamics of water mixtures at ambient and elevated pressure is influenced by the number of OH-groups and by the connectivity of the solute. Similar studies have been carried out for aqueous mixtures with ethylene glycol oligomers.

Among the numbers of new experimental findings coming from this work, three results can be mentioned, of particular interest for the current debate in literature on dynamics of aqueous systems. The first is the increasing of timescale separation between \( \alpha \)- and \( \nu \)- process in dielectric spectra at given (the same) \( \alpha \)- relaxation time, \( \tau_\alpha \), on increasing temperature and pressure. This behaviour is usual for the timescale separation between \( \alpha \)- and \( \beta \)- processes of hydrogen bonded systems (like sorbitol) and not shown in the case of van der Waals liquids where the \( \alpha \)-\( \beta \) timescale separation is the same on increasing temperature and pressure but keeping constant \( \tau_\alpha \).

This effect is related to the fact that the H-bond network in such systems is weakened by elevating temperature and pressure and the structure of the system is changing with the thermodynamic conditions.

The second result of particular interest is that, when it has been possible to clearly reveal the \( \nu \)-relaxation from the glassy state up to well above \( T_g \), a strong deviation from the glassy state trend has been found for both the temperature and pressure dependence, with an apparent kink in the relaxation map always occurring near the glass transition of the aqueous mixtures. The only explanation for such result could be that such crossover in temperature or pressure dependence of \( \nu \)-process is related to glass transition. This occurrence helps to rule out some of the hypotheses on dynamic crossover recently published in literature.

The third important result is that the dielectric strength of the water-specific relaxation also exhibits a crossover from a weaker to a stronger dependence with increasing \( T \), at the temperature where the slow process attains a very long timescale (\( > 1 \) ks) and becomes structurally arrested.

All these facts support the idea that water-specific \( \nu \)-relaxation can be identified as the Johari-Goldstein \( \beta \)-relaxation of water. This interpretation of \( \nu \)-relaxation is in full agreement with the temperature, pressure, concentration dependence of its dynamic features and dielectric strength.

Taking into account the experience gained from the work on aqueous mixtures of glycol oligomers in the first part, the second part of the thesis is devoted to the study of aqueous
mixtures with saccharides or carbohydrates (mono-, di- and polysaccharides). The main idea was to investigate, by means of dielectric spectroscopy, the dynamics and glass transition phenomena of water-sugar mixtures under pressure for possible application to cryoprotection, food preservation, biological functioning of hydrated biomolecules. In order to widen the possible applications of this study, sugars of strong interest in bio-science were chosen, such as fructose, glucose, sucrose, trehalose, dioxyribose, glycogen. For water-fructose solutions a systematic study was done in a wide pressure range by varying concentration of water. A preliminary study of the dynamics of proteins solved in sugar-water mixture was also begun.

Summarizing, our results show that the relaxation time of the ν-process, \( \tau_\nu \), represents qualitatively very similar features for all studied aqueous systems, almost universal, irrespective of the chemical and structural differences, especially for high water concentration mixtures. The ν-relaxation has an Arrhenius \( T \)-dependence at low temperature with an activation enthalpy of about 50 kJ/mol universally found in the glassy state for aqueous mixtures at ambient pressure. Such activation enthalpy is comparable with that enough for breaking two hydrogen bonds whereupon the water molecules can rotate and translate. This is because the secondary relaxation originating from water in mixtures with high water content is effectively not so different from that in bulk or confined water. Our study confirms that the aqueous mixtures can be a useful “tool” for understanding the water dynamics in the temperature and pressure regions usually unaccessible without crystallization.

**Keywords:** glass transition; pressure; aqueous mixtures; \( \alpha \)- and ν- relaxation processes; glycol oligomers; saccharides; crossover; activation energy; fragility.
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General Introduction

When a liquid upon cooling avoids crystallization, it enters the supercooled (metastable) state. If the temperature continues to decrease, the consequent increase of viscosity is reflected in the molecular mobility in such a way that the characteristic relaxation times of cooperative motions of molecules become of the same order of the longer experimentally accessible timescales. Further cooling finally transforms the highly viscous liquid into a glass, in which configurational transitions are frozen and only local motions are allowed.

It is well known that the mobility at a microscopic scale, the temperature and pressure conditions determine the macroscopic properties of the materials, which also depend strongly on their chemical structures. Macroscopic response of the material can be originated by very different microscopic motions. In the low molecular weight substances, for example, simple (local) movements can consist in rotations or in very limited translations of the whole molecule. On the other hand, complex movements require cooperative motions with neighbour molecules. Moreover, it is interesting to note that materials with very different chemical structures exhibit molecular mobility with similar features. In the molten state, one of the characteristics of the equilibrium liquid is the high rate of molecular or segmental (in the case of polymeric chains) mobility, both translational and rotational mobility are present. This dynamical behaviour suffers drastic changes when the temperature decreases or pressure increases (i.e., increasing of density) and the liquid becomes an amorphous solid (glass).

The evolution from supercooled liquid to a glassy solid is called glass transition. However this phenomenon is a kinetic process, not a proper thermodynamic transition, produced by the impossibility of the material to reach the equilibrium state (within reasonable observation time) when the temperature decreases. In other words, the glassy state is an out-of-equilibrium state in which the material lacks any molecular order: the material in this sense continues to be a liquid, but the conformational mobility is mostly frozen [1]. As a consequence, the substance presents a mechanical behaviour similar to that of solid materials (it cannot flow, it sustains a shear force, etc.), while it keeps a disorder typical of liquids, i.e. without long-range order.
Far from being an exceptional situation, there are many materials that easily form a supercooled liquid and a glass, thus named as glass formers, such as polymers, sugars, and their mixtures with water. Also in ordinary life, it is common to find situations where the glassy state is crucial. The preservation of life under extremes of cold dehydration and the stabilization of labile biochemicals [2], the processing of foods [3-5], the improvement of bioavailability in pharmaceutical products [6, 7] are some of several examples in which the glassy state plays an important role.

The most abundant substance in our planet Earth is water, which is present in significant proportion in all living organisms, and without which life is impossible. Since pure bulk water easily crystallizes on cooling, its relaxation dynamics in the supercooled state cannot be deduced from various experiments without uncertainty and controversy including its glass transition temperature, $T_g$. Therefore, the study of water mixtures, which do not crystallize on cooling, serves yet another purpose that is, to infer, from the observed relaxation dynamics of water in the mixtures at various concentrations, the properties of supercooled pure water in its inaccessible temperature range below about 235 K.

That is why the study of the molecular dynamics of glass-forming binary mixtures of water with other hydrophilic substances is very interesting not only for practical purposes but for fundamental understanding of the glass transition.

The reorientational dynamics of water molecules, thanks to their very strong molecular dipole, can be successfully studied by broadband dielectric spectroscopy. This technique, present in Physics Department laboratory of the University of Pisa, allows for a very wide dynamic range from 10 ps up to 1 ks and can be applied both at ambient and very high pressure.

The thesis is organized as follows: Chapter 1 will introduce the general topics and phenomenology of glassforming liquids. The experimental setup and practical procedures will be described in Chapter 2. Chapters 3 and 4 will present the main results of our study. The effect of temperature and pressure on the structural and secondary relaxation in aqueous mixtures with glycol oligomers will be discussed in Chapter 3. In particular, the effect of water concentration and molecular weight of solute on dynamics will be reported. Chapter 4 will presents the results from experiments where the solutes are saccharides (mono-, di- and polysaccharides). The possible application of the results concerning the dynamics of saccharide-water mixtures to bio-relevant systems will be also discussed in this Chapter.
In Chapter 5 we will contribute to the discussion about common features in aqueous systems such as water mixtures, confined water in nanoporous media and water present in the hydration layer at the protein surfaces. A schematic picture about the general mechanisms of the dynamics of bulk water will be also presented.
Polarization, Dielectric Relaxation Spectroscopy and Glass Transition

The interaction between an electric field and matter can be studied by Dielectric Relaxation Spectroscopy (DRS) in a wide range of frequencies \((10^{-6}–10^{11} \text{ Hz})\). The variation of the dielectric constant with frequency and temperature is very useful for getting information about dipolar reorientational motions and electric conduction that arises from translational motions of charge carriers. With this information it is possible to infer about the molecular reorientational motions and even about the molecular structure and arrangement of the system. Since 1927, when Debye established the relationship between the dielectric relaxation and the orientational motions of molecular dipoles [8], the technique of DRS has been gaining progressively interest within the scientific community.

As this work is based in its majority in results acquired with this technique, it is important to present the basic concepts of BDS and theory that supports it.

1.1 Polarization

Since matter is constituted by electric charges, when an electric field is applied, an interaction is produced, taking, at equilibrium, to an arrangement of the charges different from that with no applied field. If free charges are present in the material, that interaction, together to some friction mechanism, results into a charge carrier drift that originates the conduction phenomenon. On the other hand, if the material is a dielectric, such a long range movement is not possible (or only in a weak way); nevertheless, the electric field is able to induce a deformation in the charge distribution with respect to the equilibrium situation. This displacement, with low intensity, is at the origin of polarization.

The basis of the theory of electric polarization is the development of electric potential \(\phi(P)\) into the elementary charge distributions (unipolar, dipolar, quadrupolar, … terms):

\[
\phi(P) = e \frac{1}{r} - m \cdot \nabla \frac{1}{r} + Q : \nabla \nabla \nabla \frac{1}{r} - U \nabla \nabla \nabla \frac{1}{r} + ..., \tag{1.1}
\]

where \(m, Q, U\) are dipole, quadrupole and octupole moments, respectively, \(e\) electric point charge, \(r\) radius vector.
In most of the systems moment of unipole is equal to zero (electrically neutral) and contributions to the polarization field due to the higher order dipole moments could be considered negligible. If so, the polarization $P$ is defined as a vector quantity that expresses the magnitude and direction of the overall electric dipole moment per unit volume in the material:

$$ P = \frac{1}{V} \sum_i p_i, \quad (1.2) $$

where $i$ counts all dipole moments in the system, $p_i = q_i r_i$, i.e. the product of charge times the position vector. Molecules have a dipole moment if there is a mismatch between positive and negative electric charge average. It is important to define the concept of dipole moment: two charges $q$ with opposite polarity, separated by distance $d$, can be characterized with the dipole moment $p = q d$. For any distribution of charges the dipole moment can be expressed by $p = \int V r \rho(r) d^3 r$ [9].

At first approximation, in the following, we will consider that the overall electric potential related to the charge distribution in our systems can be expressed completely in terms of electric dipole moment. We will not consider any multipole expansions. Moreover, due to the low electric field that we applied (less than $10^5$ V/m), non-linear effects can be neglected. Moreover, the systems we studied can be considered isotropic, a fact that will allow us to consider the polarization vector always parallel to electric field and to expressing permittivity as a scalar quantity and not as a tensor (unlike, for instance, the case of ferroelectric materials).

According to a very simplified approach, at microscopic level three main different mechanisms can induce polarization in a dielectric material when it is subjected to an electric field: electronic, atomic and orientational [10].

**Electronic polarization:** it happens when the electrons undergo a displacement with respect to the nucleus by the action of the electric field. Actually, the intensity of the electric field inside the atom ($\sim10^{11}$ V·m$^{-1}$) is higher than those applied in the experiments (less than $10^8$ V·m$^{-1}$); so this difference induces usually a weak polarization. This dipole moment can be induced by the external applied electric field or by the interaction with other molecular dipoles.

**Atomic polarization:** It is the result of the modification in the relative positions of atomic nuclei inside the molecule or in an atomic network as a result of the application of the external field. It is typical, for instance, in ionic crystals. The timescale on which such a displacement occurs is the same of movements of internal degrees of freedom like bending, twisting or stretching of molecules. All these movements are slower than those that originate the electronic polarization.
*Orientational polarization*: Only appears in polar materials, i.e. those systems possessing a static molecular or ionic dipole moments, and it is a result of the preferential orientation of these permanent dipole moments in the direction of the applied electric field.

The times of response of the three types of polarization are very different in condensed matter: around $10^{-17}$ and $10^{-14}$ s for electronic, $10^{-13}$ to $10^{-12}$ s for atomic polarization, and between $10^3$ and $10^{-12}$ s for orientational one (strongly dependent on temperature and material). Thus, the orientation of molecular dipoles is a relatively slow process in comparison with electronic transitions or molecular vibrations. Moreover, it does not mean that all molecules rearrange uniformly and instantly: It looks more like slight changes in their average orientations which proceed thermal fluctuations. The maximum polarization will be reached in material only when time after applying external electric field is sufficiently long to allow all molecules approach their equilibrium conditions. The physical quantity that describes how an electric field affects and is affected by a dielectric medium, and determines the ability of a material to polarize as a response to the field is called dielectric permittivity. The highest observable relative permittivity (or static dielectric constant), $\varepsilon_s$, in a material corresponds to the maximum value of its polarization (see fig. 1.1).

![Fig. 1.1. Mechanisms of polarization and frequency dependence of real and imaginary parts of dielectric permittivity.](image-url)
On the other hand, if the polarisation is measured immediately after the field is applied (i.e. there is no time for dipole orientation to take place), then the observed instantaneous relative permittivity, denoted \( \varepsilon_\infty \), will be low and due to deformational (electronic and atomic) effects alone. Therefore, somewhere in between these extremes of timescale there must be a dispersion from a high to a low relative permittivity.

Figure 1.1 shows the frequency-dependent real and imaginary parts of dielectric permittivity upon application of an oscillating electric field with frequency \( \nu \), putting in evidence several facts: i) the frequency location of the different mechanisms involved in the polarization is quite distinct; ii) the intensity of each process is also quite different but the relative intensity could depend on the system; and iii) the width of the loss peaks is higher in orientational polarization due to the resistance that the medium puts up to the dipole’s motion [10] being far from an instantaneous response as the other two polarization mechanisms. Actually, the main difference between electronic and atomic polarization response on one side and orientational polarization response on the other side is the resonant behaviour of the first two, while the latter shows the characteristic non-resonant decay in the simplest case described by the Debye equation. Indeed, while in the first case the equation for polarization is similar to that of a damped harmonic oscillator (with a quite high \( Q \) factor), the second case can be obtained for an overdamped oscillator, where the system returns or relaxes (exponentially decays) to equilibrium without oscillating. Actually the orientational motion of molecular dipoles in liquids is subjected to several frictional interactions with the surrounding medium.

1.2 Phenomenological description of dielectric measurement

In the thesis we will focus on the dielectric relaxation phenomena. The relaxation phenomena are very similar in the case of dielectric and viscoelastic response, as they occur, respectively, after application of electrical or mechanical stresses. The dielectric relaxation processes as well as mechanical can be described by means of general formalism, introducing a generalized force \( F \) and a generalized response \( x \). In our case the generalized force or disturbance is the electric field \( E \), the associated generalized response is the polarization \( P \) of the system. The relation between them is included in the linear-response theory (i.e. when the strength of the force is small, the response is proportional to that [10]). Thus the dependence of polarization \( P(t) \) on time dependent electric field \( E(t) \) can be written as:
\[ P(t) = \chi \varepsilon_0 E(t), \quad (1.3) \]

where the proportionality factor \( \chi \) is called the dielectric susceptibility and \( \varepsilon_0 = 8.854 \cdot 10^{-12} \) F/m is universal constant, called permittivity of vacuum. If the electric field has very high intensity the proportionality no longer holds, and the polarization \( P \) can be expressed by a power series expansion of \( E \):

\[ P = \chi \varepsilon_0 E + \sum_i \beta_i E^{(i+1)} . \quad (1.4) \]

From now and on only the linear approximation (Eq. (1.3)) will be considered, that is fully justified by the fact that the values of the electric field used in the experiment (less than \( 10^5 \) V/m) and the molecular permanent dipoles \( \mu \) involved bring to values of energy \((-\mu \cdot E)\) much smaller than the thermal energy \((k_B T \approx 1/40 \text{ eV})\) or bond’s energy (10 eV) that correspond to the values of electrical field of order \( E \approx 10^9 \text{ - } 10^{11} \text{ V/m} \).

From the definition of the vector of dielectric displacement the relation between susceptibility \( \chi \) and dielectric permittivity \( \varepsilon \) follows:

\[ \varepsilon = 1 + \chi . \quad (1.5) \]

It is important to note that \( \varepsilon \) depends on the material properties (structure and chemical composition) and physical parameters such as temperature and density. In the case of time-varying electric fields, if there is the dispersion phenomenon, the permittivity \( \varepsilon \) may depend on the frequency of the applied field. In fact, Eq. (1.3) implies an instantaneous response by the charge distribution of the system and it is true only for quasi-static case. On the contrary, when \( E \) changes in time faster than the characteristic time of the microscopic motion of the molecules, this latter will not be sufficiently rapid to build up the equilibrium polarization. On the other hand, it gives rise to a delayed response and a phase displacement between \( P \) and \( E \), depending on the frequency of the field: this phenomenon is called dispersion. Following the principle of causality the value of the polarization assumed at time \( t \) depends on the values of the applied electric field at all previous moments:

\[ P(t) = \varepsilon_0 \chi \int_{-\infty}^{t} f(t,t') E(t') dt'. \quad (1.7) \]

The function \( f(t,t') \) is called response function and it depends only on difference in times, \( f(t,t') = f(t-t') \). For a system with an instantaneous response in respect to the characteristic
timescale of the process (i.e. $f(t, t') = \delta(t - t')$, the Dirac’s delta function), we obtain Eq. (1.3), with $\chi_s$ which is called static dielectric susceptibility, reflecting the value of susceptibility that is obtained with time variation of the electric field much longer than the characteristic timescale of the system.

According to the formalism of linear response theory [11-14] Eq. (1.7) is nothing but the convolution integral between the response function (or Green function) $f(t - t')$ and the electric field $E$. In other terms, the function $f(t - t')$ is the response of the polarization of the system at time $t'$ on the pulse electric field $E = E_0 \delta(t - t')$. If the electric field of intensity $E_0$ applied to the system is kept constant for some time and then suddenly removed at $t = 0$, it can be represented with $E_0 \cdot \theta(-t)$, Heaviside step function. In that case, the produced electronic and atomic polarizations (also designed by induced polarization, $P_{\text{in}}$) disappear very fast (on a time scale shorter of ps). In contrast, the orientational polarization falls down slowly (comparatively to those ones) with an exponential decay (as a first approximation, usually there is a distribution of such functions). The polarization response $F(t)$ to a step function describing such a decay is called the relaxation function and related to $f(t)$ by the following relation [11-13]:

$$f(t) = -\frac{dF(t)}{dt}.$$  \hspace{1cm} (1.8)

After sufficiently long time after removal of the electric field the polarization of the system (and the relaxation function $F(t)$ associated with it) vanishes: limit values assigned to the relaxation function are therefore $F(t=0)=1$ and $F(t\rightarrow\infty)=0$ [11-13] (see also fig. 1.2).

![Fig. 1.2. Time dependence of the response $f(t)$ and relaxation $F(t)$ functions.](image-url)
In other words, the evolution of the system towards its equilibrium after removal of the electric field is called the relaxation phenomenon. This lag in response is due to the internal friction of the material, and it can be related to viscosity $\eta$. For viscoelastic relaxation, in fact, according to the Maxwell model, the shear relaxation time is proportional to viscosity $\eta G_\infty$, being $G_\infty$ the infinite frequency shear modulus [15]. More is the viscosity of the medium, slower is the relaxation. Keeping this in mind, naturally arises the necessity to define a parameter that describes the polarization loss dynamics when the electric field is turned off. This parameter is the characteristic time, known also by relaxation time (required time to polarization decreases a factor $1/e$ from its initial value), and its average value can be measured by the integral of the relaxation function:

$$\langle \tau \rangle = \int_0^\infty F(t)dt.$$  \hspace{1cm} (1.9)

To analyse phenomena characterized by an arbitrary time dependence is useful to move the analysis of phenomena from the time domain to the frequency domain. This is possible due to the linearity of the response of the system: applying the Laplace transform to Eq. (1.7) with respect to $i\omega$ ($\omega=2\pi v$, angular frequency of the applied field), it is obtained from the relation of direct proportionality between transformed electric field and polarization which defines the complex dielectric susceptibility $\chi(\omega)$:

$$P(\omega) = \varepsilon_0 \chi(\omega) E(\omega).$$  \hspace{1cm} (1.10)

The $\chi(\omega)$ is, in contrast to the static susceptibility, the Laplace transform of the response function $f(t)$ of the system:

$$\chi(\omega) = \chi'(\omega) - i \chi''(\omega) = \chi_s \int_0^{\infty} f(t)e^{-\omega t}dt.$$  \hspace{1cm} (1.11)

Substituting Eq. (1.8) in Eq. (1.11) and partially integrating one can obtain the relation between the relaxation function $F(t)$ and the complex dielectric susceptibility $\chi(\omega)$:

$$\chi(\omega) = \chi_s \left[ 1 - i\omega \int_0^{\infty} F(t)e^{-\omega t}dt \right].$$  \hspace{1cm} (1.12)

On the basis of Eqs. (1.5) and (1.6) the complex dielectric permittivity can be defined in the frequency domain, $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$:

$$\varepsilon(\omega) = 1 + \chi(\omega).$$  \hspace{1cm} (1.13)

From Eq. (1.13) the static dielectric permittivity can be obtained $\varepsilon_s = \varepsilon(0) = 1 + \chi(0) = 1 + \chi_s$.  

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The real part of susceptibility $\chi'$ and the permittivity $\varepsilon'$ is the polarization component (in phase with applied electric field) which is related to a measure of the oriented molecules with electric field and of the fraction of the stored electromagnetic energy per period. On the other hand, the imaginary part of two variables is related to dissipated energy during the process (out-of-phase component) [11-13]. It can be also calculated the power $L$ dissipated by the system in a period by the time averaging of the expression $E \cdot (dP/dt)$ [11-13] and the result, for a harmonic electric field with amplitude $E_0$ and frequency $\omega$, is $L = \pi E_0^2 \omega \varepsilon_0 \chi''(\omega)$. For this reason the imaginary part of permittivity, $\varepsilon''$, is also called dielectric loss factor and the ratio $\tan(\delta) = \varepsilon''(\omega)/\varepsilon'(\omega)$, corresponding to the ratio between dissipated and stored energy for the period of oscillation, it is called the dielectric loss factor or dissipation factor [16]. It contains no more information than $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, but this ratio can be obtained directly from complex capacitance independently of the capacitor geometry. This is particularly important if the capacitor geometry is not well defined. Furthermore, $\tan(\delta)$ is used as a measure of the sensitivity of dielectric equipment. Recently, dielectric equipment able to measure $\tan(\delta) \approx 10^{-5}$ has become available [17].

Dielectric relaxation spectroscopy apparatuses are precisely based in the measure of the loss of polarization (i.e. dielectric relaxation) after the step removal of an external electric field at a certain temperature or pressure. The way as these dipoles relax will be rationalized in terms of molecular mobility existing in the system. Alternatively, a field sinusoidally changing with time is applied and the gain and phase displacement of the polarization response at different frequencies are acquired, taking to the so-called dielectric spectra.

When a relaxation happens, this can be detected either as a peak in the imaginary part or as an inflexion in the curve of the decrease of real part of susceptibility (and thus permittivity). That means that the two components are not independent: in fact, for a system that is linear, causal and stationary (i.e. independent of the choice of the time axis origin), as previously hypothesized, the real and imaginary parts are connected by the Kramers-Kronig (KK) dispersion relations [10, 18, 19]:

$$\chi'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\xi \chi''(\xi)}{\xi^2 - \omega^2} d\xi; \quad \chi''(\omega) = -\frac{2}{\pi} \omega P \int_0^\infty \frac{\xi \chi'(\xi)}{\xi^2 - \omega^2} d\xi. \quad (1.14)$$

The letter $P$ indicates that it is needed to calculate the main part of the integrals [14].

On the basis of Eqs. (1.6) and (1.14) the Kramers-Kronig relations for complex dielectric permittivity can be written:
\[ \varepsilon'(\omega) - \varepsilon_\infty = \frac{2}{\pi} \int_0^\infty \frac{\xi \varepsilon''(\xi)}{\xi^2 - \omega^2} d\xi; \quad \varepsilon''(\omega) = -\frac{2}{\pi \omega} \int_0^\infty \frac{\varepsilon'(\xi) - \varepsilon_\infty}{\xi^2 - \omega^2} d\xi. \]  

(1.15)

For the derivation of the Kramers-Kronig relations it has been used that:

\[ \int_0^\infty \frac{d\xi}{\xi^2 - \omega^2} = 0. \]  

(1.16)

Eqs. (1.15) give the opportunity to obtain one part of the complex dielectric permittivity (real or imaginary) if another part (imaginary or real) is known from experiment. Actually, two singularities occur in Eqs. (1.15) when it is not possible to obtain unequivocally real part from imaginary and vice versa. First, when the real part of dielectric permittivity is constant with \( \omega \) (in practice equal to \( \varepsilon_\infty \) or \( \varepsilon_\infty' \)) Eq. (1.15 right) leads to Eq. (1.16), i.e. to 0. Second, when the imaginary part of dielectric permittivity is proportional to \( 1/\omega \) (it could be in the case of dc conductivity term in dielectric spectra) Eq. (1.15 left) leads again to Eq. (1.16).

It is important to note that if only real part of the complex dielectric permittivity, \( \varepsilon'(\omega) \), is known from experiment it is not possible to obtain dc conductivity using Kramers-Kronig relations (a true conductivity term proportional to \( 1/\omega \) in the \( \varepsilon''(\omega) \) spectra gives no contribution to the real part), and on the other hand, if only \( \varepsilon''(\omega) \) is known from experiment it is not possible to obtain the value of \( \varepsilon_\infty \). It is so clear the importance to analyse simultaneously both real and imaginary part of permittivity.

### 1.3 Debye model and related empirical models

Debye in 1929 presented a work on dielectric properties of polar liquids [20] where he proposed that for a dipolar system in non-equilibrium, relaxation takes place with a rate that increases linearly with the distance from equilibrium.

This statement can be written by a first order differential equation such as:

\[ \frac{dP(t)}{dt} = -\frac{P(t)}{\tau_D}, \]  

(1.17)

where \( \tau_D \) is a characteristic relaxation time. Three assumptions were made: (i) negligible interactions between dipoles, (ii) only one type of process brings to the equilibrium (i.e. either a transition above a potential barrier either a rotation with friction) and (iii) all the dipoles can be considered equivalents, that is, all of them relax in average with only one characteristic time.
Eq. (1.17) leads to an exponential decay for the correlation decay function $\Phi(t)$:

$$\Phi(t) = \exp\left(-\frac{t}{\tau_D}\right).$$  

(1.18)

The relation for the complex permittivity in the frequency domain can be obtained as [21]:

$$\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} = \left(\varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\omega\tau)^2}\right) - i\left(\frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2}\right).$$  

(1.19)

This is the well-known Debye dispersion equation. Plots of the characteristic shapes of real and imaginary parts of $\varepsilon^*$ against $\nu = \omega/2\pi$ ($\nu$ is the frequency of the outer electrical field) for this model are shown in fig. 1.3 (a). The imaginary part exhibits a symmetric peak whose maximum value occurs at $\omega_\text{max} \tau = 1$ and has an amplitude of $\varepsilon^*_{\text{max}} = (\varepsilon_s - \varepsilon_\infty)/2$. The breadth of the peak at half the height covers 1.14 decades of frequency [11].

The real part shows dispersion falling from $\varepsilon_s$ to $\varepsilon_\infty$ with increasing frequency. The most probable relaxation time of the process, $\tau$, is defined as the inverse of $\omega_\text{max}$ ($\tau = 1/2\pi f_\text{max}$).

The Debye response behaviour is observed in very few materials among which are organic liquids (acids and monohydroxy alcohols) [22-24] and liquid crystals [25]. For more complex systems as it is the case of supercooled liquid and polymers, this model fails to represent experimental data since most of the Debye assumptions are not satisfied: in fact molecular dipoles strongly interact, multiple processes bring to relaxation (with a distribution of activation barriers and of relaxation times), and not all the dipoles are equivalent, since, even in homogeneous systems, a dynamic heterogeneity sets up at molecular scale.

![Graph](image)

Fig. 1.3 (a) Frequency dependence of the real, $\varepsilon'$, and imaginary, $\varepsilon''$, parts of permittivity in a simple Debye process. (b) Imaginary part vs. real part of $\varepsilon^*$.
Treating dielectric data, it is sometimes useful to construct the plot of imaginary part vs. real part of permittivity, known by Cole-Cole plot. In this representation, the Debye model corresponds to a symmetric semicircle arc (see fig. 1.3(b)).

Usually the measured dielectric functions in most of systems are much broader than predicted by the Debye function. Moreover, in many cases the dielectric function is asymmetric, i.e. that means that the short time (high frequency) behaviour is more pronounced than the long time (low frequency) one. This is called non-Debye or sometimes non-ideal dielectric relaxation behaviour. To take into account such phenomena Wagner proposed to use a continuous distribution of relaxation times [26]:

\[
\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_S - \varepsilon_\infty} = \int_{\tau=0}^{\tau=\infty} \frac{G(\ln \tau)}{1 + i \omega \tau} d \ln \tau, \tag{1.20}
\]

with logarithmic distribution function:

\[
\int_{\tau=0}^{\tau=\infty} G(\ln \tau) d \ln \tau = 1. \tag{1.21}
\]

The corresponding expression for the response function is:

\[
F(t) = \int_{\tau=0}^{\tau=t} \exp(-t/\tau) G(\ln \tau) d \ln \tau. \tag{1.22}
\]

In the literature, much attention has been paid to the problem of obtaining information about distribution function from experimental results, although not in all cases the distribution function has a direct meaning. Mostly, the experimental results are represented as values of \(\varepsilon'(\omega)\) and \(\varepsilon''(\omega)\) at a number of frequencies. And approximate relations between \(G(\ln \tau)\) and frequency dependence of \(\varepsilon'(\omega)\) and \(\varepsilon''(\omega)\) at \(\omega = 1/\tau\) can be obtained only if the width of the distribution function \(G(\ln \tau)\) is large with respect to that of the graph for \(\varepsilon''(\omega)\) against \(\ln \omega\) for a single relaxation time [10].

In many cases the non-Debye relaxation behaviour in the time domain is empirically described by the Kohlrausch-Williams-Watts (KWW) function [27, 28] (KWW-function) also named “stretched exponential function”, that is:

\[
\Phi(\tau) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right]. \tag{1.23}
\]

The stretching parameter \(\beta_{KWW}\) \((0 < \beta_{KWW} \leq 1)\) leads to an asymmetric broadening of \(\Phi(\tau)\) at short times compared with exponential decay \((\beta_{KWW} = 1)\), the case of simple Debye relaxation
behaviour). \( \tau_{KWW} \) is the related relaxation time. KWW function has not analytic Fourier transform to the frequency domain. In the frequency domain the relaxation data are often described by the empirical function of Havriliak and Negami (HN) [29] which reads

\[
\varepsilon_{HN}^* (\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega\tau_{HN})^{\alpha_{HN}}}^{\beta_{HN}}. \tag{1.24}
\]

The fractional shape parameters \((1 - \alpha_{HN})\) and \(\beta_{HN}\) \((0 < (1 - \alpha_{HN}); (1 - \alpha_{HN})\beta_{HN} \leq 1)\) describe symmetric and asymmetric broadening of the complex dielectric function. Moreover \((1 - \alpha_{HN})\) and \(\beta_{HN}\) are related to the limiting behaviour of the complex dielectric function at low and high frequencies, that are asymptotically described by power laws:

\[
\varepsilon_0 - \varepsilon'(\omega) \sim \omega^m; \varepsilon'' \sim \omega^n \quad \text{for} \quad \omega \ll 1/\tau_{HN} \quad \text{with} \quad m = (1 - \alpha_{HN}), \tag{1.25}
\]

\[
\varepsilon'(\omega) - \varepsilon_\infty \sim \omega^{-n}; \varepsilon'' \sim \omega^{-m} \quad \text{for} \quad \omega \gg 1/\tau_{HN} \quad \text{with} \quad n = (1 - \alpha_{HN})\beta_{HN}. \tag{1.26}
\]

Some examples of the behaviour described by Havriliak-Negami function are shown in fig. 1.4.

![Graph](image)

Fig. 1.4. (a) Frequency dependence of the real, \(\varepsilon'(\omega)\), and imaginary, \(\varepsilon''\), parts of permittivity. (b) Imaginary part vs. real part of \(\varepsilon^*\). Continuous lines show the Debye function case, dotted lines show the HN function with \(\alpha_{HN}=0.6\) and \(\beta_{HN}=1\) (symmetric case) and dashed lines show the HN function with \(\alpha_{HN}=0\) and \(\beta_{HN}=0.4\) (asymmetric case).

The frequency of maximum \(\varepsilon''\), \(f_{max}\), can be analytically calculated from the HN fitting parameters by:

\[
f_{max} = \left(2\pi\tau_{HN}\right)^{-1} \sin^{\frac{1}{1-\alpha}} \left(\frac{\pi(1-\alpha)}{2(1+\beta)}\right)^{\sin^{\frac{1}{1-\alpha}} \left(\frac{\pi(1-\alpha)\beta}{2(1+\beta)}\right)} \tag{1.27}
\]
The most significant parameter of a single relaxation process is the characteristic relaxation time \( \tau \), which is also the average time, that is the area below the peak curve of the different relaxation spectra. In the case of a distribution of relaxation times, a significant value is which represents the most probable time. It can be easily obtained from Eq. (1.27) as \( \tau = (2\pi \cdot f_{\text{max}})^{-1} \), which is usually preferred to \( \tau_{\text{HN}} \) since it is a model-independent parameter.

It is important to note that Eqs. (1.19) and (1.24) are theoretically compatible with Kramers-Kronig relations (Eqs. (1.15) and (1.16)).

The quantity \( \Delta \varepsilon = (\varepsilon_s - \varepsilon_a) \) in Eq. (1.24) is named dielectric relaxation strength and it is a measure of the orientational contribution to polarization. It can be obtained from the difference between low and high frequency of the real part of permittivity or from the area below the imaginary part versus logarithm of frequency of the loss peak (see fig. 1.1). In a molecular liquid dielectric strength can be described by the equation [30]:

\[
\Delta \varepsilon = \frac{4\pi C}{3k_B T} F g_K N_A \mu^2,
\]

where \( N_A \) is the Avogadro number, \( k_B \) the Boltzmann constant, \( \mu \) is the molecular dipole moment, \( C \) is the number of effective dipoles per unit volume, \( F \) is the local field correction, \( g_K \) is the Kirkwood correlation factor which gives the local static angular correlations between the dipoles.

Eq. (1.28) was generalized on the basis of Debye formula [30] by Onsager [31] and later by Kirkwood [32-34] and Fröhlich [21]. Onsager obtained it for polar molecules by the theory of the reaction field [31] which considers the enhancement of the permanent dipole moment of a molecule \( \mu \) by the polarization of the environment. In practice Onsager equation fails for polar associating liquids because interactions of neighbouring molecules are not considered in the derivation of the equation. Therefore, Kirkwood [32-34] and Fröhlich [21] introduced the correlation factor \( g_K \) to the model of the dipole interaction. In the first approach to calculate Kirkwood correlation factor, only the nearest neighbours of a selected test dipole are considered and \( g_K \) can be approximated by:

\[
g_K(T) = 1 + z \langle \cos \psi \rangle,
\]

where \( z \) is the coordination number and \( \psi \) is the angle between the test dipole and a neighbour [9, 30]. In practice \( g_K \) is very difficult, if not impossible, to obtain on a molecular basis, thus Eq. (1.28) cannot be used to calculate theoretical \( \Delta \varepsilon \) and, instead, it is usually used to calculate the
correlation factor $g_K$ from measured $\Delta \varepsilon$. Usually all the quantities involved have a very weak $T$ dependence, excepting $g_K$ that has a temperature dependence that can be approximated as a first order polynomial: therefore the overall temperature behaviour can be represented by a first order polynomial in $1/T$, so if the number of effective dipoles per unit volume $C$ is nearly constant, $\Delta \varepsilon$ usually decreases with increasing temperature for a structural $\alpha$-process. If the number of effective dipoles on the other hand increases on increasing temperature, as it occurs for secondary (local) relaxation processes (that usually have to overcome an activation barrier), $\Delta \varepsilon$ is found to increase with temperature.

1.4 Molecular dynamics and the glass transition problem

1.4.1 Molecular dynamics and macroscopic response

Why is the knowledge of the macroscopic electric response important for understanding the molecular dynamics? Because the linear response theory relates the macroscopic response function to microscopic dynamics, i.e. to the spontaneous fluctuations of an observable due to molecular motions [13, 35, 36]. Let’s consider the stochastic fluctuations of the microscopic variable $x(t)$ (for instance $x(t) = p(t)$ microscopic polarization). We can suppose that the expectation value $\langle x(t) \rangle$, i.e. the average on the ensemble of all the possible values of $x(t)$ in the system, is constant with time (stationary process) and it is equal with the time average (ergodic process). Assuming, for making it simple, that $\langle x(t) \rangle = 0$ (that can be always obtained by subtracting the average value), the autocorrelation function $\chi(t)$ can be defined as:

$$\phi(t) = \langle x(t')x(t'+t) \rangle.$$  \hfill (1.30)

This function describes the correlation degree of the variable $x$ at the instant $t'+t$ with the same variable at time $t$; when the autocorrelation function is zero it means that events differing more than time $t$ are statistically not related. The knowledge of $\phi(t)$ provides important information about the microscopic dynamics of the system and it allows to directly check theoretical predictions on molecular dynamics, so important to define unsolved problems as that of the glass transition. Some spectroscopic techniques allow to acquire, directly or less directly, $\phi(t)$. Concerning the spontaneous fluctuations of the microscopic polarization $p(t)$ there are some methods based on dielectric noise analysis [37, 38] that allow to obtain $\phi(t)$, with very strong limitation in sensitivity. It is therefore very important to relate $\phi(t)$ and the data, very accurate,
that can be obtained from a dielectric relaxation experiment (by means of permittivity). Conventional dielectric spectroscopy provides information on the autocorrelation function of the macroscopic polarization. In fact, according to Kubo relation [13], the relaxation function \( \Phi(t) \) and the autocorrelation function are related as:

\[
\Phi(t) = \frac{1}{k_B T} \langle \vec{P}(0) \cdot \vec{P}(t) \rangle = \frac{1}{k_B T} \left[ \langle \vec{p}_i(0) \cdot \vec{p}_i(t) \rangle + \sum_{j \neq i} \langle \vec{p}_i(0) \cdot \vec{p}_j(t) \rangle \right] = \phi(t) + \Psi(t), \tag{1.31}
\]

where \( T \) is the temperature in Kelvin and \( k_B \) is the Boltzmann constant, \( \vec{P} \) is overall electric dipole moment per unit volume defined by Eq. (1.2), \( \vec{p} \) is microscopic dipole moment, \( \phi(t) \) is the microscopic autocorrelation function, \( \Psi(t) \) is the cross-correlation term. Therefore, only when the cross-correlation term is negligible, i.e. when microscopic dipoles are non-interacting, dielectric spectroscopy can give information on the microscopic dynamics. Unfortunately, this case occurs very rarely, for instance in very diluted dipolar solutions.

