Organization versus frustration: low temperature transitions in a gelatine-based gel

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Abstract. A commercial physical gel composed of gelatine, water and glycerol shows a sol–gel transition which has been resolved by optical rotation measurements by step-wise heating the gel. This transition is not observable in the longitudinal acoustic mode measured at hypersonic frequencies with Brillouin spectroscopy. Depending on the thermal treatment of the investigated material during the sol–gel transition and within the gel state, Brillouin spectroscopy reflects tremendously different hypersonic dynamics. These distinct dynamics are responsible for the formation of different glassy states at low temperatures including that of a glass-ceramic. The large variety of super-cooled and glassy states is attributed to distinct distributions of the gel’s constituents within the samples. Surprisingly, the same gel state can be produced either by annealing the gel over months or by the non-equilibrium effect of thermo-diffusion (Soret effect) in the course of some minutes.

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1. Introduction

Gels undergo so-called sol–gel transitions as a function of temperature, composition, solvent exchange with the environment and other external parameters. The large number of different types of gels can be roughly classified into chemical and physical gels, respectively (e.g. [1]–[5]). Their sol–gel transitions have been extensively investigated [1]–[13]. This paper focuses on the transition behaviour of a gelatine-based physical gel at temperatures well below the sol–gel transition. The related objective concerns the competition between organization of the gel state and frustration mechanisms caused by mutual molecular association tendencies between the constituents of the gel.

The investigated model system is Kaiser’s glycerol gelatine (KGG) from Merck®, composed mainly of glycerol and water, and 7 mass% of gelatine. It shows a thermo-reversible sol–gel transition at about 308 K. The temperature of the sol–gel transition of KGG depends little on the thermal history of the sample. It will be shown that the rate of temperature change has a strong influence on KGG’s molecular dynamics and low temperature states.

The crucial role of water for the molecular dynamics of KGG will be interpreted in terms of its affinity to gelatine, as well as to glycerol. In order to clarify the competing role of glycerol and water in the gelatine-based gel, we have studied the hypersonic properties of different glycerol/water mixtures. In addition, the non-equilibrium process of thermo-diffusion, also called the Soret effect [14, 15] will be discussed for the low temperature behaviour of KGG.

High performance Brillouin spectroscopy, optical investigations, polarimetry and wide-angle x-ray scattering (WAXS) are used as experimental techniques.

2. Experimental

2.1. Samples

As model system, a commercial gel from Merck® called Kaiser’s glycerol gelatine (KGG) was chosen, consisting of 48.3 mass% glycerol, 43.5 mass% water, 7.2 mass% gelatine and 1 mass% phenol. The practical use of this gel is to embed and protect biological samples during investigations with an optical microscope. Because of the high glycerol content, KGG remains amorphous even in the neighbourhood of the freezing temperature of water. The phenol is included in this gel for its antibacterial properties and is supposed to affect KGG’s properties only in an insignificant manner. At ambient temperature, this gel is a transparent soft solid showing static shear stiffness. Its basic molecular network is formed of polypeptide molecules (gelatine) which are interconnected by physical network knots made of triple helices [1, 2], [5]–[9], [12, 13]. These triple helices consist of three single polypeptide helices showing chirality [6, 8, 12, 13]. While heating KGG above its gel–sol transition temperature, the physical network knots disappear continuously [6]–[9], [12].

To study the influence of the gelatine molecules on the hypersonic properties of KGG, three samples consisting only of glycerol and distilled water were investigated. For this purpose, pure glycerol from Merck® containing less than 0.5% water was used. The sample compositions are (glycerol/water mass ratios): G/W (52.6/47.4), G/W (65/35) and G/W (100/0), where the first sample contains the same glycerol/water ratio as KGG.
2.2. Experimental methods

For this work Brillouin spectroscopy was performed on optically transparent samples in order to obtain their longitudinal hypersonic properties. A modified tandem Brillouin spectrometer of the Sandercock type [16] was used in the so-called 90A scattering geometry [16, 17]. For propagating sound modes in an amorphous sample the longitudinal sound velocity \( v_L \) for a given acoustic wave vector \( \vec{q}_{90A} \) (selected by the 90A scattering geometry) is given by

\[
v_L(\vec{q}_{90A}) = f_L(\vec{q}_{90A}) \lambda_{90A} = f_L(\vec{q}_{90A}) \frac{\lambda_{\text{LASER}}}{\sqrt{2}},
\]

where \( f_L(\vec{q}_{90A}) \) is the longitudinal hypersonic frequency, \( \lambda_{\text{LASER}} \) the vacuum laser wavelength and \( \lambda_{90A} \) the acoustic wavelength related to the 90A scattering geometry.

