On the origin of the \( \lambda \)-transition in liquid Sulphur

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(Dated: February 1, 2008)

PACS numbers: 62.60.+v,64.70.Ja,62.10.+s,82.35.-x

Developing a novel experimental technique, we applied photon correlation spectroscopy using infrared radiation in liquid Sulphur around \( T_\lambda \), i.e. in the temperature range where an abrupt increase in viscosity by four orders of magnitude is observed upon heating within few degrees. This allowed us - overcoming photo-induced and absorption effects at visible wavelengths - to reveal a chain relaxation process with characteristic time in the ns range. These results do rehabilitate the validity of the Maxwell relation in Sulphur from an apparent failure, allowing rationalizing the mechanical and thermodynamic behavior of this system within a viscoelastic scenario.

Common wisdom holds that liquids become less viscous as the temperature is raised. On a microscopic ground, indeed, viscosity can be regarded as arising from continual brushing of molecules which are close to each other. On increasing temperatures the more vigorous thermal motion of the molecules is expected to render such mutual friction progressively less effective. This naive description provides a qualitative interpretation of the decrease in viscosity normally observed in almost all substances as the temperature increases. There exist, however, a few remarkable exceptions exhibiting complex behavior, which can be regarded as extreme examples of how critically viscosity depends upon molecular interactions. Specifically, there are ranges of temperatures in which the viscosity of Sulphur exhibits anomalous temperature dependence. In the liquid state, just above melting (\( T_m=119^\circ C \)), eight-membered rings (S8) are the most abundant species, and the viscosity slightly decreases with temperature as normally expected, reaching values as low as 0.01 Pa·s at \( T = 157^\circ C \). Further increase of temperature causes a dramatic increase of viscosity \( \mu \), accompanied by gross changes in optical \( \bar{\alpha}, \overline{\alpha} \) and thermodynamic \( \tau, \tau' \) properties, which, at \( T\approx 185^\circ C \), reaches a maximum value of 100 Pa·s. Beyond this temperature, a gradual viscosity decrease is observed. Although this phenomenon, known as \( \lambda \)-transition \( (T_\lambda = 159^\circ C) \), has been tackled for more than 150 years, its comprehension is still far from being reached: to rationalize this puzzling temperature dependence of viscosity, indeed, a liquid-liquid transition from a monomeric (i.e. a S8 rings liquid) to a polymeric phase has been invoked \( 2,4,8 \). The temperature dependence of the mass fraction of S atoms participating in the polymeric component turns out to be a central parameter for extracting information on many thermodynamic aspects of the \( \lambda \)-transition \( 9,10 \). This phenomenon has been classified as a living polymerization \( 11 \) transition that essentially involves two steps, the initiation (formation of diradicals through opening of S8 rings) and propagation (concatenation of species to form long polymeric chains). Thermo-chemical models were developed in the past \( 12,13,14 \) to relate the transport properties of liquid sulphur to the underlying polymerization phenomenon. There are, however, provocative aspects of the \( \lambda \)-transition still not fitting into the proposed pictures. These are mostly related to the difficulty of casting the mechanical properties of S within the usual viscoelastic scenario, up to the extent that a break down of the Maxwell relation has been proposed for this liquid \( 15 \).

In this Letter, we report on the experimental evidence of a previously unobserved low frequency relaxation, detected in the 1-10 kHz region by means of infrared photon correlation spectroscopy (IR-PCS). The application of optical spectroscopy techniques is critical in liquid Sulphur, since its absorption spectrum is considerably different \( 2,4 \) between the monomeric and the polymer-dominated phase. Specifically, undesired absorption and photo-induced changes occur when studying the liquid with visible laser wavelengths on increasing temperature above \( T_\lambda \) \( 16 \). To overcome these problems, we developed a new technique employing a near infrared radiation as probing field (\( \lambda=1064 \) nm), namely Infra-Red Photon Correlation Spectroscopy (IRPCS). The revealed relaxation, which implies the existence of a temperature dependent plateau \( 17 \) of the elastic modulus, allowed us to give a coherent picture of mechanical and thermodynamic properties of S within a viscoelastic scenario through a modified version of the Maxwell relation.

Infrared Photon Correlation Spectroscopy (IRPCS) was performed using a solid state laser source operating at \( \lambda = 1064 \) nm. The detector was a Perkin Elmer avalanche photodiode retaining a 2% quantum efficiency at the probe wavelength, with a dark count rate of 50 counts/sec and an after pulse probability lower than 0.3%. The incident beam was focused onto the sample and the scattered radiation was collected by a lens and
then collimated onto an optical fibre through an IR optimized collimator from OZ-Optics. The scattering angle $\Theta = 90^\circ$ defines the momentum transfer, $Q$, of the experiment through the relation $Q = \frac{4\pi n}{\lambda} \sin \frac{\Theta}{2}$, where $n$ being the refractive index of Sulphur ($n_{1064} \approx 1.847(1.863)$ - the first value refers to 140 °C while the second one in parenthesis to 183 °C). The sample was heated in a furnace whose temperature, measured by means of a platinum resistance thermometer, was stabilized within 0.1 °C. The digital signal coming out from the detector was acquired by a National Instruments card and processed by a software package (PhotonLab [29]) performing real time autocorrelation. Correlation functions were collected at constant temperatures during an upscan in the range 145 $^\circ$C $< T < 250$ $^\circ$C, with an integration time of 30 min after 20 min stabilization time at each temperature. The temperature step was half degree around the transition, and coarser far from the transition.

