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Transient grating experiment on supercooled water

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Abstract

We measured the acoustic and thermal relaxation dynamics on supercooled water in the temperature range from 42 to −17°C by heterodyne-detected transient grating (TG) experiments. The TG signal shows some particular and interesting features that are produced by the anomalous behaviour of the thermodynamic parameters of water. In particular, the thermal diffusion effects disappear in the TG data for a temperature of about 0°C. We found that this effect has to be ascribed to the combination of two different physical phenomena: the anomalous temperature dependence of water density and the contribution to the TG signal from the dielectric variation induced directly by the temperature. This term is usually neglected in both light scattering and TG studies; our data show clearly a non-negligible thermal decay that has to be addressed. The data are analysed using a model based on a simple formulation of the linearized hydrodynamic equations. A Markovian approximation for the memory function is used, since the structural relaxation times are much faster than the other responses analysed.

§ 1. Introduction

During the last few years, transient grating (TG) experiments have been confirmed as one of the most interesting and promising spectroscopic tools for obtaining new information on the dynamics of supercooled liquids (Yang and Nelson 1995a,b,c, Torre *et al.* 2001). The quality and the richness of dynamic information yielded by these experiments are definitely unique. It has recently been shown, both experimentally and theoretically, that a better definition of the signal measured in TG experiments is really needed (Taschin *et al.* 2001) and that different contributions to the signal, coming from several excited material modes, have to be taken into account. For example, the TG measurements in supercooled liquids with an anisotropic molecular polarizability revealed new contributions in the signal that has to be addressed by the rotational dynamics (Pick *et al.* 2003); the TG pattern shows

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the presence of a non-exponential decay in the long-time window that has to be attributed, in molecules with isotropic polarizability, to the coupling of structural and entropic modes (Di Leonardo *et al.* 2003a,b). So these studies clearly explain how the TG signal has to be carefully considered depending on the material investigated.

We performed a TG experiment on supercooled bulk water in order to measure the acoustic processes and the thermal diffusivity. We found a very peculiar temperature dependence of the TG signal. These effects can be interpreted according to a simple hydrodynamic model where the induced dielectric variation includes the standard density effect and the unusual temperature effect.

§ 2. Experiment and results

In a TG experiment (Torre *et al.* 2001), two high-power laser pulses obtained by dividing a single pulsed-laser beam interfere inside the sample to produce a spatially periodic variation in the dielectric constant. This modulation can be probed by a third continuous-wave laser beam of a different wavelength to that of the pump. It impinges on the induced grating and is subsequently diffracted by it. Measurement of the diffracted intensity permits one to obtain dynamic information on the relaxation of the induced TG. The experimental results presented in this paper have been performed with a laser system and optical set-up exhaustively described by Torre *et al.* (2001). In a heterodyne-detected transient grating (HD-TG) experiment the measured signal can be directly connected with the dielectric response function R^{ε} of the material and hence with the induced dielectric constant variation $\delta\varepsilon$. When the excitation pulses have very short duration and large spot size, that is impulsive limits in time and space, the TG signal can be defined by the following expression (Di Leonardo *et al.* 2003b, Pick *et al.* 2003):

$$S^{\mathrm{HD}} \propto R^{\varepsilon}(q,t) \propto \delta\varepsilon(q,t). \tag{1}$$

So the HD-TG signal is proportional to the time evolution of the induced dielectric constant variation.

Supercooling bulk water is not a trivial task and only a very pure sample can reach and maintain this condition. The supercooling ability is also strongly reduced by any sharp edge present in the cell. So we performed the measurements on a sealed ampoule of cylindrical shape, prepared for pharmaceutical purposes by the Collalto Company, which allowed us to reach a temperature of -17°C. In the experimental set-up, the sample temperature is controlled by a home-made cryostat with a stability of 0.1 K. The ampoule is inserted into an aluminium holder fixed to a cold plate of a Peltier cooler, and the temperature is controlled by a thermoresistance in thermal contact with the aluminium holder. In order to limit the optical distortions induced by the cylindrical lens as a result of the ampoule shape, the scattering plane has been rotated by 90° with respect to the standard experimental configuration (Torre *et al.* 2001). In this way, the wave vector q characterizing the induced TG has the same direction as the ampoule cylindrical axis.