A Verdi laser from Coherent with a wavelength of \( \lambda_{\text{LASER}} = 532 \) nm is used for all investigations. This laser wavelength in combination with the 90A scattering geometry leads to an acoustic wavelength of \( \lambda_{90A} = 376 \) nm. The output power of the laser was kept low enough in order to avoid thermal deterioration of the samples. It should be stressed that in the 90A scattering geometry the acoustic wavelength is strictly independent of the sample's refractive index [16, 17].

Whether the investigated material stays in equilibrium with respect to the probe depends on the ratio between the sample’s structural relaxation times \( \tau \) and the hypersonic frequency \( f_L \) [17]. Either in the low frequency equilibrium state \( (2\pi f_L \cdot \tau \ll 1) \), also called the ‘fast motion regime’, or in the high frequency clamped state \( (2\pi f_L \cdot \tau \gg 1) \), called the ‘slow motion regime’, the acoustic attenuation can be neglected and the measured hypersonic frequencies for the longitudinally polarized sound mode can be considered as real quantities. If the sound attenuation is not negligible \( (i.e. 2\pi f_L \cdot \tau \approx 1) \), Brillouin spectroscopy yields information about the complex hypersonic frequency.

For most Brillouin spectroscopic investigations mentioned in this paper, the samples were placed into block-shaped glass cuvettes sealed either by Teflon plugs or by gluing aluminium foil on the top. These cuvettes are appropriate for our optical continuous flow cryostat. One KGG sample (\( KGG-3 \), see section 3) was put into a self-built disc-like aluminium cuvette possessing two glass windows.

The degree of chirality of KGG was determined around the gel–sol transition by a Sucromat automated polarimeter from Anton Paar OptoTec during time domain measurements. This method consists of heating the sample step-wise by 2 or 5 K and recording the temporal isothermal evolution of the rotation angle. In contrast to many polarimetry studies of gelatine’s sol–gel transition [6, 8, 12, 13], the relaxation response of the rotation angle at a given temperature could be accessed close to the transition. Polarized light with a wavelength of 589.4 nm was used. The temperature of the cylindrical, 5 cm long closed cuvette and that of the sample were stabilized and recorded via a water bath thermostat.

The \( \theta - 2\theta \) x-ray measurements were performed with an automatic two-circle x-ray diffractometer from Panalytical.

3. Results and discussion

As mentioned above, KGG loses its static shear stiffness at the gel–sol transition. This results from the disappearance of a gelatine network through the whole sample, as the number of triple

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helices decreases. Due to the chirality of the network knots and of polypeptide chain segments in between having helical conformation [13], polarimetry can be used to determine the temperature range of the gel–sol transition [6, 8, 12, 13]. As a matter of fact, the evolution of triple helices and polypeptides with helical conformation in the course of the sol–gel transition as a function of temperature and time is still a matter of debate (e.g. [6, 8, 12]).

The inset of figure 1 shows the time evolution of the optical rotation angle $\alpha$ (black line) of KGG after changing the temperature from 296.2 K to 298.1 K (blue line). The final $\alpha$-values of the total step-wise heating experiment are indicated in figure 1. The uncertainty of these data is below the size of the data points. Apparently, the gel–sol transition takes place at about $T_{GS} = 307$ K. A simple Debye model is used for describing the temporal evolution of the rotation angle after a temperature increase, leading to the relaxation times $\tau$ indicated in figure 2. The statistical error bars of the $\tau$-data are smaller than the data points. For five data points, we have estimated enlarged error bars in comparison to the statistical errors as deviations from the fits were apparent.

Before trying to give an interpretation of figures 1 and 2, a general comment about gelatine/water systems is necessary: according to the thorough investigations of Djabourova et al [6], even after a month and a half the amount of gelatine’s triple helices is not saturated in the gel phase after cooling the sample from the sol to the gel state. In addition, comparing the temporal evolution of the rotation angle during cooling and heating a gelatine/water sample through the sol–gel transition with the same temperature rate of 0.5 K min$^{-1}$, it turns out that longer relaxation times are involved in physical network formation than in the network disintegration [12].