Moreover, it is possible to relate the autocorrelation function \( \Phi(t) \) to the power spectrum \( I(\omega) \) of the fluctuations of \( P(t) \) and the latter to the imaginary part of the susceptibility, using the Wiener-Kintchine theorem and the fluctuation-dissipation theorem [13, 36]:

\[
\frac{1}{2\pi} \int_{-\infty}^{+\infty} \Phi(t) e^{-i\omega t} dt = I(\omega) = 2k_B T \frac{\chi''(\omega)}{\omega}. \tag{1.32}
\]

Thanks to the above mentioned relations, we can affirm that the data obtained in relaxation experiments in a system with linear response provide information on the fluctuation dynamics of the examined system. Moreover, due to this achievement, it is equivalent to acquire data in time domain (through the response or relaxation function) or in frequency domain (through susceptibility to permittivity). If the microscopic polarization \( p(t) \) can be associated to reorientational motions of the molecular dipoles, dielectric spectroscopy experiments allow the direct study of microscopic molecular dynamics.

### 1.4.2 Slow Dynamics and Glass Transition

The motions of molecules constituting a liquid are known to slow down when the temperature is decreased or the pressure (or density) is increased. Eventually, if the liquid can be supercooled below its melting point or compressed beyond the melting curve without forming a crystal and kept in that metastable state also to much lower temperature or higher pressure, the dynamics of liquid can become so slow that eventually the molecules cannot attain their dynamic equilibrium
configurations on the time scale of observation, and the system becomes structurally arrested, with its structure similar to that of a liquid \textit{(i.e.} without long range order). The amorphous solid so obtained is called glass.

This falling out of equilibrium occurs across a narrow transformation temperature or pressure range where the characteristic molecular relaxation time becomes of the order of $10^2$ s, and the rate of change of volume or enthalpy with respect to temperature decreases abruptly to a value comparable to that of a crystalline solid \cite{39}. Figure 1.5 illustrates the temperature dependence of a liquid's specific volume (or enthalpy) at constant pressure. The glass transition is defined by the change of slope in the temperature dependence of the considered quantity (thermodynamic definition). In this figure, a slow cooling rate will bring the system out of equilibrium later and at a lower glass transition temperature $T_{g_{\text{slow}}}$ corresponding to a smaller specific volume or enthalpy, whereas a faster cooling rate will lead to a glass transition at a higher $T_{g_{\text{fast}}}$ with a bigger specific volume or enthalpy. So, $T_g$ increases with cooling rate.

![Figure 1.5. Temperature dependence of the specific volume (or enthalpy) of a glass former. $T_m$ is the melting temperature, $T_g$ is defined as the temperature at which the liquid and the glass $V(T)$ curves intersect. $T_g$ depends on cooling rate which is faster for “glass 1” (reproduced from ref. [40]).](image)

The glass transition temperature is not associated to the discontinuity of any thermodynamic variable but to the temperature range where the transition to the out-of-equilibrium amorphous solid state occurs. The common definition of $T_g$ in terms of thermodynamic properties is reported
above. According to dynamic properties, $T_g$ is the temperature at which the shear viscosity reaches $10^{13}$ poise or the structural relaxation time (usually proportional to viscosity) reaches 100 s (as was mentioned above, more viscous is system slower is the relaxation process, \textit{i.e.} the relaxation time is proportional to the viscosity of the material).

Thus the glass transition or vitrification is nothing but the manifestation of the dramatic slowing down of kinetic processes, such as diffusion, viscous flow and molecular reorientations. Such a phenomenon is very general and it has been found in organic, inorganic, metallic, polymeric, colloidal, and biomolecular materials. It is not typical of some material: usually molecular liquids with complex chemical structure are more prone to form glasses, as well as some disordered systems like atactic polymeric melts, but recently vitrification was shown in simulation also for very simple systems like argon [41]. The most important variable seems to be the cooling rate: if one is able to quench a liquid fast enough, a glass will be obtained.

In summary, as a phenomenon, it is recognized that glass transition is the arrest of the structure from reaching equilibrium, and is well understood simply from kinetics consideration. Its main cause is the slow structural relaxation (see section 1.5.1). A fundamental understanding of glass transition requires the knowledge of the dynamics of the structural relaxation and the identification of the factors that make $\tau_a$ to slow down drastically with decreasing temperature or increasing pressure. Surprisingly, in spite of the long history of the phenomenon and technological significance of glass, there is still no universally accepted view on the dynamics of the structural relaxation, so that this is one of the unsolved question of condensed matter physics (see [42, 43]). There is no consensus on the factors governing the dramatic slowing down of the structural relaxation and related kinetic processes, such as viscous flow and diffusion. Development of a microscopic and quantitatively accurate theory of the glass transition that is generally applicable to real materials, has become even more challenging with the improvement of experimental techniques and the introduction of new ones. These advances have led to the discovery of an increasing number of general properties of the dynamics of glass-forming materials spanning the range from picoseconds to years. In fact, accurate spectroscopy techniques show that not only the slow structural relaxation is important for glass transition, but also other faster processes. An accurate theory should take into account all these phenomena spanning the whole dynamic range.

Glass transition is currently still the subject of active research with many participants, and the theme of many international scientific conferences [44-46]. Its study is no longer limited to the
few traditional areas concerning the amorphous structural materials (silicate and polymer
glasses), but has branched out to electronics and opto-electronics, metallurgy, geoscience,
materials for energy source applications, and others. The study of glass transition has recently
received a boost from activities in nanoscience and nanotechnology, where the changes found in
the dynamics of the structural relaxation and glass transition temperature present new challenges
[47-50]. Other recent fields where glass transition is of great interest are biology, pharmacy,
medicine and food industry: protein dynamics seem to resemble that of very complex glass-
forming polymers [51]; drugs have been found to be more soluble (so more bio-available) in
their amorphous (glassy) state than in their crystalline [7]; aqueous mixtures with glycols and
sugars are commonly used for the food storage, conservation and for the cryo-preservation of the
biological systems [52, 53].

1.5 Relaxation phenomena in glassy systems

In physics, the relaxation phenomenon means the return of the macroscopic system to the
thermodynamic equilibrium after removal of an external perturbation. For example, in our case a
system can be perturbed from its equilibrium state by the electric field, whereby the energy from
the external source can be dissipated in the system in characteristic time-regions which are
determined by the molecular structure of the glassy system. These are the relaxation processes in
which configurational rearrangement of atomic or molecular constituents of the glass is induced
by the external stress (electric field) which must be small compared with, for example, the
electrical forces acting between the constituent particles. These relaxation processes may be
monitored by different ways, some of which determine the volume or enthalpy of the system,
while others the permittivity or the optical density at frequencies characteristic of specific
subunits of the glass structure are determined. Moreover, the characteristic time scales of the
relaxations are of particular interest in material science because, in contrast with frequencies of
resonant phenomena, they are highly temperature-dependent, varying over 13-15 orders of
magnitude between the glass temperature and the normal melting temperature. Generally,
relaxation processes are named successively by the order of appearance at fixed frequency on
cooling the system, by the Greek letters $\alpha$, $\beta$, $\gamma$, $\delta$ and can be classified according to their time
scale in the following order:
(i) At the longest time scale structural changes are allowed by collective, cooperative motions that involve the rearrangement of groups of molecules or the segmental motions of polymer chains. In this case the dynamics is controlled by the $\alpha$-relaxation, named also the structural relaxation which is the main universal dynamical process related to the glass transition (see fig. 1.6) and describes the situation near $T_g$ with the $\alpha$-peak situated at a rather low frequency. On increasing temperature it will rapidly shift to higher frequencies.

(ii) At shorter times, the molecular motions are non-cooperative. These faster and non-cooperative processes are present as well in the viscous liquid state as in the glassy state and are generally more localized than the cooperative $\alpha$-process. Their behaviour in the glassy state is purely activated. They are usually called secondary or $\beta$-relaxation processes. Because of the disordered structure of the glass, a large distribution of the barrier energy can be present. In some systems with several degrees of freedom, several secondary relaxations can be present (they are labelled as $\beta$, $\gamma$, $\delta$, etc.).

(iii) At some THz a second loss peak shows up, which can be identified with the so called *boson peak* (see fig. 1.6) known from neutron and light scattering [9]. The boson peak is a universal feature of a glass system and corresponds to a low frequency excess in the vibrational density of states.

![Fig. 1.6. Schematic view of the dielectric relaxation loss spectra in glass-forming systems for one temperature. The $\alpha$-relaxation related to the dynamic glass transition, the excess wing, the fast $\beta$-process, the boson peak and infrared bands (intramolecular modes) at the highest frequencies are shown (reproduced from ref. [54]).](image-url)
In the following sections, we will introduce and discuss the main features of the structural $\alpha$-relaxation and secondary $\beta$-relaxation.

### 1.5.1 The structural relaxation

The central and most important dynamical phenomenon in glass-forming systems is the $\alpha$-relaxation. It is undoubted that every glass shows this type of dynamics and certain characteristics are always observed [55]. On decreasing temperature $T$ or increasing pressure $P$, the structural relaxation time $\tau_\alpha$ of supercooled liquids becomes increasingly long. The most prominent features of the $\alpha$-relaxation resulting from structural disorder are non-exponential relaxation patterns and a non-Arrhenius temperature dependence of the characteristic timescale [41, 56].

**a) Non-exponentiality and dynamic heterogeneity:** As was mentioned before (see section 1.3), differently to a simple Debye relaxation phenomenon in which the correlation function is described by a simple exponential function, the structural relaxation appears more slowly and it can be described by the empirical stretched exponential [10] or the Kohlrausch-Williams-Watts type decay [27, 57] for a very broad class of materials [27, 41]. The deviation from the simple to the stretched exponential function describing the time dependence of the relaxation functions when a liquid is supercooled should be related to two reasons:

- The “cage effect” which is already present in the normal liquid but should become more pronounced on increasing density, *i.e.* when temperature decreases or pressure increases. “Thus, the long time dependence of the relaxation functions should have a larger temperature dependence on approaching the glass transition than the short time dependence and the motion will be more and more cooperative as the molecular packing increases, whereas the latter is related to ‘in cage’ motions and is thus less affected by the freezing of the cages. This difference explains the stretching as well as the increased temperature dependence of the relaxation times, which are dominated by the long time dependence” [58].

- **Dynamic heterogeneity** which is now recognized as a fundamental feature of the slow dynamics of supercooled fluids and glasses in condensed matter. Heterogeneity regarding the dynamics refers to the picture in which fast and slow relaxing modes exist [56, 58-63]. There is a long history of heterogeneous models of translational and rotational dynamics in supercooled liquids:
for a comprehensive review on heterogeneity and dynamics see the papers by Prof. Sillescu [58] and Prof. Richert [56]. The sizes of these domains, which are dynamically distinct, are assumed to be of the order of several nm [59-62]. Taking a snapshot of a glass-forming system, in the same environment some molecules are characterized by fast motions, while others are much slower, acting as cages for the faster. This picture is dynamic, in the sense that, few moments later (usually on the time scale of the structural relaxation $\tau_\alpha$) due to the mutual interactions, the fast molecules could become slow and vice versa. Fast and slow molecules are usually clustered in domains. One could be tempted to explain the stretched exponentiality character of the relaxation in glass-forming systems, simply assuming that, in each spatial domain, relaxation occurs exponentially but with a different relaxation time in each domain: averaging over the ensembles, this should lead to a distribution of relaxation times. Following this idea, Ediger et al. [63] proposed a spatially heterogeneous model of translational and rotational diffusion in supercooled liquids, i.e. the different temperature behaviour of the two quantities reported in the region $T_g < T < 1.2T_g$. In fact translational diffusion was found less temperature dependent than the rotational one. According to Ediger the decoupling could be due to the different prominences that fast and slow motions have on translational and rotational diffusion, respectively: therefore, if spatial heterogeneity reflects into a given distribution of relaxation times for the $\alpha$-relaxation, wider is the distribution stronger is the decoupling between translational and rotational diffusion. On the contrary, some experimental evidences for organic glass-formers (for instance $aa\beta$-tris-naphthylbenzene (TNB) [64, 65], showed that the width of the relaxation peak (and so the distribution of relaxation times) was temperature independent over a broad temperature range, while in the same temperature range a decoupling between translational and rotational diffusion was found. An alternative explanation was proposed by the coupling model (CM) (see section 1.6) according to which decoupling of translational and rotational diffusion in glass-forming liquids is a special case of a more general phenomenon, i.e. that different dynamic observables weigh the many-body relaxation differently and have different coupling parameters $n$ (i.e. different degrees of intermolecular cooperativity) that enter into the stretch exponents $\beta_{KWW}$ of their Kohlrausch correlation functions but also in the temperature dependent considered observable [66, 67].

Concerning the homogeneous scenario, among the models proposed in recent years, the one that received the most attention is the Mode Coupling Theory (MCT) developed by Götze and Sjögren [68]. This theory gives one of the interpretation of the complex microscopic dynamics of
simple supercooled liquids. The MCT predicts and explains a wide range of phenomena relating
to the glass transition with a small number of basic assumptions and concepts borrowed from the
dynamics of simple liquids. Despite of the validity and applicability of this theory it is still a
matter of debate [69, 70]. Some results of this model are certainly interesting and shown below
along with the main features of the MCT model.

The Mode Coupling Theory directly calculates the autocorrelation function of the density
fluctuations of a liquid \( \phi(t) \), through which one can go back to the relaxation function (see § 1.2)
and monitor the dynamics of the system. The function \( \phi(t) \) describes the correlation between the
positions of the molecules, i.e. it measures the probability of finding a molecule in certain
position \( \mathbf{x} \) at time \( t \) (initial conditions: \( \mathbf{x} = 0 \) at time \( t = 0 \)). According to the MCT for \( \phi(t) \) the
following equation is valid [68-70]:

\[
\frac{d^2 \phi(t)}{dt^2} + \Omega_0^2 \phi(t) + \gamma \frac{d\phi(t)}{dt} + \int_0^t m(t-t') \frac{d\phi(t')}{dt'} dt' = 0
\] (1.33)

Eq. (1.33) is generalized equation of motion (Langevin equation) of an overdamped harmonic
oscillator: the elastic collisions between the molecules lead to the fluctuations with frequency
\( \Omega_0 \), related to phonon frequency, and to a dissipative term (\( \gamma \) is the friction coefficient). The
fourth term of Eq. (1.33) is called memory term since it describes the effects happened at time \( t' \)
before the density fluctuations occurred \( (t' < t) \) and represents the feedback exerted on the
molecule by the surrounding molecules. Since the memory term \( m(t) \) depends on the product of
the density correlation functions, obtained solution of Eq. (1.33) is self-consistent. At low
density (i.e. high temperature) the collisions are statistically independent and the uncorrelated
ones contribute only to the friction term \( \gamma \) and the memory term disappears. The result, when the
friction term overwhelms the inertial one (i.e. the second derivative), is the same as in Debye
model, and so the correlation function is an exponential decay. On increasing density collisions
are more correlated and a molecule, at shorter times, becomes caged by the surrounding
particles. Increase of the damping motion is represented by Eq. (1.33) when the memory term
increases. At longer times the molecule can escape from the fluctuated "cage" and further
diffuse. The corresponding friction coefficient apparently relates to the memory term. According
to this view, the relaxation is developed in two stages: first the vibrational component relaxes
related to the motion of the molecule inside the "cage") and then slower motions related to the
decay of the "cage" effect and to the diffusion.
The simplest version of MCT [68] is provided for the arrest of the slow processes around some critical temperature $T_C > T_g$ and the universal scaling law for all diffusion coefficients is written as:

$$\eta \propto \tau \propto |T - T_c|^\gamma$$

(1.34)

Vibrational processes remain on the contrary active for $T < T_C$. The predictions of MCT are related also to the shape of the relaxation function: apparently non-Debye relaxation is approximated by KWW function (see § 1.3). Moreover, invariance of the shape of relaxation for temperatures above $T_C$ is expected, even though revealed by different techniques.

In fact, the divergence of $\tau$ at $T_C$ is not observed. According to the extended version of MCT [69, 71] the structural relaxation is possible even under $T_C$ due to activated processes allowing to overcome the barrier of the "cage" effect: mechanism of the movement has no longer the diffusion character typical of liquid, but it proceeds as jumps (phonon assisted hopping) as in amorphous solids.

According to these predictions different coefficients of the diffusion dynamics, when there are probabilities of different hopping, should decouple below $T_C$. Some of these phenomena, as the clear change in the dynamics of different diffusion coefficients at the critical temperature $T_C \approx 1.3 \cdot T_g$ and their decoupling, have been recently experimentally tested [72-75].

b) Arrhenius and Non-Arrhenius temperature dependence: Another characteristic feature of the $\alpha$-relaxation of glass-forming systems is the deviation of its temperature dependence from that expected for thermally activated processes, namely the Arrhenius law in which it is assumed the existence of unique energy barrier $E$ that controls the transition from two different states. In reality, the activation energy barrier $E$ increases on decreasing $T$ and approaching $T_g$:

$$\tau = \tau_0 \exp\left(\frac{E}{k_B T}\right).$$

(1.35)

The extent of this deviation is very different for different glass-forming materials leading to a categorization by A. Angell [76, 77] into ‘strong’ glasses following Eq. (1.35) and ‘fragile’ ones which show a bent curve in the normalized activation plot $\log(\tau)$ or $\log(\eta)$ versus $T_g/T$ (see for the shear viscosity fig. 1.7). In experiments with fragile glasses, temperature dependence of the $\alpha$-relaxation time was described empirically with the Vogel-Fulcher-Tamman (VFT) law [40]:
\[
\tau_{\alpha}(T) = \tau_{0}^\alpha \exp\left(\frac{DT_0}{T - T_0}\right),
\]

(1.36)

where \(T_0\) is the Vogel-Fulcher temperature which indicates the divergence of the relaxation time at infinite viscosity, corresponding to the complete blocking of the structural relaxation, \(\tau_{0}^\alpha\) is the high temperature limit of relaxation time, and \(D\) is the strength parameter whose value is related to the degree of deviation of the \(\tau_{\alpha}(T)\) curve from the Arrhenius equation [40]. Typically, for a fragile system \(D\) is quite small (down to about 3) and in strong one is much bigger (reaching up to about 100).

Fig. 1.7. Angell plot of the viscosity against \(T_g/T\) in log-scale. In this representation, strong glassformers such as SiO\(_2\) with their Arrhenius dependence of timescales on temperature give straight lines, while the super-Arrhenius (such as VFT) divergence in fragile glasses (for example, OTP) leads to curved plots (reproduced from ref. [40]).

Another relevant relaxation parameter that deserves to be considered is the steepness index or fragility, \(m\), related to the apparent activation energy of the structural relaxation measured at \(T_g\). It can be estimated for isobaric data from the apparent activation energy at \(T_g\), normalized by \(T_g\) value, using the well-known relation [39]:

\[
m = \left. \frac{d \log(\tau)}{d(T_g / T)} \right|_{T=T_g}.
\]

(1.37)
The parameters of the VFT Eq. (1.36) are also applied to find the fragility $m$ using the following formula:

$$m = \log_{10} e \frac{D T_i T_\alpha}{(T_g - T_\alpha)}.$$  

(1.38)

All the glass-forming systems were classified according to their fragility [39]. Prototypical examples of fragile systems ($m=70-150$) are the van der Waals molecular liquids (like o-terphenyl), whereas strong glass-formers ($m=17-35$) are characterized by strong covalent directional bonds, forming space-filling networks (like silica). Hydrogen bonded materials (like glycerol or propylene glycols) have intermediate values, with $m$ ranging between 40 and 70. Experiments can assess isobaric fragility $m_P$ also at high pressure: $m_P(P)$ turns out to be a constant or a decreasing function of pressure for common glass-forming systems [78], with some exceptions, like hydrogen-bonded systems, whose fragility is steadily increasing with pressure up to GPa range, then decreases again [79].

All experimental evidences indicate the complex dependence of the structural relaxation time on the temperature. Actually, there are several experimental and numerical simulation results that reported that the slowing down of the dynamics on approaching $T_g$ and the increasing of the apparent activation energy could be related to the onset of cooperative motions, involving molecules on an increasing correlation length [56, 63, 80]. The size of the cooperative rearranging region has been found to be related to the fragility and to the complementary as well as to $\beta_{KWW}$ parameter [59-61, 81], leading to the increase of the activation energy and so of the fragility. An old but still popular model that tried to rationalize the increase of activation energy and to link it to the size of the cooperative regions is that of Adam and Gibbs [82]. According to the Adam and Gibbs (AG) model the slowing down of $\alpha$-relaxation time $\tau_\alpha$ in glass-forming systems is linked to the increasing size $N_{CRR}$ of the cooperatively rearranging regions (CRR). AG model postulates that the free energy activation barrier for a CRR relaxation is linearly increasing with $N_{CRR}$, that is reciprocal of configurational entropy $S_c$ of the system (i.e., $N_{CRR} \propto 1/S_c$). Thus, on approaching the glass transition by cooling or compressing, the reduction of configurational entropy implies a slowing down of structural dynamics, according to the equation:

$$\tau(T, P) = \tau_\alpha \exp\left(\frac{C_{AG}}{T S_c(T, P)}\right),$$  

(1.39)
where $\tau_0$ is the value of $\tau$ in the limit of infinite ($T_{Sc}$), and $C_{AG}=(s_c^* \Delta \mu / R)$, with $R$ the gas constant ($R = 8.314$ J mol$^{-1}$K$^{-1}$), $s_c^*=k_B \ln 2$ and $\Delta \mu$ is the free energy activation barrier for an elementary transition, \textit{i.e.} at high temperatures where cooperativity does not take place and $N_{CRR}=1$. Eq. (1.39) has been recently successfully applied to reproduce the dynamics of supercooled liquids above the glass transition in many cases [83-86]. The determination of configurational entropy $S_c$ is usually obtained from the difference of the total entropy and the vibrational $S_{vib}$. Since $S_{vib}$ is not directly accessible, a common approximation for $S_c$ in literature is to calculate the excess entropy $S_{exc}$ of the supercooled liquid with respect to the crystal. This approximation gave rise to several criticisms [87]. The main one is that the vibrational properties of a crystal are different from that of the supercooled liquid at the same $T$-$P$ conditions and so a vibrational excess term is considerably contributing to $S_{exc}$. Nevertheless, the Eq. (1.39) is successfully applied to explain the temperature and pressure dependence of structural dynamics. In particular, if $S_c$ can be expressed in terms of a first order polynomial of $1/T$, Eq. (1.39) turns into the VFT equation for $\tau_\alpha(T)$.

1.5.2 The secondary relaxation

It is well known that glass-forming liquids, in addition to the $\alpha$-relaxation, show secondary $\beta$-relaxation active also in the glassy state, whose dielectric loss spectra appears as a broad peak, more often symmetrical [10, 88], slowly moving to lower frequency on decreasing temperature. Microscopically, two different mechanisms can contribute to the $\beta$-process: firstly, motions of molecular subunits that can relax independently from the whole molecules (intramolecular origin); secondly, non-cooperative motion of the entire molecule (intermolecular origin).

The first contribution can be well detected in systems with complex molecular structure such as polymers, where the motion of a part of molecule can originate relaxation processes independent from the structural one [11]. The second contribution was singled out by G. Johari and co-workers, who found a secondary relaxation process in simple glass forming system, having no internal degree of freedom [89]. The intermolecular origin of this process makes it ubiquitous to any amorphous packed molecular systems.

Two approaches have been proposed to explain the origin of the intermolecular $\beta$-relaxation (called Johari-Goldstein (JG) relaxation). Johari considered the concept of the “islands of mobility” which are responsible for the $\beta$-process [89]. The islands of mobility are isolated
regions of loosely packed molecules caged in the glassy matrix. Consequently, only molecules within these regions possess enough space to perform relatively fast and independent motions which appear as the $\beta$-relaxation. These defects are due to freezing-in of local density fluctuations during the vitrification process. According to the Johari’s model, the $\beta$-relaxation is a non-homogenous process, which originates only from molecules within the islands of mobility [90, 91].

A completely different interpretation was later put forward by Williams et. al. [92]. They postulated that the $\beta$-process could be attributed to a faster, small angle (thermally-activated) reorientational motion of all molecules. Thus, it has a homogenous character, in contrast to Johari’s concept. However, recently G. P. Johari proposed arguments to show that a spatially homogenous motion is inconsistent with the properties of the secondary processes usually observed in the dielectric spectra [91]. Although Johari’s concept was proposed over 40 years ago it still remains a subject of very hot debate in the literature. The debate results from the fact that there is no unambiguous experimental evidence for the existence of the islands of mobility. Consequently, the origin of the $\beta$-relaxation still remains as an open question.

There are currently strong efforts by many researchers to explain its real nature. There is an additional fact: in various glass-formers, beyond the structural relaxation no additional secondary relaxation processes is observed in the loss spectra, but an excess contribution to the high-frequency power law of the $\alpha$-peak, called excess wing. It has been postulated that the excess wing and $\beta$-relaxations could be different phenomena and even the existence of two classes of glass-formers was proposed – “type A” with an excess wing and “type B” with a $\beta$-process [93].

A little bit later the dielectric experiments performed below the glass temperature $T_g$ after long aging times gave evidence that, generally, the excess wing results from a $\beta$-relaxation peak submerged under the dominating $\alpha$-peak [94, 95]. Based on experimental observations it seems natural to explain Johari-Goldstein $\beta$-processes and excess wing as manifestation of the same phenomena. Indeed it was recently confirmed by a broadband dielectric spectroscopy study that in binary mixture of polar rigid molecules in apolar solvent, the so-called “excess wing”, characteristic of the spectra of neat simple and quite rigid molecular glass formers, evolves in a well resolved $\beta$-relaxation, when a mixture with a more viscous apolar solvent is carried out [96, 97]. Besides, the polyalcohols with small chain length present an excess wing but in the sample with longer chain length the excess wing reveals as secondary relaxation peak [98-100].
At temperature below the glass transition temperature when the structural relaxation moved out the frequency interval of the measurement, the temperature dependence of the secondary $\beta$-relaxations is usually Arrhenius-like following Eq. (1.35):

$$\tau_\beta = \tau_0^\beta \exp\left(\frac{\Delta E_\beta}{RT}\right), \quad (1.40)$$

where $R$ is the gas constant, $\tau_0^\beta$ the relaxation time at high temperature and $\Delta E_\beta$ is the activation energy.

Other broadband studies have shown a more complicated behaviour of the temperature dependence of the secondary relaxation time around and below $T_g$ [101-106]. The dielectric strength for secondary $\beta$-relaxation shows almost constant or slightly increasing value with temperature below $T_g$. On increasing temperature above $T_g$, $\Delta \varepsilon_\beta$ also increases showing a crossover from a weaker to a stronger temperature dependence. This behaviour of $\Delta \varepsilon_\beta$ is usually observed for secondary relaxation in neat glass-formers and for a component in binary mixtures, and it mimics the changes observed in the enthalpy $H$, entropy $S$, and volume $V$ of neat glass-formers when crossing the glass transition temperature [97, 101, 107-109] (see also an example in fig. 1.8).

![Fig. 1.8. Temperature dependences of the relaxation strengths $\Delta \varepsilon$ for structural $\alpha$-, secondary $\beta$-processes and for total dielectric strength ($\Delta \varepsilon_{\text{tot}} = \Delta \varepsilon_\alpha + \Delta \varepsilon_\beta$) of 16 wt.% TBP/3Styrine mixture. Solid lines are linear regressions (reproduced from ref. [97]). $\Delta \varepsilon_\beta$ shows change of slope (in vicinity of $T_g$) from a weaker $T$-dependence to a stronger one on heating.](image)
1.6 Interdependence between structural and secondary relaxation: Coupling Model

Basing on the thermodynamic and dynamic properties of the glass systems, two different types of theories of the glass transition have been inspired during years. The thermodynamic theories view the experimentally observed transition as a kinetics controlled manifestation of the ideal glass transition occurring at \( T < T_g \). This transition is then described in term of static (thermodynamic) properties. This viewpoint underlines the free volume [111] and the previously mentioned entropy theory of Adam and Gibbs [82]. In contrast, there are many non-thermodynamic approaches to the glass transition, according to which the vitrification is mainly governed by kinetics aspects. Among these theories can be mentioned the Mode Coupling Theory [68] (see also § 1.5.1), the potential energy landscape approach [112, 113] and the coupling model (CM) [114-116]. Because of lack of the space in the thesis we will introduce the one of the recent models that we used in our work: the coupling model, proposed by K. L. Ngai [114-116], which is an approach to the glass transition mainly based on many-body dynamics.

It is considered that glass-formers are made of units having nontrivial mutual interactions. Therefore, structural relaxation of glass-forming substances is a many-body relaxation problem. This unfortunately is still an unsolved problem in statistical mechanics and therefore also the glass transition is an unsolved problem. Conventional theories and models of glass transition avoid giving a solution to this problem, and often take into account the effect of the mutual interactions according to a mean field approach, \( i.e., \) by averaging the effect of the surrounding molecules on the relaxing one. There are plenty of experimental evidences for the many-body relaxation dynamics. Even though a full solution of the many-body relaxation problem is not given by the coupling model, its predictions can explain the properties of structural relaxation originating from many-body relaxation and their relations to its precursor, namely the independent relaxation, identified by K. Ngai as the Johari-Goldstein secondary relaxation [117].

In the framework of the coupling model, it exists a temperature independent crossover time \( t_c \), at which transition from the non-cooperative dynamics characterized by a single exponential to a cooperative one characterized by stretched exponential occurs [118]. A schematic description of the dynamic evolution can be described as following: at very short time \( t << t_c \), molecules try to rearrange independently with the exponential relaxation function:

\[
\Phi(t) = \exp \left( -\frac{t}{\tau_o} \right), \quad (1.41)
\]
which has the form of a Debye function with characteristic time $\tau_0$ called primitive relaxation time in CM. $\tau_0$ is the independent characteristic time for the non-cooperative relaxation of the molecule, and represent the inverse of the rate $W_0 = \tau_0^{-1}$ at which the molecule tries to relax, if it would be independent.

Starting at $t_c$, the many-molecule dynamics prevent all attempts of molecules to relax independently and simultaneously. In other words, the probability that molecules can rearrange (which is proportional to $\exp(-t/\tau_0)$) is high so that single molecule relaxation processes are no more isolated, resulting in different molecules relaxing with faster and slower motions, i.e. heterogeneous dynamics. In this dynamic region ($t \gg t_c$) the corresponding correlation function of the model can be well approximated by the KWW stretched exponential function (see Eq. (1.23)):

$$\Phi(t) = \exp \left[ -\left( \frac{t}{\tau_\alpha} \right)^{1-n} \right], \quad (1.42)$$

and the crossover at $t_c$ leads to a relation between $\tau_\alpha$ and $\tau_0$ given by

$$\tau_\alpha = \left( t_c^{-n} \tau_0 \right)^{1-n}, \quad (1.43)$$

where $n$ is the coupling parameter of the CM and $0<n<1$. Higher is the degree of the dynamic heterogeneity (and non-exponentiality), stronger is the slowing down effect of the many-molecule dynamics, larger is the coupling parameter $n$ and vice versa.

The experimental evidences [119-121] and numerical simulations [122-124] show that the crossover from the primitive relaxation to Kohlrausch relaxation appears at $t_c \approx 2$ ps for molecular liquids. The correspondence between the independent (primitive) relaxation time of the coupling model (CM), $\tau_0$, and the Johari-Goldstein (JG) $\beta$-relaxation time, $\tau_\beta$ or $\tau_{\text{JG}}$, was predicted and demonstrated by K. L. Ngai [104, 116]. Evidently, the concepts of primitive and the JG relaxation processes are not identical, but they are closely related. The first is the relaxation process in which molecular unit could undergo in absence of many-body dynamics, the second is an independent motion of the entire molecule as a whole. Actually, it was shown that this relation holds for many small molecular and polymeric glass-formers, where $\tau_{\text{JG}}$ is from experiment and $\tau_0$ obtained by calculation [104, 125-127]. The CM was also applied to other areas including blend dynamics [128, 129], polymer viscoelasticity and to ionic conductors [118].
In most glass-formers where a secondary $\beta$-relaxation has been identified as a true JG process, its time scale $\tau_\beta$ is in good correspondence with $\tau_\alpha$ calculated from $\tau_\alpha$ and the coupling parameter $n$ of the $\alpha$-process by Eq. (1.43) for various temperatures and pressures in the supercooled liquid state down to glass transition [104]. According to the Coupling Model, should Eq. (1.43) continue to hold deep in the glassy state [127]? An unequivocal answer cannot be given because a direct test for Eq. (1.43) can be performed only when the $\alpha$-loss peak is observed, but in the glassy state $\tau_\alpha$ exceeds the time that is experimentally accessible in the laboratory. Nevertheless, $\tau_\alpha$, the activation energy and the shape of structural relaxation in the glassy state can be estimated [130-132] and a test is possible under some assumptions. The structure of a glass, as well as its specific volume and its configurational entropy [82], depend on the thermal history and is characterized by, at least, one parameter called the fictive temperature $T_f$. Hodge [131, 132] proposed that the $\alpha$-relaxation time, $\tau_\alpha$, depends on $T$ and $T_f$ according to the following equation:

$$\tau_\alpha(T, T_f) = A \exp\left(\frac{B}{T(1-T_0/T_f)}\right),$$  \hspace{1cm} (1.44)

where $A$, $B$ and $T_0$ are the parameters of the VFT equation (1.36), fitting the temperature dependence of $\tau_\alpha$ in the equilibrium liquid state. If the system is at equilibrium, $T_f = T$ and Eq. (1.44) becomes identical to Eq. (1.36). In this case Eq. (1.44) is equivalent to an apparent activated process:

$$\tau_\alpha(T, T_f) \equiv A \exp\left(\frac{E_a(T_f)}{T}\right),$$  \hspace{1cm} (1.45)

with activation enthalpy $E_a(T_f)$ (see fig. 1.9) given by:

$$E_a(T_f) = \frac{R \cdot B}{1-T_0/T_f},$$  \hspace{1cm} (1.44)

where $R$ is the gas constant. After cooling to some temperature below $T_g$ the structure of the glass remains frozen thereafter, the glass is in an “isostructural” state and its $T_f$ is constant throughout the glassy state. From one point of view, what occurs could be described as the freezing of the configurational entropy below a certain temperature: the system cannot follow the change of $T$ so that configuration becomes frozen below $T_f$. Thus, from Eq. (1.44), $\tau_\alpha$ of the isostructural glassy state has the Arrhenius temperature dependence of:
\[ \tau_a(T, T_f) = A \exp \left( \frac{E_a}{T} \right). \]  

(1.47)

From this and the relation between \( \tau_{JG} \) and \( \tau_a \) (Eq. (1.43)), the JG relaxation time also has an Arrhenius temperature dependence in the isostructural glassy state, with an activation enthalpy equal to:

\[ E_{JG}(T_f) = (1 - n) E_a(T_f). \]  

(1.48)

The intermediate regime, where the system is not at equilibrium but its fictive temperature is dependent on \( T \) as well as the thermal history, bridges the non-Arrhenius (VFT) dependence of the equilibrium state and the Arrhenius dependence of the isostructural state (see fig. 1.9). Therefore, different conclusions could be obtained from data of \( \tau_\beta \) in glassy states having different \( T_f \), consequences of different cooling rates, annealing temperatures and thermal histories.

![Fig. 1.9. Schematic representation of the temperature dependences of the specific volume, \( V_{sp} \), enthalpy, \( H \), (upper panel) and activation enthalpy, \( E_\alpha(T) \), (lower panel). Vertical dash-dotted lines mark \( T_g \) for fast and slow cooling rates. In the region below \( T_g \), \( T_f = T \) and \( E_\alpha(T) \) is obtained from Eq. (1.43), for \( T > T_g \), \( T_f = \text{const} \) and hence \( E_\alpha(T) = \text{const} \). The values of \( V_{sp}, H \) and \( E_\alpha(T) \) in glassy state depend on cooling rate.](image)
Indeed Hodge proved with calorimetric experiments that $\tau_\alpha$ in glassy state, when relaxation time becomes much longer, changes its temperature dependence from a stronger VFT to a weaker Arrhenius one [131, 132].

It was proved by experiments and application of CM that the change of slope in the temperature dependence of $\tau_\alpha$ in the vicinity of $T_g$ reflects in that for $\tau_\beta$ [126, 127]. Moreover the change of slope of the relaxation times corresponds to that for temperature dependences of enthalpy, specific volume, etc. (see figs. 1.5 and 1.9).

1.7 Relaxation dynamics of confined and mixed water

Water is the most abundant liquid on earth (it covers almost two thirds of the surface of the planet). It is also undoubtedly one of the most important substances conditioning the existence of living organisms. This explains the strong research interest on the structure and dynamics of water: this system has been indeed extensively studied since some centuries. Nevertheless, many fundamental aspects on its physico-chemical properties are still a mystery and their explanation is an especially important assignment for researchers. Many anomalies of thermodynamic and dynamic properties of water (e.g. unusual temperature dependences of isothermal compressibility $\kappa_T$, isobaric heat capacity $C_P$, isobaric expansivity $\alpha_P$) become more pronounced in the metastable supercooled liquid state (see fig. 1.10 and refs. [133-135]). In the literature, studies have been made on the dynamics of supercooled water in the region between melting point (273 K) and the homogeneous nucleation temperature (231 K) [133, 136-140]. There are also experimental evidences that water can exist as an amorphous solid (glass) at very low temperatures (lower than 130 K), but, once heated above the glass transition temperature, it transforms into a highly viscous liquids and then immediately crystallizes [141, 142]. Therefore, dynamics of water is experimentally inaccessible for the liquid state in a wide temperature range (140-230 K at atmospheric pressure, see phase diagram in fig. 1.11).

Recent theories [144-147] predict within this range a phase transition between two different forms of liquid water, each of them characterized by a different local structure: at low temperatures an hydrogen bond network dominates, bringing to a highly ordered tetrahedral structure with a low packing (low density liquid), while at higher temperatures the weakening of hydrogen bond network allows for a more compact local structure (high density liquid). This last form of liquid water is also predicted to dominate at high pressure. The coexistence and the
competition between these two forms of liquid water and the transition from one to the other (occurring in the unaccessible region) could explain, according to the above mentioned theories, the number of observed anomalies of the physical properties of water, that should show a critical behaviour below 230 K [134, 148, 149].

Fig. 1.10. Temperature dependences of the measured thermodynamic response functions of water: (a) the temperature derivative of the water density (expansivity); (b) the temperature derivative of the measured fractional chemical shift, the specific heat at constant pressure, $C_P$, measured in bulk water in the supercooled regime, and $C_P$ calculated for the TIP5P model of water. Figures are reproduced from ref. [143].

Fig. 1.11. Schematic phase diagram of water (reproduced from ref. [150])
Very few experimental results on the dynamic, thermodynamic and structural behaviour of water in
its metastable amorphous form exist in the region below 230 K and their interpretation in agreement
with the coexistence of the two forms of water is still very controversial [143, 151, 152]. A
systematic study on this issue is therefore of strong interest for the fundamental research.

The goal of this thesis is to study the dynamic properties of water systems in the metastable
supercooled state at ambient and very high pressure. In the literature, two alternative strategies are
employed to obtain information on water dynamics in the usually unaccessible temperature region
(140-230 K): 1) mixing with “cryoprotectants”, 2) confinement on the nanometer length-scale.

The first strategy consists in obtaining homogeneous mixtures of water and hydrophilic glass-
forming solutes that hinder the formation of ice crystals by strongly modifying the hydrogen
bonding dynamics and the local structure with respect to that characteristic of bulk water.
Examples of some systems suitable to form homogeneous solutions with water (up to 50% in
weight), that can be easily supercooled down to form a glass, are alcohols and polyalcohols (like
glycerol), ethylene and propylene glycols, sugars or carbohydrates (mono-, di- and
polysaccharides) and some hydrophilic macromolecular systems, including biopolymers (from
polypeptides to several proteins) [103, 153, 154]. Examples for temperature dependences of
water related relaxation process in mentioned water mixtures are shown in fig. 1.12.

