Origin of the λ Transition in Liquid Sulfur

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Developing a novel experimental technique, we applied photon correlation spectroscopy using infrared radiation in liquid sulfur around T_λ, i.e., in the temperature range where an abrupt increase in viscosity by 4 orders of magnitude is observed upon heating within few degrees. This allowed us—overcoming photoinduced and absorption effects at visible wavelengths—to reveal a chain relaxation process with characteristic time in the millisecond range. These results do rehabilitate the validity of the Maxwell relation in sulfur from an apparent failure, allowing rationalizing of 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 sulfur exhibits anomalous temperature dependence. In the liquid state, just above melting ($T_m = 119\,°C$), eight-membered rings (S_8) 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 $T = 157\,°C$. Further increase of temperature causes a dramatic increase of viscosity [1], accompanied by gross changes in optical [2–4] and thermodynamic [5,6] properties, which, at $T \approx 185\,°C$, reaches a maximum value of $100\,Pa\,s$. Beyond this temperature, a gradual viscosity decrease is observed. Although this phenomenon, known as λ transition ($T_\lambda = 159\,°C$), 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., an S_8 ring liquid) to a polymeric phase has been invoked [7,8]. 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 λ 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

S_8 rings) and propagation (concatenation of species to form long polymeric chains). Thermochemical models were developed in the past [12–14] to relate the transport properties of liquid sulfur to the underlying polymerization phenomenon. There are, however, provocative aspects of the λ 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 breakdown 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 (IRPCS). The application of optical spectroscopy techniques is critical in liquid sulfur, since its absorption spectrum is considerably different [3,4] between the monomeric and the polymer-dominated phase. Specifically, undesired absorption and photoinduced changes occur when studying the liquid with visible laser wavelengths on increasing temperature above T_λ [16]. To overcome these problems, we developed a new technique employing a near infrared radiation as probing field ($\lambda = 1064\,nm$), namely, 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.

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 fiber through an IR optimized collimator from OZ-Optics. The scattering angle $\Theta = 90°$

defines the momentum transfer Q of the experiment through the relation $Q = (4\pi n/\lambda)\sin(\Theta/2)$, n being the refractive index of sulfur [$n^{1064} \simeq 1.847(1.863)$—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 [18]) performing real time autocorrelation. Correlation functions were collected at constant temperatures during an upscan in the range $145 < T < 250$ °C, with an integration time of 30 min after 20 min stabilization time at each temperature. The temperature step was a half degree around the transition, and coarser far from the transition.

Selected normalized autocorrelation functions of the scattered intensity measured in a broad temperature range around the λ 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 time scale at T_λ, 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 modeled by a stretched exponential function, representing the decay displayed by the raw data, according to the equation

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

where $\phi_Q(t)$ is the normalized density autocorrelation function [19]. In Fig. 2 we report both the average relaxa-
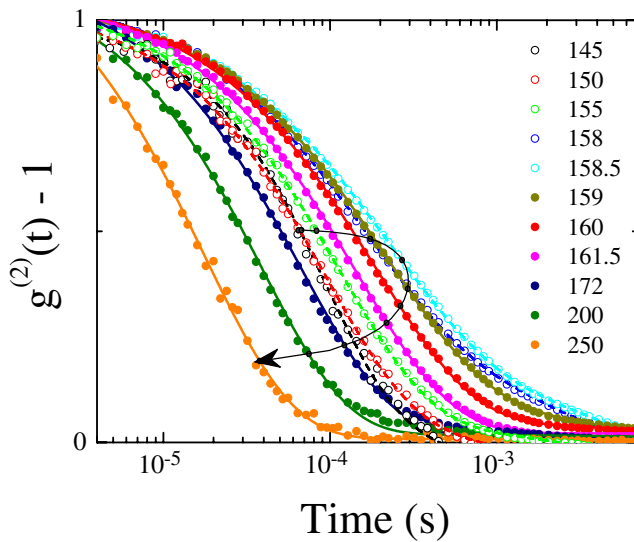
tion time $\tau_c = \langle\tau\rangle = \beta^{-1}\Gamma(\beta^{-1})\tau$ (Γ is the Euler gamma function) and the stretching parameter β as a function of T. The temperature behavior of τ_c clearly indicates its tight relation with the λ transition.

