



## Slow dynamics of liquid Se studied by Infrared Photon Correlation Spectroscopy

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### ABSTRACT

We report on the study of the slow dynamics of supercooled and molten Selenium by means of dynamic light scattering. To achieve this in the present case, where the opaqueness of Se prevents visible light scattering measurements, we have developed a novel experimental setup using infrared radiation as the light source. By measuring the scattered intensity autocorrelation function we have been able to extract the average size of the Se clusters in the liquid state and determine the temperature dependence of the related diffusion coefficient which was found to exhibit Arrhenius behavior.

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### 1. Introduction

The metastable glassy and supercooled states of matter have been, and still are, the subject of numerous investigations, both theoretically and experimentally. The main aim, which still remains a challenge for the 'glass' community, is the formulation of a coherent microscopic picture of the glass transition [1,2]. The rapid – often non-Arrhenius – increase of the shear viscosity  $\eta$  on decreasing the temperature of a supercooled liquid, approaching the glass transition temperature, has long ago been recognized as one of the salient features of the dynamical glass transition effect. Specifically, the  $T$  dependence of  $\eta$  has been found to follow the relation:

$$\eta(T) = \eta_{\infty} \exp\left(\frac{DT_0}{T - T_0}\right), \quad (1)$$

where  $DT_0$  is an energy,  $\eta_{\infty}$  is the infinite temperature limit for the viscosity, while the limit of infinite viscosity is attained for  $T$  approaching the so called Vogel temperature  $T_0$ . Both these asymptotes are far away from the range of application of Eq. (1). The behavior of the shear viscosity is accompanied by the equivalent behavior of the structural relaxation time, two quantities related

through the Maxwell relation:  $\eta = G_{\infty}\tau$ , where  $G_{\infty}$  is a glass shear modulus of order  $10^9$ – $10^{12}$  Pa. The glass transition temperature  $T_g$  is conventionally defined by  $\tau = 100$  s, or by a viscosity attaining  $10^{13}$  P. The divergence of  $\tau$ , as well as of  $\eta$ , predicted by Eq. (1) at a temperature  $T_0$  well below  $T_g$ , is characterized by a structural relaxation timescale lying outside any experimentally accessible window, and its possible physical interpretation is still debated [2]. The temperature behavior of  $\eta$  has stood as the basis for the *strong* and *fragile* classification of supercooled liquids [3]. Among other poorly understood phenomena accompanying the glass transition, there is the non-exponential nature of the relaxation functions, whose decay is normally well described by the Kohlrausch–Williams–Watts (KWW) stretched exponential

$$\Phi(q, t) = \Phi(q, 0) \exp\left[-(t/\tau)^{\beta}\right], \quad (2)$$

where  $\beta \leq 1$  is the stretching parameter. The non-linear response of glasses to perturbations completes the three non's paradigm [4]. A further important aspect of supercooled liquids concerns their structural heterogeneity. Structural heterogeneity usually manifests through long-range density fluctuations [5]. Such very slow modes have been attributed to the existence of long-range density fluctuations having their origin to clusters of molecules which can be found in the normal liquid state above the melting temperature  $T_m$ . Such effects cannot be considered universal to all glass-forming liquids since in some strong glasses the alpha-relaxation was shown

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to be the final step to equilibrium [6,7]. In this work we have undertaken a Dynamic Light Scattering (DLS) study of the ‘inorganic polymer’ Selenium over a temperature range covering the molten and the supercooled liquid state.

Liquid Se is one of the most interesting elemental liquids owing to its twofold coordination property that is the basis for the formation of one-dimensional (chain-like) polymeric molecules. Entanglement between long chains leads to an unusually high viscosity of the liquid above the melting point. Chains (trans configuration) are not the only molecular species in the melt and the glass.  $Se_8$  rings (cis configuration) are also present in an extent considerably lower than that of the  $Se_n$  chains [8,9]. Further, ring-like fragments may also exist as parts of a long chain and they contribute to the structural features accounting for the  $Se_8$  isolated rings. It was found experimentally [8] that the population of ringlike fragments decreases with temperature as was predicted by simulations. The polymer content was found to be of about 85% around the glass transition temperature with a light increase with temperature rise. At high temperatures, at  $\sim 400^\circ\text{C}$ , experiments [10] have shown that the  $Se_8$  rings are almost absent from the liquid. Coordination defects that inevitably will change the dynamics of liquid Se appear with increasing temperature. In particular, onefold and threefold coordinated Se atoms are the main defects where the fraction of the former is expected to increase faster with temperature and the latter can be considered responsible for the formation of clusters in the liquid state.