From the dynamic and structural properties of the water mixtures with variations of the solutes
and concentrations, attempts were made to infer, by extrapolations, the properties of supercooled
pure water in the unaccessible region below 230 K [155, 156]. Moreover, these studies are
important by themselves because aqueous mixtures are often present in biological systems [157]
and the knowledge of the dynamics in their supercooled and glassy states is important in the field
of cryoprotection of living organisms and biopharmaceuticals [53].

The second strategy uses the nanoscale confinement in order to reduce the water molecular clusters
down to sizes smaller than the critical size necessary for homogenous nucleation. Another effect of
the confinement is the disorder induced by the interfaces that prevent the water molecules to form a
crystalline lattice. Nanoconfined supercooled water was obtained in nanoporous systems as silica
gels [158], Vycor glasses [159], zeolites, mesoporous molecular sieves [160], and other systems.
Crystallization does not occur in water dispersed in biorelevant materials, such as polymeric
nanoporous hydrogels [161, 162], and in the water present in the hydration layer at the protein
surfaces [51, 154, 163]. The temperature dependences for the water related process of confined water
and water present in hydration shell of various proteins are shown in fig. 1.13.
The experimental findings reported in the literature on the dynamics of supercooled water are remarkably similar for most of the above mentioned systems, irrespective of the structure and chemical composition of the aqueous systems. At least two relaxation processes were always reported, both can be detected by the highly sensitive adiabatic calorimetry or by broadband dielectric spectroscopy [103, 164]. There is a slower process coming from the structural relaxation of the solute molecules hydrogen bonded to water or from motion of molecules of the confining wall that are hydrogen bonded to water in the case of confined water. Also present in the dielectric spectra at higher frequency is a faster process, which is related to reorientational motions of the water molecules and has been called the $\nu$-process, from νερω, the name in modern greek of the water [103, 165]. The relaxation time $\tau_\nu$ of the $\nu$-relaxation shows qualitatively very similar features for many aqueous systems, almost universal, irrespective of the chemical and structural differences [153] (see also figs. 1.12 and 1.13).

![Fig. 1.12. log$_{10}(\tau_\nu)$ vs 1000/$T$, of the $\nu$-relaxation of water component in various aqueous mixtures: 35 wt.% water mixture with PEG600 (black inverted open triangles) [103]; 48 wt.% water mixture with DPG (blue open triangle) [166]; 50 wt.% water mixture with TPG (black open circles) [167]; 50 wt.% water mixture with 5EG (magenta crosses) [167]; 50 wt.% water with PVP (green open squares) [168]; 50 wt.% water mixture with PVME (red open asterisks) [169]; 50 wt % of water with PHEMA (olive triangles with pluses) [170]; bulk water (Buchner et al.) located at the lower left corner) [171]. All data were obtained by dielectric relaxation spectroscopy. Red open circle with plus is $T_g$ obtained from DSC studies of glassy water [141].]
Fig. 1.13. Dielectric data of relaxation time of water confined in MCM-41 with pore diameter 2.14 nm at hydration level 12 wt.% (open magenta asterisks), 22 wt.% (red open squares) and 55 wt.% (violet pluses) [172]. The green closed circles are translational relaxation time determined by neutron scattering of water confined in nanoporous MCM-41-S with pore diameters of 14 Å [148]. Black open circles – $\tau$ of fast relaxation process of water confined in 10 Å molecular sieves obtained by dielectric spectroscopy [173]. Also shown are the relaxation times $\tau_r$ of water in hydration shell of various proteins: bovine serum albumin (BSA) (cyan open triangles) [154] and lysozyme (orange inverted open triangles) from dielectric measurements [174]. The dielectric relaxation times of bulk water at higher temperatures and shorter times are also shown (red open diamonds located at the bottom in the left corner) [171]. Red open circle with plus is $T_g$ obtained from DSC studies of glassy water [141].

The literature about the dynamics of this water related process became recently inflamed by a heated debate. Liu et. al. [148] reported high-resolution quasielastic neutron scattering (QENS) measurements at different isobaric conditions on water confined in nanopores of a silica glass (MCM-41-S). They determined the temperature dependence of the average translational-relaxation time $\langle \tau_r \rangle$ which exhibits a crossover from VFT-like behaviour at high temperature to Arrhenius-like at low temperature (see fig. 1.14). Authors concluded that the change of slope in the temperature dependence of $\langle \tau_r \rangle$ is manifestation of so called “fragile-to-strong” dynamic transition [147]. The crossover was found at around 220 K ($T_L = 224$ K) in the short timescale (tens of ns). Results obtained by Liu et. al. are in good agreement with theories already
mentioned above which predict a phase transition between two different forms of supercooled liquid water [144-147]. Same authors later found similar results in hydrated protein [175]: the fragile-to-strong dynamic transition occurred at $T_c = 220$ K and at $\tau \approx 10$ ns for hydrated lysozyme.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig14.png}
\caption{Temperature dependence of the average translational-relaxation time $\langle \tau_r \rangle$ for the supercooled water confined in nanopores of a silica glass at ambient pressure (reproduced from ref. [148]).}
\end{figure}

On the other hand, Cerveny et. al. in their comment to ref. [148] pointed that the crossover in temperature dependence of the relaxation related to the water occurs for many systems at different $T$, not only at 220 K [176]. According to them, until now it is observed in various systems: pure glass formers, binary mixtures [97, 177-179], confined water [169, 173, 180], water mixtures [79, 156, 165, 181, 182] (see fig. 1.15). Such crossover always appears in the range of glass transition of the systems. Authors of ref. [176] suggested that observed water-specific relaxation in many different water systems is the $\alpha$-relaxation, with its relaxation time having the usual VFT $T$-dependence above $T_g$, which then becomes confined (in the frozen matrix of solute, for mixtures) below $T_g$ with Arrhenius $T$-dependence due to finite size effect. Moreover, following this hypothesis, authors estimated, by extrapolation from water/glycol mixtures, the glass transition temperature of the bulk water as $T_g \approx 160-170$ K [156, 183]. It is worth to note that the time of crossover found for all these systems in the temperature dependence of water-related relaxation process for water mixtures and confined water is much longer (from $\mu$s to seconds) than found by Liu and Chen (tens of ns) (see figs. 1.14 and 1.15).
Later Khodadadi *et. al.* [174, 185] used dielectric spectroscopy to investigate dynamics of hydrated proteins on the same systems studied by Chen *et. al.* [175]. Their results show absence of the cusplike fragile-to-strong transition in temperature dependence of water-related relaxation process at $T = 220$ K postulated by Chen *et. al.* (see fig. 1.16). Moreover, results of neutron scattering experiments on the hydrated lysozyme ($h = 0.4$) [174, 186] also did not confirm results of Chen *et. al.* By dielectric spectroscopy authors observed in spectra the appearance of a new relaxation process around $T = 220$ K (see spectra in fig. 12 of ref. [174]) whose temperature behaviour well corresponds with that observed by Chen at low $T$ (see also fig. 1.16). Authors of ref. [155] suggest that the observed dynamic transition on increasing temperature in water systems originates from the water-related relaxation process (as called above $\nu$-process) entering the time window of the neutron scattering spectrometer.

The issue of the crossover in temperature dependence of the water-specific relaxation and origin of the relaxation processes observed in the literature for water systems will be discussed in the thesis in further details step by step.
Fig. 1.16. Temperature dependence of characteristic relaxation times of the three dielectric processes in the hydrated ($h = 0.37$) sample: (●) the main, (▲) the fastest, and (■) the slowest processes. The fastest process splits from the main process at $T \approx 220-225$ K. The ○ symbol presents the protein’s relaxation time for hydrated ($h \approx 0.4$) lysozyme estimated from neutron scattering experiments (data from ref. [186]); the solid line presents the relaxation time for the lysozyme’s hydration water estimated from neutron scattering experiments (data from ref. [175]). Figure is reproduced from ref. [174].

The project of this thesis is to study dynamics of supercooled aqueous systems, using both the mixing and confining strategies, but with more emphasis on the water mixtures. Actually, we have studied water confinement only by investigating the behaviour of water dispersed at very low concentration in biomacromolecules with very high glass transition temperature, like glycogen or some lyophilised protein/sugar solutions. While the study of water in confinement were performed at ambient pressure, in the cases of mixtures the experiments have been carried out both at ambient and high pressure (up to around 1.8 GPa), the first time that this occurs for aqueous systems in literature. The use of pressure as additional variable is important to validate the models on the liquid-liquid transition since there are already theoretical predictions and numerical simulation tests [187, 188]. Few pressure experiments have been performed in literature on nanoconfined water systems, but with very limited pressure (up to 0.2 GPa) and dynamic scale (10 ps - 10 ns) range [148]. Moreover the possibility to study bio-relevant systems (like cryoprotectants and proteins) at very high pressure is appealing for the study of the life at very extreme conditions, like those present in deep sea [189] or on other planets [190].
From what shown above, it emerges that this issue has a potential impact also on applied research in different fields.

1.8 General remarks on the investigated experimental quantities and relevant parameters

The transition towards the glassy state has influence on different physical properties of the system and in particular on the relaxation dynamics of several macroscopic observable, such as the polarization or the density fluctuation. Dielectric spectroscopy is a sensitive technique to investigate the relaxation dynamics of the orientational polarization due to the permanent dipole moment of the polar molecular groups. From dielectric relaxation measurement one can gather information on a relaxation process according to the following main points:

(i) the most probable relaxation time $\tau_{\text{max}}$ (related to the inverse frequency of the maximum of the dielectric loss $\varepsilon''$) at a specific temperature and pressure;
(ii) the relaxation time distribution (related to the relaxation shape parameters), which reflects the dynamic heterogeneity of the relaxing unit;
(iii) the relaxation strength, which is proportional to the concentration of the active relaxing dipoles and their dipole moment.

These three quantities will be extracted from our experiments done at ambient and elevated pressure on different aqueous systems and their behaviour will be shown in the Chapters 3-5.
Chapter 2

The Experimental Details

2.1 Low frequency (1 mHz - 10 MHz) dielectric spectroscopy measurements

In our dielectric relaxation spectroscopy studies, the experimental complex dielectric permittivity \( \varepsilon(\omega) \) was mainly measured covering the frequency range from 1 mHz-10 MHz. We performed these measurements employing a frequency impedance measurement technique where the complex impedance \( Z(\omega) = Z'(\omega) + iZ''(\omega) \) of a capacitor, with empty capacity \( C_0 \), filled by the sample material, is measured. The principle of the impedance measurement is as follow. A sinusoidal voltage \( U_1(t) = U^* \exp(i\omega t) \) at fixed frequency \( \omega \) is applied to the cell and the current across it \( I_S(t) = I^* \exp(i\omega t + \phi) \) is measured. Generally the measured current is shifted with respect to the applied voltage by a phase angle \( \phi \), which depends on the properties of the sample and on the frequency. After measuring the applied voltage and the generated current the value of \( Z \) is obtained by the complex ratio \( U^*/I^* \) and consequently the complex permittivity \( \varepsilon = \varepsilon' - i\varepsilon'' \) is obtained by impedance measurement through the relation \( \varepsilon = (i\omega C_0 Z(\omega))^{-1} \).

The experimental setup is shown in fig. 2.1. The device under test (DUT) is mounted in a special sample holder (see fig. 2.2) for dielectric measurements which is directly connected to the input terminals of the impedance analyser. The sample cell is constituted generally by two gold-plated electrodes. A special cell for the measurements on water mixtures was developed during the activity of the first year of Ph. D. and it will be described into details later. The temperature is measured using Platinum resistor sensor (PT100) placed in thermal contact (but electric insulation) with one of the capacitors plates. The sample holder is part of a cryostat which belongs to the QUATRO cryosystem. The DUT is heated and cooled with conditioned dry nitrogen gas with controlled temperature. The Impedance Analyser as well as the cryosystem are fully remote controlled by a personal computer. The Novocontrol Alpha high resolution dielectric analyser was used to measure the impedance or complex dielectric function in a frequency range from 1 mHz to 10 MHz. The covered temperature range was between 100 K and 500 K.
The measuring circuit on which the Alpha Analyser is based is presented in fig. 2.3 in simplified form. The voltage signal $U_1$ generated by the digital sine-wave generator is applied to the cell, then the generated current across it is converted to the voltage $U_2$ by a current to voltage converter. This latter is amplified, filtered and converted in two digital data streams, which are analysed with discrete Fourier transform technique in order to gain information about the amplitude and the phase of the voltage $U_2$ (for this reason, the device is called vector analyser). Once the two voltages are known the value of the sample impedance $Z_S$ is calculated as follows:
\[ Z_S = \frac{U_1}{I_S} = -\frac{U_1}{U_2} Z_x , \]  

(2.1)

where \( Z_x = (R_x^{-1} + j\omega C_x)^{-1} \) is the feedback impedance of the inverting amplifier used in the current to voltage converter. The parameters \( R_x \) and \( C_x \) of the impedance \( Z_x \) are very well known and they can be suitably changed by an automatic procedure following the different needs of the measurement and adapted on the base of the values of the sample impedance \( Z_S \). In this type of measurement the main errors are the detection of the phase of \( U_1 \) and \( U_2 \) and of the contribution of \( Z_x \). To reduce this errors, the Alpha analyser has the capability of replacing the sample by a precision low loss variable impedance, \( Z_R \), used for reference.

Fig. 2.3. Scheme of the circuit of Alpha dielectric analyser (reproduced from ref. [191]).

Depending on the value of the sample impedance, the Analyser automatically selects the appropriate reference impedance \( Z_R \) for the measurement. Since the value of the reference capacitor is well known, by this measurement, the value of \( Z_x \) can be calculated from:

\[ Z_x = \frac{U_1^R}{U_2^R} Z_R , \]  

(2.2)

and finally the value of the sample impedance is:

\[ Z_S = \frac{U_1^R}{U_1^R} \frac{U_1}{U_2} Z_R . \]  

(2.3)

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The procedure is repeated each time before a set of data is acquired. The sensitivity of the Alpha Analyser is very high: its resolution limit of the Analyser for low losses is less than $10^{-5}$ for $\tan \delta = \varepsilon'' / \varepsilon'$.

**Dielectric cell for mixtures**

We developed a special dielectric cell for measurements on water mixtures, following the main concepts at the base of the design of the cell shown in ref. [192]. The main requirements for our experiments is that the concentration of water in our solution should not change throughout the temperature range investigated. The evaporation of water has to be prevented, by using a sealed cell. On the other hand, the cell has to be easy to be mounted, air bubbles should be avoided in the liquid under study, a high empty capacitance $C_0$ should be provided. Moreover a constant geometric capacitance $C_0$ versus the temperature variations should be assured, and the cell should have very high thermal conductivity in order to prevent temperature gradient across the sample and to allow fast temperature variation with short time stabilization.

The sample cell (see fig. 2.4) usually used in low frequency dielectric measurements is a parallel plate capacitor that can be filled by the sample. In our case the sample capacitor consists of parallel plates of 24 mm $\varnothing$ having a uniform separation of $\approx 114 \mu$m.

![Fig. 2.4. Drawing of the vacuum-sealed sample capacitor cell used for dielectric measurements on liquid samples. Housing (1) and counter (2) electrodes are gold-plated brass parts; the insulating window (3) is sapphire. Screw (4) and copper-beryllium spring (5) are for sealing the sapphire window. The O-ring (6) is required only for volatile liquids. The capacitor diameter is 24 mm, the electrode separation is $\approx 114 \mu$m.](image-url)
This cell can be sealed to be vacuum-tight, it has a small drain channel to degas the sample and avoid bubbles (not shown in figure), its geometry is temperature-insensitive, and the electrode separation is defined without the need of spacer material between the electrodes. Figure 2.4 shows the design of this capacitor, which turned out to be very useful for high-definition dielectric measurements on liquid and glassy samples. Figure 2.5 shows pictures of the cell made in our workshop. The shape of the upper electrode reduces electric stray field effects and allows for a sufficient material reservoir outside the electrode gap. Upper electrode is mounted on a window made of sapphire that allow a stable placement of the two electrodes in a parallel way. Sapphire is good electrical insulator, but it has high thermal conductivity. The sapphire window allows to avoid the leakage of volatile liquids (concentration of mixtures inside the cell remains constant during experiment) and can be sealed with an rubber O-ring hosted in a suitable groove. The cell was temperature controlled by a Novocontrol Quatro nitrogen-gas cryostat to a relative accuracy of ±0.1 K.

Fig. 2.5. Pictures of the cell for dielectric measurements on liquid samples

The geometric arrangement used for this cell provide an almost constant value for the empty capacitance $C_0$ on varying temperature. In this way, once the capacitance of the cell filled by the sample will be acquired, every temperature variations will be ascribed only to the sample permittivity. The empty capacitance for a parallel plate capacitor can be expressed as $C_0 = \varepsilon_0 S/d$, where $S$ is the surface of the electrodes and $d$ their separation. The separation $d$ will change very little, as both electrodes are of the same material (gilded brass) and their length with respect of the plane of sapphire window is very similar. So the main source of change in $C_0$ is the expansion of the surface with temperature. We can estimate:
\[
\frac{\Delta C_0}{C_0} \approx \frac{\Delta S}{S} \approx 2\alpha_l \Delta T ,
\]

(2.4)

where \(\alpha_l\) is the linear thermal expansivity of brass (\(\alpha_l = 20.3 \times 10^{-6} \text{ K}^{-1}\)) and \(\Delta T\) is the temperature variation. For a change of 200 K we have a change less than 0.8 % for geometrical capacitance. Figure 2.6 shows the good agreement between the experimental check and this estimate.

2.2 High pressure (0.1-700 MPa) setup for dielectric spectroscopy measurements

Dielectric measurements at high pressure were carried out using a Novocontrol Alpha-Analyzer (\(\nu = 10^3 - 10^7 \text{ Hz}\)). A sample-holder multilayer capacitor (geometric capacitance 30 pF) was filled with the sample under test and isolated from the pressurizing fluid (silicon oil) by a Teflon membrane of thickness of 50 mm. The design of the cell was inspired by that of ref. [193], that is shown in fig. 2.7.

Alternatively, we used a simple capacitor with two steel parallel plates separated by Teflon spacers and isolated from the silicon oil by Teflon membrane and lattice wrapping.

The dielectric cell was then placed in a Cu-Be alloy high pressure chamber, provided by UNIPRESS. Pressure from 0.1 to 700 MPa was applied to silicon oil using a manually operated pump with a pressure intensifier and measured by a Nowa Swiss tensometric sensor with a resolution of 0.1 MPa. A different arrangement for the pressure pump allows to reach higher
pressure (up to 1.8 GPa). Temperature was varied in the interval 200-350 K and controlled within 0.1 K by means of a thermally conditioned liquid flow (Huber thermal bath circulator). Figure 2.8 shows the experimental set-up.

Fig. 2.7. Dielectric cell for high pressure experiments (design taken from ref. [193]): 1 – clamp nut, 2 – pressure ring, 3 – cylindrical encapsulation of capacitor, 4 – clamp cover plate, 5 – screws, 6 – quartz spacer, 7 – plates, 8 – Teflon insulator, 9 – Teflon washer, 10 – filler hole, 11 – connection wires, 12 – capacitor base, 13 – sample, 14 – Teflon membrane for transmission of pressure, 15 – bushing.

Fig. 2.8. High-pressure dielectric cell using a pressure-transmitting liquid. Hydraulic connections are denoted by dashed lines and electrical connections by solid lines. Adapted from ref. [78].
Calibration measurements (empty cell and short-circuit) were performed before each pressure scan experiment. The extremely low losses obtained for empty cell allow to measure relaxations with small amplitude (that is the case of secondary relaxation) also at very high pressures and low temperatures: in fact, the signal coming from the relaxation process of the material is enough higher than that coming from the empty cell and the contribution of the latter can be neglected or singled out and subtracted. Moreover, the good insulation assured between sample and pressure transmitting medium allow to keep constant the level of concentration in our mixtures. Measurements were performed on increasing and decreasing pressure, checking their reproducibility.

2.3 Very high pressure (0.1 MPa - 3 GPa) setup for dielectric spectroscopy measurements

For the very high pressure setup (see fig. 2.9), used in this thesis work during a period spent in Silesian University Katowice at the laboratory of Prof. Paluch, the cylindrical pressurizing cell is filled with the sample, which is squeezed by pistons in conjunction with a hydraulic press in which the pressure transmitting medium is oil [194-196]. Thus, in this method the sample serves as its own pressure-transmitting fluid, and pressures of as high as 3 GPa can be achieved [197, 198]. A limitation of the approach is that for experiments below \( T_g \), the sample solidifies and can no longer exert hydrostatic stress. Another potential problem is friction between the cylinder and piston. Up and down pressure scans are useful to check hysteresis of the measurements. The usual ways to measure the pressure are calibrated bourdon gauges and tensometric manometers. For temperature control, the very high-pressure cell was immersed in air thermostatic bath. Dielectric spectra were measured in the temperature range from liquid to the deep glassy state on cooling by isothermal steps, after stabilizing the temperature within 0.1 K for an appropriate equilibration time.
2.4 High frequency dielectric measurements

The complex permittivity was obtained in the frequency range 50 MHz - 20 GHz by means of Frequency Domain Reflectometry (FDR) technique. FDR technique is based on the measure of the reflection coefficient of a coaxial line ended with an open probe cell (see fig. 2.10). The open probe is immersed into the sample under test in a manner that all the region explored by the probe is completely filled with the material under test. In this way the spatial distribution of the electric field is homogeneously covered (infinite sample configuration).

The measurements were mainly carried out by means of the Vectorial Network Analyser Agilent HP 8722D. The measurement of the complex reflection coefficient $\rho(\omega, \varepsilon) = \rho'(\omega, \varepsilon) + i \rho''(\omega, \varepsilon)$, obtained from the ratio of the incident and reflected sinusoidal ac voltage, $\rho(\omega, \varepsilon) = U_{\text{ref}}(\omega)/U_{\text{inc}}(\omega)$, allows the calculation of the complex impedance.
\[ Z_m(\omega, \varepsilon) = Z_m'(\omega, \varepsilon) + iZ_m''(\omega, \varepsilon) \] measured in the initial part of the line (Analyser-Line connection), i.e. the impedance measured at the \( S_{11} \) port of the Analyser, by means of the equation:

\[ Z_m(\omega, \varepsilon) = Z_0 \frac{1 + \rho(\omega, \varepsilon)}{1 - \rho(\omega, \varepsilon)}, \]

(2.5)

where \( Z_0 \) is the characteristic impedance of the line (50 \( \Omega\)). Knowing \( Z_m(\omega, \varepsilon) \), it is possible to get the complex permittivity \( \varepsilon(\omega) \) of the material that is in contact with the end probe, once the equivalent circuit of the transmission line is known. Such a circuit in our case can be represented by the \( T \) system shown in fig. 2.10(a), where the three impedances \( Z_1, Z_2 \) and \( Z_3 \) take into account, in particular, of the spurious effects introduced by possible lacks of uniformity of the transmission line (bends of the coaxial cables, slight impedance mismatches of the connectors, etc.) that are not completely corrected by the standard calibration of the Network Analyser (see [199] for more details).

The values of the three complex impedances \( Z_1, Z_2 \) and \( Z_3 \) are usually determined by measurements on three materials of known permittivity, according to the formula \( Z = \frac{1}{i\omega C_0 \varepsilon} \), where, \( C_0 \) is the empty capacitance of the terminal part of the coaxial line, and \( \varepsilon \) is the complex permittivity of the material. The best procedure consists in three measurements: first, the empty cell, i.e. filled with air \( (\varepsilon' = 1, \varepsilon'' = 0) \), and then two measurements with the cell filled by two reference liquids with very different dielectric properties, known from literature. It is better if the permittivity values of the reference liquids are close and span those of the sample under test. Usually, in addition to air, a polar (like water, methanol, propanol, chloroform, chlorobenzene) and an apolar liquid (like ciclohexane, \( \varepsilon' = 2.015, \varepsilon'' = 0 \)) are chosen. In most of our cases, when the samples showed a not negligible conductivity and a permittivity higher than or around 10, a different procedure was chosen. In fact, for determining \( Z_1 \) we measured with the probe in air, for \( Z_2 \) we measured double distilled water \( (\varepsilon' = 78, \varepsilon'' \text{ dependent on frequency and temperature, but whose data are tabulated in literature}) \) and to a short-circuit measurements \( (Z_3 = 0) \), obtained contacting the probe with a special tool assuring a very good contact with a metallic surface covered by gold. This last procedure is what is suggested in the manual of the Agilent open ended coaxial probe [200].

The coaxial termination must have an enough large diameter to assure a good sensitivity and to average on possible inhomogeneities but, at the same time, it should have a size much less than the used wavelength. Moreover, to have a infinite sample configuration, for the cell of fig. 2.10(b) the length penetration \( l \) of fringing field must be smaller than the cell height, in order to
avoid that the discontinuity of the interface air-liquid could affect the distribution of electric fields in the sample. Fringing field reflects in an effective $l$, related to $D_{crit}$, the critical penetration depth of the field. In our case the size of the sample was always bigger than the spatial extent of the fringing field.

Fig. 2.10. (a) Schematic representation of the measurement apparatus; (b) detail of the terminal part of the coaxial line with the open ended coaxial probe, the dotted lines show the fringing electric field lines; (c) the equivalent circuit representing the impedance of the transmission line.

The terminal impedance $Z(\omega)$ of the coaxial line, filled with a dielectric material, isotropic and homogeneous is [201]:

$$Z(\omega, \varepsilon) = \frac{Z_0}{\sqrt{\varepsilon}} \cdot \coth\left(\frac{i \omega l}{c \sqrt{\varepsilon}}\right),$$

(2.6)

where $l$ is the effective length of the line and $c$ the light speed in vacuum. The cell conditions above mentioned require that $2\pi l/\lambda<<1$, or $\omega \varepsilon^{1/2} l/c<<1$. In such a case we can approximate the Eq. (2.6) in a way that it is possible to represent the impedance $Z(\omega)$ according to the following equation [199]:
$$Z(\omega, \varepsilon) = \left( i\omega\varepsilon \cdot C_0 + i\omega C_f \right)^{-1},$$  \hspace{1cm} (2.7)$$

where $\varepsilon C_0$ takes into account the effects of the electric field coupled to the material under test and $C_f$ represents the contribution of the fringing field that involves the insulator inside the probe. The equivalent circuit shown in fig. 2.10(c) allows to write a simple relation between the input impedance measured by the Analyser port $Z_m(\omega)$ and the impedance $Z(\omega)$ at the interface line-sample at the end of the coaxial line [199]:

$$Z(\omega, \varepsilon) = Z_0 \cdot \frac{\Delta' - \Delta'_{23} Z_m(\omega, \rho)}{Z_m(\omega, \rho) - \Delta'_{12}}$$  \hspace{1cm} (2.8)$$

$$\Delta' = Z_1 Z_2 + Z_2 Z_3 + Z_3 Z_1$$  \hspace{1cm} (2.9)$$

$$\Delta'_{12} = Z_1 + Z_2$$  \hspace{1cm} (2.10)$$

$$\Delta'_{23} = Z_2 + Z_3$$  \hspace{1cm} (2.11)$$

Comparing Eq. (2.7) and Eq. (2.8), from the measured complex $\rho(\omega)$ (Eq. (2.5)) it is possible to obtain the value of real and imaginary part of permittivity as a function of frequency.

The calibration procedure should be repeated any time that the configuration of coaxial line and open ended probe is modified and perturbed.

The standard cable we used for the coaxial line is the APC-3.5 mm Precision (outer conductor diameter is 3.5 mm) that allows measurements without spurious effects up to 20 GHz. The cable is also designed to have dielectric properties stable and not affected by temperature variations in the range from 210 K up to 400 K.

For the measurements we used the Network Analyser Agilent HP8722D in the frequency range 50 MHz - 20 GHz. We used the value 10 dBm for the ac power. The typical sweep used was 201 points equally spaced in a logarithmic scale, with integration at bandwidth IF=10 Hz, 45 seconds for sweep.

The open ended coaxial probe we used was the Agilent HP85070E-020 (High Temperature Probe, see fig. 2.11). The Agilent probe has an external steel flange of diameter 19 mm and the active central area constituted by a coaxial cable, with an outer conductor with 3.5 mm diameter and characteristic impedance 50 $\Omega$. 

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2.5 Materials

All the materials used in this thesis are commercial product, stored in dry nitrogen atmosphere and used as received; their chemical structure and properties are listed in the Table 2.1. Additionally we performed preliminary studies of the properties of water solutions of glycogen, a biorelevant material prepared in Chemistry Department, University of Pisa.

Distilled and deionised water with an electric conductivity lower than 18.3 $\mu$S/m was obtained from a Pure Water Productor present in Chemistry Department (Millipore, MILLI-Q Laboratory).

Samples were mixed with water to form solutions in different concentration ranges. Mass and molar fractions of water in the mixtures were calculated using following formulae, respectively:

\[
e_{H_2O} = \frac{m_{H_2O}}{m_{H_2O} + m_{solute}}, \tag{2.5}
\]

\[
x_{H_2O} = \frac{\nu_{H_2O}}{\nu_{H_2O} + \nu_{solute}}, \tag{2.6}
\]

where $m_{H_2O}$ and $m_{solute}$ – masses of water and solutes, respectively; $\nu_{H_2O}$ and $\nu_{solute}$ – number of moles of water and solutes, respectively.
Table 2.1. Materials characteristics

<table>
<thead>
<tr>
<th>Names</th>
<th>Chemical structure</th>
<th>$T_g$ (at 100 s) [K]</th>
<th>$M_w$ [g/mol]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>fructose</td>
<td><img src="image1" alt="fructose structure" /></td>
<td>288.5 [202]</td>
<td>180.16</td>
<td>Wako Pure Chemical Industries</td>
</tr>
<tr>
<td>glucose</td>
<td><img src="image2" alt="glucose structure" /></td>
<td>307.6 [202]</td>
<td>180.16</td>
<td>Fluka</td>
</tr>
<tr>
<td>deoxyribose</td>
<td><img src="image3" alt="deoxyribose structure" /></td>
<td>249 [203]</td>
<td>134.13</td>
<td>Aldrich</td>
</tr>
<tr>
<td>trehalose</td>
<td><img src="image5" alt="trehalose structure" /></td>
<td>371 [204] 396 [208] 373 [209] 391 [210]</td>
<td>342.30</td>
<td>Fluka</td>
</tr>
<tr>
<td>glycogen</td>
<td><img src="image6" alt="glycogen structure" /></td>
<td></td>
<td></td>
<td>Aziende Chimiche Angelini Francesco ACRAF s.p.a.</td>
</tr>
<tr>
<td>monomer of propylene glycol (PG)</td>
<td><img src="image7" alt="monomer PG structure" /></td>
<td>169 [211]</td>
<td>76.09</td>
<td>Aldrich</td>
</tr>
<tr>
<td>trimer of propylene glycol (TPG)</td>
<td><img src="image8" alt="trimer TPG structure" /></td>
<td>192.4 [181]</td>
<td>192.26</td>
<td>Aldrich</td>
</tr>
<tr>
<td>polypropylene glycol (PPG400)</td>
<td><img src="image9" alt="polypropylene glycol structure" /></td>
<td>196.9 [212]</td>
<td>400</td>
<td>Fluka</td>
</tr>
<tr>
<td>polyethylene glycol (PEG400)</td>
<td><img src="image10" alt="polyethylene glycol structure" /></td>
<td>-</td>
<td>400</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
For all the systems, dielectric measurements were performed in different temperature and pressure intervals. An overview of the experimental activity can be found in Tables 2.2 and 2.3 where all the details are provided. The main results will be shown in the following sections together with related discussion.

Table 2.2. List of experiments done on aqueous mixtures with glycol oligomers at different isobaric and isothermal scans

<table>
<thead>
<tr>
<th>Concentration of water, %</th>
<th>Concentration of solute, %</th>
<th>Isobars, MPa</th>
<th>Isotherms, °C/K</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>weight molar</td>
<td>[isobaric $T$ range scan]</td>
<td>[isothermal $P$ range scan]</td>
</tr>
<tr>
<td>Water + PG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>66.5</td>
<td>68.0</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>weight molar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.1 [148.2-213.2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>[200.2-257.1]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>[198.7-263.2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water + TPG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>83.4</td>
<td>68.0</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>weight molar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.1 [158.2-293.2]</td>
<td></td>
<td>-39.0 / 234.2 [0.1-500]</td>
</tr>
<tr>
<td>500</td>
<td>[209.3-253.5]</td>
<td></td>
<td>-60.0 / 213.2 [0.1-500]</td>
</tr>
<tr>
<td>620</td>
<td>[210.0-247.9]</td>
<td></td>
<td></td>
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<td>Isotherms, °C/K</td>
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Table 2.3. List of experiments done on saccharides-water mixtures at different isobaric and isothermal scans

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<th>Isotherms, °C/K</th>
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Chapter 3

Study of Relaxation Dynamics of Aqueous Systems at Low Temperature and High Pressure: A) Mixtures of Water and Glycol Oligomers

3.1 Relaxation dynamics of water in propylene glycols oligomers

3.1.1 Experimental Details

Propylene glycol oligomers (n-PG) belong to diols which means that independently on molecular weight of n-PG each molecule has 2 hydroxyl groups at the ends of chain (see Table 3.1). Because of OH groups, oligomers of PG characterize a strong tendency to form a hydrogen bonded network. They are highly hygroscopic and easily miscible with water. Oligomers of PG are very popular cryoprotectants for their properties to prevent ice crystal formation [52, 220-223]. This fact is a unique opportunity that enables us to study properties of water in the supercooled state by modifying the hydrogen bonding network.

Propylene glycol (PG) and tripropylene glycol (TPG) were obtained from Aldrich Chemical Company (purity > 99.5% and 97 %, respectively). These materials have the chemical formula H-(C₃H₆O)ₙ-OH with \( n = 1 \) and 3 and molecular weight of 76.09 g/mol and 192.26 g/mol, respectively. Propylene glycol contains less than 0.2 % of residual water by weight. Mixtures of PG and TPG have been studied both with 32 wt.% mass fraction of water.

Polypropylene glycol oligomer of molecular weight of 400 g/mol (PPG400) was purchased from Fluka (purity > 97%). Molecule of PPG400 has 7 repeating units \( (N = 7) \). Polypropylene glycol PPG400 and water were mixed to form solutions in a wide range, starting from small amount of water, 2.0 wt.%, up to 36.0 wt.% mass fraction of water. Among these, two systems, one with small (4 wt.%) and another with high (26 wt.%) mass fraction of water, were chosen to study how the dynamics of water mixtures with different water concentration is influenced by the pressure.

Distilled and deionised water (electric conductivity lower than 18.3 \( \mu \)S/m) was prepared by an ultra-pure water distiller (Millipore, MILLI-Q Laboratory). Both mixing of components and loading of the sample holder were performed in controlled atmosphere with dry nitrogen.
New data on dynamics of aqueous mixtures with propylene glycol oligomers at ambient and high pressure (up to 1.8 GPa) have been obtained with all equipments and procedures reported in Chapter 2. Dielectric spectra were measured in the temperature range from liquid to the deep glassy state on cooling by isothermal steps, after stabilizing the temperature within 0.1 K for an appropriate equilibration time. Pressure was continuously stabilized at a fixed value during isobaric measurements. In the case of isothermal compression, the pressure was slowly changed in subsequent steps and, once the target pressure was reached, the dielectric measurements were performed after an appropriate equilibration time (several tens of minutes). The pressure range from 1000 to 1800 MPa had been covered by the setup situated in Katowice (Poland) with collaboration of Prof. M. Paluch group. The description of the very high pressure ($P = 0.001-3$ GPa) technique can be found in Chapter 2. An overview of the experimental activity on aqueous mixtures with propylene glycol oligomers can be found in Table 2.2 (Chapter 2) where all details are provided. Studied aqueous mixtures at the chosen concentration range do not demix or crystallize in the explored temperature range [156, 211].

Our discussion begins with aqueous mixtures of PPG400 because those systems have been very well studied in a wide dynamic range and among the other systems studied in the thesis PPG400-water mixtures cover the biggest range of temperature and pressure. Later we will show effects of water concentration, molecular weight of solute and pressure on molecular dynamics of aqueous mixtures with the other glycol oligomers.
3.1.2 Effect of water concentration at ambient pressure

To study the effect of water on molecular dynamics we performed dielectric measurements of aqueous mixtures of PPG400 with different concentration of water, as listed in Table 2.2. Examples of dielectric spectra of PPG400-water mixtures with small (4.0 wt.%) and large (26.0 wt.%) amount of H\textsubscript{2}O (corresponding to mole fraction of water of $x_{H_2O} \approx 0.48$ and $x_{H_2O} \approx 0.89$, respectively) measured at ambient pressure and in the wide temperature range are presented in fig. 3.1.

As can be seen in fig. 3.1 relaxation dynamics of investigated mixtures strongly depends on the following factors: (i) temperature and (ii) amount of water in the solution. Generally, a decrease in temperature causes a rapid slowing down of molecular dynamics of the mixtures, whereas an increase in amount of water in the solution leads to speed up of the dielectric processes.

It is clearly seen that water significantly changes the relaxation dynamics of propylene glycol oligomers: adding even a small amount of water to PPG400 causes the appearing, in dielectric spectra, of a new additional relaxation, that we call $\nu$-relaxation (see § 1.7) which is not visible in the case of anhydrous PPG400. The $\nu$-process is faster than structural $\alpha$-relaxation and can be observed in the range of frequency in which anhydrous PPG400 exhibits a resolved secondary $\beta$-relaxation (see fig. 3.2 and refs. [79, 212]). The origin of this $\beta$-relaxation is controversial but however it is ubiquitous in all the pure glycol oligomers [181, 212, 217-219]. Authors of ref.
assume that occurrence of the $\beta$-relaxation in anhydrous $n$-PG oligomers is associated with the presence of residual water which is absorbed during manufacturing or preparation of the samples. On the other hand, it was shown that all anhydrous $n$-PG oligomers exhibit JG $\beta$-relaxation (for small oligomers $\beta$-relaxation is present as an excess wing) [218, 219] and adding water only enhances its intensity but water is not its cause [181, 212]. Moreover, $n$-PG oligomers with higher molecular weight (bigger number of repeating units) exhibit a stronger JG $\beta$-process which is less sensitive to adding water.

As the content of water in the mixture becomes larger, the intensity of the $\nu$-process significantly increases and its loss peak shifts to high frequency. Apart from $\beta$-relaxation, anhydrous PPG400 exhibits also a faster process ($\gamma$-relaxation process), probably originating from hydroxyl group rotation [212]. The strength of $\gamma$-relaxation of PPG400-water mixtures decreases with amount of water and $\gamma$-relaxation peak completely disappears for 12 wt.% water concentration. It could indicate that reorientations of OH groups of PPG400 are hindered by hydrogen bond formed between water molecules and hydroxyl groups of PPG400. Actually, the different character of the observed $\beta$- and $\gamma$-relaxation in anhydrous $n$-PG oligomers was clearly demonstrated by the application of pressure [218, 219]: whereas the former is very sensitive to pressure application, the latter is almost not affected by the reduction of density, showing the inter-molecular (JG) versus intra-molecular character of the $\beta$-one [104].