Since figures 1 and 2 are measured on heating, we are concerned with the much faster decomposition of triple helices (network knots) and disappearance of helical conformation of the polypeptides [12]. As the static shear stiffness of KGG disappears on heating the gel to the transition temperature $T_{G\sigma}$, this transition temperature coincides with the percolation threshold.
of the polypeptide network. According to figure 1, the angle of optical rotation \( \alpha(T < T_{GS}) \), i.e. the average chirality decreases in the transition regime almost linearly on heating the gel to the gel–sol transition. Surprisingly, related to this decrease is an almost linear increase of the relaxation time \( \tau(T < T_{GS}) \) as derived from the time domain measurements (see figure 2). This means that below \( T_{GS} \) the decrease of chirality needs increasingly more time. From the linear relationships of \( \alpha \) and \( \tau \) versus temperature, we conclude that none of the measured properties couple directly to the order parameter of the percolation transition (no critical behaviour) [3, 4].

According to figures 1 and 2, \( \alpha(T) \) and \( \tau(T) \) change in a nonlinear way above \( T_{GS} \). In contrast to the opposite temperature evolution of \( \alpha \) and \( \tau \) just below \( T_{GS} \), in the temperature regime just above \( T_{GS} \) the relaxation time \( \tau \) decreases in concordance with the average chirality \( \alpha \). In fact, between the relaxation time \( \tau \) and the rotation angle \( \alpha \) a linear relationship exists below, as well as above the vicinity of \( T_{GS} \) (see inset of figure 2). However, the slope and the sign of the piecewise linear function \( \tau(\alpha) \) changes at \( T_{GS} \), indicating the importance of the percolation phenomenon for this relation. Whereas the slope \( d\tau/d\alpha \) is about +9 min per degree below \( T_{GS} \), it is about −94 min per degree above.

The presented database is so small that at this time only a preliminary concept concerning the thermal evolution of molecular conformation, structure formation and related relaxation times is proposed.

Considering the complicated temperature behaviour of the relaxation time \( \tau \) given in figure 2, a pure thermal activation cannot be responsible for this temperature dependency. As the relaxation time \( \tau \) is longest around the temperature of the percolation threshold, additional influences originally introduced by the formation of a macroscopically extended network seem to play a prominent role for the \( \tau(\alpha) \) relation in the gel phase. It seems that on approaching \( T_{GS} \) from below the decomposition of the physical network provides two contributions to the

**Figure 2.** Relaxation times \( \tau \) versus the temperature close to the gel–sol transition temperature \( T_{GS} \). Inset: relaxation times \( \tau \) versus the rotation angle \( \alpha \) close to \( T_{GS} \).
diminishing chirality:

1. The decrease of the amount of helical segments as a consequence of a reduction of mechanical constraints on the molecular network strands due to the loss of triple helices.
2. The decomposition of the triple helices themselves.

As a consequence of this concept and in accordance with the experimental results the decrease of chirality in the gel phase takes increasingly more time when approaching \( T_{GS} \) from below. The diminution of triple helices within the percolated network lowers those mechanical constraints which help to overcome the barriers between helix and coil conformations. As a consequence, the relaxation time \( \tau \) of the remaining helical structures increases. Single polypeptide molecules, which take part in a triple helix are assumed to lose their helical structure only over a certain distance (correlation length). We claim therefore that in the vicinity of the gel–sol transition there exist different correlations above and below \( T_{GS} \) between the average distance between triple helices and the relaxation time \( \tau \) for a given gel. Above the percolation threshold, the action of thermal activation dominates and the number of triple helices drops rapidly with increasing temperature. This leads to the experimentally observed drastically increased slope of \( \tau(\alpha) \) with negative sign.

In contrast to polarimetry, other techniques do not show the sol–gel transition at all since they do not couple to the order parameter of the transition. This seems to be the case for the longitudinally polarized acoustic mode as detected by Brillouin spectroscopy (see below).

