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Correlation spectroscopy in molten and supercooled antimony trichloride

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Correlation spectroscopy measurements performed on molten and supercooled antimony trichloride with the homodyne technique show correlation functions that have a nonexponential behavior. Two well-defined distributions of correlation times can be observed in different temporal regions. This behavior is discussed in terms of a structural relaxation of clusters dynamically formed by intermolecular and interchain bonds. The Arrhenius plot of these correlation times shows a linear behavior with the same activation energy for both. In contrast, the activation energy of shear viscosity has a different value, showing that the processes determining the temperature behavior of τ and η_s are different.

INTRODUCTION

It is well established that the normal and supercooled molten $SbCl_3$ behaves as an associated liquid in which the basic molecular unities (pyramidal $SbCl_3$) are bonded together with chlorine bridges to create chains of several molecules. Moreover, these chains are interacting via van der Waals forces,[1] giving a long-range bond connectivity that can explain some anomalous chemical physical properties such as high dielectric constant, low electrical conductivity with respect to a typical molten salt. The existence of such a cooperative phenomenon has been investigated by means of elastic wide angle neutron and x-ray scattering experiments.[1,2] The dynamics of breaking and making intermolecular chlorine bridges has been studied by means of depolarized Rayleigh-Wing[3] experiments. Moreover, measurements of hypersound velocity and absorption by the Brillouin scattering technique[4] have shown the presence of a relaxation phenomenon. A dispersion in the sound velocity between 5 GHz and 15 MHz and the related excess of absorption respect to the classical one can be connected to a relaxation between two states, in a bond-lattice model characterized by the existence of "intact" and "broken" bonds.

The above measurements have shown a large amount of scattering light in the quasielastic region ($10-10^6$ Hz) due to slow fluctuations of the dielectric tensor. On the other hand the presence, in a fused salt, of a contribution in the very low frequency region of the spectra is not surprising. In fact, recent photon correlation studies on molten and supercooled $ZnCl_2$,[5] have shown the existence of slow fluctuations in the dielectric tensor that was connected with a local configurational relaxation. Although these fluctuations occur in a liquid with a viscosity ($\eta_s \sim 10$ P) higher than molten $SbCl_3$, the low-frequency contribution of the scattered light in the latter sample is qualitatively similar to that of liquid $ZnCl_2$. Recently much work[6] has been done on glass-form liquids in the deeply supercooled region in order to explain the ability of these systems to solidify without crystallization. In these system the viscosity becomes very large as the glass transition is approached reaching values of 10^{13} P. For this reason structural relaxations observed by ultrasound and hypersound measurements, in the nanosecond time scale, can be frozen as the temperature is lowered and can be observed in the quasielastic light scattering region by photon counting measurements.[7] Our system presents a low viscosity in the normal phase as well as in the supercooled one, and this makes us unable to deeply supercool the liquid with low cooling rate in order to approach the glass transition. Therefore, we think that the observed phenomenon cannot be completely set in the frame of current theories on the glass transition, but is due to peculiar collective properties of this strongly associated liquid. On the other hand, the observed fluctuations of the dielectric constant are not due to the thermal diffusion in a pure liquid, because this generally occurs in a frequency scale higher than that found in liquid $SbCl_3$ and $ZnCl_2$. Therefore, the explanation of fluctuations in the dielectric tensor should be made within a theory which accounts for structural relaxations of local environment of molecules due to the breaking and reforming of interchain bonds. In order to clarify the nature of this scattering in $SbCl_3$, we have made measurements of light-beating spectroscopy by photon correlation technique.

EXPERIMENTAL PROCEDURES, DATA ANALYSIS, AND RESULTS

Photon correlation spectra on molten and supercooled antimony trichloride were obtained with a standard procedure[8] using a homemade clipped correlator with the homodyne technique. The ultrapure sample was prepared by G. P. Smith of Oak Ridge National Laboratory with a technique previously described.[9] It was contained in a special sealed multioptical cell, in order to permit sublimation in an argon atmosphere shortly before measurement, without exposing the sample to air and humidity. The lack of fluorescence of the samples as well as the ability to supercool deeply ($\sim 40\,^\circ\mathrm{C}$) for several hours is an indication of their high degree of purity and should rule out the presence of oxychlorides. We used a optical thermostat which assures a temperature control better than 0.02 °C in the entire temperature range of measurements (37.5–90 °C). We used a 90° scattering geometry with a 5-mW He-Ne laser. Measurements were made also at angles of 45° and 135° in order to test an eventual k^2 dependence of obtained linewidths. No dependence was observed in the spectra at various angles. The samples were first heated above the melting point at 90 °C and left for two days at this temperature to be sure of absence of gas microbubbles in the bulk.

We also performed polarization analysis of the spectra. In the following we report only the spectra analysis related to the VV polarization because apart from an overall intensity factor ($I_{VH}/I_{VV} \sim 0.15$) I_{VV} and I_{VH} are essentially the same.

Following a well-defined procedure,[10] from the experimental clipped correlation function $C_k(t)$, we can derive the square of the first-order correlation function $\Phi^2(t)$ according to the relation

$$C_k(t)=\left[\frac{1+k}{1+\langle n\rangle}f(A,T)\Phi^2(t)+1\right]n_B\ ,$$

where $n_B=\langle n_k\rangle\langle n\rangle N$ is the theoretical value of the correlation function $t\rightarrow\infty$, $\langle n_k\rangle$ and $\langle n\rangle$ represent the rate of clipped and total counts, respectively, N is the number of sampling times, k is the clipping level, and finally $f(A,T)$ is a factor which takes into account the sampling time and coherence area.