In the upper inset in fig. 3.2 one can observe a spectacular increase in the dielectric strength of the new process $\Delta\varepsilon_\nu$ with increasing of water content in the solution. This dramatic change in dielectric spectra due to water adding is an experimental evidence that the $\nu$-relaxation reflects mainly the water dynamics in the mixture. It is important to report that in general for aqueous mixtures there is a threshold concentration (mole fraction of water $\sim$0.8 in our system, fig. 3.2), above that dielectric strength of $\nu$-process rapidly increases with water concentration and the relaxation times are not so much dependent on the concentration [167, 181]. In this concentration regime the $\nu$-process is believed to reflect the true dynamics of water molecules mainly surrounded by other water molecules.

Water also affects the structural $\alpha$-relaxation which is always observed as a single peak in the dielectric loss spectra for studied mixtures. Moreover, water added to anhydrous PPG400 causes a broadening of the structural process (see the lower inset in fig. 3.2). Thus, the $\alpha$-relaxation is related to global cooperative dynamics of the system formed by both water and polymer PPG400 molecules and it is connected with the glass transition of the mixture, as demonstrated by the
coincidence of the calorimetric glass transition with the temperature where $\alpha$-relaxation time reaches around 100 seconds (see refs. [156, 182, 220]. The broadening of the structural relaxation peak is usually attributed to an increase in degree of cooperativity of the molecular dynamics in supercooled liquids but it could be due also to the dynamic heterogeneity related to the presence of the very mobile water molecules or to the fluctuation concentration that is always present in mixtures [221].

Fig. 3.2. Dielectric loss spectra of aqueous mixtures of PPG400 with various concentrations of water in the glassy state at $T = 178$ K and $P = 0.1$ MPa. The upper inset shows the dependences of dielectric strength for the $\alpha$- (closed red circles), $\nu$- (closed blue triangles) relaxations and their sum, $\Delta \varepsilon_{\text{tot}}$, (open black stars) against mole fraction of water; arrows indicate the concentrations of water in the mixture compared in § 3.1.7. The lower inset presents spectra of the water mixtures with the same $\alpha$-relaxation times in the liquid state.

Due to H bonding water molecules surround solute molecules and the water molecules that are bounded to the side of the solute molecules are feeling the dynamics of the solute. That is why for low concentration of water (below the certain concentration threshold) actually the dynamics
that water is probing is similar to the dynamics of the solute (see § 3.1.7). Dipole moment of water molecules is quite big that even at low concentration of water in the mixtures the contribution coming from the water molecules is observed: dielectric strength of the $\alpha$-process as well as of the $\nu$-process increases on adding water up to certain threshold concentration (see upper inset in fig. 3.2). At high enough water concentration $\Delta \varepsilon_{\alpha}$ tends to slightly decrease whereas $\Delta \varepsilon_{\nu}$ rapidly increases with water concentration. Following the idea that $\alpha$-relaxation originates only from the solute, the dielectric strength for the $\alpha$-relaxation should rapidly decrease with water concentration (for $x_{H,O}$ higher than threshold concentration) since amount of solute component is decreasing. And that is not observed for studied water mixtures.

It is important to stress that for studied systems one $\alpha$-relaxation and one $\nu$-relaxation are observed in water mixtures. On the contrary, in van der Waals mixtures and polymeric blends several primary and secondary relaxations are resolved corresponding to each component in the solution. Secondary processes of solute ($\beta$-, $\gamma$-, etc.) are also present in the water mixtures but because of their low strength comparatively to the $\nu$-process could not be observed in the dielectric spectra.

Such behaviour in dielectric spectra and dielectric strength on varying concentration is similar as in the case of many other water mixtures [79, 165, 181, 182].

Actually, the experimental findings reported in the literature on the dynamics of supercooled water mixtures are remarkably similar, irrespective of the structure and chemical composition of the aqueous systems. At least two relaxation processes were always reported, both can be detected by the highly sensitive adiabatic calorimetry or by broadband dielectric spectroscopy [103, 164]. There is a slower process coming from the structural relaxation of the solute molecules hydrogen bonded to water. Its relaxation time has the Vogel-Fulcher-Tammann (VFT) $T$-dependence, typical of cooperative structural $\alpha$-relaxation in glass-formers, and attains values between $10^2$-$10^3$ s at the glass transition temperature $T_g$, where a jump in heat capacity is observed by differential scanning calorimetry. Also present in the dielectric spectra at higher frequency is a faster process, that is usually called $\nu$-process. From the above mentioned increase of its dielectric strength with water content in the mixtures (see upper inset in fig. 3.2) [103, 165], as well as the increase of its relaxation time, on replacing the protonated water by deuterated water [156], it is clear that this faster relaxation is a process originating specifically from the water component [103, 165].
3.1.3 Quantitative analysis of dielectric spectra

To study the dynamics of “rich-in-water” mixtures of PPG400 under high pressure we chose one concentration, 26 wt.% (mole fraction of water ~ 0.89), that is above the mentioned threshold concentration. This system was well studied at ambient pressure in collaboration with Prof. M. Paluch group from Katowice (Poland).

Dielectric measurements of the mixture PPG400+26% H$_2$O performed under high pressure provide us new information about relaxation processes of the solution and especially about dynamics of water. Similarly as it is observed at $P = 0.1$ MPa, the spectra of the mixture PPG400+26% H$_2$O obtained at elevated pressure of 360 and 500 MPa exhibit two well-resolved relaxation peaks: the slower ($\alpha$-process) and faster ($\nu$-process) (see figs. 3.2-3.4), whereas in the case of spectra measured at the highest pressure 1.8 GPa the loss peak of the $\alpha$-relaxation was hidden by the large contribution of dc-conductivity to dielectric loss. Nevertheless some information about the $\alpha$-relaxation was obtained from the real part of permittivity.

The real and imaginary parts of the dielectric constant, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, of PPG400+26% water mixture are displayed in figs. 3.3-3.4 at selected pressures and temperatures. The isobaric and isothermal permittivity data were analysed in terms of linear superposition of relaxation and conductivity contributions, with each relaxation process described by a Havriliak–Negami (HN) function:

$$\varepsilon'(\omega) = \sum_{k=\alpha,\nu} \frac{\Delta \varepsilon_k}{1 + (i\omega\tau_{HN,k})^{1-\alpha_k}} - \frac{i\sigma_{DC}}{\varepsilon_0\omega} + \varepsilon_\infty .$$  \hspace{1cm} (3.1)

In Eq. (3.1) the index $k$ runs over the relaxation processes and the conductivity effect is taken into account by the term $-i\sigma_{DC}/(\varepsilon_0\omega)$ ($\varepsilon_0$ is the dielectric permittivity of vacuum). $\varepsilon_\infty$ is the high-frequency limit of $\varepsilon'$ outside the dispersion zone, and $\Delta \varepsilon_k$ is the dielectric strength of each process. The simultaneous fit of real and imaginary part of permittivity with this phenomenological function allows us to extract characteristic parameters for the different relaxation peaks, i.e., the frequency of maximum loss, the dielectric strength and the peak shape. The frequency of maximum $\varepsilon''$, $f_{\text{max}}$, can be analytically calculated from the HN fitting parameters (see Eq. (1.27)). The characteristic relaxation time (most probable time), can be easily obtained $\tau = (2\pi \cdot f_{\text{max}})^{-1}$ (see also § 1.3).
Fig. 3.3. Frequency dependences of real and imaginary parts of dielectric function for PPG400+26% water mixture at 204.2 K and ambient pressure. The solid curves were obtained by the fitting procedures. Close and open circles are $\varepsilon'$ and $\varepsilon''$ data, respectively; the dashed, dotted and dotted-dashed lines indicate the $\alpha$-process, $\nu$-process, and dc conductivity, respectively.

Fig. 3.4. Frequency dependences of real and imaginary parts of dielectric function for PPG400+26% water mixture at 239.4 K and 500 MPa. The solid curves were obtained by the fitting procedures. Close and open circles are $\varepsilon'$ and $\varepsilon''$ data, respectively; the dashed, dotted and dotted-dashed lines indicate the $\alpha$-process, $\nu$-process, and dc conductivity, respectively.
The real and the imaginary parts of $\varepsilon^*(\omega)$ have been fitted simultaneously by using the non-linear least-squares Levenberg–Marquard routine: a distribution of fitting parameters was found, with average values and standard deviations. An estimate of the error of each parameter has been obtained by the standard deviation of the probability distribution of the fitting parameters.

The use of simultaneous fitting on real and imaginary parts has several advantages: i) the use of a Kramers-Kronig compatible fitting function allows to check the Kramers-Kronig compatibility of the data; ii) a simultaneous fit allows the determination of the parameters $\varepsilon_\infty$ and $\sigma_{DC}$, that can be determined only from real and imaginary part, respectively; iii) the procedure makes possible to reveal relaxation processes from the real part of permittivity, when the low frequency range of the imaginary part is masked by the conductivity contribution and no loss peak can be revealed directly. Figures 3.3-3.4, for instance, show a case where the simultaneous fit of real and imaginary part provides a reliable representation of the data.

### 3.1.4 Similarity of $\nu$-process to secondary relaxation

From inspection of the spectra we found that the $\nu$-process has similar features (its sensitivity to pressure and temperature) to those of the secondary (non-cooperative) relaxation found in many other pure glass-forming liquids. In fact, for isobaric and isothermal data, we observe that both relaxations, $\alpha$- and $\nu$-, slow down with decreasing temperature $T$ and increasing pressure $P$, but the $\alpha$-relaxation time have always a much stronger $T$ and $P$ dependence. Moreover, the $\nu$-relaxation is much less sensitive to changes of pressure than temperature. Consequently, a greater separation between $\alpha$- and $\nu$- processes may be achieved by isothermal rather than isobaric experiments. Figure 3.5 shows the dielectric loss spectra for anhydrous PPG400 and PPG400+26% water mixture plotted at the same $\alpha$-relaxation time at different isothermal-isobaric conditions. Adding the water does not change too much the position of $\alpha$-peak at ambient pressure, only its broadness increases. On the other hand, pressure strongly changes the dynamics: when we increase pressure both $\alpha$- and $\nu$- processes slow down and to make comparison with the spectra at ambient pressure at the same $\alpha$-relaxation time we have to increase temperature. Combination of $P$ and $T$ allows to plot isochronal spectra which are shown in fig. 3.5 where it is clearly seen that the separation between $\alpha$- and $\nu$- processes increases for about one decade for measurement at elevated pressure (500 MPa) and higher temperature (232.15 K) comparing to that of ambient pressure.
It was experimentally recognized that such properties are typical for secondary process, especially in hydrogen bonded liquids, for example in glycerol, sorbitol, xylitol, threitol etc. [104, 197, 198]. In this respect the $\nu$-relaxation can be considered as a secondary relaxation reflecting some “independent” (i.e. involving motions of single molecule, without cooperativity with the surroundings) dynamics of water component in the aqueous mixtures, as recently discussed by Capaccioli et. al. for many aqueous systems at ambient pressure [103, 182, 222].

Fig. 3.5. Comparison of dielectric spectra with the same $\alpha$- relaxation times, obtained at different $P$ and $T$ for water mixture of PPG400+26% H$_2$O and anhydrous PPG400. Solid lines denote fits of entire spectra as a superposition of the two HN functions (dotted lines).

3.1.5 Effect of high pressure on the parameters of the relaxation dynamics

a) Analysis of dynamics: $T$ and $P$ dependence of $\tau_\alpha$ and $\tau_\nu$ relaxation times

From dielectric spectra we found the relaxation maps for aqueous mixture of PPG400 with 26% content of water obtained at different isobaric conditions ($P = 0.1, 360, 500, 1800$ MPa). Figure 3.6 shows the temperature dependence of $\alpha$- and $\nu$- relaxation times for PPG400-26% water mixture at ambient and elevated pressure. The logarithm of $\tau_\alpha$ shows the typical Vogel-Fulcher-
Tamman-like behaviour (see fig. 3.6(a)), with a curved behaviour vs. $1/T$, meaning an apparent activation energy that increases on decreasing temperature $T$:

$$\log_{10} \tau_\alpha = \log_{10} \tau_{\alpha\text{VFT}} + \frac{A}{T - T_0},$$  \hspace{1cm} (3.2)$$

where $\tau_{\alpha\text{VFT}}$, $A$ and $T_0$ are empirical VFT parameters. The VFT behaviour is typical of structural process in glass-forming material. It can be also seen that pressure effect moves $\alpha$-relaxation times to higher temperatures.

![Fig. 3.6. Plots of logarithm of relaxation times against reciprocal temperature for the $\alpha$- (a) and $\nu$- (b) processes of PPG400+26% water mixture for various isobars: 0.1 MPa (circles), 360 MPa (triangles), 500 MPa (squares), 1800 MPa (stars). Solid lines represent VFT fitting curves, dashed lines are Arrhenius fitting.](image)

Figure 3.6(b) shows the temperature dependence of logarithm of $\nu$-relaxation time for PPG400-26% water mixture. This relaxation has linear (Arrhenius) behaviour vs. reciprocal temperature below $T_g$:

$$\log_{10} \tau_\nu = \log_{10} \tau_{\nu\text{Arr}} + \log_{10} \left( e^{\frac{\Delta E}{RT}} \right),$$ \hspace{1cm} (3.3)$$

where $\tau_{\nu\text{Arr}}$ is the preexponential factor, $R$ the gas constant and $\Delta E$ the apparent molar activation energy. It can be seen that pressure less affects the timescale of $\nu$-relaxation than that of $\alpha$-relaxation.

In general, we observed that compression significantly slows down water dynamics in mixtures. Relaxation times considerable increases on increasing pressure, at odds with what observed and
predicted for bulk pure water [148, 188, 223]. So, although \( \nu \)-relaxation time could have some resemblance with pure water dynamics at ambient pressure, its behaviour at high pressure is quite different. This is a remarkable fact that should invite to be careful when data of water mixtures are extrapolated to the bulk behaviour [156].

Besides isobaric we performed also isothermal experiments (at, for instance, \( T = 213.2 \) K, 233.8 K): at constant temperature we elevated the pressure step by step, and we measured after equilibrating at each point for a time long enough to reach equilibrium conditions (not less than 15 minutes but up to some hours, in some cases). Figure 3.7 shows an example of the pressure dependence of \( \alpha \)- and \( \nu \)-relaxations for PPG400-26% water mixture at \( T=213.2 \) K. We can see that the behaviour is similar to that of isobaric data. There is a strong effect of pressure on \( \alpha \)-relaxation, which has slightly curved dependence, a kind of VFT-like behaviour. There is also a weaker effect of pressure on \( \nu \)-relaxation which has linear behaviour in liquid and glassy states, but with different slopes. The pressure dependences of \( \tau_\alpha \) and \( \tau_\nu \) were fitted by Eq. (3.4) [195, 224] and Eq. (3.5), respectively:

\[
\tau_\alpha(T,P) = \tau_\alpha(T,0) \exp \left( \frac{D_\nu P}{P_0 - P} \right),
\]

\[
\log \tau_\nu = \log \tau_0^* + \frac{P \Delta V^*}{RT},
\]

where \( P \) – pressure, \( D_\nu \) and \( P_0 \) – empirical VFT parameters, \( \tau_0^* \) – the preexponential factor, \( \Delta V^* \) – the apparent molar activation volume, \( \Delta V^* = RT \cdot \partial (\ln \tau)/\partial P \). The fitting parameters of Eqs. (3.2)-(3.5) for isobaric and isothermal scans for PPG400+26% water are shown in Table 3.2.

Actually, the results obtained for isobaric temperature and isothermal pressure dependences of \( \nu \)-relaxation times \( \tau_\nu \) are unusual and very surprising for aqueous systems. We observed that the relaxation dynamics of water reflected in the \( \nu \)-process is sensitive to the glass transition of the mixture, which is manifested by a change in the character of the dependence \( \log[\tau_\nu(T,P)] \) vs. \( 1/T \) or \( P \) that occurs always close to \( T_g \) (at a crossover temperature \( T_{\text{cross}} \)) or \( P_g \) (at a crossover pressure \( P_{\text{cross}} \)) for isobaric and isothermal measurements, respectively (see examples in figs. 3.6-3.7). For isobaric measurements \( \log[\tau_\nu(T)] \) changes behaviour from a stronger Vogel-Fulcher-Tamman to a weaker Arrhenius dependence on cooling. Moreover, in the case of
isothermal scans, $\log[\tau_\alpha(P)]$ shows a transition between two Arrhenius behaviours with a stronger dependence in the liquid than in glassy state.

Fig. 3.7. Plot of logarithm of relaxation times against pressure of the $\alpha$- (closed symbols) and the $\nu$- (open symbols) processes of PPG400-26% water mixture for isotherm $T = 213.2$ K. $\tau_\nu^{\text{cross}}$ and $P_\nu^{\text{cross}}$ the crossover time and the crossover pressure, respectively. Solid line represents VFT fitting curve for the $\alpha$-process and dashed lines represent Arrhenius fitting above and below $P_\nu^{\text{cross}}$.

Table 3.2. Parameters of the VFT Equation (3.2), (3.4) and Arrhenius Equation (3.3), (3.5) for PPG400 + 26% water at different isobaric and isothermal scans

<table>
<thead>
<tr>
<th>$P$ [MPa]</th>
<th>$T_\nu$ [K]</th>
<th>VFT parameters of the $\alpha$-process</th>
<th>Arrhenius parameters of the $\nu$-process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\log_{10}[\tau_{\alpha,VFT}(s)]$</td>
<td>$A$ [K]</td>
</tr>
<tr>
<td>0.1</td>
<td>194.4</td>
<td>-11.8</td>
<td>413.4</td>
</tr>
<tr>
<td>360</td>
<td>219.8</td>
<td>-13.2</td>
<td>573.4</td>
</tr>
<tr>
<td>500</td>
<td>227.4</td>
<td>-12.1</td>
<td>483.8</td>
</tr>
<tr>
<td>1800</td>
<td>270.6</td>
<td>-14.0</td>
<td>1093.0</td>
</tr>
</tbody>
</table>

Isothermal scans

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$P_\nu$ [MPa]</th>
<th>$\log_{10}[\tau_\alpha(T,0)]$</th>
<th>$D_p$</th>
<th>$P_0$</th>
<th>$\log \tau_0^*$</th>
<th>$\Delta V^*$ [cm$^3$/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>233.9</td>
<td>644</td>
<td>-6.0</td>
<td>47.6</td>
<td>2290.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>213.2</td>
<td>249</td>
<td>-3.2</td>
<td>30.4</td>
<td>882.3</td>
<td>-3.67</td>
<td>0.165</td>
</tr>
</tbody>
</table>
Figure 3.8 shows examples of temperature dependences of $\tau_\alpha$ and $\tau_\nu$ for 26% water-PPG400 mixture at ambient pressure and 500 MPa. We estimated the dielectric glass transition temperature $T_g$ by extrapolation of VFT equation to a time that is equal to 100 s. It can be seen that $T_g$ moves to higher temperature on increasing pressure.

![Plot of logarithm of relaxation times against reciprocal temperature for the $\alpha$- (close symbols) and the $\nu$- (open symbols) processes of PPG400-26% water mixture for ambient (circles) and elevated, 500 MPa, (squares) pressures. $\tau_\nu$ cross and $T_{\text{cross}}$ the crossover time and the crossover temperature, respectively. Solid lines represent VFT fitting curves for the $\alpha$-process and for $\nu$-process above $T_{\text{cross}}$, dashed lines represent linear fitting below and above $T_{\text{cross}}$.](image)

Fig. 3.8. Plot of logarithm of relaxation times against reciprocal temperature for the $\alpha$- (close symbols) and the $\nu$- (open symbols) processes of PPG400-26% water mixture for ambient (circles) and elevated, 500 MPa, (squares) pressures. $\tau_\nu$ cross and $T_{\text{cross}}$ the crossover time and the crossover temperature, respectively. Solid lines represent VFT fitting curves for the $\alpha$-process and for $\nu$-process above $T_{\text{cross}}$, dashed lines represent linear fitting below and above $T_{\text{cross}}$.

To estimate actual values of the crossover parameters $(T_{\text{cross}}, P_{\text{cross}}, \tau_{\nu \text{ cross}})$ the temperature (pressure) dependences of $\tau_\nu$ for isobaric (isothermal) scans in glassy and in supercooled liquid state (in the vicinity of the crossover) were fitted by linear regression (see fig. 3.8) and intersection of two straight lines was taken as the crossover. The deviation of the $\nu$-relaxation time from extrapolation of the Arrhenius behaviour in a glassy state to higher temperature at $T_{\text{cross}}$ was more than one standard deviation. Such procedure is quite empirical, however, it gives the possibility to estimate simply precise values of the crossover parameters, instead of analysis of the derivative
\(d(\log_{10}[\tau_v(T)])/d(1/T)\) for isobaric and \(d(\log_{10}[\tau_v(P)])/dP\) for isothermal scans, procedure which could give very noisy data. Another effect of pressure on the crossover is to move it to higher temperature and shorter time. It is worth noting that the correspondence of the measured \(T_{cross}\) with \(T_g\) is valid for the whole pressure range from 0.1 MPa up to 1.8 GPa (see fig. 3.11).

The change of \(T\) or \(P\) dependences of the \(\tau_v\) in vicinity of \(T_g\) is a true phenomenon characteristic of the fast dynamics in glass-formers: it involves the amplitude of mean square displacements [106] related to the cage dynamics and relaxation time and strength of the \(\beta\)-process [101-105, 222]. Such phenomena, involving fast dynamics, mimic the transition in temperature behaviour found for volume or enthalpy around \(T_g\), caused by the arrest of structural relaxation (see § 1.4.2).

Some authors [156] claimed that the change of slope of \(\tau_v\) on crossing \(T_g\) in aqueous systems could be nothing but an apparent effect due to the fitting procedure, as it was reported for \(\alpha\)- and \(\beta\)-relaxation. This fact could happen in the case for which \(\alpha\)- and \(\beta\)-timescales are close each other: in that case the results could depend on the deconvolution method used. In reality, there are several examples of typical secondary \(\beta\)-relaxations of organic compounds where no merging with the \(\alpha\)-process occurs at temperatures just above \(T_g\), and the observed change of temperature dependence of its relaxation time \(\tau_\beta\) is real because the two relaxations are widely separated at \(T_g\) and no fitting procedure is needed to determine \(\tau_\beta\). Examples include the studies by Blochowicz et. al. [96] and by Kessairi et. al. [97] on component dynamics of binary mixtures where a clear change of activation energy of \(\tau_\beta\) at \(T_g\) was reported. Another example is sorbitol and xylitol subjected to high pressure studies by Paluch and co-workers [198]. In all the mentioned cases and other examples, the secondary relaxation time changes its Arrhenius \(T\)-dependence in the glassy state after crossing \(T_g\). This effect was seen directly without the use of any fitting procedures, such as the so-called “Williams-ansatz” or by simple superposition of the two processes. In this case of well resolved \(\alpha\)- and \(\beta\)-relaxations, even by subjecting the data to analysis by the Williams-ansatz procedure Blochowicz found the change of activation energy of \(\tau_\beta\) at \(T_g\) [96]. According to Williams-ansatz procedure, the total correlation function can be expressed in the time domain as a linear combination of the \(\alpha\)-correlation function and a product between \(\alpha\)- and \(\beta\)-correlation function:

\[
\Phi(t) = a \cdot \Phi_\alpha(t) + (1-a) \cdot \Phi_\alpha(t) \cdot \Phi_\beta(t). \tag{3.6}
\]

As a consequence, in the frequency domain Eq. (3.6) gives rise to the usual superposition of two loss peaks, but with the faster one being an “effective” secondary relaxation peak, resulting from
the convolution in Fourier transform. In principle, $\alpha$- with $\beta$- relaxation time could have any kind of temperature dependence (see for instance ref. [96]), but many authors [225, 226] arbitrarily fix $\tau_\beta$ to have an Arrhenius behaviour for all temperatures. If the $\beta$-relaxation would have an Arrhenius behaviour in the whole temperature range, when its timescale approaches that of the $\alpha$- (with a VFT behaviour), a change of the temperature dependence of the “effective” secondary relaxation to a stronger dependence than the assumed Arrhenius dependence of $\tau_\beta$ could be expected. It is worthwhile to point out that the Williams-ansatz is an hypothesis that has not yet been given a proof to be fundamentally correct, and also its assumption that $\Phi_\alpha(t)$ and $\Phi_\beta(t)$ are independent functions seems to contradict the experimentally observed connection between the $\alpha$- and $\beta$- relaxation as demonstrated in refs. [104, 116, 227]. Moreover, we stress that, in several examples where the secondary relaxation time deviates from the temperature behaviour of the glassy state, the separation between structural and secondary relaxation in their relaxation times is quite large, more than five decades at ambient pressure and even larger at very high pressure. We can see such examples from the mixture, PPG400+26% wt. fraction of water, in fig. 3.9, where the supposed influence of the $\alpha$-relaxation should be negligible on the much faster timescale of the secondary $\nu$-relaxation. Whether it is at ambient or elevated pressure, the change in $T$-dependence of $\tau_\nu$ occurs close to $T_g$, which increases with pressure. Concomitantly, the separation between $\alpha$- and $\nu$-processes increases with pressure (see fig. 3.5 and also next Chapter 4) and the $\tau_\nu$ at the crossover becomes shorter on increasing pressure, at odds with the prediction of recent theories [188].

The data in fig. 3.9 offer an opportunity to test the effect of the convolution of the $\alpha$- and $\beta$-relaxations according to the Williams ansatz. We used the same procedure described in refs. [225, 226]. First we determined the Arrhenius $T$-dependence of the $\nu$-relaxation time in the glassy state, then we extrapolated this dependence to higher temperatures up to where it merges with the $\alpha$-relaxation. Following Eq. (3.6), we calculated the “effective” relaxation time for the convoluted $\alpha$-and $\nu$-relaxation, and examined whether it can account for the observed change in $T$-dependence of $\tau_\nu$. The “effective” $\nu$-relaxation times from this exercise using the Williams ansatz are shown in fig. 3.9. It is clear by inspection of fig. 3.9 that the Williams ansatz analysis brings only a milder deviation of the “effective” $\nu$-relaxation times from the Arrhenius behaviour and at temperature significantly higher than $T_g$. These results are both in disagreement with experimental observation, and therefore the Williams ansatz procedure is not able to explain the
large deviation from the Arrhenius dependence of $\tau_v$ after crossing $T_g$ which is experimentally observed at ambient and elevated pressures. Irrespective of the fitting procedure adopted (Williams ansatz convolution or simple superposition), the dynamic crossover can be described only with a real change in the behaviour of $\log[\tau_v(T,P)]$.

![Semilog plot of relaxation times vs. reciprocal T of 26% wt. fraction of water in PPG400](image)

Fig. 3.9. Semilog plot of relaxation times vs. reciprocal $T$ of 26% wt. fraction of water in PPG400. Close and open circles indicate $\alpha$- and $\nu$- process, respectively. Asterisks are the relaxation times of the “effective” relaxation obtained from the convolution procedure indicated by the Williams ansatz. Black and red symbols indicate isobaric scan done at $P = 0.1$ and 500 MPa, respectively. Dotted lines are Arrhenius fits to the data in the glassy state.

**b) Analysis of dynamics: effect of pressure on $T_g$ and $T_{cross}$ on fragility and on activation energies**

The strong dependence of $\tau_\alpha$ and $T_g$ on pressure are clearly shown in figs. 3.6-3.9. As a summary, we will show now the values for $T_g$ (or $P_g$) for isobaric (or isothermal) conditions, obtaining by extrapolating the VFT function up to the corresponding $\tau_\alpha = 100$ s. Longer are the relaxation times measured, less error we found in the extrapolation.
Figures 3.10-3.13 show how pressure affects all parameters defined above and characterizing the variation of dynamics with $T$ and $P$. Similarly to other glass formers, the glass transition temperature $T_g$ of the considered mixture increases with increasing pressure (see fig. 3.10). The experimental dependence of $T_g$ on $P$, obtained from combining both isobaric and isothermal measurements, is well-fitted with the Andersson equation [228]:

$$T_g = k_3 \left(1 + \frac{k_2 P}{k_3}ight)^{1/k_2},$$  \hspace{1cm} (3.7)

where $k_3 = T_g \bigg|_{P=0}$, $k_2$ is reciprocal of the fractional exponent and $k_3 = T_g \bigg|_{P=0} \cdot \left[\frac{dT_g}{dP}\bigg|_{P=0}\right]^{1}$ is the pressure coefficient. There is another model for representing pressure dependence of $T_g$ in literature proposed by Avramov [229] which brings to similar mathematical function. The fitting parameters of Eq. (3.7) for PPG400+26% water mixture are shown in Table 3.3.

The low pressure derivative of glass transition temperature, $dT_g/dP$, is 90 K/GPa, a value typical of H-bonded systems and much lower than that of pure polypropylene glycol (nearly 160 K/GPa) [78].

![Graph showing the pressure dependence of glass transition temperatures for PPG400-26% water mixture.](image)

**Fig. 3.10.** The pressure dependence of glass transition temperatures obtained from both isobaric (closed triangles) and isothermal (open circles) measurements for PPG400-26% water mixture. Solid and dashed lines represent Andersson fitting curve and derivative $dT_g/dP$ at low values of $P$, respectively.
As was mentioned above, the ν-process changes its behaviour from a weaker Arrhenius dependence to a stronger VFT-like temperature dependence on increasing temperature and crossing $T_g$ region. We define here precisely the crossover temperature $T_{\text{cross}}$ and the crossover time $\tau_{\nu \text{cross}}$ as the value where the ν-relaxation time deviates (from more than one standard deviation) from extrapolation of the Arrhenius behaviour in a low temperature glassy state (see fig. 3.8). We can also easily define pressure of glass transition at certain temperature, $P_g$, and the crossover parameters, $P_{\text{cross}}$ and $\tau_{\nu \text{cross}}$ for isothermal measurements (see fig. 3.7), using the same concepts already illustrated for isobars.

Table 3.3. Fitting parameters of Eq. (3.7) for water solutions with propylene glycol oligomers and for PEG400+35% water mixture

<table>
<thead>
<tr>
<th>Systems</th>
<th>$k_1$ [K]</th>
<th>$k_2$</th>
<th>$k_3$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG400 + 26% H$_2$O</td>
<td>194.3</td>
<td>5.1</td>
<td>2100</td>
</tr>
<tr>
<td>TPG + 32% H$_2$O</td>
<td>183.6</td>
<td>6.0</td>
<td>2270</td>
</tr>
<tr>
<td>PG + 32% H$_2$O</td>
<td>161.0</td>
<td>2.7</td>
<td>4900</td>
</tr>
<tr>
<td>PPG400 + 4% H$_2$O</td>
<td>195.9</td>
<td>5.1</td>
<td>1330</td>
</tr>
<tr>
<td>PEG400 + 35% H$_2$O</td>
<td>182.4</td>
<td>5.4</td>
<td>3400</td>
</tr>
</tbody>
</table>

We have observed that $T_{\text{cross}}$ for PPG400-26% water mixture at different isobaric scans always occurs few degrees below the glass transition temperature $T_g$ at times exceeding 1000 s. For such a value of $\tau_\alpha$, the structural dynamics of the system is completely frozen and water reorientation can occurs in an environment that is structurally invariant: its dynamics is completely controlled by the interactions that the single molecule experiences only on a very local scale. Both $T_{\text{cross}}$ and $T_g$ are moving with pressure and they are strongly correlated. This can be shown in fig. 3.11, where the couple $T_{\text{cross}}$ vs. $T_g$ is plotted for PPG400+26% water mixture at different isobaric conditions. The correlation of $T_{\text{cross}}$ and $T_g$ will be discussed in more details in Chapter 4.

The value of ν- relaxation time at the dynamic crossover, $\tau_{\nu \text{cross}}$, is also pressure-dependent, that is, it decreases with compression in a way that can be fitted exponentially, approaching $\tau_{\nu \text{cross}} (P \to \infty) = 3 \mu$s (see fig. 3.12). It is noteworthy that the timescale of $\tau_{\nu \text{cross}}$ attains an order of magnitude similar to that found by dielectric spectroscopy in other aqueous mixtures [103, 167, 181] and also for water confined or present in hydration shells of proteins [163]. Only in
some neutron scattering studies a much shorter crossover time scale (tens of ps) was found [148, 230]. Moreover, it is remarkable that the crossover temperature at ambient pressure is much lower than the critical temperature (225 K) usually characterizing some anomalous behaviour of the dynamics, viscosity, and transport coefficients of water confined in different environments with different effective dimensions and even in water-rich aqueous mixtures [231].

Fig. 3.11 Correlation between $T_{\text{cross}}$ and $T_g$ with pressure for PPG400-26% water mixture at different isobaric conditions. Dashed line is guide for the eyes.

Fig. 3.12. Pressure dependence of logarithm of $\tau_{v \text{cross}}$ for PPG400+26% water mixture. Solid line is exponential fitting curve.
We also found unusual pressure dependences of activation energies $E_a$ for the $\nu$ relaxation, which exhibit maxima over pressure variation both for the liquid and glassy state behaviours. As it can be seen in fig. 3.13(a), initially $E_a$ increases but eventually decreases with pressure in the GPa range. It may indicate that initially the increase in pressure can facilitate the hydrogen bonds forming, whereas the reversal of the direction of change in $E_a$ during compression may be due to significant reduction of hydrogen bonds in PPG400+26% H$_2$O system when $P > 1$ GPa. It is noteworthy that at that high pressure, measurements have been done in the temperature range 270-300 K, where hydrogen bonds are known to be weakened [232]. Actually, both types of $E_a$ in fig. 3.13(a) have been determined in vicinity of $T_g$, and even the number of H-bonds frozen in the glass (affecting $E_a$ below $T_g$) should be related to the temperature of glass formation. In the literature, an increase of the strength of H bond with increasing pressure was usually found [233-235], although a negligible effect or even a decrease was sometimes reported, especially due to the distortion that pressure imposes to the bond angles [236, 237].

It is intriguing that a similar effect of pressure on H bond formation was observed for the pure samples (i.e. without water) of small oligomers of propylene glycol (DPG [238] and TPG [79]), reflecting the non-monotonic pressure dependence of isobaric fragility $m_p=\frac{d\log \tau_\alpha}{d(T_g/T)}|_{P=T_g}$ (see fig. 3.13(b)). Values of $m_p$ for these materials were reported to increase up to nearly 1 GPa and then to decreases. It is contrary to what occurs usually for non-associated liquids, which reveal a quite different variation of the function $m_p(P)$: fragility monotonically slightly decreases with increasing pressure. In analogy to DPG and TPG, also here (see fig. 3.13(b)) we found an initially increasing character of the dependence $m_p(P)$ for the $\alpha$-relaxation times of mixture PPG400+26% H$_2$O, followed by a smaller value reported at 1.8 GPa. It indicates that, similarly to the case of pure PG oligomers, dynamics of H bonds considerably influences also the $\alpha$-relaxation of the water mixture.
c) **Analysis of dielectric strength: evidence of local mechanism for water relaxation**

The analysis of dielectric strength can provide information on the character of the relaxation processes. According to Eq. (1.28) in a molecular liquid dielectric strength can be written as [30]:

\[
\Delta \varepsilon = \frac{4\pi C}{3k_BT} F g_K N_A \mu^2,
\]

where \(N_A\) is the Avogadro number, \(k_B\) the Boltzmann constant, \(\mu\) is the molecular dipole moment, \(C\) is the number of effective dipoles per unit volume, \(F\) is the local field correction, \(g_K\) is the Kirkwood correlation factor. As was mentioned in § 1.3, usually all the quantities in Eq. (1.28) have a very weak \(T\) dependence, excepting \(g_K\) (\(T\) dependence of \(g_K\) can be approximated...
as a first order polynomial). Therefore the overall temperature behaviour can be represented by a first order polynomial in $1/T$. For a structural $\alpha$-process $\Delta \varepsilon$ usually decreases on increasing temperature. This is what we found for $\alpha$-process in studied PPG400-water mixtures. Such behaviour is observed only if the number of effective dipoles per unit volume is constant. On the other hand, when the number of effective dipoles increases on increasing temperature, $\Delta \varepsilon$ increases on increasing $T$, that is typical for secondary relaxation process.

In general, in PPG400+26% H$_2$O mixture for different isobaric conditions, the dielectric strength, $\Delta \varepsilon_{\nu}$, of the $\nu$-process increases monotonically with temperature with an elbow shape that indicates a change of slope in vicinity of $T_g$. In figs. 3.14 and 3.15 an example of the temperature dependence of $\Delta \varepsilon_{\nu}$ is shown together with $\Delta \varepsilon_{\alpha}$ from PPG400+26% H$_2$O mixture at ambient and elevated (500 MPa) pressures.

This behaviour of $\Delta \varepsilon_{\nu}$ is typical of secondary relaxation of a component in non-aqueous mixtures shown in [103] and also neat glass-formers [101, 102, 104, 105], and it is another evidence that the local water relaxation is strongly affected by the vitrification of the mixture.

![Graph showing temperature dependence of $\Delta \varepsilon$ for PPG400+26% H$_2$O mixture at ambient pressure.](image)

**Fig. 3.14.** Temperature dependence of the relaxation strength of the $\alpha$- (squares) and the $\nu$- (circles) processes for the PPG400+26% H$_2$O mixture at ambient pressure.
In summary, we found that pressure considerably affects the relaxation dynamics of water in a rich-in-water aqueous mixture of PPG400. For isobaric and isothermal data, we observed that both relaxations, $\alpha$- and $\nu$-, slow down with decreasing $T$ and increasing $P$, but the $\alpha$-relaxation time have a much stronger dependence. Moreover, the $\nu$-relaxation is much less sensitive to changes of pressure than temperature.

We also observed the dynamic crossover in the water related $\nu$-relaxation near the glass transition of the mixture in the whole pressure range (0.1 MPa - 1.8 GPa). It is characterized by the VFT-to-Arrhenius transition of $\tau_\nu(T)$ on cooling similarly to that established for water in confined systems. Other pressure-dependent properties of the crossover of water relaxation in the aqueous mixture are significantly different from properties observed for confined water: (i) Contrary to what occurs for aqueous systems of confined geometry [148, 187, 188, 230], the dependence $T_{\text{cross}}(P)$ for our water mixture has an increasing character, and therefore, we cannot relate it to the liquid-liquid phase transition line (associated to crossing the Widom line) in a $T$-$P$ space.
plane. (ii) The crossover relaxation time $\tau_{\nu \text{cross}}$ decreases exponentially with increasing $P$ for the mixture PPG400+26% H$_2$O, whereas $\tau_{\nu \text{cross}}(P) \approx \text{const}$ for confined water. These two findings can indicate that the $\nu$-process is not the structural relaxation of water, but it reflects a more local dynamics of H$_2$O molecules. (iii) Moreover, the pressure dependence of the Arrhenius activation energy $E_a$ for the $\nu$-relaxation is non-monotonic and reveals a maximum at about 1 GPa, while the Arrhenius activation energy for the confined water process decreases with increasing $P$ at $T < T_{\text{cross}}$. The dependences $E_a(P)$ for the $\nu$-process and the isobaric fragility $m_P$ for the aqueous mixture correspond well with each other. It is shown that the compression effect on hydrogen bonding in water mixtures is strongly dependent on pressure value: increasing pressure reinforces the structuring of a H-bonded network until a certain pressure value after which the degree of H bonds decreases due to the increase of temperature following $T_g(P)$. Thus, the values of $E_a$ for the $\nu$ process and $m_P$ for the aqueous mixture depend on the dynamics of H bonds, whereas the crossover relaxation time $\tau_{\nu \text{cross}}$ depends on the system density, which manifests the well-known “elbow shape” temperature dependence with a change of slope at $T_g$ as a consequence of the structural arrest. (iv) The relaxation strength, $\Delta\varepsilon_{\nu}$, of the $\nu$-process changes near $T_{\text{cross}}$ from a weaker dependence below $T_{\text{cross}}$ to a stronger one above $T_{\text{cross}}$ on heating through the glass transition temperature. This change is similar to $\Delta\varepsilon_{JG}$ seen before in secondary relaxation of a component in non-aqueous mixtures and in neat glass-formers, and is a mimicry of the changes observed in the enthalpy $H$, entropy $S$, and volume $V$ of neat glass-formers when crossing the glass transition temperature.