The best-annealed KKG which was at our disposal was the one from the original bottle. The material was at rest least for three months at room temperature (298 K) in our laboratory. This sample is called \( KGG-1 \). At room temperature, \( KGG-1 \) shows a hypersonic velocity for the longitudinally polarized phonon mode of \( v_L = 1830 \text{ m s}^{-1} \) (see figure 3(a), black filled squares). The hypersonic attenuation of this acoustic mode (see figure 3(b), black open squares) has on the high temperature branch a significant slope. Thus, the related sound velocity has only approximately reached its static value. On cooling this sample with a mean rate of \( -0.25 \text{ K min}^{-1} \) the hypersonic velocity and the attenuation increase. The maximum attenuation is observed at about 240 K. The temperature position of the damping maximum indicates that the sound velocity data at ambient temperature are close to the fast motion regime confirming that almost quasi-static properties are measured [16, 17].

At about 220 K, \( KGG-1 \) starts to become opaque in the whole cuvette, preventing further Brillouin spectroscopic investigations. This opacity is finally so strong that even films with a thickness of 0.1 mm are completely intransparent for the laser light. Such a sample looks similar to the one shown in figure 6(d). Optical heterogeneities within \( KGG-1 \) on the length scale of the optical wavelengths must be responsible for this strong elastic Mie scattering. This Mie scattering is attributed to segregation within \( KGG-1 \). Optical inspection of this sample while heating shows that the opacity disappears at about 260 K to 265 K, which indicates the existence of melting ice.

The presence of ice in the segregated sample could be confirmed by wide-angle x-ray diffraction. Figure 4 shows for comparison an x-ray spectrum of the demixed sample measured at 100 K and of an original \( KGG-1 \) gel at 295 K. The x-ray peaks of the segregated sample belong all to ice crystals of hexagonal symmetry [18, 19], which were also observed at low temperatures in a water/gelatine mixture of similar gelatine concentration [20]. The \( KGG-1 \) gel shows at 295 K only the expected amorphous halo. A similar double-peak halo exists in the background curve of the demixed sample. The latter result is indicative of an amorphous matrix.
within the demixed KGG-1 sample. Stress cracking in the segregated sample proves that it is completely rigid at 100 K. Consequently, the sample consists of a kind of glass ceramic (glass 1) composed of ice crystals embedded in a glassy glycerol/gelatine/phenol matrix. It is likely that this glassy matrix also contains water molecules [21, 22].

The question is whether KGG-1 gel can be super-cooled sufficiently quickly to form a homogeneous glassy state. In order to elucidate this question KGG-1 was quenched from ambient temperature as rapidly as possible in a liquid nitrogen bath. Beside the appearance of some fissures a transparent sample was obtained (KGG-2) which could be used for Brillouin spectroscopy on heating (see figures 3 and 5(a)). In figure 5(a), the black parts of the cuvette picture are the completely transparent regions of the quenched sample. According to the Brillouin spectroscopic investigation, KGG-2 appears as a glass (glass 2) below the transition

\[ T_{SG} \]

**Figure 3.** Temperature dependence of the (a) longitudinal hypersonic velocity \( v_L \) and (b) longitudinal hypersonic attenuation for four differently prepared KGG samples. Green/red squares: cooling/heating of KGG-3. Other measurements performed on cooling.

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Figure 4. WAXS intensity for KGG-1 at 295 K (black line; counting time 20 min) and the demixed sample at 100 K (red line; counting time 85 min).

Table 1. Thermal history of the KGG samples.

| Sample   | Thermal history                                                                 |
|----------|---------------------------------------------------------------------------------|
| KGG-1    | Stayed at least for three months at 298 K.                                      |
| KGG-2    | KGG-1 quenched to 77 K in a liquid nitrogen bath.                               |
| KGG-3    | A KGG-1 sample heated up into the sol state, cooled from 323 K to about 250 K   |
|          | at $-20\, \text{K}\, \text{min}^{-1}$ and heated up to 300 K.                  |
| KGG-4    | A KGG-1 sample heated up into the sol state, cooled from 323 K to about 250 K   |
|          | at $-5\, \text{K}\, \text{min}^{-1}$, and heated up to 300 K.                  |
| KGG-5    | A KGG-3 sample cooled from 298 K down at $-5\, \text{K}\, \text{min}^{-1}$.     |

The conservation of this bubble during the heating procedure indicates that a network structure is preserved in the KGG-2 sample. Otherwise the bubble would have collapsed after leaving the glassy state.