We report in figure 1 the HD-TG data at $q = 0.630\,\mu\mathrm{m}^{-1}$ with the polarization configuration of two pumps, probe and detection beams orthogonal to the scattering plane (called in previous work the VVVV configuration). As expected on the basis of the previous studies, the data show a damped oscillation produced by the acoustic phonons superimposed on a slow exponential decay, generated by the thermal

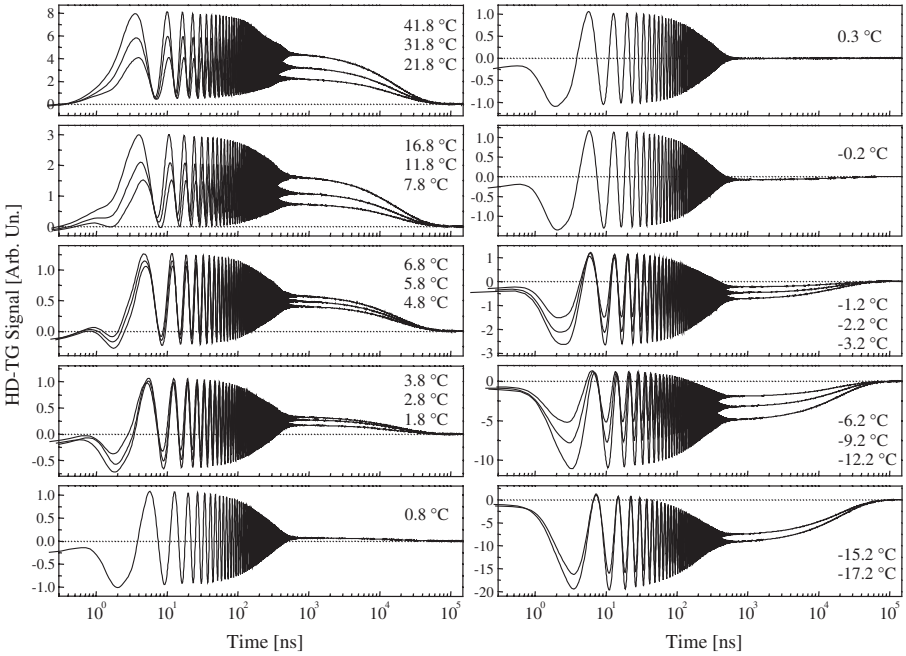

Figure 1. HD-TG data on water at $q = 0.630\,\mu\text{m}^{-1}$ at several temperatures. The data are reported in the same order as the listed temperatures (e.g. in the upper left graph, 41.8°C corresponds to the upper curve, 31.8°C to the middle curve and 21.8°C to the lower curve). The data show acoustic oscillations with an almost temperature-independent damping rate and slow thermal exponential decay. In particular, the amplitude of the thermal mode vanishes at a temperature of 0°C and changes sign for lower temperatures.

processes. However, even a simple look at the temperature dependence of the signal features gives a clear indication of the anomalous behaviour of the TG signal of water. In particular, the amplitude of thermal decay shows anomalous temperature behaviour; it vanishes at a temperature of about 0°C and changes sign for lower temperatures in the supercooled phase. On the basis of the previous model used in the TG analysis, the amplitude of the thermal decay is directly proportional to the thermal expansion coefficient. In water this thermodynamic parameter becomes zero at 4°C, where water has the maximum density. Our experimental results present the disappearance of the thermal decay at a different temperature, at about 0°C, in conflict with the predictions of the previous models. So, to explain the TG data for water, the definition of the measured signal has to be reconsidered.

§ 3. Hydrodynamic model and data analysis

In order to analyse the TG data for water we need a theoretical model to describe and calculate properly the variation $\delta\varepsilon(q, t)$ (see equation (1)). This observable can be linked to the material modes using the following equation (Boon and Yip 1980):

$$\delta\varepsilon \propto \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \delta\rho + \left(\frac{\partial\varepsilon}{\partial T}\right)_\rho \delta T, \tag{2}$$

where $\delta\rho$ and δT are the variations, with respect to the equilibrium values, of the local density and temperature respectively in the sample.