The discovery of this new relaxation process in the millisecond time scale allows reconciling the unusual behavior of sulfur 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 (η) observed at T_λ should trigger an equivalent increase of the structural relaxation time τ_α which should rise from 1 ps to 10 ns [21].

This should imply the detection of the α relaxation in the gigahertz 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 ω satisfies the condition $\omega\tau_\alpha = 1$, relevant effects are expected on both sound velocity and damping. More specifically, as sketched in Fig. 3(a) 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 BLS experiments on sulfur. On the contrary, both M' and M'' display a continuous smooth decreasing trend across the λ transition [22,23] testifying a decrease of the structural relaxation time (the orthodox behavior in ordinary liquids), and not the increase expected on the basis of the Maxwell relation. The situation becomes even more puzzling considering ultrasonic (US) experiments [15,24,25] performed in the 1–10 MHz window, where the time scale of the probe is much longer than the 10 ns expected for the relaxation time. In this
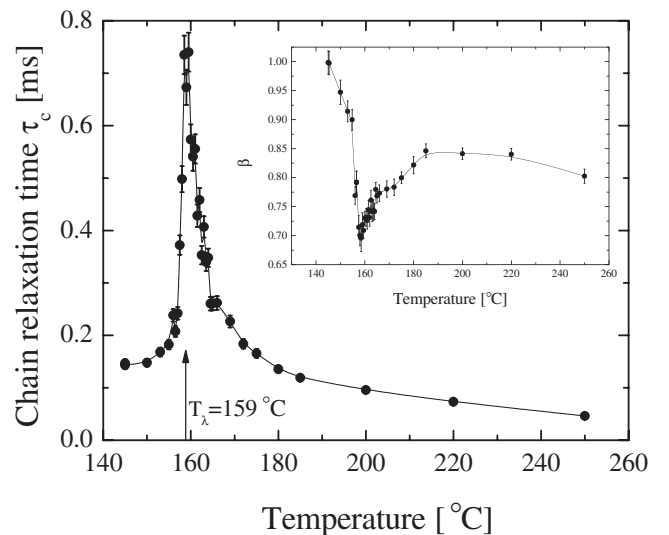

FIG. 1 (color online). Homodyne IR correlation functions at selected temperatures (°C) for $T < T_\lambda$ (○) and $T > T_\lambda$ (●). The T dependence of the chain relaxation is indicated by the arrow.

FIG. 2. Temperature behavior of the chain relaxation, as measured by IRPCS. The line is a guide for the eyes. Inset: T dependence of the stretching parameter.
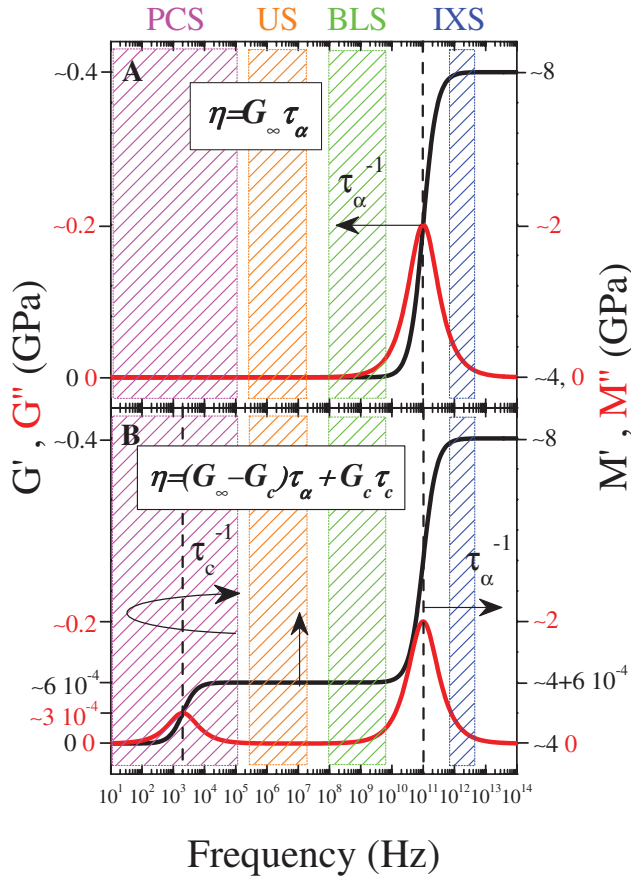
FIG. 3 (color online). The Maxwell relation at work in liquid S. (a) Sketch of the wrong scenario which would lead into an apparent failure [15] of the Maxwell equation. The increase of η with temperature should reflect an increase in τ_α ($\eta = G_\infty \tau_\alpha$), ultimately moving the resonance condition ($\omega \tau_\alpha = 1$) from the terahertz [inelastic x-ray scattering (IXS)] down to the gigahertz region (BLS). (b) The working scenario: Upon heating, the α process shifts towards higher frequencies as in any ordinary fluid (due to the decrease of τ_α), while the rapid emergence of a secondary plateau at T_λ (graphically emphasized for presentation reasons), observed in M' and G' between 10 kHz and 10 GHz, accounts for the unusual viscosity increase observed in S.