To improve the understanding of the thermal history’s influence on the acousto-dynamical properties of KGG, a further preparation scenario was chosen (table 1). A gel sample was taken from the original bottle, heated up into the sol state (323 K) and filled in a cuvette. This sample was first cooled at a rate of about $-20\, \text{K}\, \text{min}^{-1}$ to about 250 K and then heated immediately to 300 K. Brillouin measurements were performed on this sample (called KGG-3) on cooling...
Figure 5. Evolution of \textit{KGG-2} on heating, after quenching the sample to liquid nitrogen temperatures. Photos taken at: (a) 124 K, glassy state containing many fissures; (b) 158 K, disappearing fissures in the molten state; (c) 201 K, important Mie scattering of the laser light due to the appearance of optical heterogeneities; (d) 260 K, the laser light cannot penetrate the totally opaque state anymore; and (e) 291 K, transparent gel state.

until 100 K (see figure 3, green squares, mean cooling rate: $-0.4 \text{ K min}^{-1}$). Subsequently, the hypersonic properties were recorded on heating until 350 K with a mean heating rate of $0.09 \text{ K min}^{-1}$ (see figure 3, red squares). Comparing these hypersonic properties to those of the aforementioned samples, several remarks arise.

In contrast to \textit{KGG-1}, \textit{KGG-3} shows no demixing on cooling below 220 K. \textit{KGG-3} remains transparent until 100 K and undergoes a quasi-static glass transition at $T_{\text{gs}}^{\text{KGG-3}} = 165$ K. Remarkably no hysteresis is observed in the hypersonic properties while cooling/heating, which is obviously not the case for the segregating \textit{KGG-1}. Moreover the temperature corresponding to the hypersonic attenuation maximum of \textit{KGG-3} (about 340 K) is about 100 K higher than that of \textit{KGG-1} (240 K)! The hypersonic velocity value of \textit{KGG-3} differs at room temperature also considerably from that of \textit{KGG-1}: almost 3000 m s$^{-1}$ instead of 1830 m s$^{-1}$. As the hypersonic attenuation decreases and the sound velocity increases while lowering the temperature of \textit{KGG-3}, it trespasses an acoustic relaxation process from the acoustic excess damping regime to the slow motion regime attained at about 200 K. The significant discrepancy between the sound properties of \textit{KGG-1} and \textit{KGG-3} is attributed to different molecular dynamics at GHz frequencies.

From figure 3(a), we conclude that no distinct hypersonic anomaly is observed while the sample passes from the sol to the gel state. This means that the order parameter of the sol–gel transition does not couple to the longitudinal sound velocity (at least not at hypersonic frequencies).

The glass transition temperature of \textit{KGG-3}, determined during slow cooling is positioned about 15 K above that of the quenched \textit{KGG-2}. The reverse would be expected if only cooling rates are taken into account. Consequently, the reverse shift of the glass transition temperature indicates that the two glassy states have different morphologies. This means that a further rigid amorphous state of KGG exists (glass 3) having the same overall composition as \textit{KGG-1} and \textit{KGG-2}.

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A reasonable explanation for the described diverse dynamical and morphological behaviour of KGG could be different distributions of the constituents, depending on the thermal treatment of the sample.

Having established the existence of three different glassy states of KGG which cannot be transferred into a common morphological picture, several questions arise: (a) does another thermal treatment of the KGG lead to a sample with further differing hypersonic properties? (b) Is the quasi-static glass transition temperature of KGG-3 shifted to higher temperatures when cooling such a sample faster?

Concerning question (a), the data coloured in grey of figure 3 clearly demonstrate the success of finding a state showing intermediate hypersonic properties. In order to obtain this KGG-4 sample, the KGG was heated to 323 K, then cooled at about $-5 \text{ K min}^{-1}$ to 250 K and immediately heated to 300 K. Thus, the thermal treatment is similar to that of KGG-3, except for slower cooling. Figure 3(b) shows a hypersonic loss maximum at around 260 K which is in between those of KGG-1 and KGG-3. This sample shows no demixing during cooling until the lowest measured temperature of 130 K. The glass branch of the hypersonic velocity curve of KGG-4 is rather short as the quasi-static glass transition takes place around $T_{gs}^{KGG-4} = 155 \text{ K}$. As a matter of fact, this glass transition temperature is positioned in between those of KGG-3 and KGG-2.