The reported equation (2) has been extensively investigated in light scattering (LS) experiments. In fact, the LS signal is proportional to the Fourier transform of the dielectric correlation functions $\langle \delta\varepsilon(t)\,\delta\varepsilon(0)\rangle$, $\delta\rho$ and δT being produced by the spontaneous fluctuations. Typically, in a LS experiment the signal is dominated by the first term $(\partial\varepsilon/\partial\rho)_T\,\delta\rho$, since $(\partial\varepsilon/\partial\rho)_T \gg (\partial\varepsilon/\partial T)_\rho$, and the magnitudes of $\delta\rho$ and δT are of the same order.

In the case of water the identification of this contribution in the LS signal is complicated by the anomalous temperature dependence of density. In fact, even if the ratio $(\partial\varepsilon/\partial T)_\rho/(\partial\varepsilon/\partial\rho)_T$ is about 10^{-5}°C cm^3 g^{-1} for all temperatures, the magnitude of $\delta\rho$ is strongly temperature dependent because the coefficient of thermal expansion is zero at 4°C. So around this temperature the thermally induced density variation is negligible, $(\delta\rho)_T \approx 0$, and it has been shown (O'Connor and Schlupf 1967) that the Rayleigh signal is dominated by the second term, $(\partial\varepsilon/\partial T)_\rho\delta T$.

In a TG experiment the density change $\delta\rho$ and temperature change and δT are not spontaneous. In fact, in molecular liquids, the variation in the dielectric constant is produced by two main channels of excitation: firstly, the excitation laser beams are partly absorbed, generating a local heating that consequently results in a change in the local temperature and density; secondly, they create an instantaneous electrostrictive pressure, causing again a density perturbation. Typically the temperature grating, also called Impulsive Stimulated Thermal Scattering (ISTS), dominates the TG signal in the slow-time window and it produces the density change that can be evaluated by the following equation:

$$|\delta\rho| = \left|\left(\frac{\partial\rho}{\partial T}\right)_P \delta T\right|. \tag{3}$$

Since in water $\left|(\partial\rho/\partial T)_P\right|$ is of the order of 10^{-5}–10^{-4}°C^{-1} g cm^{-3}, the induced $(\partial\varepsilon/\partial\rho)_T\,\delta\rho$ term, in a TG experiment, is of the same order as $(\partial\varepsilon/\partial T)_\rho\,\delta T$ term, for all temperatures.

The data, as in other TG experiments (Yang and Nelson 1995b,c, Torre *et al.* 2001), can be analysed using the linearized hydrodynamic equations (Boon and Yip 1980) as motion equations for density and temperatures change. In the range of temperatures analysed, the structural relaxation times of water (typically some picoseconds) (Winkler *et al.* 2002) are always faster than the other material responses (larger than 1 ns). Therefore, we used a simple formulation of the hydrodynamics with a Markovian approximation for the longitudinal viscosity memory. Under this hypothesis the hydrodynamic equations in the q space are (Yang and Nelson 1995b):

$$\begin{aligned} &\frac{1}{q^2}\frac{\partial^2}{\partial t^2}\delta\rho + \frac{c_0^2}{\gamma}\delta\rho + \frac{c_0^2}{\gamma}k\rho_0\delta T + v_{\mathrm{L}}\frac{\partial}{\partial t}\delta\rho = F(q,t),\\ &\rho_0 c_V\frac{\partial}{\partial t}\delta T - \frac{c_V(\gamma-1)}{k}\frac{\partial}{\partial t}\delta\rho + q^2\lambda\delta T = Q(q,t), \end{aligned} \tag{4}$$

where c_0 is the adiabatic sound velocity, γ is the specific heat ratio, $k = -\rho_0^{-1}(\partial\rho/\partial T)_P$ is the thermal expansion coefficient, v_{L} is the longitudinal viscosity, c_V is the isobaric specific heat, ρ_0 is the equilibrium density and λ is the thermal conductivity coefficient. $F(q,t)$ and $Q(q,t)$ are the thermal and electrostrictive driving forces respectively which, in the limit of infinitely short pump–laser pulses and slowly varying envelope approximation of fields, can be written as $F(q,t) = F_0\delta(t)\delta(q \pm q_0)$