"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 [26]. The attitude of sulfur escaping for more than a century the established scenario valid for any other molecular liquid warranted the labeling of a "viscous but nonviscoelastic liquid" [15].

The discovery of the relaxation process reported here around and above T_λ allows one to reformulate the Maxwell equation within a two relaxation processes framework.

$$\eta = (G_\infty - G_c)\tau_\alpha + G_c \tau_c, \quad (2)$$

where G_c is the shear modulus related to the new relaxation

process [27]. Since $\tau_\alpha < \tau_\alpha(T_m) \approx 10^{-11}$ s, $\tau_c \gg \tau_\alpha$ holds, and being $G_\infty \approx 5 \times 10^8$ Pa [30] the first term of (2) becomes progressively less important as temperature is raised above T_λ. The increase of viscosity with temperature, therefore, is triggered by the appearance of the low frequency relaxation, which largely compensates for the decrease of τ_α. Hence, one can estimate the magnitude of G_c as

$$G_c = \left[\frac{\eta - G_\infty \tau_\alpha}{\tau_c - \tau_\alpha}\right]_{T > T_\lambda} \approx \left[\frac{\eta}{\tau_c}\right]_{T > T_\lambda}. \quad (3)$$

As can be seen from Fig. 4, G_c extracted through Eq. (3) displays an abrupt temperature dependence growing by 5 orders of magnitude in 10 °C above the onset temperature T_λ and then asymptotically reaches values in the narrow range 4–8×10^5 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. 3(b). More importantly, at variance with the α-relaxation plateau G_∞, the plateau value G_c turns out to have significant temperature dependence around T_λ and, in spite of its small value ($G_c \approx 10^{-3} G_\infty$), the large contribution to η is brought about by the large value of τ_c.

The discovery of this low frequency plateau above T_λ also allows one to rationalize the abrupt decay of the shear modulus measured by stress relaxation technique [30], in the range $-40 < T < -30$ °C, in sulfur rapidly quenched from $T = 250$ °C, and substantiates the hypothesis made in Ref. [26]. Indeed, the strong increase of the plateau with temperature just above T_λ reported in the present study can be traced back to the formation of polymeric chains of
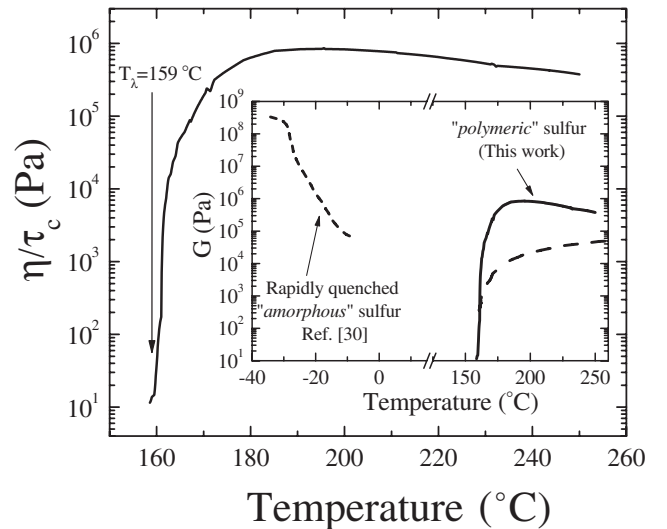

FIG. 4. Shear modulus G_c, as determined by the ratio $[\eta/\tau_c]$, η is from [1]. Inset: Shear modulus on an extended scale with low temperature measurements in a quenched sulfur sample [30] (dotted line) along with a theoretical prediction [14] for the high temperature modulus (dashed line).