Investigating question (b) leads to a really surprising result. Cooling a KGG-3 sample down with a rate of $-5 \text{ K min}^{-1}$, lead to the strange segregation witnessed by the photo sequence of figure 6. KGG samples having undergone such a treatment will be called KGG-5 in the following. Instead of observing a homogeneous transparent sample until 100 K, a segregation process starts from the borders of the cuvette in the form of ball-like structures. On the surfaces of these balls seen below 230 K further balls start to grow until the whole volume of the cuvette is opaque (see figure 6(d)). One should keep in mind that all demixing processes noticed hitherto evolved homogeneously in the whole cuvette volume. The special kind of super-structure development observed for this KKG-5 sample is probably due to the important temperature rate

Figure 6. Growth of ball-like white structures while cooling KGG-3 at $-5 \text{ K min}^{-1}$ below about 230 K. Dimensions of the glass cuvette: $30 \times 15 \times 5 \text{ mm}$. 

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Figure 7. Temperature evolution of the longitudinal hypersonic velocity $v_L$ (filled squares) and of the hypersonic attenuation (open squares) for KGG-1 and KGG-5 (after annealing at 300 K).

compared to the low cooling rate applied to KKG-3. This rather important cooling rate seems to induce significant temperature gradients in the cuvette. According to thermo-diffusion, also called the Soret effect [14, 15], these temperature gradients can provoke concentration gradients of the constituents, e.g. of water. These gradients would be responsible for the initially spherical super-structures which appear according to our observation at first in the corners of the cuvette, which are the coldest parts.

There is no difference in the optical appearance between the fully demixed states of KGG-1, KGG-2 and KGG-5. Heating KGG-5 until 265 K confirmed the vanishing of the opacity already described for KGG-1. It should however be stressed that in general the opacity did not disappear instantaneously. An intermediate, almost transparent state appeared which is interpreted as water droplets suspended in the gelatine/glycerol/phenol matrix. This state disappeared while annealing the material.

To find out whether the similarities between KGG-5 and KGG-1 are restricted to the optical properties, the hypersonic properties of the annealed, transparent KGG-5 were studied on cooling. According to figure 7, the similarity, especially for the hypersonic velocities of both samples is striking (within the margin of error, which is roughly given to be the diameter of the data points). Attenuation data, as obtained by Brillouin spectroscopy, are usually by an order of magnitude less accurate. The good agreement between the sound velocity curves indicates that KGG-3 can be forced via the non-equilibrium Soret effect into a state showing similar optical and hypersonic properties as the one obtained by annealing the gel at ambient temperature for months.

Figure 8 concludes the drastic influence of the thermal history on the low temperature behaviour of KGG. As a function of the thermal history, three different homogeneous glassy states and two glass-ceramic states could be discriminated. This complex thermal behaviour suggests a competition between the association tendencies of water, gelatine and glycerol molecules.

The observed dynamical behaviour is untypical for structural glass formers for which the primary freezing dynamics (the so-called $\alpha$-process) follows over a wide temperature range a
Figure 8. The different low temperature states of KGG depending on the thermal history of the sample.

Vogel–Fulcher–Tammann (VFT) law \[17, 23, 24]\:

\[
\tau_\alpha = \tau_\alpha^0 e^{[\Delta G/R(T - T_0)]},
\]

(2)

where \(\tau_\alpha\) is the \(\alpha\)-relaxation time, \(\tau_\alpha^{-1}\) is the so-called attempt frequency, \(\Delta G\) is the free activation energy for the translational molecular diffusion process, \(R\) is the general gas constant and \(T_0\) is the so-called VFT-temperature at which the \(\alpha\)-relaxation time possibly diverges \[24\]. It is generally believed that in the course of freezing the parameter values of the VFT-law remain invariant during temperature change. In the frame of the kinetic interpretation of the structural glass transition, the operative glass transformation takes place at the temperature at which the relevant experimental time constant crosses the relaxation time \(\tau_\alpha\) \[24\]. The situation is completely different for KGG since the \(\alpha\)-relaxation time depends itself on the thermal history of the samples.