and $Q(q,t)=Q_0\delta(t)\delta(q\pm q_0)$. Equations (4) with these forcing terms have a simple analytic solution which can be written as follows:

$$\begin{aligned} S^{\mathrm{HD}} &\propto \delta\varepsilon \\ &\propto \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \delta\rho + \left(\frac{\partial\varepsilon}{\partial T}\right)_\rho \delta T \\ &= A\exp(-\Gamma_{\mathrm{A}}t)\cos(\omega_{\mathrm{A}}t) + B\exp(-\Gamma_{\mathrm{A}}t)\sin(\omega_{\mathrm{A}}t) + C\exp(-\Gamma_{\mathrm{H}}t), \end{aligned} \tag{5}$$

where Γ_{A} is the acoustic damping rate, $\omega_{\mathrm{A}}=c_0q$ is the sound frequency and Γ_{H} is the thermal relaxation.

Defining $E=(\partial\varepsilon/\partial T)_\rho/(\partial\varepsilon/\partial\rho)_T$, the amplitudes A, B and C at the lowest order of q are

$$\begin{aligned} A &= -\frac{Q_0}{c_p}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T\left(k+E\frac{\gamma-1}{\rho_0}\right), \qquad B = -\frac{qF_0}{c_0}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T\frac{1}{k}\left(k+E\frac{\gamma-1}{\rho_0}\right), \\ C &= \frac{Q_0}{c_p}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T\left(k-\frac{E}{\rho_0}\right). \end{aligned} \tag{6}$$

The vast literature on water provides the values of all thermodynamic parameters appearing in the hydrodynamic equations for almost the full temperature range analysed. ρ and γ values can be taken from O'Connor and Schlupf (1967) and Hare and Sorensen (1986), c_p from Johari *et al.* (1996) and from NIST (2003) and λ from IAPWS (1998). Furthermore in the paper by Hare and Sorensen (1986) we can find the values of the isothermal compressibility k_T, the refractive index n and its derivatives $(\partial n/\partial T)_P$ and $(\partial n/\partial P)_T$. Hence we calculate the E ratio, using the standard formula connecting dielectric with the index derivatives $(\partial\varepsilon/\partial\rho)_T=(\partial n/\partial P)_T 2n/\rho k_T$ and $(\partial\varepsilon/\partial T)_\rho=2n\left[(\partial n/\partial T)_P+(\partial n/\partial P)_T\,k/k_T\right]$, and the parameters obtained from literature. Furthermore we can estimate the $\left|E(\gamma-1)/k\rho_0\right|$ value which turns out to be less than 10^{-3}, in the whole temperature range available. This result allows us to simplify the expressions for the amplitudes A and B. In fact they can be approximated by the following equations:

$$A \approx -\frac{kQ_0}{c_p}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T, \qquad B \approx -\frac{qF_0}{c_0}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T. \tag{7}$$

The E ratio that will not modify the amplitude of the oscillating part of the TG signal does not appear in these equations. Also the expression for the amplitude C cannot be approximated. So a measurement of this amplitude allows an experimental investigation of this physical parameter.

Figure 1 shows how the damping rates of the acoustic phonons appear almost temperature independent in our TG data. This is due to an experimental limit and not to a real physical effect. In fact, when the damping rates are very small, as in water, the acoustic oscillations are damped because the two induced counter-propagating waves arise in the probing area and not for the effective damping processes present in the material (Yan and Nelson 1987). For this reason the experimental results are fitted with the following equation:

$$S^{\mathrm{HD}} \propto Af(t)\cos(\omega_{\mathrm{A}}t) + Bf(t)\sin(\omega_{\mathrm{A}}t) + C\exp(-\Gamma_{\mathrm{H}}t), \tag{8}$$

where ω_{A}, Γ_{H} and the amplitude constants A, B and C are free-fitting parameters and the acoustic exponential damping has been substituted by $f(t)$. This function is

defined as the envelope of the acoustic oscillations, extracted from the each data. $f(t)$ is equal to 1 for $t=0$ and decreases for $t>0$ following the extracted profile. This fitting procedure, which includes an instrumental response convolution, allows us to extract safely the values of the amplitudes A, B and C.