Selected examples of the autocorrelation functions of the scattered intensity measured in a broad temperature range around the $\lambda$-transition are reported in Fig. 1. The existence of a previously unobserved relaxation process can be easily observed and, already from the raw data, an unusual behavior is detected: Upon heating above the melting point the relaxation time is in the $10^{-4}$ s range, and it rapidly increases reaching its longer timescale at $T_\lambda$, then it decreases up to the higher measured temperature $T=250$ °C. To extract the relevant parameters, the reduced homodyne intensity autocorrelation functions, the so called $g^{(2)}(t)$, have been modelled by a stretched exponential function, representing the decay displayed by the raw data, according to the equation:

$$g^{(2)}(t) - 1 = \phi(Q, t) = \left[e^{(t/\tau)^\beta}\right]^2$$

where $\phi(Q, t)$ is the normalized density autocorrelation function [30]. In fig. 2 we report both the average relaxation time $\tau_c = \langle \tau \rangle = \beta^{-1}\Gamma(\beta^{-1})\Gamma$ (the Euler gamma function), and the stretching parameter $\beta$ as a function of $T$. The temperature behaviour of $\tau_c$ clearly indicates its tight relation with the $\lambda$-transition.

The discovery of this new relaxation process in the ms timescale allows reconciling the unusual behaviour of sulphur with the usual viscoelastic framework: in principle, according to one of the most venerable phenomenological equations of physics, namely the Maxwell relation $\eta = G_\infty \tau_\alpha$, the abrupt increase in viscosity ($\eta$) observed at $T_\lambda$ should trigger an equivalent increase of the structural relaxation time $\tau_\alpha$ which should rise from 1 ps to 10 ns [31]. This should imply the detection of the $\alpha$-relaxation in the GHz domain by means of those techniques, like Brillouin light scattering (BLS), that measure the longitudinal modulus $M = K + \frac{4}{3}G$ (K being the bulk modulus). Indeed, when the Brillouin peak position, $\omega$, satisfies the condition $\omega \tau_\alpha = 1$ relevant effects are expected on both sound velocity and damping. More specifically, as sketched in Fig. 3A for a prototypical Debye-like relaxation, one should have an increase of both the real ($M'$) and imaginary ($M''$) parts of the longitudinal modulus, observed as an increase in the measured sound velocity and acoustic absorption, respectively. Interestingly, none of the two effects has ever been detected in Brillouin light scattering experiments on Sulphur. On the
unusual viscosity increase observed in S. λ decreasing trend across the in M (graphically emphasized for presentation reasons), observed around and above Tλ, allows to reformulate the Maxwell equation within a two relaxation processes framework.

\[ \eta = (G_\infty - G_c) \tau_\alpha + G_c \tau_c \]  

(2)

where \( G_c \) is the shear modulus related to the new relaxation process \[32\]. Since \( \tau_\alpha < \tau_\alpha(T_m) \approx 10^{-11} \text{ s} \), \( \tau_c \gg \tau_\alpha \) holds, and being \( G_\infty \approx 5 \cdot 10^8 \text{ Pa} \) \[23\] the first term of (2) becomes progressively less important as temperature is raised above \( T_\lambda \). The increase of viscosity with temperature, therefore, is triggered by the appearance of the low frequency relaxation, which largely compensates for the decrease of \( \tau_\alpha \). Hence, one can estimate the magnitude of \( G_c \) as:

\[ G_c = \tau_c(\frac{\eta_\alpha}{\tau_\alpha})_{T>T_\lambda} \approx \frac{\eta}{\tau_c} \]  

(3)