## 2. Experimental

Performing DLS on glassy Se is a non-trivial task due to the low bandgap energy and the increased absorption at visible wavelengths. Absorption problems become more important at elevated temperatures above the melting point of Se. To overcome this obstacle we employ for the first time a near-infrared, single longitudinal mode, laser operating at 1064 nm. The experimental spectroscopic technique used to perform DLS, namely Photon Correlation Spectroscopy (PCS) was also accordingly modified. Indeed, as Fig. 1 shows, the intrinsic adsorption edge of liquid Se is located at energies higher than the energy of the 1064 nm (1.16 eV) laser used in this work, even up to temperatures as high as  $350^\circ\text{C}$ . In amorphous Se the structural relaxation has been investigated by means of different techniques such as calorimetric

[11], viscosimetric [12–14], and dielectric [15]. A comparison of these data with light scattering studies of the dynamics of Se has been prevented, up to now, by the optical properties of this system, which in its amorphous and liquid states – for temperatures higher than, let’s say,  $200^\circ\text{K}$  – is completely opaque (see Fig. 1, [16]). In the present case we worked at a  $90^\circ$  scattering angle. The scattered intensity was detected by means of a thermoelectrically cooled avalanche silicon photodiode detector (Perkin–Elmer). Intensity correlation functions were recorded employing a digital correlator developed in our laboratories (Photonlab, R. Di Leonardo), covering the vast range of about 7 decades, from the lower limit of few  $\mu\text{s}$ , up to 100 s. The sample temperature was measured by an iron-constantane, J-type thermocouple, and it was stabilized by means of a PID software capable of reaching a precision of  $\Delta T \sim 0.1^\circ\text{C}$ .

Selenium (5N purity) has been subjected to further purification by distillation. Proper amounts of Se were loaded in carefully cleaned with hydrofluoric acid, quartz tubes with dimensions 6 mm o.d.–4 mm i.d. After loading the cells, Se was subjected to heating under vacuum in order to remove possible water or oxide traces and then was sealed, still under vacuum. Light scattering data were recorded by lowering the temperature in steps of  $10^\circ\text{C}$  over the temperature range  $270$ – $160^\circ\text{C}$ , which included both the normal molten state as well the supercooled liquid state. Before each measurement the liquid was kept at least 20 min at each temperature for equilibration. Several acquisitions were performed to ensure reproducibility of the results. Glassy Se has a glass transition temperature at  $\sim 35$ – $40^\circ\text{C}$  (depending on the quenching rate) while crystallization sets in at about  $90$ – $100^\circ\text{C}$ ; the crystal melts at  $221^\circ\text{C}$ .

## 3. Results

In a PCS experiment, when the homodyne technique, as in our case, is used, the time correlation function of the scattered intensity  $g^2(t) = \langle I(t)I(0) \rangle$  is measured. For a Gaussian process  $g^2(t)$  is related to the autocorrelation function of the scattered field  $I_1(t) = \langle E_s^*(0)E_s(t) \rangle$ , through the equation [17]

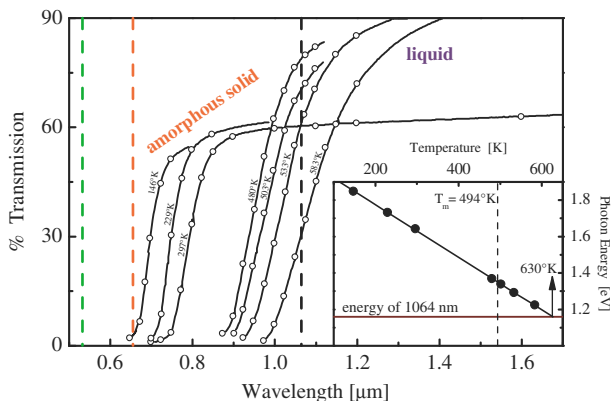
$$g^2(t) = \langle I \rangle^2 \left( 1 + f \frac{|I_1(t)|^2}{|I_1(0)|^2} \right), \quad (3)$$

where  $f$  is a constant. The scattered field also depends on the exchanged momentum  $q$  between the probe and the sample, given by the relation

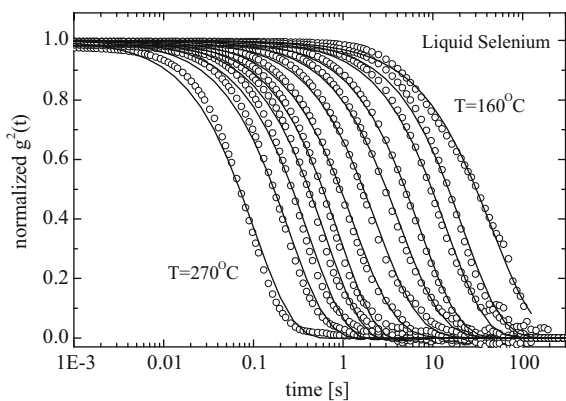
$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2},$$

where  $n$  is the refractive index of liquid Se ( $n \sim 2.4$ , [16]),  $\lambda$  is the laser wavelength, and  $\theta$  is the scattering angle.