In figure 2 we report the sound velocity, obtained by our TG data, versus temperature compared with literature data (O'Connor and Schlupf 1967, NIST 2003). Figure 3 shows the temperature behaviour of the thermal diffusivity

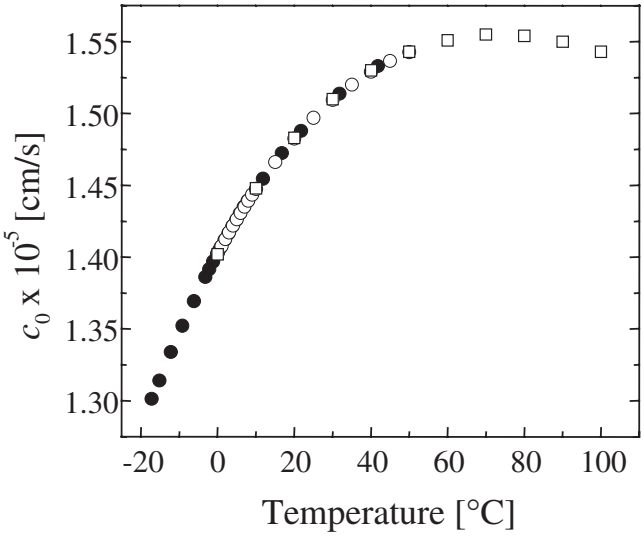

Figure 2. Temperature dependence of the adiabatic sound velocity c_0 from the literature and the present study: (●), data from our study; (○), from O'Connor and Schlupf (1967); (□), from NIST (2003).

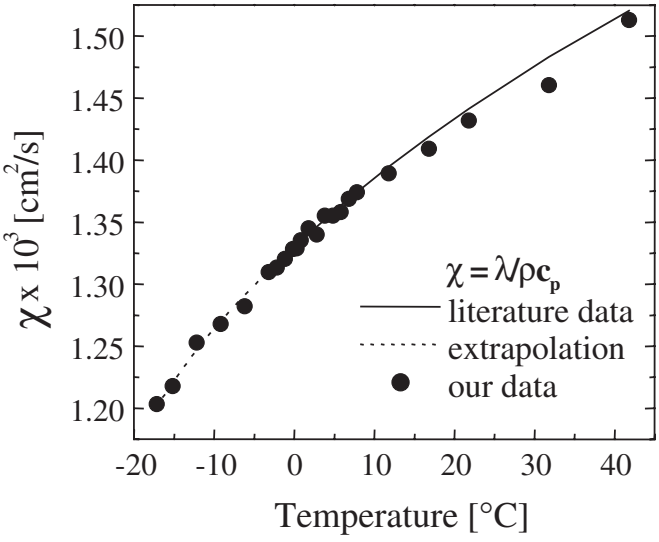

Figure 3. Thermal diffusivity $\chi=\lambda/\rho_0 c_p=\Gamma_H/q^2$ versus temperature. Our data (●) are compared with the second-order polynomial fit (——, - - - -) of reference data from IAPWS (1998).

$\chi = \lambda/\rho_0 c_p = \Gamma_H/q^2$. The χ values corresponding to 0.8, 0.3 and -0.2°C are not reported because the thermal decay amplitude is so weak that we could not extract any safe value for Γ_H. The diffusivity data are compared with the second-order polynomial fit of the literature data (IAPWS 1998). The sound velocity and the thermal diffusivity found in the present experiment extend over a large temperature range which includes the supercooled water phase, where the literature data are not available. Nevertheless, in the overlapping temperature range, very good agreement is obtained.