As can be seen from Fig. 3, \( G_c \) extracted through Eq. (3) displays an abrupt temperature dependence growing by five order of magnitude in ten degrees above the onset temperature \( T_\lambda \) and then asymptotically reaches values in the narrow range \( 4 \pm 8 \cdot 10^5 \text{ Pa} \). The presence of this additional relaxation, leading to the reformulation of the Maxwell equation given in Eq. (2), manifests itself through the existence of this "intermediate" plateau in \( G' \) (and consequently \( M' \)), as sketched in Fig. 3B. More importantly, at variance with the α-relaxation plateau \( G_\infty \), the plateau value \( G_c \) turns out to have significant temperature dependence around \( T_\lambda \) and, in spite of its small value (\( G_c \approx 10^{-3} G_\infty \)), the large contribution to \( \eta \) is brought about by the large value of \( \tau_c \). The discovery of this low frequency plateau above \( T_\lambda \) also allows to rationalize the abrupt decay of the shear modulus measured by stress relaxation technique \[23\], in the range \(-40 < T < -30 \text{ °C} \), in sulphur rapidly quenched from \( T_\approx 250 \text{ °C} \), and substantiates the hypothesis made in Ref. \[22\]. Indeed, the strong increase of the plateau with temperature just above \( T_\lambda \) reported in the present study can be traced back to the formation of polymeric chains of growing average length \[24, 25\] (living polymerization \[11\]). Upon an ideal, instantaneous quenching from the polymeric phase, one can reasonably expect the polymer structure and ultimately the average chain length to be frozen, i.e. equivalent to those of the initial equilibrium state. In this respect, we believe that the large difference \( G_\infty - G_e \) that we observe can be related with the decay of the shear modulus reported in Ref. \[23\]: the value of the plateau in \( G_e(T) \) reported here is \( \approx 8 \cdot 10^5 \text{ Pa} \), while in the decay observed in Ref. \[23\] the lowest measured value upon heating is \( \approx 6 \cdot 10^4 \text{ Pa} \). We consider such difference as remarkably small, in view of the large variation of the

contrary, both \( M' \) and \( M'' \) display a continuous smooth decreasing trend across the α-transition \[18, 19\] testifying a decrease of the structural relaxation time (the orthodox behaviour in ordinary liquids), and not the increase expected on the basis of the Maxwell relation. The situation becomes even more puzzling considering ultrasonic experiments \[15, 20, 21\] performed in the 1-10 MHz window, where the timescale of the probe is much longer than the 10 ns expected for the relaxation time. In this “relaxed”, \( \omega \tau_\alpha \ll 1 \), regime one should measure the viscosity directly from the attenuation of an ultrasonic pulse. Surprisingly, no critical temperature dependence of the acoustic damping has ever been observed, as recently emphasized \[22\]. The attitude of Sulphur of escaping for more than a century the established scenario valid for any other molecular liquid, warranted the labelling of a “viscous but non viscoelastic liquid” \[13\].
elastic modulus from the solid to the polymeric regime. Moreover, this difference could be ascribed to the finite quenching time which prevents the system from falling instantaneously out of equilibrium. As a result there is a reduction of the initial effective quenching temperature and, correspondingly, the value of the elastic modulus at which the structure is frozen is lower. Interestingly, the behaviour of the high temperature modulus can be theoretically predicted \[^{14}\] on the basis of its measured low temperature value \[^{23}\] for an ideal quenching, i.e. assuming that the average chain length is not affected by a rapid cooling. As can be seen in Fig. \[^{1}\] the predicted \(G_e(T)\) closely resembles the shape of the plateau that we found.

In conclusion, in this Letter we present the experimental proof for the existence of a KHz relaxation in liquid sulphur, providing the rationale behind the \(\lambda\)-transition and ruling out a simple coupling between viscosity and structural relaxation in this system. At variance with ordinary liquids, where the increase in viscosity is ruled by a direct proportionality (through the constant \(G_\infty\)) with the structural relaxation time, in liquid sulphur the large increase in viscosity reflects the large temperature dependence of a relatively small intermediate plateau in the real part of the shear modulus. According to the Maxwell relation, the \(T\)-dependence of the viscosity is triggered and amplified by a relatively large relaxation time. We speculate that the nature of this plateau may be analogous to that usually found in dense solutions of uncross-linked polymers (referred to as "rubbery plateau" for its small value compared to the infinite frequency one) and reflects the entanglement between the chains in the melt \[^{13}\] \[^{17}\] which, in the case of the \(\lambda\)-transition, proceeds first through a rapid increase of the average chain length, thus originating the sharp onset of the \(G_e(T)\) plateau. We are grateful A. Sokolov for useful comments.

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\[^{29}\] PhotonLab is a Python extension for the acquisition and analysis of photon counts developed by R. Di Leonardo.
\[^{30}\] The first equality in Eq. (1) holds in the gaussian approximation, assuming an isotropic polarizability \[^{23}\].
\[^{31}\] \(G_\infty \approx 10^8 \div 10^9\) Pa is the "unrelaxed" shear modulus of a
liquid, i.e. that measured in the short wavelength limit. The ground to Eq. (2) is provided by the relation between the shear viscosity $\eta$ and the memory function of the transverse current autocorrelation, $K_t(Q, t)$: $\eta = \lim_{Q \to 0} \int_0^\infty K_t(Q, t)dt = K_t(t = 0)\tau$ in which the latter equality defines the Maxwell relaxation time. In presence of two relaxation processes with significantly different timescales (as in the present case) $K_t(Q, t)$ is the sum of two contributions, as shown for instance in [28].