It was experimentally recognized that such properties are typical of secondary processes.

3.1.6 Effect of the number of repeating units of the oligomers on dynamics

To study the effect of the number of repeating units of the propylene glycol oligomers on molecular dynamics we chose rich-in-water solutions of the $n$-PG oligomers ($n = 1, 3, 7$) with more or less similar weight fraction of water (equivalent to a similar ratio of number of water molecules per monomeric units).

As examples of the relaxation processes for water mixtures of the $n$-PG oligomers with one and three repeating units (the small $n$-PG oligomers), frequency dependences of dielectric loss for propylene glycol and tripropylene glycol with 32% H$_2$O mixtures at various temperatures (at
ambient pressure) are shown in fig. 3.16. For other examples of relaxation processes for water mixtures of the \( n \)-PG oligomers with seven repeating units (the large \( n \)-PG oligomers), the frequency dependences of dielectric loss for polypropylene glycol+26\% H\(_2\)O mixture at various temperatures are shown in fig. 3.1(b).

From inspection of figs. 3.1(b) and 3.16 it can be seen that the dielectric spectra for rich-in-water solutions of the \( n \)-PG oligomers exhibit a similar scenario, with two relaxation processes: primary (\( \alpha \)-relaxation) responsible for the glass transition of the mixtures and secondary (\( \nu \)-relaxation) originated from local motions of water molecules as have been already shown above for PPG400+26\% H\(_2\)O. Both relaxations slow down on cooling. Moreover, the temperature as well as the molecular mass of dissolved \( n \)-PG oligomer determine the degree of separation \( \alpha \)-, and \( \nu \)- processes. At higher temperatures (\( T\gg T_g \)) the \( \alpha \)-, and \( \nu \)-processes in rich-in-water mixtures are strongly overlapped. As a results we observed broaden dielectric loss curve and distinguishing of both the \( \alpha \)- and \( \nu \)- processes from dielectric spectra bears some difficulties. The overlapping of the \( \alpha \)- and \( \nu \)- processes in dielectric loss spectra is more pronounced in the case of PG monomer mixture, where one relaxation peak is observed in the wide temperature range, and two relaxation peaks could be distinguished only in vicinity of the glass transition (at low frequencies). On the other hand, for the \( n \)-PG oligomers-water mixtures with 3 and 7 repeating units the separation between two relaxation peaks becomes evident at higher temperatures and consequently the identification of the relaxation processes being components of dielectric spectra becomes more straightforward.

![Dielectric loss spectra](image)

**Fig. 3.16.** Dielectric loss spectra of TPG+32\% water (a), and PG+32\% water mixtures (b) at ambient pressure.
For all studied \( n \)-PG oligomers-water mixtures elevating pressure helps to distinguish two relaxations in the dielectric loss spectra (see fig. 3.17). The separation between \( \alpha \)- and \( \nu \)-relaxation becomes already evident at higher temperatures. Thereby the combined effect of increase of pressure and temperature for the mixtures of small \( n \)-PG oligomers (PG and TPG) with 32% \( \text{H}_2\text{O} \) results in increasing the separation between two relaxation processes more and more, as similarly it occurs in the case of PPG400+26% \( \text{H}_2\text{O} \) (see figs. 3.4, 3.5).

![Dielectric loss spectra](image)

Fig. 3.17. Dielectric loss spectra of TPG+32% water (a), and PG+32% water mixtures (b) at elevated pressure – 500 MPa and 1200 MPa, respectively.

The timescale separation between \( \alpha \)- and \( \nu \)- processes in dielectric spectra could be seen also at given (i.e., the same) \( \alpha \)- relaxation time, \( \tau_\alpha \): the separation increases on increasing temperature and pressure (see figs. 3.18 and also 3.5). While at ambient pressure \( \alpha \)- and \( \nu \)- relaxation of PG+32% \( \text{H}_2\text{O} \) almost overlap and distinguishing them from the spectra is quite difficult, at elevated pressure the separation between two relaxation peaks is more evident and the frequency position of the \( \nu \) relaxation can be easily estimated (see fig. 3.18(a)). In the case of the larger \( n \)-PG oligomer (TPG) with 32% of water the clear separation between both relaxations is observed at ambient as well as at elevated pressure (see fig. 3.18(b)).
Fig. 3.18. Comparison of normalized dielectric spectra with the same \( \alpha \)-relaxation times, obtained at different \( P \) and \( T \) for the mixtures of PG+32\% H\(_2\)O (a) and TPG+32\% H\(_2\)O (b).

Figure 3.19(a) shows plot of the relaxation times for the \( n \)-PG oligomers-water mixtures against reciprocal temperature. The temperature dependence of the \( \alpha \)-relaxation time in liquid state and the \( \nu \)-relaxation time in glassy state for the \( n \)-PG oligomers-water mixtures can be described well by the VFT equation (3.2) and Arrhenius equation (3.3), respectively. The fitting parameters of those equations for PG and TPG with 32\% water are shown in Table 3.4. Moreover, the temperature dependence of the \( \nu \)-relaxation time for studied \( n \)-PG oligomers-water mixtures crosses over from a weaker to a stronger temperature dependence when temperature increases in vicinity of \( T_g \) (at \( T_{cross} \)).

From Arrhenius plot (see fig. 3.19(a)) we observe that both \( \alpha \)- and \( \nu \)-relaxations move to high temperature with increasing of repeating units of the oligomers, consequently \( T_g \) of the mixtures also increases. In other words, the smaller are the molecules of solute in the aqueous mixtures the faster is the \( \alpha \)-relaxation time. Such behaviour could be related by the relative influence of hydroxyl end groups, less and less important for longer chains. A rationale can be found in terms of the cooperative rearranging regions (CRR), hypothesized by the model proposed by Adam and Gibbs [82]. Water added to pure \( n \)-PG oligomers breaks homogenous clusters built of molecules of the small oligomers. It leads to a smaller average size of CRRs and structural relaxation times significantly becomes faster. On the other hand the dynamics of PPG400-water mixture is characterized by smaller sensitivity to water presence. Only a large amount of water noticeably influences on cooperative motions of the oligomer which results in a slight acceleration of the structural relaxation in water mixtures of PPG400 (see lower inset to fig. 3.2).
Fig. 3.19 (a) Plot of relaxation times against reciprocal temperature at ambient pressure of the $\alpha$- (closed symbols) and $\nu$- processes (open symbols) for similar mass fraction of water in various n-PG oligomers: PG+32 wt.% water (squares), TPG+32 wt.% water (circles), PPG400+26 wt.% water (triangles); (b) dielectric loss spectra at $T \approx 202$ K for the same systems plotted in figure 3.19(a).

Although the $\alpha$- relaxation time of the studied mixtures shows large variations, on the other hand, $\nu$-relaxation is quite similar for different mixtures, especially below $T_g$ (see the region highlighted by the magenta box in the fig. 3.19(a)). At temperatures below $T_{cross}$ of the mixture, $\nu$-relaxation of all mixtures has Arrhenius temperature dependence with activation energies of about 52 kJ/mol, which is not much larger than the energy of breaking two hydrogen bonds before translation or rotation of the molecule can occur and similar to the value of about 50 kJ/mol universally found in the glassy aqueous mixtures with higher water content [103]. A similar value of the activation energy at ambient pressure ($E_a \approx 55$ kJ/mol) was found also for rich-in-water solution PPG400+26 wt.% water (see fig. 3.13(a) and Table 3.2). On the other hand, the separation between $\alpha$- and $\nu$- process in the liquid state increases on increasing the number of repeating units. This effect is also shown in spectra at 202 K for studied mixtures (see fig. 3.19(b)). It is clearly seen that for mixture of monomer PG (the small $n$-PG oligomer) with water both relaxations are merged together meanwhile for the water mixture with the large $n$-PG oligomer (PPG400) the separation is clear from two well resolved peaks.

High pressure has, on molecular dynamics of $n$-PG oligomers-water mixtures, a similar effect as that caused by the increasing of the number repeating units of the oligomers. Figure 3.20 shows temperature dependence of $\alpha$- and $\nu$- relaxations at elevated pressure (1800 MPa). Both relaxations slow down on increasing of the number of repeating units of the oligomers. Such
slowing down for the $\alpha$-relaxation is more pronounced at high pressure with respect to that of ambient. On the other hand, the $\nu$-relaxation is much less sensitive to changes of pressure for different $n$-PG oligomers-water mixtures: the $\nu$-relaxation in glassy state is quite similar for different mixtures (see the region highlighted by the magenta box in the fig. 3.20).

More experimental results under pressure for $n$-PG oligomers-water mixtures could be seen in figs. 3.21 and 3.22. Arrhenius plots for PG+32 wt.% water and TPG+32 wt.% water mixtures in figs. 3.21 and 3.22 plotted for different isobaric scans show the same behaviour as was already represented in fig. 3.6 for PPG400+26 wt.%: $\alpha$-relaxation has VFT-like temperature dependence and $\nu$-relaxation change its temperature dependence from weak VFT-like to Arrhenius (in glassy state) on decreasing temperature showing the crossover for each isobaric scans which appears in vicinity of corresponded $T_g$.

Summarizing, the effect of pressure on dynamics of PG+32 wt.% water and TPG+32 wt.% water mixtures is similar to what found for PPG400+26 wt.% water: both $\alpha$- and $\nu$- relaxations slow down on increasing pressure, and such effect of pressure is stronger for $\alpha$-relaxation at that. In the case of PG+32% water mixture intermediate isobaric measurements could not be done because of temperature limitation of High Pressure setup (see Chapter 2). In the dielectric spectra

Fig. 3.20. Plot of relaxation times against reciprocal temperature at elevated pressure (1800 MPa) of the $\alpha$- (closed symbols) and $\nu$- processes (open symbols) for similar mass fraction of water in various $n$-PG oligomers: PG+32 wt.% water (squares), TPG+32 wt.% water (circles), PPG400+26 wt.% water (triangles).
of TPG+32 wt.% water mixture measured at high pressure (1.15 and 1.8 GPa) the loss peak of the \( \alpha \)-relaxation was hidden by the large contribution of dc-conductivity to dielectric loss. Nevertheless it was possible to obtain some information about the \( \alpha \)-relaxation from the real part of the dielectric permittivity (see fig. 3.22(a)).

Fig. 3.21. Plots of logarithm of relaxation times against reciprocal temperature for the \( \alpha \) (left graph) and \( \nu \) (right graph) processes of PG+32% water mixture for various isobars: 0.1 MPa (circles), 1200 MPa (triangles), 1600 MPa (squares), 1800 MPa (stars). Solid lines represent VFT fitting curves, dashed lines are Arrhenius fits to the data in the glassy state.

Fig. 3.22. Plots of logarithm of relaxation times against reciprocal temperature for the \( \alpha \)- (a) and \( \nu \)- (b) processes of TPG+32% water mixture for various isobars: 0.1 MPa (circles), 300 MPa (triangles), 500 MPa (squares), 605 MPa (stars), 1150 MPa (diamonds), 1800 MPa (inverted triangles). Solid lines represent VFT fitting curves, dashed lines are Arrhenius fits to the data in the glassy state.
Table 3.4. Parameters of the VFT Equation (3.2), (3.4) and Arrhenius Equation (3.3), (3.5) for PG + 32% water and TPG + 32% water at different isobaric and isothermal scans

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<th>P [MPa]</th>
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<th>Arrhenius parameters of the ν-process</th>
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Isothermal scans

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<th>( D_p )</th>
<th>( P_0 )</th>
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</table>

The glass transition temperatures of studied rich-in-water solutions of \( n \)-PG oligomers versus pressure are plotted in fig. 3.23. The fitting parameters of Andersson equation (see Eq. (3.7)) for representing pressure dependences of \( T_g \)s for aqueous mixtures with oligomers are shown in Table 3.3. The pressure dependence of \( T_g \) for all mixtures has non-linear character with increasing its values on increasing pressure. Moreover, the steepness of those dependences increases on increasing the number of repeating units. It can be easily seen if we calculate the low pressure derivative of glass transition temperature, \( dT_g/dP \), for studied aqueous mixtures. Figure 3.24 shows calculated derivatives \( dT_g/dP \) plotted versus the number of repeating units for \( n \)-PG oligomers-water mixtures and also for pure \( n \)-PG oligomers taken from ref. [78]. Both values for pure systems and that for mixtures increase with the number of repeating units of the oligomers (and consequently, with the dilution of the numbers of OH bonds), moreover, the values for mixtures are smaller more than 1.5 times. Such low values (<200 K/GPa) are typical of H-bonded systems [78]. The hydrogen bonds in rich-in-water solutions of \( n \)-PG oligomers are strong and quite high pressure should be applied to change noticeably the glass transition temperature of the mixture.
Fig. 3.23. The pressure dependence of the glass transition temperatures obtained from both isobaric (closed symbols) and isothermal (open circles) measurements for PPG400+26% water (triangles), TPG+32% water (squares) and PG+32% water (stars) mixtures. Lines represent Andersson fitting curves.

Fig. 3.24 Plot of the low pressure derivative of the glass transition temperature, $dT_g/dP$, against the molecular weight of the solutes ($n$-PG oligomers). Squares represent pure $n$-PG oligomers, circles represent rich-in-water solutions with $n$-PG oligomers and star is PPG400+4 %. Lines are guides for the eyes.

As it was discussed above the glass transition temperature also increases on increasing the number of repeating units of the $n$-PG oligomers at corresponding pressure. The smaller is the...
size of solute molecule the lower is the glass transition temperature of the mixture. Such behaviour can be easily seen also in fig. 3.25 where $T_g$ is plotted versus the number of repeating units for two isobaric scans (0.1 and 1800 MPa). For the highest pressure $T_g$ has steeper dependence than that of ambient pressure, so we can induce bigger difference in $T_g$ with pressure for $n$-PG oligomers with higher numbers of repeating units.

![Fig. 3.25. Plot of the glass transition temperature against the number of repeating units of solute molecules for the rich-in-water solution of $n$-PG oligomers for ambient pressure (squares) and 1800 MPa (circles). The symbols indicate the temperatures at which the relaxation times of the $\alpha$ process are 100 s. Lines are guides for the eyes.](image)

It was also possible to estimate the values of $\nu$ relaxation time at the dynamic crossover, $\tau_{\nu \text{ cross}}$, of several isobaric scans for TPG+32% water and PG+32% water mixtures. Logarithm of $\tau_{\nu \text{ cross}}$ decreases exponentially (becomes shorter) on increasing pressure, and the timescale of $\tau_{\nu \text{ cross}}$ is of the order of magnitude of that found for PPG400-26% (see fig. 3.26) and for other aqueous mixtures, and also for water confined or present in hydration shells of proteins [103, 163, 167, 181]. As also could be seen from figs. 3.19(a) and 3.20 the values of $\tau_\nu$ at the dynamic crossover become shorter on increasing of the number of repeating units of solute. The reason is quite simple: higher is the number of repeating units of solute, more separated the $\alpha$- and $\nu$- relaxation timescale are and so at $\tau_\nu(T_g)$ is shorter.
Fig. 3.26. Pressure dependence of logarithm of $\tau_{\nu_{\text{cross}}}$ for PPG400+26% water (circles), TPG+32% water (triangles) and PG+32% water (squares) mixtures. Solid and dashed lines are the exponential fitting curves and guide for the eyes, respectively.

The unusual pressure dependences of activation energies $E_a$ for the $\nu$-relaxation and isobaric fragilities for the $\alpha$-relaxation, which exhibit maxima over pressure variation was found also for TPG+32% H$_2$O mixture. As it can be seen in fig. 3.27, the maximal values of $E_a$ and $m_P$ appears in the GPa range as for PPG400+26% H$_2$O (see fig. 3.13 for comparison).

Fig. 3.27 (a) Pressure dependences of the $\nu$-process activation energies $E_a$ for mixture TPG+32% H$_2$O. The energies at $T < T_g$ are evaluated from Arrhenius equation (3.3). (b) Pressure dependences of the isobaric fragility $m_P$ determined at $\tau_a=100$ s for mixture TPG+32% H$_2$O. Lines are guides for the eyes.
3.1.7 Comparison of low (4%) and high (26%) water concentration mixtures with PPG400 at elevated pressure

In previous paragraphs it was shown that water strongly effects on dynamics of rich-in-water aqueous solution. The chosen concentration of water was 26 wt.% that is above concentration threshold (mole fraction of water ~0.8 in PPG400+H₂O corresponds to ~15 wt.%). However, how the dynamics of aqueous mixtures with small amount of water differs from that of rich-in-water solutions? And, moreover, could the pressure be a variable helping to understand the phenomenology in that case? To answer these questions we chose PPG400+H₂O mixture with 4% of water and studied different isobaric scans on applying pressure up to 1400 MPa.

From inspection of figs. 3.1(a) and 3.2 it can be easily seen that PPG400+4% H₂O mixture exhibits, like anhydrous PPG400, three resolved relaxation processes: a) a slower process, whose dynamic properties indicate that it is the structural α-relaxation of the aqueous mixture leading to glass transition at \( T \) equal to the calorimetric \( T_g \); b) a faster process (\( \nu \)-relaxation process), which appears close to \( \beta \)- (secondary) process of PPG400 in dielectric spectra (similarly as in the case of many other water mixtures) and has the characteristics of an intermolecular Johari-Goldstein secondary relaxation; c) the fastest process (\( \gamma \)-relaxation process), probably originating from hydroxyl group rotation [212], and whose strength is weaker than that of anhydrous PPG400.

As we already introduced, there is a very general trend reported before in literature (see for instance [156]) about the effect of water concentration on \( \tau_\nu \). We can show here by examples for glycerol-water mixtures and for currently studied PPG400-water mixtures. At any fixed temperature, the relaxation time \( \tau_\nu \) decreases on increasing the concentration of water in the mixture. The decrease of \( \tau_\nu \) continues until the limiting value at which the molar concentration of water is very high. Such a value of \( \tau_\nu \) is more or less independent of the specific solute [156].

This dependence of \( \tau_\nu \) on composition of aqueous mixture can be readily explained by the fact that, at very low water molar concentration, water molecules are mainly hydrogen bonded to hydrophilic groups of the solute, which usually has lower mobility than water molecule, whereas at high water molar concentration the environment of water molecule is mainly composed of the more mobile water molecules themselves. In the latter case, the activation energy in the glassy state for the relaxation time \( \tau_\nu \) is about 52 kJ/mol, which is not much larger than the energy of breaking two hydrogen bonds to enable independent relaxation of water. Not so well publicized is that the position of \( \tau_\nu \) in aqueous mixtures at very low water concentration is very close to that
of the Johari-Goldstein or the primitive relaxation of the Coupling Model (CM) [103, 125, 222] of the pure (anhydrous) system. We can show two examples in figs. 3.28 and 3.29.

![Glycerol + H2O](image)

**Fig. 3.28.** Plot of relaxation times vs. reciprocal $T$ of glycerol-water mixtures at different water mass fraction $c_{H_2O}$. Close and open symbols indicate $\alpha$- and $\nu$- process, respectively. The crossed black squares represent the primitive relaxation time for anhydrous glycerol as obtained by application of CM according to Eq. (1.43). Solid lines are VFT function fits, dotted lines are Arrhenius fits to the data in the glassy state.

Figure 3.28 shows the relaxation times for glycerol-water mixtures at different water weight fraction $c_{H_2O}$ (data are kindly obtained from Prof. Shinya Shiki, for more details see ref. [240]). Both $\alpha$- and $\nu$- relaxation processes are present in the mixtures at different $c_{H_2O}$, with the same characteristic behaviour already illustrated in figs. 3.6, 3.8 and 3.19(a). On increasing $c_{H_2O}$ both processes are moving to lower temperature, as a consequence of the plasticization effect due to water. The crossover of $\tau_\nu$ occurs always few degrees below $T_g$ as was also shown above for $n$-PG oligomers-water mixtures, and the activation energy in the glassy state approaches that one characteristic of $\nu$-relaxation. Data for anhydrous glycerol are taken from ref. [241]. From those data, the relaxation time predicted for primitive process by Eq. (1.43) (see § 1.6) can be
estimated for the anhydrous glycerol. The \( \nu \)-relaxation time \( \tau_\nu \) in mixtures at low \( c_{H_2O} \) is very close to the primitive relaxation time of anhydrous glycerol. At higher \( c_{H_2O} \), \( \tau_\nu \) move to shorter times when the interactions of water with the solute becomes less important.

Another example is shown by fig. 3.29, where relaxation times of mixtures of water with PPG400 are plotted, as well as the data for anhydrous PPG400 [212]. For anhydrous PPG400, a true intermolecular JG \( \beta \)-relaxation was identified (relaxation time \( \tau_{JG} \) is in agreement with the CM predictions for the primitive relaxation time \( \tau_0 \) from Eq. (1.43), as well as an additional secondary \( \gamma \)-process having much shorter relaxation times and originating from intra-molecular degrees of freedom [212]. At low \( c_{H_2O} \), the interaction of water molecule with its environment implied mainly the motion of PPG400 molecules which affects the \( \nu \)-relaxation. The water molecule can be considered to serve as a “probe” of the local dynamics of the solute, and hence the primitive motions of the solute are reflected in the \( \nu \)-relaxation. For example at low water fraction of \( c_{H_2O} = 0.04 \), it is evident from fig. 3.29 that \( \tau_\nu \) is not much smaller than \( \tau_{JG} \) or \( \tau_0 \) of the pure solute. This can be considered as evidence that the \( \nu \)-relaxation is to some degree coupled to the environment (glycol segments) and its local dynamics. On increasing the concentration, the \( \nu \)-relaxation becomes faster to eventually approach the \( \nu \)-relaxation time of pure water confined in two layers on the surface of vermiculite clay [242, 243], molecular sieves [173], silica gels [244], and graphite oxide [245] (see one example in fig. 3.29 and others in Chapter 5).

The \( \nu \)-relaxation with Arrhenius \( T \)-dependence and activation energy \( \sim 50 \) kJ/mol observed in aqueous mixtures at high molar concentration of water could be considered as approximately the same as the primitive or JG \( \beta \)-relaxation in bulk water, which cannot be observed over the same temperature range because of crystallization.

The effect of pressure on temperature dependences of the \( \alpha \)-, \( \nu \)- and \( \gamma \)-relaxation times of PPG400+4\% H\(_2\)O mixture is shown in an Arrhenius plot in fig. 3.30(a). For all isobaric scans temperature dependence of \( \tau_\alpha \) has a VFT-like behaviour. On the other hand, \( \tau_\nu \) relaxation time has a crossover from a weaker to a stronger temperature dependence on heating in a similar way as it occurs for JG secondary relaxation in many neat glassformers, van der Waals and aqueous mixtures. The fitting parameters of Eqs. (3.2) and (3.3) are shown in Table 3.5. \( \tau_\nu \) has a linear behaviour in studied temperature range at ambient pressure within the experimental error. On increasing pressure we observe that \( \nu \)-relaxation moves to high temperature together with \( \alpha \)-relaxation. On the other hand, \( \gamma \)-relaxation is not too much affected by high pressure and it seems
to continue the behaviour of ambient pressure. This is consistent to what observed by Casalini and Roland in pure PG oligomers [219].

Fig. 3.29. Plots of relaxation times vs. reciprocal $T$ of PPG400-water mixtures at different water weight fraction $c_{H_2O}$. Close and open symbols indicate $\alpha$- and $\nu$- process, respectively. The black asterisks represent the $\gamma$- relaxation times of anhydrous PPG400. Stars are data for water confined in vermiculite clay [242, 243]. Arrows show the evolution with increasing $c_{H_2O}$.

If the relaxation times are rescaled according to the ratio of $T_g(P)/T$, i.e. the glass transition temperature at the corresponding pressure over the temperature of measurement, a superposition of relaxation times obtained at different isobaric scans is observed for both $\alpha$- and $\nu$- relaxations (see fig. 3.30(b)). Another good indication of this isochronal behaviour for the $\alpha$- and $\nu$-relaxation processes can be seen in fig. 3.31.
Fig. 3.30. Plots of logarithm of relaxation times against (a) reciprocal temperature and (b) reciprocal temperature scaled by $1/T_g$ for the $\alpha$- (close symbols), $\nu$- (open symbols) and $\gamma$- processes (symbols with pluses) of PPG400+4% H$_2$O mixture for ambient and elevated pressures.
From the superposition of the $\alpha$-relaxation in fig. 3.30(b) it can be assumed that the fragility of the system is almost constant on increasing pressure within experimental error. It is well-known that the fragility of van der Waals glassformers and polymers does not change with pressure or slightly decreases [78]. The only exceptions to this appear to be the hydrogen-bonded materials, such as glycerol [246, 247], polypropylene glycol [228] and perhaps salol [248, 249]. Simulations also suggest an increase in fragility when the coordination number of SiO$_2$ is changed by pressure [250]. Thus, all cases of a positive pressure coefficient of $m_p$ appears to involve a change in the structure or small range order arrangement of the material, whereas the direct effect of $P$ on the dynamics is to reduce $m_p$ [78].

It is important to note that in fig. 3.30(a) crossover in temperature dependence of $\nu$-relaxation for all isobaric measurements follows $T_g$ and, moreover, it occurs always at the same time (see fig. 3.30(b)). Moreover, the fairly good superposition observed in the glassy state for $\nu$-relaxation times implies that the activation energy increases with pressure in a manner proportional to $T_g$.

Such behaviour of crossover observed in fig. 3.30(b) was not found for rich-in-water solutions as was shown above (see fig. 3.8). Moreover, if we repeat the same procedure of scale the relaxation map versus $T_g(P)/T$ for 26% of water in PPG400 (see fig. 3.32) we again can observe
that the crossover time becomes shorter with increasing pressure and there is not a superposition of the \( \nu \)-relaxation times. It could also be seen from fig. 3.32 that the fragility of PPG400+26% H\(_2\)O mixture is not constant and it changes with pressure in the way shown in fig. 3.13(b).

Fig. 3.32. Plots of logarithm of relaxation times against (a) reciprocal temperature and (b) reciprocal temperature scaled by \( 1/T_g \) for the \( \alpha \)- (close symbols) and \( \nu \)- (open symbols) of PPG400+26% H\(_2\)O mixture for ambient and elevated pressures. Olive vertical line indicates crossover in temperature dependence of \( t_\nu \).
Table 3.5. Parameters of the VFT Equation (3.2), (3.4) and Arrhenius Equation (3.3), (3.5) for PPG400+4% water at different isobaric and isothermal scans

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<td>249.0</td>
<td>-12.7</td>
<td>624.1</td>
</tr>
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<td>558.3</td>
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<td>1200</td>
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<td>-12.0</td>
<td>658.5</td>
</tr>
<tr>
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<td>281.5</td>
<td>-12.1</td>
<td>690.3</td>
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Isothermal scans

<table>
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<tr>
<th>T [K]</th>
<th>Pg [MPa]</th>
<th>log_{10}[τ_a(T,0)]</th>
<th>Dp</th>
<th>P0</th>
<th>log τ0^*</th>
<th>∆V^0 [cm^3/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>213.2</td>
<td>146</td>
<td>-2.6</td>
<td>46.1</td>
<td>829.5</td>
<td>-2.28</td>
<td>0.525</td>
</tr>
</tbody>
</table>

Interesting observation can be done on comparison of pressure dependences of the glass transition temperatures for mixtures of PPG400 with small and high amount of water. The pressure dependence of \( T_g \) for PPG400+4% water mixture was fitted using Andersson equation (Eq. (3.7)) and those parameters are presented in Table 3.2. In fig. 3.33 it is clearly seen that adding the water does not change too much the glass transition temperature at ambient pressure. It could also be seen from the spectra (see lower inset in fig. 3.2) where the position of \( \alpha \)-relaxation peak is almost similar for different concentrations of water (the temperature variation is about 3 K). Such behaviour is not typical. As was shown above for glycerol-water mixture in fig. 3.28 the effect of water on dynamics of the mixture is significant for that case: the glass transition temperature for glycerol+30% water mixture differs more than 20 K for that of anhydrous glycerol. Similar feature was also found for small \( n \)-PG and \( n \)-EG oligomer-water mixtures [181, 251, 252]: the differences in \( T_g \) between anhydrous DPG and TPG and those with 32 wt.% of water are about 15 K and 8 K [252], respectively; between anhydrous 3EG and 35 wt.% of water mixture is 15 K [251]. Admittedly, molecules of PPG400 can bind that of water (it is so-called “bound” water) but they are too large to form heterogeneous hydrogen-bonded clusters with water molecules and move cooperatively within a such network. Thus, it could be claimed that the \( \alpha \)-relaxation of studied aqueous mixtures is related to global dynamics of the system formed by both water and solute molecules and it is connected with the glass transition of
the mixture, but in the case of the water mixtures of PPG400 reflected mainly cooperative motions of PPG400 molecules.

Applying pressure to PPG400-water mixtures we observe significant difference in the glass transition temperatures for 4 % and 26 % of water in PPG400. Molecular dynamics of those mixtures are quite different as could be wrongly expected assuming only the data at ambient pressure. Moreover, the low pressure derivative is smaller for rich-in-water solution: adding water to anhydrous PPG400 causes in decreasing of $dT_g/dP$ (see fig. 3.24).

Fig. 3.33. The pressure dependence of the glass transition temperatures obtained at $\tau_a = 100$ s for PPG400+26% water (triangles), PPG400+4% water (circles). Lines represent Andersson fitting curves.

Results obtained by applying pressure to the aqueous mixtures with small and high amount of water confirm that idea that for low water concentration in mixture motions of water molecule are coupled to that of solute molecules, i.e. water molecules “feel” the dynamics of the solute, and the $\nu$-process seems to behave similarly to JG or primitive relaxation of the van der Waals polymers. When the water concentration is high the $\nu$-relaxation gains a “water-specific” character approaching the dynamics of bulk water on further increasing concentration, water molecules are surrounded by other water molecules and motions of neighbouring big and less mobile solute molecules become less important. For instance, it was observed for glycerol-water
mixtures by Towey et al. [253] that the majority of water molecules exist as single monomers in the concentrated glycerol solution (~44 wt.% of water).

3.2 Dynamics of water mixed with ethylene glycol oligomers

In previous paragraphs the effects of concentration of water, molecular weight of solute and pressure on dynamics of aqueous mixtures of \( n \)-PG oligomers were shown. The similar behaviour was found also for another class of glycol oligomers – ethylene glycols (EG).

Figure 3.34(a) shows an example of the relaxation map of a mixture of 35 wt.% fraction of water in the ethylene glycol oligomer with 5 repeat units (5EG) (data are kindly obtained from Prof. Shinyashiki, for more details see refs. [180, 254]). The typical scenario with two relaxation processes is evident. The slow process has the Vogel-Fulcher-Tammann (VFT) \( T \)-dependence, typical of cooperative \( \alpha \)-relaxation and responsible for glass transition of the mixture. The cooperative character can be confirmed by the value of the dielectric relaxation time at the calorimetric glass transition \( T_g \) [180] (172 K), that is \( \tau_\alpha(T_g) \sim 10^2 \) s. Concerning the \( \nu \)-relaxation, it has an Arrhenius \( T \)-dependence at low temperature with an activation enthalpy of 49 kJ/mol, similar to the value of about 50 kJ/mol universally found in the glassy rich-in-water mixtures [103]. On increasing temperature, at \( T_{cross} = 169 \) K, \( \tau_\nu \) changes to assume a stronger \( T \)-dependence. This crossover does not occur at 220 K as predicted in ref. [148]. On the contrary, it occurs always few degrees below \( T_g \), where \( \tau_\alpha \) exceeds 1-10 ks, where it can be identified in every aqueous mixtures investigated above and in the next Chapter 4. Moreover, \( \Delta \varepsilon_\nu \) exhibits a change of its dependence from a weaker to a stronger one with increasing \( T \) after crossing \( T_{cross} \) (see fig. 3.34(b)).

The example of coupling of the \( \nu \)-relaxation to its environment comes also from aqueous mixtures with the same water mass fraction \( c_{H_2O} = 0.35 \) but with the solute that are oligomers of different molecular weights or degree of chain connectivity, such as the ethylene glycols oligomers \( n \)-EG (with \( n = 2, 3, 4, 5, 6 \)) and PEG400 (data original from this thesis and partially kindly obtained from Prof. Shinyashiki, for more details see refs. [180, 220, 254]). The effect of the number of repeating units of the oligomers on molecular dynamics of aqueous mixtures with the same amount of water is similar to what was shown in § 3.1.6 for the case of \( n \)-PG oligomers.
Fig. 3.34 (a) Plot of relaxation times vs. reciprocal $T$ of 35% wt. fraction of water in 5EG. Close and open red symbols indicate the $\alpha$- and $\nu$- process, respectively. Solid line is the VFT function fit, dashed line is the Arrhenius fit to the data in the glassy state. The vertical line indicates the temperature where $\tau_\alpha=1$ ks. Inset shows the loss spectra for $T=173$ K. (b) Plot of dielectric strength vs. reciprocal $T$ for the $\alpha$- and $\nu$- processes. Symbols are the same as in panel (a). Lines are from linear regression for data above and below $T_g$.

Shown in the upper panel of fig. 3.35 (taken from ref. [222]) are the relaxation times of the $\alpha$-process involving cooperative motions of solute and water altogether and the fits to their $T$-dependences by the VFT relation. The lower panel shows the water-specific $\nu$-relaxation. Each vertical line marks the glass transition temperature $T_g$ at which $\tau_\alpha \approx 1$ ks. Below $T_g$, the structure is arrested, and $\tau_\nu$ changes to assume the Arrhenius $T$-dependence with activation energy close to 50 kJ/mol, similarly for all the systems. The temperature at which the change occurs, $T_{cross} \approx T_g$ increases with the molecular weight of the oligomers, and concurrently $\tau_\nu(T_{cross})$ decreases (becomes shorter). On the other hand, for $T > T_g$ the relaxation time of $\nu$-process, $\tau_\nu$, becomes shorter with smaller number of repeating units.
CM can rationalise these properties. It has been generally demonstrated in binary mixtures of van der Waals liquids that the coupling parameter $n$ of the $\alpha$-relaxation of the more mobile molecule increases on decreasing the mobility of the other component. That is also the case of the $n$-EG systems of fig. 3.35, where the molecular weight increases and the concentration of water is kept constant. According to Eq. (1.43), a larger coupling parameter $n$ makes the $\tau_\nu$ shorter at any fixed value of $\tau_\alpha$ such as $\tau_\alpha(T_g)=1$ ks. If $\nu$-process can be assumed as the JG relaxation of water and the only one $\alpha$-relaxation observed in the spectra of water mixtures is ALSO the alpha of the water, according to Eq. (1.43) and CM, $\tau_\nu$ is related to $\tau_\alpha$ as $\tau_\nu = t_c (1-\beta_{\alpha\nu}) \cdot \tau_\alpha^{\beta_{\alpha\nu}}$. In this sense, if one
considers at fixed $\tau_a=1$ ks, $\log_{10}(\tau_a/\tau_{\nu})$ can be expressed as
\[
\log_{10}(\tau_a/\tau_{\nu}) = (1 - \beta_{KWW}) \cdot \log_{10}(\tau_a/\tau_{\nu}) = (1 - \beta_{KWW}) \cdot 14.7.
\]
On increasing the coupling, $\beta_{KWW}$ decreases and the separation increases. That is exactly what happen for $\nu$-relaxation in $n$-EG-water mixtures, i.e. the separation in timescale of the two relaxations given by $\log_{10}(\tau_a/\tau_{\nu})$ at fixed $\tau_a=1$ ks, increases as the molecular weight of the solute increases (see inset of fig. 3.35). It is important to stress that, in spite of the differences in molecular weight of the solute, $\tau_{\nu}$ does not show large variations, especially below $T_g$. On the other hand, the primary $\alpha$-relaxation time of these mixtures are immensely different because of their VFT-like temperature dependences and widely different glass transition temperatures, $T_g$, as well as different steepness indices $m$.

Figure 3.36 taken from ref. [220] shows the characteristic temperatures determined for the $n$-EG oligomers-water mixtures ($n = 2, 3, 4, 5, 6, 8, 13$) against the number of repeating units of $n$-EG oligomers molecules. $T(\tau_a=100$ s) is the dynamic glass transition temperature at which the relaxation time of the $\alpha$ process is 100 s, $T_g$ is the glass transition temperature obtained by DSC, and $T(\tau_{\nu}=100$ s) was defined as the temperature at which the dielectric relaxation time of the $\nu$-process is 100 s. It is clearly seen from fig. 3.36 that $T(\tau_a=100$ s) and $T_g$ are close to each other and both increase on increasing the number of repeating units of the solute molecule. The similar trend was also found for rich-in-water solutions of $n$-PG oligomers (see fig. 3.25). On the other hand, $T(\tau_{\nu}=100$ s) is almost independent on the number of repeating units of $n$-EG oligomers molecules.

![Figure 3.36](image_url)

Fig. 3.36. Plots of temperature against the number of repeat units of EGO molecules for the $n$-EG oligomers-water mixtures. The closed square indicates the glass transition temperature determined from DSC measurement. The closed and open circles indicate the temperatures at which the relaxation times of the $\alpha$- and $\nu$- processes, respectively, are 100 s. Figure is reproduced from ref. [220].

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To see how pressure can affect on molecular dynamics on aqueous mixtures with other propylene oligomers (n-EG) the mixture of PEG400 (8 repeating units) with 35 % of water was chosen. This system is well studied at ambient pressure by dielectric and calorimetric techniques and results are shown in ref. [103, 220].

The dielectric spectra of PEG400-35% water mixture both at ambient and elevated pressure, as those of many rich-in-water solutions, exhibit two relaxation processes: at lower frequency part – primary $\alpha$-relaxation and at higher frequency – secondary $\nu$-relaxation (see fig. 3.37). The data are fitted in terms of linear superposition of Havriliak-Negami functions (Eq. (3.1)) for the $\alpha$- and $\nu$- processes.

![Fig. 3.37](image)

Fig. 3.37. Frequency dependences of imaginary part of dielectric function (dc conductivity is subtracted) for PEG400-35% water mixture at (a) 189.2 K and 0.1 MPa, and (b) 218.3 K and 600 MPa. Closed circles are data, the dashed, dotted and solid lines indicate the $\alpha$-, $\nu$- processes, and fitting curve, respectively.

The temperature dependences of the $\alpha$- and $\nu$- relaxation times obtained from the peak position of the $\alpha$- and $\nu$- processes are shown for different isobaric scans in fig. 3.38. The parameters of the VFT and Arrhenius equations for fitting $\alpha$- and $\nu$- relaxation times temperature dependences are listed in Table 3.6.