The extracted values of the amplitude constants A, B and C clearly show temperature dependences. Because in this experiment we did not record the pump pulse intensity we cannot extract accurate information from the absolute signal intensity. Otherwise, since Q_0 and F_0 are both proportional to this intensity, we can calculate the ratios A/B and A/C and overcome the problem. Considering that F_0 is proportional to the electrostrictive coefficient $\rho_0(\partial\varepsilon/\partial\rho)_T$, the theoretical expressions for the ratios are $A/B = (Q_0/q)c_0(\partial\rho/\partial T)_P/\rho_0^2 c_p(\partial\varepsilon/\partial\rho)_T$ and $A/C = -(\partial\rho/\partial T)_P/[E - (\partial\rho/\partial T)_P]$. In figure 4 we report the experimental value of these ratios and their theoretical prediction calculated from the previous expressions on the basis of the literature data (O'Connor and Schlupf 1967). To calculate the theoretical values of A/B we neglect the Q_0 temperature dependence due to the absorption

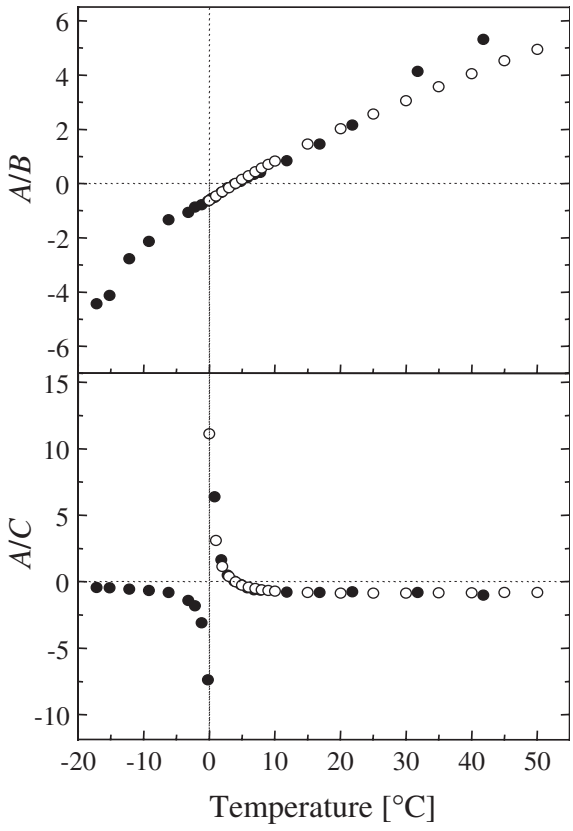

Figure 4. Comparison between the experimental (●) and theoretical (○) temperature dependences of the ratios A/B and A/C. The thermodynamic parameters necessary to calculate the theoretical ratios are extracted from O'Connor and Schlupf (1967).

coefficient and the refractive index. Since we are not able to give an absolute value of Q_0, this parameter is properly adjusted to match the A/B data, while the literature data on A/C are compared without any proportional factor. Our experimental results, A/B and A/C, verify a zero crossing point at 4°C as predicted by our hydrodynamic model. This effect is due to the disappearance of the thermal expansion coefficient and consequently of the amplitude A. Moreover the A/C ratio, obtained from TG data, presents an asymptotic behaviour around 0°C as expected by the model. In fact at this temperature the amplitude C vanishes, because the coefficient E/ρ_0 is equal to k.

§4. Conclusion

We performed measurements of the acoustic and thermal relaxation dynamics on supercooled water in the temperature range from 42 to −17°C by HD-TG experiments. The TG signal shows some particular and interesting features; in particular the thermal diffusion effects disappear in the TG data for a temperature of about 0°C. This feature cannot be explained by considering only the dielectric change induced by the density. Hence, the TG signal has to be reconsidered and all the possible contributions to it have to be taken into account. We found that the dielectric variation induced by the temperature becomes indispensable in defining the signal in water and the contribution from the $(\partial\varepsilon/\partial T)_\rho$ term must be included.

Using a simple hydrodynamic model, we calculated the complete TG response by introducing the direct effect of temperature on the dielectric function. This model is able to explain fully the TG data in all the temperature range investigated including the supercooled state. Furthermore it allows us to obtain a very good fit of the water data and to extract several interesting physical parameters. The present TG data yield new information about the sound velocity and the thermal diffusivity of bulk supercooled water. Nevertheless, this work opens up new problems concerning the TG signal definition. In fact the contribution of the $(\partial\varepsilon/\partial T)_\rho$ term must be taken into account and it cannot be considered *a priori* negligible.

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