A representative set of the measured correlation functions is shown in Fig. 2. As is clear at a first sight, the relaxation time increases as temperature decreases, coherently with the expected behavior of a cooperative structural relaxation process, but the observed relaxation process reaches a timescale of about 100 s already at a temperature of  $160^\circ\text{C}$ . This result clearly reveals that the relaxational process we monitor with PCS in this particular temperature range does not correspond to the structural relaxation of supercooled Se which is associated to the glass transition dynamics. Indeed, at these temperatures the structural relaxation is too fast to be observed in the time window of PCS and hence density fluctuations associated with the primary alpha-process are completely relaxed. Most of the correlation functions, as is shown in Fig. 2, are satisfactorily fitted with a single exponential relaxation function. However, it has been reported [18,19] that the relaxation process of supercooled Se just above the glass tran-



**Fig. 1.** Transmission curves of amorphous and liquid Selenium at different temperatures (open circles). Data are taken from Ref. [16], full lines are guides to the eye. The black dashed line indicates the wavelength of the radiation used for the present experiment, while green and red dashed lines show the wavelengths of the green and red laser lines most commonly used in conventional PCS setups. The inset reports the absorption edge (in eV) for Se as a function of the temperature. The solid horizontal line shows the energy of the source used in the present work. The melting point for Se is also reported as a dashed line.

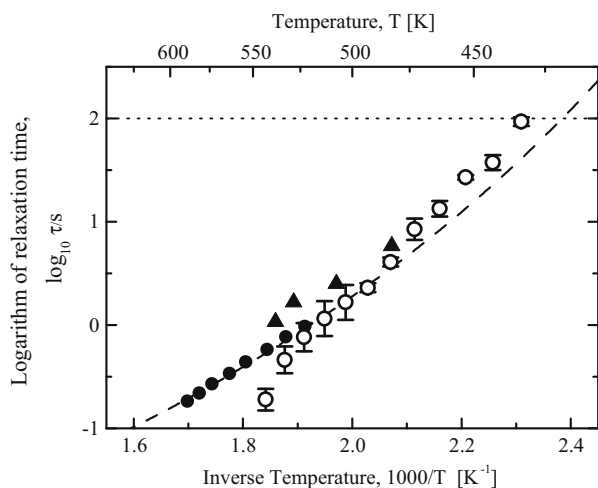


**Fig. 2.** Representative normalized intensity autocorrelation functions at selected temperatures (circles). The higher and lower experimentally accessed temperatures are reported. Temperature steps are each 10 °C. Continuum lines represent the model function: a single exponential decay. The whole measurement was performed on cooling the liquid, at  $T=160\text{ °C}$  the system probably started to crystallize.

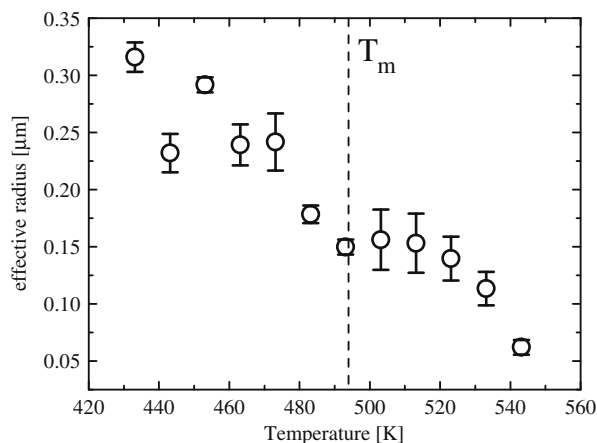
sition temperature is described by a stretched exponential function with  $\beta = 0.5$ .

#### 4. Discussion

The relaxation time, obtained from the best fit procedure, is reported as a function of the inverse temperature in Fig. 3 (open circles). The same figure also reports arbitrarily rescaled viscosity data. For this purpose, experimental results from Ref. [13] (full circles) and [14] (full triangles) have been employed, together with the model Eq. (1) (dashed line) determined in Ref. [13]. The figure shows that at high temperatures there is no matching between the trends of viscosity and relaxation time, meaning that these two quantities are not related as should be if we were dealing with a structural relaxation process. This fact, together with the exponential behavior of time correlation functions, and the inconsistency between the calorimetric  $T_g$  and the relaxation times observed in the present experiment, allows us to speculate on a different origin of the process we observed. Specifically, we may hypothesize the formation of clusters of Se atoms, whose self-diffusion gives origin



**Fig. 3.** Logarithm of relaxation time vs. inverse temperature as measured by IR-PCS (open circles). Arbitrarily scaled viscosity data are shown from Ref. [13] (full circles) and [14] (full triangles). A Vogel–Fulcher–Tammann model, Eq. (1), is also reported (dashed curve, [13]), scaled in the same way as viscosity.