The phenomenology found in pressure studies for rich-in-water solutions of $n$-PG oligomers appears to be general also for $n$-EG oligomers-water mixtures: pressure effect moves both $\alpha$- and $\nu$- relaxation to high temperature (or to longer time), consequently the glass transition temperature of the mixture increases, $\nu$-relaxation exhibits a crossover (in vicinity of $T_g$) from a weaker to a stronger temperature dependence on heating, activation energy $E_a$ of the $\nu$ process in
glassy state (at ambient pressure) is 50.8 kJ/mol that is similar to many rich-in-water solutions and enough to break two hydrogen bonds.

![Graph showing logarithm of relaxation times against reciprocal temperature for PEG400 + 35% H2O](image)

Table 3.6. Parameters of the VFT Equation (3.2), (3.4) and Arrhenius Equation (3.3), (3.5) for PEG400+35% water at different isobaric and isothermal scans

<table>
<thead>
<tr>
<th>P [MPa]</th>
<th>Tg [K]</th>
<th>VFT parameters of the α-process</th>
<th>Arrhenius parameters of the ν-process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \log_{10}(\tau_{\alpha,VFT}(s)) )</td>
<td>( A ) [K]</td>
</tr>
<tr>
<td>0.1</td>
<td>182.3</td>
<td>-13.4</td>
<td>575.5</td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
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</tr>
<tr>
<td>600</td>
<td>204.9</td>
<td>-15.4</td>
<td>870.5</td>
</tr>
</tbody>
</table>

**Isothermal scans**

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( P_g ) [MPa]</th>
<th>( \log_{10}[\tau_{\alpha}(T,0)] )</th>
<th>( D_p )</th>
<th>( P_0 )</th>
<th>( \log r_0^* )</th>
<th>( \Delta V^g ) [cm³/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>803</td>
<td>213.2</td>
<td>-4.8</td>
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<td>3980.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3.3 Conductivity: the measure of translational diffusion of ions

Another important parameter for dynamics that can be extracted from dielectric spectroscopy is dc conductivity, the mechanism of which is translational diffusion of ions. Unluckily, any liquid contains electrolyte impurities. In the case of water mixtures, dissociated protons, very mobile, can add to these impurity ions. We will consider the relationship between the translational and rotational motions, in particular the coupling or decoupling of the dielectric relaxation time and the dc conductivity, obtained by the low frequency term in loss factor depending on the reciprocal frequency: \( \sigma_{\text{DC}} = \varepsilon_0 \omega \varepsilon''(\omega) \). In the literature it is well-known that the Debye–Stokes–Einstein equation \[72\] can hold:

\[
\sigma_{\text{DC}} \tau_\alpha = \text{const}. \tag{3.8}
\]

Eq. (3.8) is valid when number of charge carriers does not change with \( T \) and the rate of translational diffusion is proportional to the rate of orientational diffusion \[255\]. In other cases the DSE relation (3.8) breaks down, and a phenomenological equation can be used \[256, 257\]:

\[
\sigma_{\text{DC}} \tau'_{\alpha} = \text{const}. \tag{3.9}
\]

Eq. (3.9) is usually called as “fractional Debye–Stokes–Einstein equation”. It was found that fractional exponent \( s \) for many systems is in the range from 0.75 to 0.91 \[78\].

To check the relationship between conductivity and relaxation times, we calculated the equivalent time of \( \sigma_{\text{DC}} \): \( \tau_{\sigma_{\text{DC}}} = \varepsilon_0 \varepsilon'' / \sigma_{\text{DC}} \). The comparison of all times (\( \tau_\alpha, \tau_\nu \) and \( \tau_{\text{adC}} \)) is shown in fig. 3.39(a) for the mixture of PPG400 with 4 wt.% of water. From fig. 3.39(a) it is seen that \( \tau_{\text{adC}} \) is curved like \( \tau_\alpha \) and longer than relaxation times of the \( \alpha \)-process in the investigated temperature range. Figure 3.39(b) shows the dependence of \( \log[\tau_{\sigma_{\text{DC}}}] \) vs. \( \log[\tau_\alpha] \) which has linear character. We also estimated the coefficient \( s \) from Eq. (3.9) which has the meaning of the slope in double logarithm plane of dc conductivity vs. relaxation time. The value of \( s \) is smaller than 1 and equal to 0.88 that is similar to the value found for pure PPG400 (0.84±0.02) in ref. \[78\].
For rich-in-water solution (PPG400+26 wt.% H₂O) the same analysis is done in fig. 3.40. In fig. 3.40(b) the logarithm of dc conductivity is plotted versus logarithm of \( \alpha \)- and \( \nu \)-relaxation times.

It is seen in fig. 3.40(a) that the relaxation times of dc conductivity are shorter than for PPG400+4 wt.% H₂O and close to the glass transition are comparable with \( \tau_{\alpha} \). Dependence of \( \log[\sigma] \) vs. \( \log[\tau_{\alpha}] \) again has linear character, whereas for \( \nu \)-relaxation this behaviour is slightly curved (fig. 3.40(b)). The slopes for both dependences are 0.75 and 1.40, respectively. The value of 0.75 is found to be a little bit smaller than for pure \( n \)-PG oligomers [78]. That for \( \nu \)-relaxation times is much bigger than 1, and it was found the similar curved behaviour for all studied water mixtures (see also fig. 3.41(b)).

For water mixture with another PG oligomer (TPG+32 wt.% H₂O) the similar temperature dependences of the \( \tau_{\alpha}, \tau_{\nu} \) and \( \tau_{\text{dc}} \) relaxation times, as for PPG400+26 wt.% H₂O are found (see fig. 3.41(a)). The slope \( s \) in fig. 3.41(b) is 0.79 that is not much different from that for pure \( n \)-PG oligomers and PPG400-water mixtures.
Fig. 3.40 (a) Plot of relaxation times vs. reciprocal temperature for the mixture of PPG400 with 26 wt.% of water: \(\tau_\alpha\) (closed blue circles), \(\tau_\nu\) (open blue circles), \(\tau_{\text{DC}}\) (closed black squares); (b) Double logarithmic plot of dc conductivity vs. \(\alpha\)-relaxation times (red stars) for PPG400+26 wt.% of water. Lines are linear regressions with slope \(b\), black line is shown for comparison.

Fig. 3.41 (a) Plot of relaxation times vs. reciprocal temperature for the mixture of TPG with 32 wt.% of water: \(\tau_\alpha\) (closed blue circles), \(\tau_\nu\) (open blue circles), \(\tau_{\text{DC}}\) (closed black squares); (b) Double logarithmic plot of dc conductivity vs. \(\alpha\)-relaxation times (red stars) for TPG+32 wt.% of water. Lines are linear regressions with slope \(b\), black line is shown for comparison.

For the case of water mixture with PG monomer (PG+32 wt.% H\(_2\)O) fig. 3.42(a) shows that the relaxation times of dc conductivity are extremely long in respect to \(\tau_\alpha\) (more than 3 decades). In fig. 3.42(b) we observed coupling of \(\log[\tau_{\text{perc}}]\) and \(\log[\tau_\alpha]\): the slope \(s\) is almost equal to 1 (\(s \approx 0.99\)). In this mixture very low values of dc conductivity were observed in dielectric spectra, probably because of extremely purity of PG sample. It is interesting to note that, when the level
of conductivity is slow, the DSE relation holds. Definitely, the translational dynamics of ions is coupled to that of $\alpha$-relaxation of mixtures, for all the systems considered, and has not a defined relation with that of $\nu$-process.

Fig. 3.42 (a) Plot of relaxation times vs. reciprocal temperature for the mixture of PG with 32 wt.% of water: $\tau_\alpha$ (closed blue circles), $\tau_\nu$ (open blue circles), $\tau_{\text{dc}}$ (closed black squares); (b) Double logarithmic plot of dc conductivity vs. $\alpha$-relaxation times (red stars) for PG+32 wt.% of water. Lines are linear regressions with slope $b$, black line is shown for comparison.

3.4 Conclusions

In summary:
- rich-in-water solutions of glycols oligomers exhibit two relaxation processes: the primary $\alpha$-relaxation which is responsible for glass transition of the mixtures, and the secondary $\nu$-relaxation originating from water component and has the characteristics of an intermolecular Johari-Goldstein secondary relaxation;
- a change of dynamics for water related $\nu$-process occurs for all isobaric scans: temperature dependence of $\log_{10}\tau_\nu$ change its behaviour from a weaker (Arrhenius – in glassy state), to a stronger one (VFT-like – in supercooled liquid state) on heating;
- crossover in temperature dependence of $\log_{10}\tau_\nu$ appears always few degrees below $T_g$ and behaves different from a similar phenomenon observed in literature for confined water: $T_{\text{cross}}$ increases and $\log_{10}\tau_\nu(T_{\text{cross}})$ decreases on increasing pressure, consequently the separation between $\alpha$- and $\nu$- relaxations at the same $\tau_\alpha$ increases on increasing $P$;
- $T_g$ increases on increasing pressure for all studied aqueous mixtures with glycol oligomers;
- the activation energy of the $\nu$- process for rich-in-water solutions at ambient pressure is equal to around 50 kJ/mol, that is enough for rotation and translation of the water molecules after breaking two hydrogen bonds;

- different is molecular weight (number of repeating units) of the glycol oligomers in the same amount of water different is the molecular dynamics of the mixtures: relaxation times of $\alpha$- and $\nu$- processes (in supercooled liquid state) becomes longer, the glass transition temperature of the mixture at different isobaric scans and low pressure derivative of $T_g$, separation between $\alpha$- and $\nu$- relaxations, all increases on increasing of the molecular weight of the solute. On the other hand, temperature dependence of the $\nu$- relaxation in glassy state is almost independent on the molecular weight of the solute at the corresponding isobaric scans in glycol oligomers-water mixtures.

- the studies under pressure revealed that the secondary relaxation in the mixtures with low content of water is in a way significantly different from that of rich-in-water solutions: it has the characteristics of the Johari-Goldstein $\beta$-relaxation occurring in van der Waals and polymeric glassformers and it is mainly influenced by the dynamics of the solute molecules; crossover in the temperature dependence of $\log_{10} \tau_\nu$, always appears at the same position for different isobaric measurements in contrary to rich-in-water solutions;

- $\alpha$- and $\nu$- relaxations speed up, the glass transition temperature of the mixtures decreases, $\nu$-relaxation time dependence approaches that of water confined in geometry, low pressure derivative of $T_g$ decreases on increasing amount of water in aqueous mixtures.

- the translational dynamics of ions (dc conductivity) is coupled to the $\alpha$-relaxation of $n$-PG oligomers-water mixtures, and has not a defined relation with that of $\nu$-process.

The discussions given above have made clear the interrelation between $\alpha$- and $\nu$- relaxation process and the properties of the water-specific nature of the primitive $\nu$-relaxation. The dynamics of water are very similar in different systems, irrespective to the chemical and structural composition of the mixtures. The interpretation and explanation are generally applicable to various situations. The results and the understanding of them gained will be very useful in studying the dynamics of saccharides as well as biomacromolecules and hydrated proteins (see Chapter 4), which are more complex because of these systems are spatially inhomogeneous.
Chapter 4

4. Study of Relaxation Dynamics of Aqueous Systems at Low Temperature and High Pressure: B) Mixtures of Water and Saccharides

The study of dynamics in water-sugar mixtures from the liquid to the supercooled and glassy states can be suggested by practical considerations (like their use as cryoprotectants for biomaterials, food preservation, biological functioning of hydrated biomolecules [53, 258, 259]) but it could be potentially a subject of interest for fundamental research [260]. In particular, mono-, di- and poly- saccharides, that as pure components are often good glass-formers, are also quite soluble in water due to the large number of hydroxyl groups. These systems were shown to be able to prevent ice formation down to very low temperatures, so that it has been possible to vitrify even mixtures where a considerable amount of water is present (up to more than 50% and almost 90% as weight and molar fraction respectively) [261]. The mechanisms that prevent ice formation from water in these systems are mainly due to hydrogen bonding, to the intrinsic disorder of the sugar component, or, in the case of hydrated samples of polysaccharides with high $T_g$, to the possible confinement of water molecules at the nanometer or sub-nanometer level between domains of the polysaccharide macromolecules. The strong dipole moment associated to water molecule allows studying its orientational dynamics by means of dielectric spectroscopy, a broadband technique able to cover more than 13 decades in timescale and that can be applied from very low to ambient temperature and even at very high pressure.

In this chapter dielectric spectroscopy is extensively used to investigate the dynamics of water in glass-forming mixtures with different saccharides: fructose, glucose, deoxyribose (monosaccharides), trehalose and sucrose (disaccharides), and glycogen (Polyglumyt@, ACRAF, a polysaccharide). Mixtures of saccharides with different concentrations of water were obtained and the dielectric study was carried out in the temperature range from liquid to the glassy state. Similar saccharides were mixed with a protein (lysozyme), freeze-dried and then hydrated: a preliminary dielectric study of the dynamics of this ternary system was carried out. In some cases, also the high frequency regime, comparable to the dynamics probed by neutron scattering, was studied. In the case of water-fructose mixtures also a systematic study of water
dynamics both at ambient and, for the first time, high pressure conditions were done and the results are shown in the following chapter.

4.1 Systematic study of dynamics of water in water-fructose mixtures at different isobaric and isothermal conditions

4.1.1. Experimental details

D(-)-Fructose purchased from Wako Pure Chemical Industries was used for preparations of all the fructose-water mixtures. Fructose and water were mixed to form solutions with 26.0 and 30.0 wt% water. To make the mixture with lower water concentration (20 wt%) approximately 40 wt% water-fructose mixture was made first. The water in this mixture was evaporated at 100 ºC under a reduced pressure to obtain water-fructose mixture with 20 wt% water. Both mixing of components and loading of the sample holder were performed in controlled atmosphere with dry nitrogen.

In studied concentration range (20-30 wt.% water) dielectric strength of the \( \nu \)-process, \( \Delta \varepsilon_\nu \), increases with increasing of water content in the fructose-water solution [182] in a similar way as it was shown in previous Chapter with example for \( n \)-PG oligomers-water mixtures that in this concentration regime the \( \nu \)-relaxation reflects mainly the water dynamics in the mixtures. The increase of \( \Delta \varepsilon_\nu \) with water content occurs both for the glassy and liquid state, as shown in fig. 4.1.

The experimental activity was carried out as exposed in the following. First, we investigated the dynamics of water-fructose mixtures at ambient pressure for the concentrations already well studied in the literature [182, 262] and in a concentration/temperature range where full miscibility and supercooling can be obtained (see fig. 4.2). Results in good agreement with the literature data were obtained. Moreover, we extended the temperature range of these studies to lower values (down to 150 K).

Finally, we performed high pressure studies up to 700 MPa. The new data on the dynamics of water-fructose mixtures were obtained by dielectric spectroscopy in the frequency range from 10 mHz to 10 MHz by means of the Novocontrol Alpha high resolution dielectric analyser for both ambient and high pressure.
Fig. 4.1. Concentration dependences of the dielectric strength at different temperatures for the \( \nu \)-process of fructose+H\(_2\)O mixtures. Orange arrow indicates roughly the concentration dependence of the glass transition temperature for fructose-water mixtures. Below that arrow is glass, above – supercooled liquid.

Fig. 4.2. Phase diagram for fructose-water mixture (reproduced from ref. [263]). Data are determined both from the dielectric and calorimetry measurements.

The one of the most known phenomenon occurring in saccharides, in particular in d-fructose, is mutarotation [264]. Mutarotation can be regarded as a process of transformation from one
tautomer to another with the open ring (chain) stage [265]. Every tautomer has its unique physical properties, and mutarotational dynamics leads to viscosity fluctuations in the system. In consequence, one can expect a change of $\alpha$-relaxation time at constant temperature during equilibrating of the sample. If equilibration time is not long enough to minimize the effect of mutarotation, the measurements performed can lead to improper estimations of the glass transition temperature of the saccharides and all the dynamics can be affected by the sample preparation [264]. Authors showed that mutarotation process in anhydrous fructose is very slow, while in solutions with ethanol and water its kinetics is several dozen times faster and its equilibrium is almost immediately obtained [264, 266-268].

To minimise the effect of mutarotation we followed the procedure proposed and done by Prof. Shinyashiki [263]. The sealed cell (to prevent the evaporation of water (see Chapter 2)) was accurately filled by the sample and placed into a cryostat where temperature was controlled by a conditioned nitrogen flow. The dielectric spectra were measured in the temperature range from liquid to the glassy state on cooling by isothermal steps, after stabilizing the temperature within 0.1 K for an appropriate equilibration time (minimum 30 minutes, but even some hours when the dynamics of the system is very slow). The glass transition temperature obtained according to the dielectric definition is well in agreement with the values obtained by calorimetry [182].

For all the water-fructose mixtures dielectric measurements were performed in different temperature and pressure intervals. An overview of the experimental activity can be found in Table 2.3 (see Chapter 2) where all the details are provided. The main results will be shown in the following section together with a discussion.

### 4.1.2 Analysis of dielectric spectra in presence of dc conductivity

Figure 4.3 shows an example of dielectric spectra for fructose-20% water mixture for two isotherms (233.2 K and 243.2 K) at ambient pressure. The two relaxation processes that are shown by the spectra as a loss peak at lower frequency and a loss peak at higher frequency mainly coincide with the dynamic processes characteristic of aqueous systems found in literature and discussed in previous Chapter: the slowest one ($\alpha$-process) is related to cooperative large scale motions of solute and water molecules together and it has a dramatic slowing down on approaching the glass transition temperature, that coincides with the structural arrest of the system. The faster process ($\nu$-process) is believed to be due to reorientational motions of water
molecules [103] and it was found to be ubiquitous in any aqueous systems, in both mixtures and confined water [153].

Moreover, the dielectric spectra of studied fructose-water mixtures exhibit conductivity and electrode polarization contributions which tend to hide the $\alpha$-process in the low frequency range.

Fig. 4.3. Frequency dependences of real and imaginary parts of dielectric function for fructose+20 wt.% water mixture at ambient pressure at 233.2 K (a) and 243.2 K (b). The curves were obtained by the fitting procedures. Close and open circles are data, the dashed, dotted and dash-dotted lines indicate $\alpha$-process, $\nu$-process, and dc conductivity, respectively.

Moreover, the dielectric spectra of studied fructose-water mixtures exhibit conductivity and electrode polarization contributions which tend to hide the $\alpha$-process in the low frequency range.
As far as electrode polarization, its contribution was minimized with respect to the contribution coming from the bulk sample by choosing appropriate geometry for the capacitor cell, i.e. larger thickness (up to 1 mm) and smaller diameter than the usual one. The isobaric and isothermal permittivity data were analysed in terms of linear superposition of two relaxations and conductivity contributions, with each relaxation process described by a Havriliak–Negami (HN) function (Eq. (1.24)). A characteristic relaxation time \( \tau = \left( 2\pi \cdot f_{\text{max}} \right)^{-1} \) was easily obtained from the frequency of maximum \( \varepsilon'' \), \( f_{\text{max}} \).

To reveal more details from the frequency dispersion at low frequencies (at low temperatures or high pressure), where sometimes conductivity can dominate, we used a one-dimensional derivative technique [10, 269]:

\[
\varepsilon''_{\text{der}}(\omega) = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \approx \varepsilon''_{\text{dielectric}}(\omega).
\]

(4.1)

which approximately equals to the Ohmic-conduction-free dielectric loss \( \varepsilon''_{\text{dielectric}} \). Eq. (4.1) can be derived from a series expansion of the Kramers-Kronig relationship [9, 10, 270], truncated to the first order. From the theory, the relaxation peak so obtained is predicted to be narrower than the original one, but the location of the maximum of the peak in \( \varepsilon'' \) should be the same. Figure 4.4 shows the results of the derivative analysis technique for fructose-20% water mixture at ambient pressure for 233.2 K and 243.2 K. Applied derivative analysis gives rather sharp peaks but for \( f_{\text{max}} \) a value coincident with that got from fitting procedure is obtained.

The derivative techniques can also reveal additional processes that are hidden by the conductivity at high pressure (see fig. 4.5). Note that the contribution from electrode polarization effects is not dominant in most of our samples, since only a small difference in \( \varepsilon'' \) and \( \varepsilon''_{\text{der}} \) is observed for low frequencies.

A good agreement between two techniques (fitting procedure and derivative analysis) is shown in figs. 4.4, 4.5 for different concentrations of water in water-fructose mixtures at various temperatures and pressures. This result confirms the reliability of the parameters estimated from fitting procedure, that agree very well with those extracted by a model-independent technique (derivative analysis).
Fig. 4.4. Frequency dependences of real and imaginary parts of dielectric function for fructose+20 wt.% water mixture at ambient pressure at 233.2 K (a) and 243.2 K (b). The black curve was obtained by the derivative analysis. Close and open circles are data, the dashed, dotted and solid lines indicate $\alpha$-process, $\nu$-process, and $\varepsilon''_{der}$, respectively.
Fig. 4.5. Frequency dependence of imaginary part of dielectric function for fructose with different concentrations of water at different temperatures at elevated pressure ($P = 500$ MPa): (a) 20 wt.% water mixture at 250.2 K, (b) 26 wt.% water mixture at 234.2 K and (c) 30 wt.% water mixture at 228.2 K. Close circles are data, the solid, dashed, dotted and dash-dotted lines indicate the simultaneous fit, $\alpha$-process, $\nu$-process, and $\varepsilon''_{\text{der}}$, respectively.
As in the case of rich-in-water solutions of n-PG oligomers, on comparing measurements done at different pressures and temperatures, the timescale separation between $\alpha$- and $\nu$- process in dielectric spectra of studied fructose-water mixtures at the same $\alpha$- relaxation time, $\tau_\alpha$, also increases on increasing temperature and pressure (see fig. 4.6). This behaviour is again similar to what reported for $\alpha$- and $\beta$-processes in hydrogen bonded systems (see § 3.1.4).

Fig. 4.6. Frequency dependence for the normalized derivative of $\varepsilon'$, $\varepsilon''_{der}/\varepsilon''_{der\ max}$ (fructose+30 wt.% water mixture) at the same $\tau_\alpha$. Separation between $\alpha$- and $\nu$- processes is increasing on increasing temperature and pressure.

4.1.3 Effect of high pressure on the parameters of the relaxation dynamics

a) Analysis of dynamics: $T$ and $P$ dependence of $\tau_\alpha$ and $\tau_\nu$ relaxation times

Figure 4.7(a) shows an example of the temperature dependence of $\alpha$- relaxation times for fructose+30% water mixture. The logarithm of $\tau_\alpha$ shows the typical Vogel-Fulcher-Tamman-like behaviour, with a curved behaviour vs. $1/T$ (see Eq. (3.2)), meaning an apparent activation energy that increases on decreasing temperature $T$. The dielectric glass transition temperature $T_g$ was defined as temperature at which $\tau_\alpha$ is equal to 100 s. It is clearly seen that pressure effect moves $\alpha$-relaxation times to higher temperature.
Fig. 4.7. Plots of logarithm of relaxation times against reciprocal temperature for the $\alpha$- (a) and the $\nu$- (b) processes of fructose+30 wt.% water mixture for different isobars: 0.1 MPa (circles), 300 MPa (triangles), 500 MPa (squares), 620 MPa (stars). Plots of relaxation times for fructose+30 wt.% water mixture at ambient pressure (pluses and crosses for $\alpha$- and $\nu$- processes, respectively) were taken from ref. [182]. Lines represent VFT fitting curves.
Figure 4.7(b) shows the temperature dependence of logarithm of $\nu$-relaxation time. The behaviour is similar to that found for many aqueous mixtures and as was shown for $n$-PG oligomers-water mixtures in previous Chapter: the $\nu$-relaxation has linear (Arrhenius) behaviour vs. reciprocal temperature in glassy state (see Eq. (3.3)) and on increasing temperature $\tau_\nu$ changes its behaviour from a weaker to a stronger dependence at a crossover temperature $T_{cross}$.

We observed that compression significantly affects water dynamics in mixtures. Relaxation time increases on increasing pressure, again at odds with what observed and predicted for bulk pure water [148, 188, 223]. So, although $\nu$-relaxation time has some resemblance with pure water dynamics at ambient pressure, its behaviour at high pressure is quite different and it is similar to what found in water-glycols mixtures (see Chapter 3).

Isothermal experiments also have been done in the case of fructose-water mixtures. Figure 4.8 shows an example of the pressure dependence of $\alpha$ and $\nu$-relaxation for 20 % water-fructose mixture.

Fig. 4.8. Plots of logarithm of relaxation times against pressure of the $\alpha$ (close symbols) and the $\nu$ (open symbols) processes of fructose+20 wt.% water mixture for two isotherms, $T = 227.0$ K (a) and $T = 248.2$ K (b). $\tau_{\nu\,cross}$ and $P_{\nu\,cross}$ the crossover time and the crossover pressure, respectively. Solid lines represent VFT fitting curve for the $\alpha$-process and dashed lines represent Arrhenius fitting above and below $P_{\nu\,cross}$.

The fitting parameters of VFT and Arrhenius equations (3.2)-(3.5) for different isobaric and isothermal scans for fructose-water mixtures are shown in Table 4.1.
Table 4.1. Parameters of the VFT equation (3.2), (3.4) and Arrhenius equation (3.3), (3.5) for mixtures of fructose with different concentrations of water for isobaric and isothermal scans

### Fructose + 20 wt.% water

<table>
<thead>
<tr>
<th>$P$ [MPa]</th>
<th>$T_g$ [K]</th>
<th>VFT parameters of the $\alpha$-process</th>
<th>Arrhenius parameters of the $\nu$-process</th>
<th>$T_v = 100$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$log_{10}[r_{\alpha,VFT}(s)]$</td>
<td>$A$ [K]</td>
<td>$T_0$ [K]</td>
</tr>
<tr>
<td>0.1</td>
<td>219.8</td>
<td>-14.0</td>
<td>734.0</td>
<td>174.0</td>
</tr>
<tr>
<td>130</td>
<td>225.8</td>
<td>-14.0</td>
<td>775.6</td>
<td>177.3</td>
</tr>
<tr>
<td>300</td>
<td>233.4</td>
<td>-14.0</td>
<td>766.7</td>
<td>185.4</td>
</tr>
<tr>
<td>500</td>
<td>241.2</td>
<td>-14.0</td>
<td>776.1</td>
<td>192.7</td>
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</tbody>
</table>

**Isothermal scans**

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$P_g$ [MPa]</th>
<th>$log_{10}[r_{\alpha}(T,0)]$</th>
<th>$D_p$</th>
<th>$P_0$</th>
<th>$log\tau^*_0$</th>
<th>$\Delta V^#$ [cm$^3$/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>227.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>248.2</td>
<td>809</td>
<td>-1.14</td>
<td>117.2</td>
<td>7495.8</td>
<td>-</td>
<td>0.181</td>
</tr>
</tbody>
</table>

### Fructose + 26 wt.% water

<table>
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<tr>
<th>$P$ [MPa]</th>
<th>$T_g$ [K]</th>
<th>VFT parameters of the $\alpha$-process</th>
<th>Arrhenius parameters of the $\nu$-process</th>
<th>$T_v = 100$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$log_{10}[r_{\alpha,VFT}(s)]$</td>
<td>$A$ [K]</td>
<td>$T_0$ [K]</td>
</tr>
<tr>
<td>0.1</td>
<td>206.8</td>
<td>-14.0</td>
<td>701.9</td>
<td>162.9</td>
</tr>
<tr>
<td>300</td>
<td>220</td>
<td>-14.0</td>
<td>720.7</td>
<td>175.0</td>
</tr>
<tr>
<td>500</td>
<td>227.5</td>
<td>-14.0</td>
<td>718.4</td>
<td>182.6</td>
</tr>
<tr>
<td>620</td>
<td>231.8</td>
<td>-14.0</td>
<td>746.6</td>
<td>185.1</td>
</tr>
</tbody>
</table>

### Fructose + 30 wt.% water

<table>
<thead>
<tr>
<th>$P$ [MPa]</th>
<th>$T_g$ [K]</th>
<th>VFT parameters of the $\alpha$-process</th>
<th>Arrhenius parameters of the $\nu$-process</th>
<th>$T_v = 100$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$log_{10}[r_{\alpha,VFT}(s)]$</td>
<td>$A$ [K]</td>
<td>$T_0$ [K]</td>
</tr>
<tr>
<td>0.1</td>
<td>199.3</td>
<td>-14.0</td>
<td>705.3</td>
<td>155.3</td>
</tr>
<tr>
<td>300</td>
<td>211.4</td>
<td>-14.0</td>
<td>698.2</td>
<td>167.8</td>
</tr>
<tr>
<td>500</td>
<td>220.6</td>
<td>-14.0</td>
<td>695.5</td>
<td>177.1</td>
</tr>
<tr>
<td>620</td>
<td>223.0</td>
<td>-14.0</td>
<td>739.1</td>
<td>175.7</td>
</tr>
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</table>

**Isothermal scans**

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$P_g$ [MPa]</th>
<th>$log_{10}[r_{\alpha}(T,0)]$</th>
<th>$D_p$</th>
<th>$P_0$</th>
<th>$log\tau^*_0$</th>
<th>$\Delta V^#$ [cm$^3$/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>227.1</td>
<td>758</td>
<td>-4.4</td>
<td>68.5</td>
<td>4359.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
This phenomenology, found for 20 % water-fructose mixture, appears to be very general. It is very common to all the systems investigated: a similar behaviour was found for other water-fructose mixtures with 26% and 30% of water and n-PG oligomers-water mixtures (see Chapter 3). Due to the larger separation between \( \alpha \)- and \( \nu \)-process timescale in this case it is not possible to see the marked change of behaviour of the pressure dependence above and below \( T_g \), but mainly its behaviour in the glassy state.

The temperature dependences of logarithm of the \( \alpha \)- and \( \nu \)-relaxation times for mixtures of fructose with 26% and 20% of water are reported in the following figs. 4.9 and 4.10. The qualitative behaviour is similar to what found for the mixture of fructose with 30% of water. Quantitatively, we will show in the next subparagraph what is the effect of pressure on \( T_g \) and fragility, as far as for structural relaxation, and how pressure affect the activation energy and the crossover time, as far as the \( \nu \)-relaxation.

**Fig. 4.9.** Plots of logarithm of relaxation times against reciprocal temperature for the \( \alpha \)- (a) and the \( \nu \)- (b) processes of fructose+26 wt.% water mixture for different isobars: 0.1 MPa (circles), 300 MPa (triangles), 500 MPa (squares), 620 MPa (stars). Plots of relaxation times for fructose+26 wt.% water mixture at ambient pressure (pluses and crosses for the \( \alpha \)- and the \( \nu \)-process, respectively) were taken from ref. [182]. Lines represent VFT fitting curves.
b) **Analysis of dynamics: effect of pressure on $T_g$ and $T_{\text{cross}}$ and on activation energies**

The strong dependences of $\tau_\alpha$ and $T_g$ on pressure for fructose-water mixtures are clearly shown in figs. 4.7(a), 4.8, 4.9(a), 4.10(a). As a summary, the values for $T_g$ (or $P_g$) for isobaric (or isothermal) conditions were obtained by extrapolating the VFT function up to the corresponding $\tau_\alpha = 100$ s. Longer are the relaxation times measured, less error we found in the extrapolation.

Figures 4.11-4.14 show how pressure effects on all parameters defined above and characterizing the variation of dynamics with $T$ and $P$. The pressure dependence of glass transition temperatures for water-fructose mixtures with different concentration of water is shown in fig. 4.11. $T_g$ increases with pressure, and this behaviour is not linear. We used the equation proposed by Andersson [228] for describing our data (see Eq. (3.7)). The fitting parameters of Eq. (3.7) for fructose-water mixtures are shown in Table 4.2. Open circles in fig. 4.11 are obtained from extrapolation of isothermal data of the studied water-fructose mixtures to higher values of pressure. They are in a good agreement with other data.
Fig. 4.11. The pressure dependence of glass transition temperatures obtained from both isobaric (closed symbols) and isothermal (open circles) measurements for water-fructose mixtures with 20 wt.% (circles), 26 wt.% (squares), 30 wt.% (triangles) of water. Lines represent Andersson eq. fitting curves.

Table 4.2. Fitting parameters of Andersson Eq. (3.7) for rich-in-water solutions with fructose

<table>
<thead>
<tr>
<th>Systems</th>
<th>$k_1$ [K]</th>
<th>$k_2$</th>
<th>$k_3$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose + 20 wt.%</td>
<td>219.5</td>
<td>8.5</td>
<td>3660</td>
</tr>
<tr>
<td>Fructose + 26 wt.%</td>
<td>206.8</td>
<td>4.1</td>
<td>4280</td>
</tr>
<tr>
<td>Fructose + 30 wt.%</td>
<td>199.2</td>
<td>5.2</td>
<td>3980</td>
</tr>
</tbody>
</table>

Also the derivative of glass transition temperature with pressure $dT_g/dP$ was calculated at $P<200$ MPa and we found for fructose+26% water (as an example) a value of $dT_g/dP \approx 42 \text{ K MPa}^{-1}$ that is similar to that for glycerol [78], a pure system that is characterized by a strong hydrogen bond network. Such a low values of $dT_g/dP$ are typical for hydrogen-bonded systems. On the contrary, molecular van-der-Waals liquids and polymers have usually a value at least 3 times larger (see Chapter 3 and ref. [78]).

As it was mentioned above an increase of pressure moves the crossover to shorter times. Pressure dependence of logarithm of $\tau_{v, \text{cross}}$ has an exponential behaviour (see fig. 4.12) and an asymptotic limit is obtained at very high pressure. This result is in agreement to what is shown in
the spectra in fig. 4.6 (effect of pressure on spectra with the same \( \tau_a \) and different \( T-P \)). The increasing of pressure and temperature enhances the timescale separation between \( \alpha \)-process and \( \nu \)-process.

Fig. 4.12. Pressure dependence of logarithm of \( \tau_{\nu \text{cross}} \) for water-fructose mixtures with 20 wt.% (squares), 26 wt.% (circles), 30 wt.% (triangles) of water. Lines are guides for the eyes.

It is noteworthy to remind that the timescale of \( \tau_{\nu \text{cross}} \) is similar to that found by dielectric spectroscopy for \( n \)-PG oligomers-water mixtures and in other aqueous mixtures [103, 167, 181]. Another relevant relaxation parameter that deserves to be considered is the steepness index or fragility, \( m \), related to the apparent activation energy of the structural relaxation measured at \( T_g \).

It was estimated for isobaric data of all studied fructose-water systems using well-known relation

\[
\frac{1}{\tau_a} \frac{d}{dT} \left( \log_{10} \frac{T_{\nu \text{cross}}}{T} \right) = \frac{\partial m}{\partial T} \bigg|_{T_g} \tag{3.9}
\]

The parameters of the VFT equation (3.2) are also applied to find the isobaric fragility \( m_P \) of the examined mixtures using Eq. (1.38) (see Chapter 1).

In our case, we have that, while fragility at ambient pressure of pure fructose is around 92 [202], that of the mixtures is much lower, about 75. So, by adding water the fragility decreases, maybe for the setup of an hydrogen bonding network. On the other hand, we found that on increasing the pressure, fragility index tends to increase for the water-fructose mixtures in studied pressure range (see fig. 4.13), as it occurs for hydrogen-bonded systems.

Pressure affects also the activation energies involved in the water \( \nu \)-relaxation. Fig. 4.14 shows the influence of pressure on activation energy of \( \nu \)-process, \( E_\nu \), calculated below \( T_{\nu \text{cross}} \), for water
mixtures with fructose. In the studied pressure range the activation energy of $\nu$-process increases with pressure, as also shown by $n$-PG oligomers-water mixtures in the pressure range lower than 1 GPa.

Fig. 4.13. Pressure dependence of fragility for water-fructose mixtures with 20 wt.% (squares), 26 wt.% (circles), 30 wt.% (triangles) of water.

Fig. 4.14. Pressure dependences of the $\nu$-process activation energies $E_\nu$ for water-fructose mixtures with 20 wt.% (squares), 26 wt.% (circles), 30 wt.% (triangles) of water. The energies in the glassy state of the mixtures are evaluated from Arrhenius equation (Eq. 3.3). Lines are guides for the eyes.
c) Analysis of dielectric strength: evidence of local mechanism for water relaxation

In general, in all neat glassformers, van der Waals and aqueous mixtures \( \Delta \epsilon \) usually decreases on increasing temperature for a structural \( \alpha \)-process, on the other hand, the dielectric strength of the secondary JG relaxation increases monotonically with increasing temperature with an elbow shape that indicates a change of slope in vicinity of \( T_g \). From inspection of fig. 4.15 for the 20% water-fructose mixture the same trend in temperature dependence for the dielectric strength of the \( \alpha \)-process, \( \Delta \epsilon_\alpha \), is clearly seen at ambient and elevated pressure. Moreover, identifying the \( \nu \)-relaxation as a secondary process is fully compatible with its dielectric strength behaviour (see fig. 4.15). In the glassy state, the spatial restriction of local motion is reflected by the low and almost constant (or weakly increasing) value of dielectric strength of the \( \nu \)-relaxation, \( \Delta \epsilon_\nu \), whereas larger reorientation amplitude is possible above \( T_g \), and hence the stronger \( T \)-dependence of \( \Delta \epsilon_\nu \) is observed. These features in the dielectric strength behaviour of the \( \nu \)-process at different isobaric conditions also have been shown in previous Chapter 3 for \( n \)-PG oligomers-water mixtures. The temperature dependences of \( \Delta \epsilon_\nu \) for all studied fructose mixtures with different concentration of water are shown in fig. 4.16 for ambient pressure measurements.

![Fig. 4.15. Plot of relaxation strength of the \( \alpha \)- (squares) and the \( \nu \)- (circles) processes against reciprocal temperature for the fructose+20 wt.% water mixture at ambient (a) and elevated (500 MPa) (b) pressure.](image-url)
Fig. 4.16. Temperature dependences of dielectric strength for the $\nu$-process of fructose-water mixtures at ambient pressure. Stars indicate the glass transition temperature for each fructose-water mixture.

The analysis of dielectric strength, often overlooked in literature for its importance, helped in identifying the water-specific $\nu$-relaxation truly as the secondary relaxation. In particular, the increase of $\Delta\varepsilon_\nu$ with $T$ is a clear evidence that its secondary relaxation character continues to temperatures above $T_g$, where $\tau_\nu$ has already changed its temperature dependence to VFT-like from the Arrhenius dependence below $T_g$. It is worthwhile to point out that both the changes from a weaker to a stronger $T$-dependence on crossing $T_{cross}$ observed for $\tau_\nu$ and $\Delta\varepsilon_\nu$ in aqueous mixtures (see example for fructose-water mixtures in fig. 4.17) are exactly analogous to that found for the secondary relaxation of a fast component in binary van der Waals liquids [96, 271-273], suggesting similar interpretation. The behaviour of $\Delta\varepsilon_\nu$ invalidates the suggestion by others [156, 176, 274] that the observed water-specific relaxation is the $\alpha$-relaxation of the water component in the mixture, with its relaxation time having the usual VFT $T$-dependence above $T_g$, but it becomes confined below $T_g$ to assume the Arrhenius $T$-dependence.

Finally, the increase of $\Delta\varepsilon_\nu$ with $T$ in the whole temperature range is not compatible with the interpretation by other authors [183, 184] either, according to which the water-specific relaxation is a merged $\alpha$- and $\beta$-process above $T_g$ and only the $\beta$-character survives in the glassy state. If so, dielectric strength of water-related $\nu$-process should decrease with $T$ above $T_g$. Actually this interpretation is refuted by the data in some aqueous solutions, where both the $\alpha$- and $\nu$-process
are present and well separated from each other above $T_g$ (see, for example, figs. 3.1b, 3.3-3.5, 4.3-4.4): the fact that the $\nu$-process is well separated from the $\alpha$-process way above $T_g$ rules out merging of the two processes and splitting apart occurring just in vicinity of $T_g$.