Taking into account that KGG consists to a major part of water and glycerol it seems reasonable to compare the hypersonic properties of our KGG samples after their different thermal treatments to those of a glycerol/water mixture of the same mass ratio G/W (52.6/47.4). Figure 9 (magenta triangles) shows the hypersonic properties of the related G/W sample. Due to segregation of this sample the Brillouin investigation is impossible below 227 K. This demixing tendency is in accordance with the observations mentioned in \[21, 22\]: G/W samples with more than 40 mass parts of water demix on sufficient cooling.

It turns out that the samples KGG-1 and G/W (52.6/47.4) show, within the margin of error, almost a coincidence of their hypersonic properties and of the segregation temperatures (see figure 10). This demonstrates that at hypersonic frequencies sound propagation of the longitudinal acoustic mode is dominated by the water/glycerol mixture and that the eight mass parts of gelatine and phenol play a negligible role.

The similar acoustic behaviour of KGG-1 and the annealed KGG-5 around ambient temperature is in favour of this view: once the ice crystals formed as a consequence of the Soret effect are molten in KGG-5, the probability is higher that molecules from the water droplets meet and associate with glycerol molecules than with gelatine molecules. Thus, the
water droplets formed above 260 K act mainly as water depots for the glycerol. Apparently, approximately the same glycerol/water/gelatine/phenol distribution as found for KGG-1 in the annealed state is obtained for KGG-5.

Comparing the longitudinal hypersonic velocity of the samples KGG-3 and KGG-4 to those of G/W (100/0) and G/W (65/35) (see figure 9) leads to a further striking result. As indicated in figure 10, the hypersonic properties of KGG-3 resemble strongly to those of pure glycerol G/W (100/0), respectively those of KGG-4 to G/W (65/35). The question of why different thermal treatments of KGG lead to hypersonic properties similar to those of different pure glycerol/water compositions arises.

Figure 9. Temperature evolution of the longitudinal hypersonic velocity $v_L$ (filled triangles) and the hypersonic attenuation (open triangles) for three different glycerol/water mixtures.

Figure 10. Comparison between the temperature evolution of the longitudinal hypersonic velocity of KGG-1, KGG-3 respectively KGG-4 and glycerol/water mixtures.
In this context, it should be stressed that water shows at ambient temperature no acoustic relaxation in the GHz frequency range, although there exists a dielectric relaxation for electromagnetic waves at about 3 GHz. Thus KGG-3 can only behave similarly to pure glycerol if on the length scale of the acoustic wavelength (376 nm) and above, the KGG-3 contains percolated regions of glycerol throughout the probe volume, like glycerol in the pores of a nanoporous glass [25]. In our case the analogue to the ‘glass matrix’ consists of an unfrozen mixture of water, phenol and gelatine molecules as percolated matrix material in that glycerol ‘network’. Moreover, the interpenetrating gelatine/water/phenol regions should have sound velocities which are not too far from those of glycerol, but with no acoustic relaxation in the temperature regime of interest. It is assumed that the small amount of gelatine does not produce significant changes of the relaxation behaviour of pure water. Under these circumstances the hydrodynamic properties of KGG are expected to be dominated by those of the glycerol regions.

Concerning the thermal treatment, the KGG-4 sample represents an intermediate situation between KGG-1 and KGG-3. Apparently, the distribution of its constituents reflects an ‘intermediate’ situation. The hypersonic behaviour of KGG-4 meets the hypersonic properties of a water/glycerol mixture of a concentration between pure glycerol and that present in KGG.

4. Conclusion

KGG is a physical gel with a sol–gel transition temperature at about 307 K. In contrast to this rather well defined transition property the transformation behaviour of the gel at lower temperatures strongly depends on the thermal history of the sample. Different thermal treatments presumably change the distribution of the water in the competing gelatine/glycerol mixture of KGG which possesses an identical over-all composition. The achievement of an equilibrium distribution of water in relation to gelatine and glycerol can easily be frustrated. The related different configurations of the constituents within KGG yield very different molecular dynamics at hypersonic frequencies. As a consequence, several homogeneous glassy states can be realized, but also demixing of ice crystals is observed. The Brillouin spectroscopic investigations on KGG are compared with those made on pure glycerol/water mixtures. The latter measurements confirm the hypothesis that different thermal treatments of KGG yield distinct molecular configurations of the constituents. The Soret effect, as a non-equilibrium process, is able to create a gel state which can be produced under normal circumstances only by annealing the KGG for months.

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