**Fig. 4.** Effective radius of the Selenium clusters vs. temperature. The melting point of crystalline Se is also reported (dashed line).

to the observed signal. It is well known that a self-diffusive dynamics of clusters of a fixed size in a viscous medium, reflects in the homodyne correlation function Eq. (3) as a purely exponential decay of  $g_2(q, t)$ , with a decay time given by  $\tau = 1/2Dq^2$ , being  $D$  the self-diffusion coefficient [17]. The temperature dependence of the diffusion coefficient is given by the Einstein relation

$$D = \frac{k_B T}{6\pi\eta(T)R}, \quad (4)$$

being  $\eta(T)$  the temperature dependent viscosity of the Se medium, and  $R$  the mean radius of diffusing clusters. The viscosity of Se is known from previous investigations [12–14]. This allowed – within the hypothesis made – an estimation of the effective radius of clusters as a function of temperature, as reported in Fig. 4. Coordination defects in liquid Se are found to depend strongly on the temperature. In particular at 570 K defects are associated with onefold and threefold atoms ( $C_1$  and  $C_3$  defects) in bound pairs, even though their concentration is low. At high temperatures defects are isolated and are mainly of  $C_1$  type [20]. The behavior of the clusters size, strongly increasing with decreasing temperature, would thus be in agreement with the interpretation of clusters as originating mainly by  $C_3$  type defects.

#### 5. Conclusions

In conclusion we exploited a recently developed Photon Correlation setup with Infrared radiation for studying the slow dynamics of the non-transparent glass-forming liquid, Se. We were able to measure the relaxation time associated to the single relaxation process observed in this liquid at different temperatures covering the normal as well as the supercooled regimes. The evolution of the correlation time with temperature has been ascribed to the self-diffusion dynamics of Selenium clusters whose effective radius has been estimated as a function of temperature. The size of clusters is found to increase as temperature decreases, ranging between 50 nm and 350 nm. In perspective we believe that a study of the size of clusters at varying exchanged momentum, as well as in function of the aging, would result in a better understanding of the dynamics of such material in the liquid state.

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## References

- [1] Lille France, F. Affouard, M. Descamps, K.L. Ngai (Eds.), Proceedings of the 5th International Discussion Meeting on Relaxations in Complex Systems, *J. Non-Cryst. Solids* 352 (2005) 4371.
- [2] C.A. Angell, K.L. Ngai, G.B. McKenna, P.F. McMillan, S.W. Martin, *J. Appl. Phys.* 88 (2000) 3113.
- [3] C.A. Angell, *J. Non-Cryst. Solids* 131–133 (1991) 13.
- [4] J.C. Dyre, *Rev. Mod. Phys.* 78 (2006) 953.
- [5] E.W. Fisher, *Physica A* 201 (1993) 183.
- [6] S.N. Yannopoulos, G.N. Papatheodorou, G. Fytas, *Phys. Rev. E* 53 (1996) R1328.
- [7] S.N. Yannopoulos, G.N. Papatheodorou, G. Fytas, *Phys. Rev. B* 60 (22) (1999) 15131.
- [8] S.N. Yannopoulos, K.S. Andrikopoulos, *Phys. Rev. B* 69 (2004) 144206.
- [9] S.N. Yannopoulos, K.S. Andrikopoulos, *J. Chem. Phys.* 121 (10) (2004) 4747.
- [10] A.I. Popov, *J. Phys. C* 9 (1976) L675.
- [11] R.B. Stephens, *J. Non-Cryst. Solids* 20 (1976) 75.
- [12] R.B. Stephens, *J. Appl. Phys.* 49 (1978) 5855.
- [13] K.M. Bernatz, I. Echeverria, S.L. Simon, D.J. Plazek, *J. Non-Cryst. Solids* 307–310 (2002) 790.
- [14] R.C. Keezer, M.W. Bailey, *Mater. Res. Bull.* 2 (1967) 185.
- [15] M. Abkowitz, D.F. Pichan, J.M. Pochan, *J. Appl. Phys.* 61 (1982) 483.
- [16] R.S. Caldwell, H.Y. Fan, *Phys. Rev.* 114 (1958) 664.
- [17] B.J. Berne, R. Pecora, *Dynamic Light Scattering*, John Wiley, New York, 1976.
- [18] D. Caprion, H.R. Schober, *Phys. Rev. B* 62 (2000) 3709.
- [19] R. Böhmer, C.A. Angell, *Phys. Rev. B* 48 (1992) 5857.
- [20] G. Kresse, F. Kirchhoff, M.J. Gillan, *Phys. Rev. B* 59 (1999) 3501.