Figure 4.17 reminds ones again that both temperature dependences of $\tau_\nu$ and $\Delta\varepsilon_\nu$ change their behaviour from a weaker to a stronger one at the same temperature ($T_{\text{cross}}$) which corresponds to the $\alpha$-relaxation time $\tau_\alpha \approx 10$ ks (for the case of fructose-water mixtures), when the structure of the systems is completely frozen and no any cooperative rearrangement is possible.

![Graphical representation](image.png)

Fig. 4.17. (a) Plot of relaxation times vs. $T_g/T$ for mixtures of fructose with 20 wt.% (squares), 26 wt.% (circles), 30 wt.% (triangles) of water. Close and open black symbols indicate $\alpha$- and $\nu$-process, respectively. Solid line is the VFT function fit, dotted line indicates the time $\tau = 100$ s. The vertical dashed and dash-dotted lines indicate the temperature where $\tau_\alpha = 100$ s and the crossover temperature, respectively. b) Plot of rescaled dielectric strength for the $\nu$-process, $\Delta\varepsilon_\nu / \Delta\varepsilon_\nu(T_g)$, vs. $T_g/T$ of fructose-water mixtures. Symbols are the same as in panel (a).
Summarising all the dielectric strength behaviour of \( \nu \)-process can be rationalized: the temperature dependence is strongly influenced by the glass transition of the mixture, while its concentration behaviour is linear in number of water molecules.

4.2 Comparison with other mono-, di-, poly- saccharides: from aqueous mixtures to hydrated bio-polymers

4.2.1 Aqueous mixtures of monosaccharides: similarities and differences in dynamic behaviour

In previous Section we showed how molecular dynamics of the rich-in-water solutions of fructose changes on applying pressure. As was discussed already before, glass transition properties of sugars and sugar-water mixtures are important for practical considerations (like the use as cryoprotectants for biomaterials [53, 259]) as well as subjects of scientific interest [260]. Therefore it is of importance to extend our study to mixtures of water with other saccharides. In particular, in this Section we will compare dynamics of aqueous mixtures with fructose and that with different saccharides: glucose and deoxyribose (monosaccharides), trehalose and sucrose (disaccharides), and glycogen (Polyglumyt\textregistered, ACRAF, a polysaccharide). Comparison will be done for ambient pressure measurements only.

Pure sugars have been studied extensively by different groups using various techniques [6, 202-210]. Also their mixtures with water were investigated in many studies [205, 259, 262, 274-277]. Glucose is a six carbon polyhydroxy-ketone. Glucose and fructose are isomers, i.e. both have the same molecular formula (\( \text{C}_6\text{H}_{12}\text{O}_6 \)), but they differ structurally. Crystalline fructose adopts a cyclic six-membered structure due to the stability of its hemiketal and internal hydrogen-bonding. The cyclic six membered form is formally called D-fructo-pyranose. The molecule of glucose, on the contrary, turns out to be a very complicated system for its ability to mutate among different structures. These structures are usually adopted by a transition through the acyclic isomer, which exists in only minor amounts in solution. Glucose is derived from hexanal, a chain of six carbon atoms terminating with an aldehyde group. The other five carbon atoms each bear alcohol groups. Glucose is also called an aldohexose. The schematic pictures of the fructose and glucose molecules are shown in Section 2.5. Like other sugars, glucose undergoes the phenomenon of mutarotation. The crystalline form of our sample, D-glucose, was \( \beta \)-
glucopyranose. In the supercooled liquid state or in aqueous solution, this tautomer can be transformed into $\alpha$-glucopyranose during mutarotation phenomenon, with a strong effect on dynamic behaviour [278]. In aqueous mixtures all mutarotation phenomena are very fast, allowing a reproducible study of dynamics in the timescale of the experiments.

The spectra of the studied rich-in-water mixtures with glucose exhibit two relaxation peaks in explored temperature range as that of water-fructose mixtures: the slower ($\alpha$-process) and the faster ($\nu$-process). The characteristic relaxation times of two processes, $\tau_\alpha$ and $\tau_\nu$, were calculated from the positions of their frequency peaks $\tau = (2\pi \cdot f_{\text{max}})^{-1}$ (see also Eq. (1.27)). The temperature dependences of $\alpha$- and $\nu$- relaxation times for aqueous mixtures of glucose with 26 % and 30% of water together with that of fructose-water mixtures are shown in fig. 4.18. Also in the inset of fig. 4.18(a) it is shown a good agreement between our data for glucose+26% of water and data from the literature for glucose+25 wt.% of water [276, 277].

From inspection of fig. 4.18 it is clearly seen that both relaxation processes for aqueous mixtures of fructose and glucose not only behaves similarly, but even they are practically identical for correspondent concentration of water. The slow process has the VFT $T$-dependence, typical of cooperative $\alpha$-relaxation and responsible for glass transition of the mixture. Concerning the $\nu$-relaxation, it has an Arrhenius $T$-dependence at low temperature with an activation enthalpy of about 54 and 53 kJ/mol for 26 % and 30 % of water in glucose, respectively (see Table 4.4), similar to the value of about 50 kJ/mol universally found in the glassy aqueous mixtures [102]. On increasing temperature, at $T_{\text{cross}} = 200$ K and 190 K for 26 % and 30 % of water in glucose, respectively, $\tau_\nu$ changes to assume a stronger $T$-dependence. This crossover does not occur at 220 K as predicted in ref. [148]. On the contrary, it occurs always few degrees below $T_g$, where $\tau_\alpha$ exceeds 1-10 ks, as it can be identified in every aqueous mixtures investigated in our study.

It is also interesting that although fructose and glucose are isomers they have quite different glass transition temperatures, 288.5 K and 307.6 K, respectively. On the other hand, the glass transition temperature of the water mixtures with fructose and glucose varies in 1.5 K for the same concentration of water in mixtures. It is possible that in aqueous mixtures with high enough water content, the structures adopted at equilibrium by the two sugars and their distribution is quite similar.
The estimated values of $T_g$ for water-glucose mixtures are in a good agreement with data from the literature (see fig. 4.19) obtained also with different techniques (e.g. calorimetry) [209, 279, 280]. This coincidence is another evidence that the slow relaxation probed by dielectric spectroscopy is related to glass transition phenomenon.
Table 4.4. Parameters of the VFT Equation (3.2) and Arrhenius Equation (3.3) for saccharides-water mixtures at ambient pressure

<table>
<thead>
<tr>
<th>$T_g$ [K]</th>
<th>VFT parameters of the $\alpha$-process</th>
<th>Arrhenius parameters of the $\nu$-process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log_{10}[r_{\alpha,\text{VFT}}(s)]$</td>
<td>$A$ [K]</td>
</tr>
<tr>
<td><strong>Trehalose + 25 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>228.0</td>
<td>-13.8</td>
<td>719.5</td>
</tr>
<tr>
<td><strong>Deoxyribose + 30 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>184.7</td>
<td>-14.0</td>
<td>732.5</td>
</tr>
<tr>
<td><strong>Glucose + 26 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>207.9</td>
<td>-14.7</td>
<td>804.5</td>
</tr>
<tr>
<td><strong>Glucose + 30 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>198.4</td>
<td>-13.8</td>
<td>678.2</td>
</tr>
<tr>
<td><strong>Sucrose + 15 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>246.7</td>
<td>-13.6</td>
<td>743.7</td>
</tr>
<tr>
<td><strong>Sucrose + 20 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230.7</td>
<td>-13.2</td>
<td>682.9</td>
</tr>
<tr>
<td><strong>Sucrose + 25 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>216.0</td>
<td>-13.5</td>
<td>737.0</td>
</tr>
<tr>
<td><strong>Sucrose + 30 % water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>204.1</td>
<td>-14.4</td>
<td>812.5</td>
</tr>
</tbody>
</table>

The same scenario shown above can be found in another water mixture with monosaccharide (deoxyribose), which is mixed with 30 % wt. water fraction (see fig. 4.20(a)): in this case the crossover of $\tau_\nu$ occurs at $T_{\text{cross}} = 180$ K, while $T_g = 185$ K. Again, in the glassy state $\tau_v$ has an Arrhenius $T$-dependence with the activation enthalpy of 49.5 kJ/mol. There is good agreement between our data for $\tau_\alpha$ and $\tau_\nu$ and those of ref. [274]. Dielectric strengths of both processes are plotted in fig. 4.20 (b). It is important to note that both temperature dependences of $\tau_\nu$ and $\Delta \varepsilon_\nu$ change the slope around the same temperature, $T \approx T_{\text{cross}}$. The general behaviour of dielectric strengths will be discussed in details in the next Chapter.
Fig. 4.19. Concentration dependence of glass transition temperatures for water-glucose mixture: solid line – approximation of the data from refs. [209, 279, 280], stars – data from this work (errors are less than the size of the symbols).

Fig. 4.20 (a) Plot of relaxation times vs. reciprocal temperature of 30 wt.% fraction of water in deoxyribose. Close and open black symbols indicate \( \alpha \)- and \( \nu \)-process, respectively. Solid line is the VFT function fit, dotted line is the Arrhenius fit to the data in the glassy state. The vertical line indicates the temperature where \( \tau_\alpha = 100 \) s. (b) Plot of dielectric strength vs. reciprocal temperature for the \( \alpha \)- and \( \nu \)-processes. Symbols are the same as in panel (a). Lines are from linear regression for data above and below \( T_g \).
If we plot both $\alpha$- and $\nu$-relaxation times versus $1/T$ for the same fraction of water in monosaccharides, 30 wt.% of water (see fig. 4.21), we observe that the temperature dependence of the $\nu$-relaxation in glassy state is similar for those mixtures: activation energies and pre-exponential factors, $\log_{10}[\tau_{\nu,\text{Arr}}]$, of Arrhenius equation (3.3) are quite compatible (see Table 4.4). On the other hand, big molecules of different solutes influence on cooperative $\alpha$-relaxation of the solute hydrogen-bonded to the water: glass transition and crossover temperatures are different for different water-sugar mixtures with the same amount of water.

![Monosaccharides + H$_2$O](image)

**Fig. 4.21.** Plot of relaxation times vs. reciprocal temperature of 30 wt.% fraction of water in monosaccharides: fructose (squares), glucose (triangles), deoxyribose (stars). Close and open symbols indicate $\alpha$- and $\nu$- processes, respectively. Solid lines are the VFT function fit.

### 4.2.2 Aqueous mixtures of disaccharides: a general scenario for water-sugar solutions

We also studied aqueous mixtures of disaccharides: sucrose with 15, 20, 25 and 30 wt.%, and trehalose with 25 wt.% of water. Figure 4.22 shows the relaxation map for those mixtures. The behaviour is typical to others water mixtures shown above. $\alpha$-relaxation has VFT temperature dependence, it depends on the kind of solute and amount of water, and $\nu$-relaxation has Arrhenius behaviour at low temperatures in glassy state and changes its dependence from a
weaker to a stronger one, crossing the crossover temperature on heating. From inspection of fig. 4.22 it is clearly seen that, on increasing amount of water in the mixtures, the $\nu$-relaxation becomes shorter. Moreover, the $\nu$-relaxation for water mixture with trehalose in glassy state is identical to that for 25 wt.% of water in sucrose. This behaviour is similar to that found above for monosaccharides-water mixtures (see fig. 4.21) where $\nu$-relaxation in glassy state is almost the same for the same mass fraction of water in different monosaccharides.

![Fig. 4.22. Plot of relaxation times vs. reciprocal temperature of sucrose with 15 wt.% (black circles), 20 wt.% (red circles), 25 wt.% (blue circles) and 30 wt.% H$_2$O (orange circles), and trehalose+25 wt.% H$_2$O (purple squares). Close and open symbols indicate $\alpha$- and $\nu$- process, respectively. Solid lines are the VFT function fit. Olive thick line is VFT fit of the viscosity data and data obtained by specific heat spectroscopy [281].](image)

It is also important to mention that the good agreement was found for 20 wt.% of water in sucrose between our dielectric data and data obtained by completely different techniques: viscosity measurements and specific heat spectroscopy [281] (see fig. 4.22). Moreover, estimated glass transition temperatures for water-sucrose, which decreases on increasing amount of water, and water-trehalose mixtures very well correspond to that found in the literature with different
techniques [205, 262, 281-285] (see phase diagrams for water mixtures with sucrose and trehalose in fig. 4.23).

It is also interesting to compare concentration dependences of $T_g$ for different saccharides-water mixtures. The comparison of our and the literature data (obtained from calorimetry) [209, 280] is shown for water mixtures with glucose, sucrose and trehalose in fig. 4.24, where very good agreement is found for glucose-water and sucrose-water mixtures. $T_g$ of trehalose+25 wt.% water mixture differs from the data from ref. [209, 280], but it is in a good agreement with data [283] (see fig. 4.23(a)). The higher is molecular weight, $M_w$, of solute (sugars) in water mixture the higher is $T_g$. For mixtures with solutes which have the same $M_w$ (sucrose and trehalose), the glass transition temperatures are higher for the water mixture with the more rigid molecule, i.e. trehalose.

![Phase diagrams](image)

Fig. 4.23. Phase diagrams for: (a) water-trehalose mixture: solid line – data taken from ref. [285], squares – data taken from ref. [283], star – data from this work; (b) water-trehalose mixture: solid lines – data taken from ref. [282], squares – data taken from ref. [205], circles – data taken from ref. [262], upward triangles – data taken from ref. [283], diamonds - data taken from ref. [284], downward triangle – data taken from ref. [281], stars – data from this work (in some cases errors are less than size of the symbols). In both figures also the data for concentration dependences of the melting temperatures, $T_m$, and homogeneous crystallization temperatures, $T_h$, for studied mixtures of water with trehalose (a) and sucrose (b) are indicated.
Fig. 4.24. Concentration dependences of the glass transition temperatures for water-mixtures with glucose (triangles), sucrose (squares), and trehalose (circles). Solid lines are guides for the eyes. Our data (symbols with pluses) compared with the literature data: open symbols [209, 280] and closed symbols [283].

Figure 4.25 shows temperature dependences of dielectric strengths for $\alpha$ - and $\nu$ - processes and also total sum $\Delta \varepsilon_{\text{tot}} = \Delta \varepsilon_{\alpha} + \Delta \varepsilon_{\nu}$ vs. reciprocal temperature water-sucrose mixtures. The typical behaviour for $\Delta \varepsilon_{\alpha}$ and $\Delta \varepsilon_{\nu}$ is observed: $\Delta \varepsilon_{\alpha}$ decreases on increasing $T$, $\Delta \varepsilon_{\nu}$ slightly increases in glassy state on increasing $T$, then in vicinity of $T_g$ it changes its dependence to much stronger (see fig. 4.25(a)). From the inset of fig. 4.25(a) it can be also seen that $\Delta \varepsilon_{\nu}$ increases on increasing amount of water, moreover, the lowest studied concentration (15 wt.% of water) seems to be already above the threshold concentration (for details see Chapter 3, and an example for PPG400-water mixture in the upper inset of fig. 3.2) where the dynamics is mainly influenced by motions of water molecules. The strength of $\alpha$ -process decreases on increasing concentration of water. It is interesting that dependence of total dielectric strength, $\Delta \varepsilon_{\text{tot}}$, vs. reciprocal temperature has linear character, $\Delta \varepsilon_{\text{tot}} = a + b/T$, where values of the coefficient $a$ are listed in fig. 4.25(b).
Fig. 4.25 (a) Temperature dependences of $\Delta \varepsilon_\alpha$ (closed symbols) and $\Delta \varepsilon_\nu$ (open symbols) for mixtures of sucrose with different amount of water: 15 wt.% (black circles), 20 wt.% (red circles), 25 wt.% (blue circles) and 30 wt.% H$_2$O (orange circles). Inset: concentration dependence of $\Delta \varepsilon_\nu$ at 183.2 K in glassy state, line is guide for the eyes. (b) $\Delta \varepsilon_{tot}$ ($\Delta \varepsilon_{tot} = \Delta \varepsilon_\alpha + \Delta \varepsilon_\nu$) plotted vs. $1000/T$. Colours of circles with pluses correspond to the same concentrations of water in sucrose as in (a), lines are linear regressions.
From temperature dependences of relaxation times it is possible to extract other important parameters, like fragility $m$, activation energy of $\nu$-process in glassy state $E_\nu$, time of crossover in temperature dependence of $\nu$-relaxation $\tau_{\nu\text{ cross}}$. Their concentration dependences are shown in figs. 4.26-4.28 for water mixtures with different saccharides. For comparison we used weight fraction of water instead of molar because the first corresponds to amount of water molecules around one glucose ring which is almost the same for different saccharides (mono- or di-) with the same weight fraction of water. Figure 4.26 clearly shows that fragility decreases on adding water. The values of $m$ for fructose-water and glucose-water mixtures are similar for different concentrations of water. From the water-saccharides mixtures with the same amount of water (30 wt.%) the mixture with the strongest behaviour is deoxyribose-water.

![Graph showing concentration dependences of fragility $m$ for water mixtures with saccharides: deoxyribose (olive diamond), fructose (black squares), glucose (red triangles), sucrose (blue circles). Line is guide for the eyes.]

Fig. 4.26. Concentration dependences of fragility $m$ for water mixtures with saccharides: deoxyribose (olive diamond), fructose (black squares), glucose (red triangles), sucrose (blue circles). Line is guide for the eyes.

Figure 4.27 shows the concentration dependence for the crossover time of the $\nu$-process for water mixtures with deoxyribose, fructose, glucose, sucrose and trehalose. $\tau_{\nu\text{ cross}}$ becomes longer on increasing amount of water, i.e. separation between $\alpha$- and $\nu$-relaxation processes in dielectric spectra decreases. Moreover, it also depends on molecular weight, $M_w$, of saccharide: water-sugar mixtures with lower molecular weight of solute have longer $\tau_{\nu\text{ cross}}$. And between
water mixtures with sucrose and trehalose (these sugars have the same $M_w$), that with trehalose (more rigid molecule) has the shortest $\tau_{\nu,\text{cross}}$.

Fig. 4.27. Concentration dependences of crossover time $\tau_{\nu,\text{cross}}$ of $\nu$-process for water mixtures with saccharides: deoxyribose (olive diamond), fructose (black squares), glucose (red triangles), sucrose (blue circles), trehalose (magenta stars). Lines are guide for the eyes.

The concentration dependences of the activation energy $E_a$ of $\nu$-process in glassy state for water mixtures with different saccharides are shown in fig. 4.28. $E_a$ has more or less exponential behaviour for water mixtures with fructose, glucose and sucrose, approaching at high concentration of water an asymptotic value of about 50 kJ/mole that is the energy enough to break two hydrogen bonds. Activation energy for deoxyribose+30 wt.% water is less than that for others mixtures ($\approx 49$ kJ/mole).
To compare dynamics of water-saccharide mixtures with the same amount of water (30 wt.%)
we plotted the spectra (derivative of the real part of permittivity, in order to remove completely
the effect of dc conductivity that was masking the low frequency part of loss factor of some
samples) for different systems in fig. 4.29. We chose the spectra in such a way that the \( \nu \)-process
for all mixtures is at about the same frequency (\( \approx 0.35 \) MHz). It is clearly seen that the separation
between \( \alpha \) and \( \nu \)-relaxations for monosaccharides is more or less similar (see also fig. 4.21).
However, the strength of the \( \nu \)-process for solutes with bigger molecules (fructose and glucose)
is higher in respect to that for \( \alpha \)-process, whereas for deoxyribose (smaller molecule) in water
the strength of \( \alpha \)-process is more prominent than for \( \nu \)-process: \( \Delta \varepsilon_{\nu} / \Delta \varepsilon_{\alpha} \) for water mixtures
with fructose and glucose is equal to \( \approx 1.2 \), for deoxyribose-water mixture the ratio \( \Delta \varepsilon_{\nu} / \Delta \varepsilon_{\alpha} \) is
more than two times smaller, \( i.e. \approx 0.5 \). For the biggest molecule of disaccharide (sucrose) in
water the separation between two processes is much more evident and the strength of the \( \nu \)-process
is also high like in the case of fructose and glucose and, \( i.e. \approx 1.3 \). Also it can be seen
from Arrhenius plot (fig. 4.30) that for water-sucrose mixture \( \tau_{\alpha} \) and \( \tau_{\nu} \) are more separated, and
relaxation times for the \( \nu \)-process \( \tau_{\nu} \) in glassy state are shorter than for monosaccharides-water
mixtures. Such behaviour is typical for the \( \beta \)-relaxation time in family of neat glassformers with

![Fig. 4.28. Concentration dependences of the activation energy \( E_a \) of \( \nu \)-process in glassy state for water mixtures with saccharides: deoxyribose (olive diamond), fructose (black squares), glucose (red triangle), sucrose (blue circles), trehalose (magenta star). Line is guide for the eyes.](image-url)
increasing complexity, like glycerol, xylitol, sorbitol etc. [78], vdW binary mixtures and also was shown in Chapter 3 for ν-process in water mixtures with n-PG oligomers.

![Graph](image)

**Fig. 4.29.** Free from dc-conductivity losses (see Eq. (4.1)) vs. logarithm of frequency for mixtures of different saccharides with 30 wt.% of water.

![Graph](image)

**Fig. 4.30.** Plot of relaxation times vs. reciprocal temperature of 30 wt.% of water in mono- and disaccharides: fructose (black squares), glucose (red triangles), deoxyribose (magenta stars), sucrose (orange circles). Close and open symbols indicate α- and ν- process, respectively. Solid lines are the VFT function fit.
4.2.3 Conductivity: the measure of translational diffusion of ions

In Chapter 3 we showed that dc conductivity for \( n \)-PG oligomers-water mixtures strongly correlates with \( \alpha \)-relaxation time and their linear dependence in double logarithm plot has fractional coefficient \( s \) similar to that found in the literature for the coupling between translational and rotational dynamics [78]. Here we provide the same analysis for the water-sugar mixtures.

The comparison of the relaxation times (\( \tau_\alpha \), \( \tau_\nu \) and \( \tau_\sigma_{\text{DC}} \)) (see also section 3.3) is shown in fig. 4.31(a) as an example for glucose+26 wt.% of water. The \( T \)-dependence of the relaxation times of the dc conductivity is curved like that for \( \alpha \)-relaxation times, but less steep. Similarly at high temperatures \( \tau_\sigma_{\text{DC}} \) is longer than \( \tau_\alpha \), whereas close to the glassy state \( \tau_\sigma_{\text{DC}} \) reaches the same values as \( \tau_\alpha \). Since the dependence of \( \log[\sigma_{\text{DC}}] \) vs. \( \log[\tau_\nu] \) is curved as it was found for \( n \)-PG oligomers, logarithm of dc conductivity is plotted only versus logarithm of the \( \alpha \)-relaxation times (see fig. 4.31 (b)). Dependence of \( \sigma_{\text{DC}} \) vs. \( \tau_\alpha \) for glucose-water mixtures has linear behaviour with the slope \( s \approx 0.67 \) that is a little bit smaller than that found for \( n \)-PG oligomers-water mixtures (see section 3.3).

---

**Fig. 4.31 (a)** Plot of relaxation times vs. reciprocal temperature for the mixture of glucose with 26 wt.% of water: \( \tau_\alpha \) (closed blue circles), \( \tau_\nu \) (open blue circles), \( \tau_\sigma_{\text{DC}} \) (closed black squares); (b) Double logarithmic plot of dc conductivity vs. \( \alpha \)-relaxation times (red stars) for glucose+26 wt.% of water. Lines are linear regressions with slope \( b \), black line is shown for comparison.
As was shown above the molecular dynamics of mixtures of glucose and fructose with equal amount of water is similar, hence the decoupling of dc conductivity and \( \alpha \)-relaxation times has similar character at ambient pressure. To see how pressure effects on degree of the decoupling we constructed the same plots as in fig. 4.31 for fructose+30 wt.% of water at 500 MPa (see fig. 4.32). The similar temperature behaviour of \( \tau_\alpha \), \( \tau_\nu \), \( \tau_{\sigma_{DC}} \) is found for pressure measurements: at high temperatures \( \tau_{\sigma_{DC}} \) is still longer than \( \tau_\alpha \), on the other hand, at low temperature \( \tau_{\sigma_{DC}} \) reaches the same values as \( \tau_\alpha \) and in close vicinity of glass transition \( \tau_{\sigma_{DC}} \) becomes even shorter \( \tau_\alpha \). The slope \( s \) in fig. 4.32(b) is not affected by pressure: the value is the same as for ambient pressure measurements \( (s \approx 0.67) \), a result that was also shown for alcohols and \( n \)-PG oligomers for different isobaric and isothermal scans [78], but it is still less than that for alcohols and \( n \)-PG oligomers.

Fig. 4.32 (a) Plot of relaxation times vs. reciprocal temperature for fructose mixture with 30 wt.% of water: \( \tau_\alpha \) (closed blue circles), \( \tau_\nu \) (open blue circles), \( \tau_{\sigma_{DC}} \) (closed black squares); (b) Double logarithmic plots of dc conductivity vs. \( \alpha \)-relaxation times (red stars) for fructose+26 wt.% of water. Lines are linear regressions with slope \( b \), black line is shown for comparison.

What shown above is obtained for monosaccharides-water mixtures. How the dc conductivity-\( \alpha \)-relaxation time decoupling can be changed if it will be disaccharide-water mixture? Figure 4.33(a) shows the temperature dependences of \( \tau_\alpha \), \( \tau_\nu \), \( \tau_{\sigma_{DC}} \) relaxation times for sucrose-water mixture, where it is clearly seen that \( \tau_{\sigma_{DC}} \) is not too much different from \( \tau_\alpha \), moreover it crosses \( \tau_\alpha \) \( T \)-dependence at much shorter times than for monosaccharides-water mixtures, i.e. the values of dc conductivity are very high in that sample. Moreover, observed slope \( s \) in fig. 4.33(b) is
smaller than for monosaccharides-water mixtures and much smaller than for $n$-PG oligomers-water mixtures.

From the shown above dc conductivity analysis it can be conclude that higher is dc conductivity in water mixtures, the stronger is decoupling of $\tau_{dc}$ and $\tau_\alpha$, i.e. smaller is the slope $s$ in double logarithm plot of $\tau_{dc}$ vs. $\tau_\alpha$ ($s < 1$).

![Fig. 4.33](image)

**Fig. 4.33** (a) Plot of relaxation times vs. reciprocal temperature for the mixture of sucrose with 30 wt.% of water: $\tau_\alpha$ (closed blue circles), $\tau_\nu$ (open blue circles), $\tau_{dc}$ (closed black squares); (b) Double logarithmic plot of dc conductivity vs. $\alpha$-relaxation times (red stars) for sucrose+30 wt.% of water. Lines are linear regressions with slope $b$, black line is shown for comparison.

On the base of what observed for rich in water mixtures of with sugars and glycols we can affirm that the translational (probed by dc conductivity) and rotational dynamics (probed by the $\alpha$-relaxation time) are always coupled through a fractional power law, as observed generally in glass-forming liquids for the Debye-Stokes-Einstein (DSE) phenomenon. The slope $s$ of the power law is goes from 1 to 0.5 on increasing the molecular weight or complexity of the solute (see, for instance, the two extreme cases propylene glycol and sucrose) and so the dynamic heterogeneity and distribution of relaxation times. Moreover, the slope $s$ appears to be independent of pressure. These features are characteristic of conventional glass-formers and do not follow the predictions about DSE relation for network-forming liquids [286] according to which DSE breakdown should occur at the emergence of an increasingly well-structured random tetrahedral network, associated to a fragile to strong transition and the slope $s$ should increase with high pressure up to reach 1. We have shown how all these conditions, probably fulfilled in bulk water, are not verified in rich-in-water mixtures and so a bigger caution (together with high
pressure studies) would be needed before to extend the results obtained for aqueous systems to the bulk case [231].

4.2.4 Mixtures of water in polysaccharides: the case of the bio-macromolecule glycogen

We present here some preliminary results of a study performed in collaboration with Dr. Monica Bertoldo (IPCF-CNR) and the Ph. D. student Dr. Giovanni Zampano of Chemistry Department. Details on the sample preparation and characterization can be found in ref. [287]. We will show how results obtained on water mixtures of this polysaccharide are similar to those presented in the previous sections for other sugar solutions and are also similar to what observed in other hydrated biomacromolecules, like proteins.

Glycogen: general features and preparation

Glycogen is a highly branched polysaccharide of glucose. It is found in most of the tissues of animals, both mammal and non-mammal [288-290]. The highest concentration of glycogen is contained in the liver and skeletal muscles, but it is also present in many other tissues. Glycogen plays a fundamental role in the glucose cycle. Its function in the liver is the maintenance and regulation of blood glucose. In muscles it functions as a source of energy for contractions. Therefore, glycogen can be defined as the main storage form of glucose. Glycogen is a polysaccharide consisting of chains of α-(1,4)-linked glucose residues, which are interlinked by α-(1,6) glycosidic bonds. The fine structure and branched nature of glycogen have been widely studied using a combination of high-performance anion exchange chromatography (HPAEC) and repeated enzymatic treatments with α-amylase and pullulanase [291, 292]. Details of glycogen structure and synthesis pathways can be seen in fig. 4.34, drawn according to the literature [293-295].

The highly branched structure of glycogen and its high hydrophilicity are promising to adsorb and affect large fraction water, preventing its crystallization. The glycogen used in the present work was kindly supplied by “Aziende Chimiche Angelini Francesco ACRAF s.p.a.”. This was obtained from mollusses Mytilus Edulis and Mytilus Gallus Provincialis in a form substantially free of nitrogenous compounds and reducing sugars [296]. For dielectric measurements water-glycogen mixtures with 23 wt.%, 34 wt.%, 53 wt.% and 77 wt.% were prepared by solution casting and drying of 90 wt.% water-glycogen solution on the
electrodes in nitrogen atmosphere. An additional study by modulated differential scanning calorimetry and thermogravimetry was performed on samples with different concentrations, spanning the range 10-79 % water weight fraction [297].

Fig. 4.34. Glycogen: structure and mechanism of synthesis. (A) Glycogen structure according to Whelan’s model. (B) Iterative mechanism of glycogen synthesis: Glycogen synthase (S) promotes the growth of the chains adding glucose units by 1→4 bonds. When a chain has at least 11 residues, the branching enzyme (B) transfers a stretch of 7 glucose residues to another chain making 1→6 bonds between glucoses, and producing the growth of new branches. (C) General view of molecular growth by means of synthesis of new tiers.

**Glycogen: dielectric spectra**

We performed dielectric spectroscopy experiments on different solutions of water and glycogen. The spectra revealed two relaxation peaks, both moving to low frequency on decreasing temperature (see fig. 4.35). Spectra were fitted with a superposition of two Havriliak-Negami functions (Eq. (3.1)), as already introduced in Chapter 3. From the fitting parameters, all the relevant quantities were obtained, like the relaxation time and the dielectric strength of both processes. The slowest peak is more intense and it is less sensitive to temperature than the faster one. The latter is visible only at higher temperatures, when its strength increases.

The relative strength of the two processes is affected by the amount of water. Of course, when the water concentration is higher the whole signal is higher, but the relative strength of the slowest process is also bigger (see fig. 4.36 where spectra related to different concentrations are compared at the same $T$).
Fig. 4.35. Frequency dependence of imaginary part of dielectric function for glycogen+77 wt.% water mixture at ambient pressure and at different temperatures.

Fig. 4.36. Frequency dependence of imaginary part of dielectric function for water-glycogen mixtures with 23 wt.% (stars), 34 wt.% (triangles), 53 wt.% (circles) and 77 wt.% (squares) of water at $T = 183.15$ K and at ambient pressure.

By normalizing the loss spectra by the total dielectric strength, we can compare the relative strength of one process with respect to the other. As it is shown in fig. 4.37(a), on decreasing the
water fraction the slowest process gives a smaller relative contribution and the faster process gains relative intensity.

Fig. 4.37 (a) Log-log plot of normalized imaginary part of dielectric function, $\varepsilon''/\Delta\varepsilon_{\text{tot}}$, vs. frequency for water-glycogen mixtures with 23 wt.% (stars), 34 wt.% (triangles), 53 wt.% (circles) and 77 wt.% (squares) of water at $T = 183.15$ K. (b) Plot of logarithm of frequency maximum against reciprocal temperature of the slow (close symbols) and the fast (open symbols) processes for water-glycogen mixtures with 23 wt.% (triangles), 34 wt.% (crosses), 53 wt.% (squares) and 77 wt.% (circles) of water. Data from ref. [298] of water relaxation in hydrated myoglobin (black line), water confined in vermiculite clay [242, 243] (green diamonds) and of pure ice [299] (violet stars) are also reported.
Roughly, the peak positions (and therefore the relaxation times) did not change too much with water concentration. An overview of the dynamics is shown in fig. 4.37(b) where data for the frequency of loss peak of glycogen mixtures and some literature data on ice [299, 300], on water confined in vermiculite clay [242, 243] and on hydrated proteins [298] are also compared. From the comparison it is clear that the slow relaxation is related to the reorientational motion of water in ice lattice, whereas the faster relaxation is nothing but the ubiquitous $\nu$-relaxation process, related to amorphous form of water. In fact, its activation energy is 54 kJ/mol and the prefactor $\log_{10}[\tau_\infty/s]=-19.9$, approaching values typical of rich-in-water mixtures (see for instance Table 4.1) and of confined water. It is also remarkable the strong similarity with the relaxation time measured for hydration water (50 wt.%) in myoglobin [298], that, on the contrary, have a change in slope around 200 K.

The dynamics of hydrated proteins will be discussed in the next session, but we can anticipate that also for this kind of systems the $\nu$-relaxation time changes its temperature dependence from weaker to stronger on heating across the glass transition temperature (for the hydrated myoglobin reported in fig. 4.37 $T_g\sim200$ K). On the contrary, in the case of glycogen, no deviation from the Arrhenius behaviour has been found. The case of glycogen, with no apparent change in the Arrhenius behaviour, is analogous to what found in hydrated collagen and elastin [301], materials having a quite high $T_g$ value.

Additional information on the glycogen-water mixtures can be obtained from calorimetric measurements. First, from the heat fusion measured in hydrated samples, the amount of crystallized water was estimated. Not all the water present in the sample crystallizes: a fraction of approximately 20 wt.% of the total mixture remains amorphous, irrespective of the total quantity of water. Moreover, while the glass transition temperature of the hydrated glycogen depends strongly on amount of water for low concentration, it levels around an asymptotic value at higher concentration values, when the additional quantity of water transforms into crystalline state (see fig.4.38) and the amount of amorphous water does not exceed 20 wt.%.

Since all the samples investigated by dielectric spectroscopy are for water concentrations higher than 20 wt.%, the glass transition temperature is, for all of them, around 260 K. Therefore, in these systems, characterized by higher $T_g$ than the dynamic range experimentally investigated, there is absence of dynamic crossover for the $\nu$-relaxation in the $T$ range investigated, as similarly observed in hydrated collagen and elastin [301].
Fig. 4.38. Glass transition temperature of hydrated glycogen vs. water fraction from modulated calorimetry measurements. The continuous line is a linear regression of the low concentration regime. The dashed line is the constant value obtained the high concentration regime.

A schematic picture of the spatial distribution of amorphous and crystalline state of water is shown in fig. 4.39. Amorphous water should surround the glycogen branched chains. At high dilution, most of the water is far from glycogen chains and crystallizes below 273 K. The only fraction that remains amorphous is that very close to the glycogen chains. For low concentration of water the amorphous region around the glycogen chains almost fills the whole volume and only a marginal fraction transform to crystals. Also the relative strength behaviour of the two processes can be explained in terms of crystallized and uncrystallizable water as already found in ref. [300].

From calorimetry measurements [297] it was estimated that the amount of uncrystallized water (20 wt.%) is almost the same for all the mixtures of water and glycogen, being located about 2-3 layers around the glycogen macromolecules (see fig. 4.39) but, on increasing the water fraction, the additional water all contributes to the fraction of crystalline water and so the relative strength of the slower process increases, up to mask the $\nu$-relaxation process. On the contrary, the ice relaxation is almost absent for water weight fraction of 23 wt.%. Glycogen is therefore a good system for obtaining large fraction of amorphous water. In summary, we were able to create a system where all the water is in amorphous state at low temperatures. By the way, the behaviour of this water is the same of the uncrystallizable water at higher concentrations and also the same for a completely different system (hydrated protein).
What we have found is a universal behaviour of water confined among bio-macromolecules. This result will be discussed more deeply in the next section.

Fig. 4.39. Schematic pictures of the spatial distribution and thermodynamic state of the water in the mixture with glycogen at different concentrations and temperatures: upper figures – 77 wt.% and lower figures – 34 wt.% of water. The black lines represent the branched glycogen chains, light blue environment with blue dots marks the amorphous water regions, with crossed regions with light blue squares mark the crystalline regions.

4.3 Dynamics of water in hydrated and solvated proteins: the example of lysozyme-glucose system

As show in the previous sections, the dynamics of water seen in many different aqueous mixtures with hydrophilic solutes always present two major relaxation processes: the slow $\alpha$-cooperative relaxation of the water together to the solute hydrogen-bonded to the water and the
ν-relaxation, originating from individual motions of the water component in the aqueous mixtures. The properties of the two processes qualitatively are general and independent of the solute. The most important result is the symbiotic relation between the two relaxations, which indicates the participation of water in both processes. Changes of the two processes with content of water and molecular weight of solute conform to a regular pattern that can be rationalized from the degree of coupling of water to the solute and the molecular mobility of the neat solute or its \( T_g \). A class of hydrated materials that attracts a large interest is proteins. The situation of hydrated proteins and biomolecules in general is different from aqueous mixtures. Only about two layers of water (called the hydration shell) surrounding the folded protein are of importance for the consideration of the dynamics responsible for full activation of the protein functionality [302]. From this, the dynamics of proteins is coupled to that of water or other solvents surrounding the protein molecules. However, in the literature, different views of this coupling and explanation of the dynamics have been offered [154, 185, 303-305]. It is a general achievement that the dynamics of the solvents, both slow and fast can influence strongly the dynamics of the proteins. In particular, it has been shown that how relevant is the dynamics of hydration layer or of the first layers of solvents surrounding the protein [51]. The study of dynamics of hydrated biomolecules is often performed by Mössbauer spectroscopic and neutron scattering measurements of the mean square displacement (MSD), \(<u^2>\), of fast processes that can be observed within the time window typically shorter than the instrument resolution time, which is 140 ns for Mössbauer spectroscopy and 1 ns to 10 ps for various neutron scattering measurements.

The most relevant phenomenon shown by these techniques is the so-called ‘dynamic transition’, i.e. a change in slope of \(<u^2>\) vs. temperature, occurring at some temperature \( T_D \) above \( T_g \), that has been shown to be related to the biological functioning of the protein [306-308]. The transition temperature and the amplitude of the \(<u^2>\) of solvated protein has been shown to be strongly influenced by the solvent, as shown in fig. 4.40 higher is the \( T_g \) of the solvent, smaller the amplitude of the motions and higher the temperature \( T_D \) of dynamic transition.