growing average length [31,32] (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 $G_\infty - G_c$ that we observe can be related with the decay of the shear modulus reported in Ref. [30]: The value of the plateau in $G_c(T)$ reported here is $\approx 8 \times 10^5$ Pa, while in the decay observed in Ref. [30] the lowest measured value upon heating is $\approx 6 \times 10^4$ Pa. We consider such difference as remarkably small, in view of the large variation of the 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 behavior of the high temperature modulus can be theoretically predicted [14] on the basis of its measured low temperature value [30] 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. 4, the predicted $G_c(T)$ 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 kilohertz relaxation in liquid sulfur, providing the rationale behind the λ 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_∞) with the structural relaxation time, in liquid sulfur the large increase in viscosity reflects the large temperature dependency 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 [14,17] which, in the case of the λ transition, proceeds first through a rapid increase of the average chain length, thus originating the sharp onset of the $G_c(T)$ plateau.

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[1] R. F. Bacon and R. Fanelli, J. Am. Chem. Soc. **65**, 639 (1943).
[2] A. Donaldson and A. D. Caplin, Philos. Mag. B **52**, 185 (1985).
[3] S. Hosokawa, T. Matsuoka, and K. Tamura, J. Phys. Condens. Matter **6**, 5273 (1994).
[4] R. Sasson and E. T. Arakawa, Appl. Opt. **25**, No. 16, 2675 (1986).
[5] E. D. West, J. Am. Chem. Soc. **81**, 29 (1959).
[6] A. M. Kellas, J. Chem. Soc. **113**, 903 (1918).
[7] A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc. **81**, 780 (1959).
[8] S. C. Greer, J. Phys. Chem. B **102**, 5413 (1998).
[9] A. G. Kalampounias, K. S. Andrikopoulos, and S. N. Yannopoulos, J. Chem. Phys. **118**, 8460 (2003).
[10] J. C. Koh and W. J. Klement, J. Phys. Chem. **74**, 4280 (1970).
[11] S. C. Greer, Adv. Chem. Phys. **94**, 261 (1996).
[12] R. Powell and H. Eyring, J. Am. Chem. Soc. **65**, 648 (1943).
[13] F. J. Touro and T. K. Wiewiorowski, J. Phys. Chem. **70**, 239 (1966).
[14] A. Eisenberg, Macromolecules **2**, 44 (1969).
[15] V. F. Kozhevnikov, W. B. Payne, and J. K. Olson, J. Chem. Phys. **121**, 7379 (2004).
[16] Y. Sakaguchi and K. Tamura, J. Phys. Condens. Matter **7**, 4787 (1995).
[17] J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley & Sons, New York, 1980).
[18] F. Ianni *et al.*, Phys. Rev. E **75**, 011408 (2007).
[19] The first equality in Eq. (1) holds in the Gaussian approximation, assuming an isotropic polarizability [20].
[20] B. Berne and R. Pecora, *Dynamic Light Scattering* (John Wiley & Sons, New York, 1976).
[21] $G_\infty \approx 10^8$–10^9 Pa is the ''unrelaxed'' shear modulus of a liquid, i.e., that measured in the short wavelength limit.
[22] F. Scarponi *et al.*, Philos. Mag. **87**, 673 (2007).
[23] A. D. Alvarenga *et al.*, J. Phys. Chem. **100**, 11 456 (1996).
[24] D. L. Timrot, M. A. Seredniskaya, and T. D. Chkhikvadze, Sov. Phys. Dokl. **29**, 961 (1984).
[25] V. F. Kozhevnikov, J. M. Viner, and P. C. Taylor, Phys. Rev. B **64**, 214109 (2001).
[26] G. Monaco *et al.*, Phys. Rev. Lett. **95**, 255502 (2005).
[27] The ground to Eq. (2) is provided by the relation between the shear viscosity η 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 [28]. In the presence of two relaxation processes with significantly different time scales (as in the present case), $K_t(Q, t)$ is the sum of two contributions, as shown, for instance, in [29].
[28] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
[29] D. Levesque, L. Verlet, and J. Kürkijarvi, Phys. Rev. A **7**, 1690 (1973).
[30] A. V. Tobolsky *et al.*, Polymer **4**, 423 (1963).
[31] J. A. Poulis *et al.*, Trans. Faraday Soc. **58**, 474 (1962).
[32] J. A. Poulis and W. Derbyshire, Trans. Faraday Soc. **59**, 559 (1963).