More surprising, the dynamics probed by neutron scattering has been shown to be the same in solvated proteins and in pure solvent, as shown in fig. 4.41: a striking coupling between solute and solvent is evident.
Finally, studying ternary systems, i.e. protein solvated in aqueous mixtures, the fast dynamics has been shown to be influenced by the water concentration (more water, faster is the dynamics, higher is the $T_D$) and by the viscosity of the mixture (for the same concentration of water, higher $T_D$ is obtained for the mixture of higher $T_g$, see fig. 4.42.
In this section we will show a preliminary study conducted by dielectric spectroscopy in samples of freeze-dried solution of glucose and lysozyme, kindly provided by Prof. Paciaroni of University of Perugia. These samples have been rehydrated in a saturated vapour environment at different levels of hydration (estimated by weighting method) and their dynamics have been studied by dielectric spectroscopy, using also high frequency spectrometers. Dielectric properties of hydrated lysozyme have been studied recently by the group of Prof. Sokolov [174, 185, 186]. They found in their spectra several relaxation processes, and among them, a water related relaxation with characteristic of the $\nu$-process. The relaxation time of this process is affected by the concentration of water, levelling, for concentration enough high to values shown by rich-in-water mixtures and confined water (see fig. 4.43).

The $\tau_\nu$ shows a change of slope on crossing $T_g$, as observed in mixtures. If the relaxation process observed here is the same water related process we observed in mixtures, we can expected that the $\nu$-process observed in lysozyme/glucose/water systems should show the same behaviour of what observed in glucose-water systems.
Fig. 4.43. Relaxation time of the water $\nu$-process vs. temperature for different hydration levels ($h=$ weight water/weight protein). The vertical lines mark the inverse of glass transition temperature of the different mixtures (reproduced from ref. [185]).

In fig. 4.44 we compare the loss spectra at 183 K for hydrated lysozyme at 27 wt.% water fraction and two of our systems of hydrated glucose-lysozyme at different hydration levels, i.e. 32 wt.% and 36 wt.% water. The water relaxation shifts to lower frequencies as well as it occurs to conductivity. The strong conductivity contribution masks the low frequency region, making impossible to reveal the $\alpha$-relaxation.

Fig. 4.44. Loss spectra for solvated lysozyme in different solvents measured at 183 K. (data for hydrated lysozyme are from ref. [185]).
The effect of solvent on the dynamics of hydration water (and so on the protein dynamics) can be better understood through an Arrhenius plot, where also the $\alpha$- and $\nu$-relaxation time of the glucose-water mixtures are also displayed (see fig. 4.45). What emerges is that, on increasing the glucose quantities, the $\nu$-relaxation times of the ternary system glucose/lysozyme/water slow down, coinciding with the $\nu$-relaxation times of the glucose-water mixtures with corresponding water fraction. It is worth noting that the $\nu$-relaxation times observed in hydrated lysozyme are almost coinciding with those characteristic of confined water. We have shown in the previous sections that the effect of solvent on the dynamics of aqueous systems is twofold: both $\alpha$- and $\nu$-relaxations are slowed down but with a different extent, bigger and smaller, respectively. The effect of on the $\nu$-relaxation time of solvated proteins is analogous to what happens in aqueous mixtures.

![Arrhenius plot](image)

**Fig. 4.45.** Relaxation map for solvated lysozyme in different solvents compared with the relaxation times in glucose-water mixtures with the same water fraction. Data of hydrated lysozyme (closed green stars) are from ref. [185]. Data of water confined in MCM-41 (open black stars) are from ref. [172]. Crossed squares are data of mean square displacement from neutron scattering taken from ref. [311] and indicate $X = 1000/T_D$ and $Y = \log(\tau_{NS})$, where is $\tau_{NS} = 4$ ns for IN10 and $\tau_{NS} = 500$ ps for IN13.
It is interesting to note in fig. 4.45 that the dynamic transition occurs at the temperature $T_D$ corresponding to which the water relaxation time is entering in the characteristic relaxation time $\tau_{NS}$ of the neutron spectrometer. In fact, as explained in ref. [51] in case of neutron scattering or Mössbauer experiments, as long as the fluctuations related to the conformational or local orientational motions are slower than the characteristic time of the spectrometer (140 ns for Mössbauer, the resolution $\tau_{NS}$ for neutron scattering) only vibrational and caged motions contribute to $<u^2>$, whose amplitude has an approximately linear increase with $T$. As shown for usual glass-formers [312], the amplitude of caged motions has a mild change on crossing $T_g$, and this phenomenon should occur also in solvated proteins. Moreover, at higher temperatures, as soon as the relaxation processes begin to enter into the experimental spectrometer window, the $<u^2>$ deviates from the linear behaviour. Our data can show that this is the case also for water/glucose/lysozyme. Let’s assume that the coincidence between $\tau_{\nu}$ in glucose-water mixtures and those in glucose/water/lysozyme holds also at high frequencies. In fig. 4.46 we show measurements on two glucose-water mixtures extended to very high frequencies. In the insets it can be noted as at high temperature the $\alpha$- and $\nu$-relaxation processes merge in a single process, whose loss peak has a full width at half maximum (FWHM) of nearly 2 decades. So, we can expect two changes in the slope of $<u^2>$: one coinciding with $T_g$ (due to the caged motions) and another coinciding with the entrance of the relaxation motions into the timescale $\tau_{NS}$ of the neutron spectrometer, that should be located in the vicinity of the temperature $T_D$ for which the loss peak is located one decade slower than $\tau_{NS}$.

In fig. 4.47 we show $<u^2>$ versus temperature obtained for different solvated lysozyme, obtained using IN13 neutron spectrometer [313]: vertical arrows show two temperatures $T_g$ and $T_D$ as obtained from dielectric relaxation data for 38 wt.% water fraction. The coincidence with two changes in slope is evident. The phenomenology illustrated here is general for all the hydrated systems and will be subject of further studies.
Fig. 4.46. Plots of logarithm of relaxation times against reciprocal temperature at ambient pressure of the $\alpha$- (closed stars) and $\nu$- processes (open stars) for 30 wt.% (a) and 38 wt.% (b) of water in glucose. Solid and dashed lines are VFT and Arrhenius fitting, respectively. Horizontal dashed and dotted lines mark respectively $\log(\tau_{NS})$, the time resolution of IN13 spectrometer, and $\log_{10}(\tau_{NS})$. Insets of figures (a) and (b) are examples of spectra for real (closed circles) and imaginary (open circles) parts of dielectric permittivity obtained by high and low frequency measurements for concentrations of water in glucose specified above at 293.2 and 268.2 K, respectively. Solid lines were obtained by the fitting procedure, and dashed lines indicate merged $\alpha$- and $\nu$- processes. The vertical lines show the frequency threshold corresponding to the inverse of the time resolution of Neutron Scattering spectrometer IN13.
Fig. 4.47. Mean square displacement versus $T$ for lysozyme in glucose-water at 38 wt.% water fraction (asterisks) (reproduced from ref. [313]).
Chapter 5

Overview of the Characteristics of Water (ν-) Relaxation in the Metastable Amorphous State of Aqueous Systems

In this final chapter we summarize the dynamic properties of the water specific relaxation in the systems investigated in this thesis work. Three relevant properties will be discussed: the characteristic relaxation time, the dielectric strength and the shape of the relaxation.

5.1 Relaxation time ($\tau_\nu$) of mixed, confined and bulk water

As we have shown in the previous chapters, the dynamics of water mixtures is characterized by two processes, the slower $\alpha$-relaxation, related to the cooperative motions of solute and water, and the $\nu$-process, related to individual motions of the water molecules. The $\nu$-relaxation time at low amount of water is quite affected by the water concentration [307] and by the size of the solute, but, once that the water molar fraction is quite high (80 %), the $\nu$-relaxation times approach similar values, irrespective of the solute, and very close to those obtained for confined water (see Chapter 1).

Figure 5.1 shows the relaxation map for studied water-mixtures in this thesis. As can be seen, the $\alpha$-relaxation depends not only on amount of water but also on kind of solute: it has VFT-like behaviour, but $T_g$ and consequently $T_{cross}$, the temperature marking a crossover between two regimes for $\nu$-process, is different for each system. On the other hand, the $\nu$-relaxation in glassy state almost does not depend on the solute (see also figs. 3.20(a) and 3.37), only the concentration dependence is clearly seen: relaxation time of $\nu$-process becomes shorter on increasing amount of water, moreover, mixtures with $\approx25$ wt.% and $\approx30$ wt.% of water form two groups with more or less similar activation energies but different values of preexponential factor in Arrhenius equation (see Eq. (3.3)).
We have observed that for all studied aqueous mixtures $T_{\text{cross}}$ always occurs few degrees below the glass transition temperature $T_g$ at times exceeding 1-10 ks. For such a value of $\tau_\alpha$ the structural dynamics of the system is completely frozen and water reorientation can occur only on a very local scale. Position of the crossover, i.e. crossover temperature, $T_{\text{cross}}$, as $T_g$ depends on the solute ($T_{\text{cross}}$ increases for solute with higher $M_w$), concentration of water ($T_{\text{cross}}$ decreases on increasing content of water), pressure ($T_{\text{cross}}$ increases on increasing pressure). Both $T_{\text{cross}}$ and $T_g$ are strongly correlated. This can be seen in fig. 5.2, where the couple $T_{\text{cross}}$ vs. $T_g$ is plotted for various systems with different concentration of water, and for some systems at different isobaric conditions. We suggest that the crossover in temperature dependence of $\nu$-process is a manifestation of the glassy state of the overall system. Such crossover usually was found for secondary (local) relaxation of neat and mixed systems of van der Waals liquids [102] when one goes from glassy to liquid state. It is to point out that a good agreement is found also within the same family of systems, like oligomers of ethylene and propylene glycols ($n$-EG and $n$-PG) with increasing molecular weight.
Fig. 5.2. Correlation between $T_{cross}$ and $T_g$. Most of the data are from this work obtained for various rich-in-water solutions at different isobaric scans. Data for ethylene glycols oligomers with two to six repeating units (closed magenta squares) were taken from ref. [182]. $T_{cross}$ and $T_g$ increase on increasing pressure and the number of repeating units of solvent ($M_w$), decrease on increasing of water content ($c_{H_2O}$). Dashed line is linear regression with slope $b = 0.97$.

To summarise, the general trend for the water-related relaxation times, $\tau_v$, on increasing concentration of water in aqueous mixtures was found in this work and in the literature. On increasing amount of water, $\tau_v$ becomes shorter for all isothermal scans above and below $T_g$. In the glassy state where $\tau_v$ has Arrhenius $T$-dependence, the activation energy also decreases, levelling to a constant value around 50 kJ/mol. For example, for water mixtures with low molecular weight solutes such as oligomers of ethylene glycol, 3EG and PEG600, the $\nu$-process at significantly higher concentration than 35 wt.% of water cannot be studied because of water crystallization in it, and hence the limiting Arrhenius dependence of $\tau_v$ at higher water content cannot be obtained. However, higher molar concentration of water in mixture can be achieved by using solute of higher molecular weight such as the polymers, poly(vinylpyrrolidone) (PVP) [168, 300], PVME [167], and hydrogel of poly(2-hydroxyethyl methacrylate) (PHEMA) [170]. The examples of $\tau_v$ determined by dielectric relaxation measurements on mixtures of 35 wt.%
water with 3EG and PEG600 [102, 165], 48 wt.% of water with DPG [166], 45 wt.% of water with PPG400 [222], 50 wt.% of water with PVME [167, 169], 50 wt.% of water with PVP [168], and 50 wt.% of water with PHEMA [170] are shown in fig. 5.3. All these mixtures have a glass transition effected by the $\alpha$-relaxation. Since we concentrate on the water-related process ($\nu$-), for most systems only temperature dependences of $\tau_{\nu}$ are shown in fig. 5.3. Two vertical solid arrows and two vertical dashed arrows indicate the glass transition temperatures and crossover temperatures, respectively, for the water mixtures with 3EG, and with PPG400. $T_{\text{cross}}$ corresponds to the temperature where $\tau_{\nu}$ changes its $T$-dependence from a weaker Arrhenius below $T_g$ to a stronger dependence above $T_g$. This is the case for all aqueous mixtures including those with PEG600, DPG, 5EG, PVME, PVP, and PHEMA, although not illustrated as such. For all those mixtures activation energy of $\tau_{\nu}$ below $T_g$ is within the range from 45 to 50 kJ/mol.

Fig. 5.3. $\log_{10}(\tau_{\nu})$ vs. $1000/T$, of the $\nu$-relaxation of water component in various aqueous mixtures: 35 wt.% water mixture with 3EG (violet left-oriented closed and open triangles for the $\alpha$- and $\nu$- relaxations, respectively); 45 wt.% water mixture with PPG400 (black closed and open squares for the $\alpha$- and $\nu$-relaxations, respectively); 35 wt.% water mixture with PEG600 (black inverted open triangles); 48 wt.% water mixture with DPG (blue open triangle); 50 wt.% water mixture with TPG (black open circles); 50 wt.% water mixture with 5EG (magenta crosses); 50 wt.% water with PVP (green open squares); 50 wt.% water mixture with PVME (red open asterisks); 50 wt % of water with PHEMA (olive triangles with pluses). All data were obtained by dielectric relaxation spectroscopy. Red open circle with plus is $T_g$ obtained from DSC studies of glassy water [141].
The JG relaxation time of bulk water, $\tau_{JG \text{ w} \text{a}}$, can be considered ideally as the limiting value of $\tau_v$ as the molar fraction of water $x_{H_2O}$ approaching 1. Unfortunately, bulk water or water systems with highest amount of water cannot be studied at low temperature because of water crystallization. But from general trend shown in previous Chapters it was observed monotonic decrease of $\tau_v$ on increasing $x_{H_2O}$ in the aqueous mixtures, i.e. it can be assumed that $\tau_{JG \text{ w} \text{a}}$ is shorter than $\tau_v$ observed in all the aqueous mixtures shown in fig. 5.3. In other words, the shortest $\tau_v$ of the mixtures shown can be considered as an upper bound of $\tau_{JG \text{ w} \text{a}}$ at all temperatures.

Figure 5.4 shows the relaxation times, $\tau_{\text{conf}}$, of water nanoconfined in molecular sieves MCM-41 obtained by dielectric relaxation [172], and translational relaxation time determined by neutron scattering of water confined in nanoporous MCM-41-S with pore diameters of 14 Å [148]. Included also are the relaxation times at $10^3$ s of the fast and slow processes of water confined in MCM-41 determined by adiabatic calorimetry [158], relaxation times of water confined in silica hydrogels [244] and the relaxation times of bulk water [138, 315].

The correlation length associated with the $\alpha$-relaxation of water should be suppressed partially if not completely by the reduction of correlation volume caused by nano-confinement. If the observed relaxation is the $\nu$-process of water, then its relaxation time $\tau_{\text{conf}}$ should be close to $\tau_{JG \text{ w} \text{a}}$ of bulk water. It can be seen in fig. 5.5 that the shortest $\tau_v$ of the mixtures is almost indistinguishable from $\tau_{\text{conf}}$ of water confined in MCM-41 and graphite oxide, and this further supports that the shortest $\tau_v$ of the mixtures as well as $\tau_{\text{conf}}$ of water confined in MCM-41 is an upper bound of $\tau_{JG \text{ w} \text{a}}$.

The most convincing way we can demonstrate that the fast water specific relaxation observed in hydrated biomolecules is the primitive or JG relaxation of water is to compare their relaxation times $\tau_v$ shown above in Chapters 1 and 4 (see figs. 1.13 and 4.45) with the primitive or JG $\beta$-relaxation times of the water component in several aqueous mixtures and water nanoconfined shown in figs. 5.3 and 5.4. All data of $\tau_v$ of hydrated biomolecules are shown now in fig. 5.5. Added are the data of $\tau_v$ found in hydrated lysozyme from dielectric relaxation measurements [174], hydrated myoglobin from neutron scattering data [305], D$_2$O-hydrated myoglobin from deuteron NMR [316], and hydrated c-phycocyanin (C-PC) from neutron scattering [317]. Also shown data for water mixture with 1-propanol [165]. We can see that $\tau_v$ of the water specific
process in hydrated biomolecules when it becomes short ($< 10^{-4}$ s in the examples here) is nearly indistinguishable in all the systems and it is very close to that from $\tau$ of aqueous mixtures and confined water.

![Fig. 5.4](image)

Fig. 5.4. Plots of water relaxation times vs. reciprocal $T$ for different confined systems. Dielectric data [172] of $\tau_v$ of water confined in MCM-41 with pore diameter 2.14 nm at hydration levels $h = 0.12$ (black open squares), 0.22 (red open diamonds), 0.55 (blue open squares with + inside). The red solid diamond indicates the relaxation time of slow process of water confined in MCM-41, $h = 0.22$ [172]. Two red crossed circles are relaxation time of slow and fast processes ($\tau = 10^3$ s) of water confined within 1.2, 1.6 and 1.8 nm nano-pores of MCM-41 obtained by adiabatic calorimetry at $T=115$ and 165 K respectively [160] (see right panel). The black open stars are translational relaxation times determined by neutron scattering of water confined in nanoporous MCM-41-S with pore diameters of 14 Å [148]. The olive triangles are relaxation times of water confined in silica hydrogels [244]. The green asterisks and the black open circles are relaxation times of bulk water from [138] and [315], respectively.
Fig. 5.5. Combinations of some data from figs. 5.3 and 5.4 and other data of \( \log_{10}(\tau_v) \) plotted against reciprocal \( T \). Exactly the same symbols and colours are used for aqueous mixtures shown in fig. 5.3: water mixtures with DPG, PHEMA, PVME, PVP, 5EG; and for confined water in: MCM-41 with different pore diameter, MCM-41-S, silica hydrogels (see fig. 5.4). Also shown are the relaxation times of bulk water from [138, 315]. New added data are: the relaxation times of bulk water at higher temperatures and shorter times are shown (red right-oriented triangles) [171]. Also added in the figure are times \( \tau_v \) of water in hydration shell of various proteins: hydrated lysozyme from dielectric relaxation measurements (black diamonds with pluses inside) [174], hydrated myoglobin from neutron scattering data (olive crossed circles) [305], D_2O-hydrated myoglobin from deuteron NMR (olive circles with pluses inside) [316], and hydrated c-phycocyanin (C-PC) from neutron scattering (cyan left-oriented triangles) [317]. Also shown data for water mixture with 1-propanol (black closed circles) [165], water nanoconfined in graphite oxide by dielectric relaxation (violet inverted closed triangles) [245] and by neutron scattering (violet inverted open triangles with pluses inside) [318, 319]. Also added the relaxation times of amorphous ice at 1 GPa (orange open circles) [320]. The red crossed circle is \( T_g \) obtained from DSC studies of glassy water [141].

Not mentioned so far and represented by closed black circles in fig. 5.5 are the relaxation times of water \( \tau_v \) in a mixture of 20 wt.% water with 1-propanol obtained by Shinyashiki and co-workers [165]. It was found in dielectric spectra of 1-propanol-water mixture a new loss peak at
the frequency range lower than all the 1-propanol loss peaks [165]. This new process originates from the motion of water in the mixture with 1-propanol [155, 165] and its relaxation times have been included in the relaxation map of fig 5.5.

What distinguishes 1-propanol from all other solutes in aqueous mixtures discussed so far is that the $\alpha$-relaxation time of 1-propanol, either pure or in the 20 wt.% water mixture, is by far shorter than even $\tau_{\nu}$ of the mixtures as well as $\tau_{\text{conf}}$ of water confined in MCM-41 or in graphite oxide. It can be seen from the low $T_g$ of 1-propanol, which lies below 100 K. Due to this unusual situation, the relaxation process of water found in the mixture is slower than all processes associated with 1-propanol [155, 165]. The monotonic decrease of the relaxation strength with increasing temperature and nearly constant dispersion width parameter $\beta_{CC}$ (Cole-Cole parameter) over a considerable range of temperature above $T_g$ of this process actually reflect that the found process is the $\alpha$-relaxation of water in the mixture [155, 165]. However, this a rather unusual $\alpha$-relaxation because the temperature dependence of the relaxation times of this process is nearly Arrhenius, and not far from the shortest water relaxation times $\tau_{\nu}$ in some of the mixtures as well as $\tau_{\text{conf}}$ of water confined in MCM-41 and graphite oxide as shown in fig. 5.5.

These characteristics of the $\alpha$-relaxation of 20 wt.% water in 1-propanol suggest it has negligible intermolecular cooperativity and a smaller coupling parameter than even bulk water. This can be readily understood because the $\alpha$-relaxation of water in the mixture is facilitated by the presence of the much more mobile 1-propanol.

Thus the $\alpha$-relaxation of 20 wt.% water in 1-propanol effectively is not much different from the secondary relaxation of water, and its relaxation times in fig. 5.5 offer another estimate of the primitive or the JG $\beta$-relaxation time of bulk water $\tau_{\text{JG, bulk}}$, consistent with the estimate given before from the shortest $\tau_{\nu}$ of the mixtures as well as $\tau_{\text{conf}}$ of water confined in MCM-41 and graphite oxide. These facts inspire the construction of the region limited by the dashed lines placed diagonally in fig. 5.5. The vertical span of the rectangle is only one decade, but it seems to encompass the $\tau_{\nu}$ of aqueous mixtures of PVME, PVP, PEHMA, and other aqueous mixtures expected in the high water concentration limit, the $\tau_{\text{conf}}$ of water confined in MCM-41 and graphite oxide, and part of the relaxation times of water in mixture with 1-propanol. Furthermore, it covers the much shorter relaxation times of hydration water in hydrated
myoglobin, lysozyme, and c-phycoceanin, the very short dielectric relaxation time of pure bulk water [138, 171, 315] and amorphous ice at 1 Gpa [320].

All these relaxation times mentioned above are good estimates of the JG $\beta$-relaxation time of bulk water $\tau_{JG}^{bulk}$, and thus the rectangular box limited by dashed lines in fig. 5.5 approximately locates within it the Arrhenius or near Arrhenius temperature dependence of $\tau_{JG}^{bulk}$ over 14 orders of magnitude.

The $\tau_\nu$ in the glassy state of the 48 wt.% water mixture with DPG and 50 wt.% water mixture with 5EG lie conspicuously outside the rectangle but the deviations are due to the fact that water content in these mixtures cannot be increased beyond 50 wt.% without encountering crystallization, which pre-empts measurement of $\tau_\nu$. Thus, the deviation of the $\tau_\nu$ in the glassy state of those water mixtures with DPG and 5EG from the rectangle shown in fig. 5.5 should not be interpreted as violation of the behaviour. It has activation energy of about 46-50 kJ/mol according to the slope of the box. Since the strength of a hydrogen bond is approximately 20 kJ/mol, this corresponds to the energy required to break two hydrogen bonds in order to allow local rotation and translation of the water molecule. Actually, the energy of $E_a \approx 50-55$ kJ/mol coincides with simulation results and theoretical predictions based on a distorted structure with respect to a nearly perfect tetrahedral local order for water molecules, where in some cases the diffusion is possible only breaking three H-bonds [321]. After breaking the hydrogen bonds, the water molecule is free to rotate and translate and the JG relaxation time can be expressed as $\tau_\beta = \tau_\infty \exp(E_a / kT)$. The change from hydrogen-bonded to free rotation translation engenders entropy change, which can explain the prefactor $\tau_\infty$ is of the order of $10^{-19}$ s deduced from the Arrhenius $T$-dependence of $\tau_\beta$ in fig. 5.5. The ability of the water molecule to translate distinguishes itself from secondary relaxation of conventional glass formers such as in amorphous polymers and van der Waals glass formers, where there is only local rotational motion. Moreover, the small size of the water molecule can allow big reorientation jumps, contrarily to what happens in van der Waals glass formers, where usually JG relaxation is related to small amplitude motions.
5.2 Dielectric strength of the \( \nu \)-relaxation: another evidence of the individual nature of water relaxation

In previous Chapters 3 and 4 we have shown already for aqueous mixtures with PPG400 and fructose the temperature dependences of dielectric strengths for \( \alpha \)- and \( \nu \)-processes. Here we would like to summarize the results for all studied mixtures. Figure 5.6(a) shows the temperature dependences of \( \Delta \varepsilon_\alpha \) and \( \Delta \varepsilon_\nu \) for water mixtures with ethylene and propylene glycols and saccharides at ambient pressure. As was discussed before, both \( \Delta \varepsilon_\alpha \) and \( \Delta \varepsilon_\nu \) have general behaviour typical for primary and secondary processes, respectively, in common glassformers: \( \Delta \varepsilon_\alpha \) decreases and \( \Delta \varepsilon_\nu \) increases monotonically on increasing temperature. Moreover, temperature dependence of \( \Delta \varepsilon_\nu \) for all systems change its behaviour from a weaker to a stronger one on heating with an elbow shape that indicate a change of slope in vicinity of \( T_g \) (This behaviour indicates that the glass transition, besides the \( \alpha \)-relaxation, also strongly affects the \( \nu \)-relaxation). It is clearly seen in fig. 5.6(b) where \( \Delta \varepsilon_\alpha \) and \( \Delta \varepsilon_\nu \) are plotted versus rescaled by \( T_g \) temperature. It is worth to note that the change of slope in temperature dependence of \( \Delta \varepsilon_\nu \) corresponds to the temperature where the crossover is observed for the temperature dependence of \( \log_{10}(\tau_\nu) \) (see figs. 3.14, 3.15, 3.34, 4.15, 4.17, 4.20, 4.25). Such behaviour of \( \Delta \varepsilon_\nu \) in aqueous mixtures, that is typical for secondary JG relaxation of a component in non-aqueous mixtures and also in neat glass-formers [96, 271-273], once more confirms the idea that \( \nu \)-relaxation is a secondary process originated from water component [103].

A combined study of NMR and dielectric spectroscopy in polyols [322] demonstrated that there is an empirical relationship between the ratio of dielectric strength of secondary \( \beta \)-over structural \( \alpha \)-relaxation and the cone semi-angle \( \theta \) related to dipole jump reorientation:

\[
\frac{\Delta \varepsilon_\beta}{\Delta \varepsilon_\alpha} = (\sin \theta)^2
\]

(5.1)

In the glassy state, the spatial restriction of local motion is reflected by the low and almost constant (or weakly increasing) value of \( \Delta \varepsilon_\beta \), whereas larger reorientation amplitude is possible above \( T_g \), and hence the stronger \( T \)-dependence of \( \Delta \varepsilon_\beta \) is observed. Identifying the \( \nu \)-relaxation as a secondary process is fully compatible with its dielectric strength behaviour. Nevertheless, we have to bear in mind that it is a water-specific process with hydrogen bonding to the solute. Therefore, some differences in details of the motion of water in the \( \nu \)-relaxation compared with secondary relaxation in van der Waals liquids and polymers can be expected. For instance, in organic glass-formers, the
ratio of dielectric strengths of Eq. (5.1) close to $T_g$ is often quite small (0.08 is the maximum value reported in [322]), while in water specific process the ratio between $\Delta \varepsilon_v$ and $\Delta \varepsilon_\alpha$ can be of the order of unity (see fig. 5.6), corresponding to large jump reorientation angle in the glassy state and possible participation of translation above $T_g$. Such large angle comparable to the tetrahedral angle expected from the dielectric strength of the $\nu$-relaxation have actually been found by NMR in hydrated biomolecules [323]. Actually this result is not surprising if we consider that water is the smallest molecule in Nature that involves hydrogen bonding. The mechanism of this water specific JG relaxation is therefore quite different from the JG relaxation in van der Waals glass formers and polymers. After breaking two/three hydrogen bonds, as suggested by the activation energy $\approx 52$ kJ/mol of the $\nu$-relaxation in most aqueous systems, the water molecule is free to rotate and translate and there is no reason that local reorientation of the small water molecule has to be restricted to small angles, especially above the $T_g$ of the host system.

Fig. 5.6 (a) Dielectric strengths $\Delta \varepsilon_\alpha$ and $\Delta \varepsilon_\nu$ of the mixtures of ethylene and propylene glycol oligomers (PPG400, TPG, PEG400) and saccharides with different mass fraction of water plotted vs. $T$ for ambient pressure measurements. Full symbols are for $\Delta \varepsilon_\alpha$ of the $\alpha$-relaxation and open symbols are for $\Delta \varepsilon_\nu$ of the $\nu$-relaxation. (b) $\Delta \varepsilon_\alpha$ and $\Delta \varepsilon_\nu$ of the studied mixtures are plotted vs. $T/T_g$. Vertical line indicates the temperature $T=T_g$ for correspondent water mixtures. Exactly the same symbols and colours are used for each data set as in fig. 5.6(a).

5.3 Relaxation shape of the $\nu$-relaxation

The dielectric loss spectra of the $\nu$-process were fitted by the Havriliak-Negami function in the manner as usually done for secondary relaxations in glassformers. The broadness parameter, (1-
\( \alpha \), was determined for each aqueous mixture as a function of temperature. The results for studied mixtures with different mass fraction of water are shown altogether as a function of \( T/T_g \) in fig. 5.7. The values of \( 1-\alpha \) only slightly increase on increasing temperature in glassy state for all water mixtures, while in liquid state \( 1-\alpha \) has much stronger temperature dependence and approaches the unit value that is characteristic of Debye process. It is to point out that a good agreement is found also within the same family of systems, like oligomers of ethylene and propylene glycols (PPG400, TPG, PEG400) or saccharides. Moreover, such behaviour of \( 1-\alpha \) shown in fig. 5.7 is compatible with that found for 35% of water with different ethylene glycol oligomers \cite{103, 180, 220} and is similar to that found in \( 1-\alpha \) of the JG relaxation in other glass-formers.

Hence, both the temperature dependences of \( \Delta\alpha \) and \( 1-\alpha \) of the \( \nu \)-process are strong indications that the \( \nu \)-process is the secondary JG relaxation of the water component in the aqueous mixtures.

Fig. 5.7. The broadness parameter of Havriliak-Negami equation (3.1), \( 1-\alpha \), of the \( \nu \)-process in studied aqueous mixtures with different mass fraction of water at ambient pressure shown altogether as a function of \( T/T_g \). Vertical line indicates \( T_g \) for all water mixtures.
The other fractional shape parameter of HN equation $\beta$ (see, Eq. (3.1)) describes symmetry of the relaxation peak ($\beta=1$ for symmetric processes). We found that for the $\nu$-relaxation in water mixtures when fraction of water in a mixture increases, the value of parameter $\beta$ also increases – peak of the secondary process becomes more symmetric on adding water. And at high enough amount of water the $\nu$-relaxation peak becomes symmetric, as generally observed in literature. An example of the temperature and concentration dependences of the $\beta$ parameter are shown for water-sucrose mixtures in fig. 5.8. At some temperatures the values of $\beta$ were fixed to perform meaningful fitting of the spectra.

![Fig. 5.8](image)

Fig. 5.8. Temperature dependences of the shape parameter of HN equation for different concentrations of water in sucrose: 15 wt.% (black squares), 20 wt.% (red circles), 25 wt.% (blue triangles), 30 wt.% (orange stars).

We also performed a line shape analysis of $\varepsilon''(\omega)$ proposed and done by Gainaru et. al. [301] for hydrated collagen and elastin. The dielectric loss can be written in terms of distribution of energy barriers $G(E)$ [301, 324, 325] as:

$$\varepsilon''(\omega) = \Delta\varepsilon \int \frac{2\pi\omega \tau(E)G(E)dE}{1 + [2\pi\omega \tau(E)]^2}$$  \hspace{1cm} (5.2)

If the thermally activated loss peaks and hence $G(E)$ are so broad, like in our case, one can directly obtain a distribution of energies $G(E) = G(T \ln(\omega_0/\omega)) \approx 2\varepsilon''(\omega)/\pi T\Delta\varepsilon$ [301], where $\omega$ –
frequency, $\omega_0$ – preexponential factor in Arrhenius equation ($\tau = (2\pi \omega_{\text{max}})^{-1} = \omega_0^{-1} \exp(E_a/T)$), $\Delta\varepsilon$ – dielectric strength of $\nu$-process.

The results of line shape analysis could be seen in fig. 5.9 where rescaling of dielectric loss spectra of $\nu$-process is shown for PPG400+26% water below glass transition. Moreover, a Gaussian distribution, $G(E) \sim \exp[-(E-E_0)^2/(2\sigma^2)]$ with a standard deviation $\sigma \approx 580$ K, a value typical for $\beta$-processes in small-molecule glass formers [93], is also shown in fig. 5.9 for comparison with resulting distribution of energies for studied water mixture in the glassy state. It is clearly seen that there is only a rough superposition in the spectra: the broadness of the peaks increases on increasing temperature; and shape of the resulting distribution cannot be well approximated by Gaussian one. The deviation from the distribution at large energies is due to $\alpha$-relaxation and dc conductivity. On the other hand, for lower energies (corresponding to higher frequencies) a better scaling occurs.

Fig. 5.9. Frequency dependence of dielectric losses below $T_g$ represented as coloured lines. Rescaled data are obtained for the given choice of $\omega_0$ and a maximum appears at $E_0\approx6800$ K. The circles represent a Gaussian distribution of energy barriers with a variance $\sigma = 440$ K.

The same procedure can be also applied for water mixtures with saccharides. An example for glucose+30% water below $T_g$ is shown in fig. 5.10. The behaviour is similar to that found for PPG400+26% water: broadness of the peaks increases on increasing temperature. Maximum of the distribution of energies appears at $E_0\approx6200$ K. In this case Gaussian distribution is plotted.
with a standard deviation $\sigma \approx 500$ K and again cannot approximate the rescaled distributions. In this case the superposition seems to fail at lower energies, maybe due to the presence, at higher frequencies than the $\nu$-relaxation, of additional secondary relaxation originating by the sugar molecule.

![Graph](image)

**Fig. 5.10.** Frequency dependence of dielectric losses below $T_g$ represented as coloured lines. Rescaled data are obtained for the given choice of $\omega_0$ and a maximum appears at $E_0 \approx 6200$ K. The circles represent a Gaussian distribution of energy barriers with a variance $\sigma = 500$ K. The deviation from the distribution at large energies is due to $\alpha$-relaxation and dc conductivity.

Such deviations of the resulting distributions from the Gaussian ones shown in figs. 5.9 and 5.10 for PPG400+26% and glucose+30% water mixtures and the increasing of broadness of the peaks could be explained that the shape of $\nu$-process for studied water mixtures is not symmetric in glassy state – in other words, the water concentration is still not so high to allow to the $\nu$-relaxation to gain a completely “water-specific” character like in the case of very high water fractions: 35 wt.% with ethylene glycol oligomers [180] or more (around 50 wt.% with different polymeric systems) [156, 167, 326] where the shape of the $\nu$-relaxation peak is symmetric in whole temperature range.
Conclusions

In this work, we studied by means of dielectric spectroscopy aqueous systems in supercooled and glassy state at different isobaric conditions.

Our results show that in aqueous mixtures there are at least two coexisting relaxations. The slower one has properties indicating that it is the structural $\alpha$-relaxation of the aqueous mixture leading, when its relaxation time exceeds 100 s, to glass transition at $T=T_g$. We proved that the faster $\nu$-relaxation originates from water and has the characteristics of the secondary relaxation. The two relaxations are connected as shown by interrelations of their properties in several ways. The interrelations are the same as found in binary mixtures of van der Waals glass-formers, except for some variations caused by the prevalence of hydrogen bondings and the small size of the water molecule compared with other glass-formers.

The water-specific $\nu$-relaxation is ubiquitous in aqueous mixtures, confined water, and hydrated biomolecules. Its relaxation time $\tau_\nu$ and relaxation strength $\Delta\varepsilon_\nu$ change their $T$-dependence from a weaker to a stronger one when crossing $T_{cross}$ (in the vicinity of $T_g$) similar to the same quantities of the faster component in binary mixtures of van der Waals glassformers. Also $\tau_\nu$ and $\Delta\varepsilon_\nu$ are dependent on the molar concentration of water and the molecular weight of the solute. This is due to coupling of water to the solute by hydrogen bonding. The monotonic increase of $\Delta\varepsilon_\nu$ with temperature below as well as above $T_g$ prevents interpretation of the $\nu$-relaxation either as the $\alpha$-relaxation or the merged $\alpha$- and $\beta$-relaxation of water. Instead it is a special kind of primitive relaxation of the Coupling Model or equivalently the Johari-Goldstein (JG) $\beta$-relaxation. Moreover, the relaxation time $\tau_\nu$ of the water-specific $\nu$-relaxation in the glassy state of the aqueous mixtures and hydrated biomolecules assumes the nearly universal Arrhenius $T$-dependence independent of the solute wherever the molar fraction of water in the mixture is sufficiently high. This common $T$-dependence of $\tau_\nu$ of aqueous mixtures is approximately the same as the relaxation of water confined in nano-meter space. It is special because water molecules can translate and rotate after breaking two hydrogen bonds (the activation energy of the $\nu$-relaxation in the glassy is about 50 kJ/mol, the energy needed for that), which distinguish
the \( \nu \)-relaxation from conventional primitive or JG \( \beta \)-relaxation in van der Waals and polymeric glassformers.

Moreover, we observed, by means of dielectric spectroscopy that pressure strongly changes dynamics in rich-in-water solutions:
- the \( \alpha \)-relaxation time, \( \tau_\alpha \), becomes longer on increasing pressure, hence, the glass transition temperature increases.
- a change of dynamics for water related \( \nu \)-process occurs for all isobaric scans: temperature dependence of \( \log_{10} \tau_\nu \) change its behaviour from a weaker (Arrhenius – in glassy state), to a stronger one (VFT-like – in supercooled liquid state) on heating;
- crossover in temperature dependence of \( \log_{10} \tau_\nu \) appears always few degrees below \( T_g \) and behaves different from a similar phenomenon observed in literature for confined water: \( T_{cross} \) increases and \( \log_{10} \tau_\nu(T_c) \) decreases on increasing pressure, consequently the separation between \( \alpha \)- and \( \nu \)-relaxations at the same \( \tau_\alpha \) increases on increasing \( P \).

The secondary relaxation in the mixtures with low content of water is in a way significantly different from that of rich-in-water solutions: it has the characteristics of the Johari-Goldstein \( \beta \)-relaxation occurring in van der Waals and polymeric glassformers and it is mainly influenced by the local dynamics of the solute molecules. Moreover, the studies of the low concentration water mixtures under pressure revealed that crossover in the temperature dependence of \( \log_{10} \tau_\nu \) always appears at the same position for different isobaric measurements in contrary to rich-in-water solutions.

The dynamics of hydrated proteins and biomolecules are similar to aqueous mixtures. Principally there are one slow \( \alpha \)-relaxation responsible for glass transition of the hydrated protein, and one fast relaxation originating from water, which is no different from the \( \nu \)-relaxation in aqueous mixtures in properties, and in values as well as the \( T \)-dependence of its relaxation time \( \tau_\nu \), provided the hydration level is sufficiently high. The dynamic transition in the mean square displacements often observed in protein dynamics studies by neutron scattering or Mössbauer experiments is caused by the entrance of \( \nu \)-process in the experimental window.
Aqueous mixtures of glycols and sugars are also called cryoprotectants for their ability to be supercooled, their bio-compatibility with living matter and their use in cryopreservation. Biological functions are influenced by kinetic and dynamic processes and we showed how dynamics of bio-relevant molecules can be affected by the dynamic properties of these solvents. We hope that this small piece of experimental work could be, in the future, of some utility for life science.
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List of publications and conference contributions

Publication in International Journals


Contributions to Conferences

1. S. Ancherbak, S. Capaccioli, D. Prevosto, K. Grzybowska, M. Paluch, Dynamics of aqueous mixtures at low $T$ and high $P$, 6th International Conference on Broadband Dielectric Spectroscopy, Madrid (Spain), 7-10 September 2010. (Oral)


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