The first-order correlation function $\Phi(t)$ is connected to the correlated fluctuations of the dielectric tensor in the sample induced by a time dependence of the polarizability tensor $\boldsymbol{\alpha}$

$$\Phi(t)=\frac{\langle\Delta\epsilon(t)\Delta\epsilon(0)\rangle}{\langle\Delta\epsilon^2\rangle}\ .$$

In Fig. 1 we report a plot of $\Phi^2_{VV}(\tau)$ versus $\ln(\tau)$ for two temperatures, 90 °C and 37.5 °C. As it can be seen, the data cannot be fitted by a single exponential, moreover a long-time tail is present in a scale that is about three orders of magnitude higher than the slower one. In order to understand the origin of the $\Phi(\tau)$ behavior, we have tentatively fitted the experimental data with Williams-Watt (WW) function,

$$\Phi(\tau)=\exp\left[-\frac{\tau}{\tau_s}\right]^{\beta}\ , \tag{1}$$

where β ($0<\beta\leq 1$) represents the width of the relaxation times distribution. This expression has already been successfully used in our previous works[5,8] and in other works[11,12] of photon correlation spectrscopy in liquids that undergo structural relaxation in supercooled phase, and near the glass transition. A mean relaxation time can be drawn by

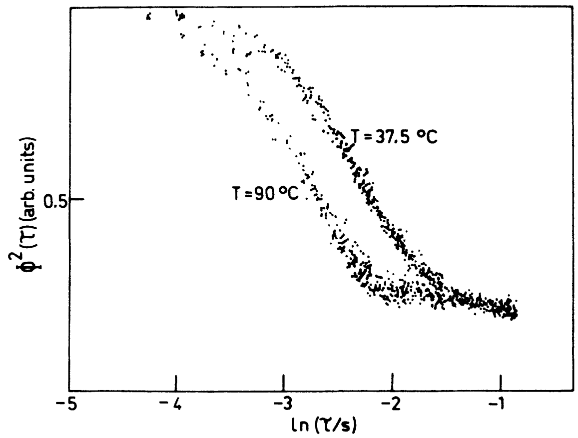

FIG. 1. Experimental values of $\Phi^2(\tau)$ vs $\ln(\tau)$ for the extreme temperatures studied in this paper.

$$\langle\tau_s\rangle=\frac{\tau_s}{\beta}\Gamma(\beta^{-1})\ ,$$

where Γ is the gamma function.

A plot of $\ln[-\frac{1}{2}\ln\Phi^2(\tau)]$ versus τ should give a straight line whose slope is β, while the intercept at the origin is related to the logarithm of relaxation time τ_s. In Fig. 2 we make such a plot for the two above-mentioned temperatures. As it can be seen the WW function well fits the experimental data in the short-time region, while in the long-time region, there is a deviation from linearity. In order to take into account the long-time behavior we have introduced in Eq. (1) a second temporal contribution to the correlation function characterized by a single relaxation time. In this way we can use a modified bimodal equation to fit the data

$$\Phi(t)=(1-P)\exp\left[-\frac{t}{\tau_s}\right]^{\beta}+P\exp\left[-\frac{t}{\tau_L}\right]\ . \tag{2}$$

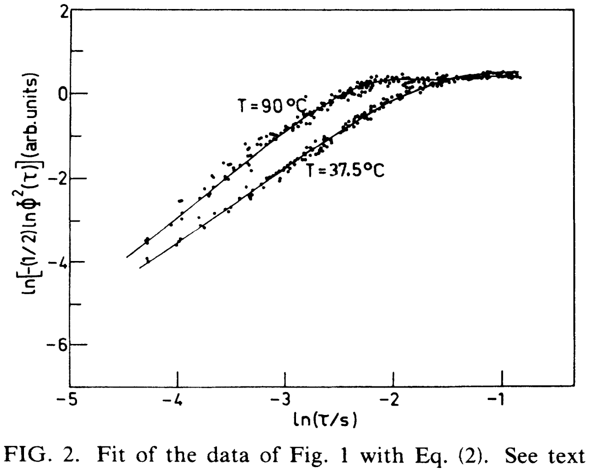

FIG. 2. Fit of the data of Fig. 1 with Eq. (2). See text for more details.

TABLE I. Fitting parameters P, β, τ_s, τ_L, and $\langle \tau_s \rangle$ of data to Eq. (2) of text.

T (°C)	90	80	70	60	50	45	40	37.5
P	0.49	0.40	0.39	0.39	0.49	0.45	0.49	0.44
β	0.99	0.98	0.94	0.90	0.85	0.82	0.81	0.79
τ_s (ms)	2.4	3.1	3.7	4.6	5.7	6.6	7.0	7.7
τ_L (s)	1.9	2.3	2.9	3.6	4.7	5.6	6.2	7.0
$\langle \tau_s \rangle$ (ms)	2.4	3.1	3.7	4.8	6.1	7.3	7.9	8.8

Figure 2 shows the results of fitting experimental data to Eq. 2 while Table I reports the fitting parameters P, β, τ_s, and τ_L together with $\langle \tau_s \rangle$.

DISCUSSION

As far as the polarization analysis is concerned, photon correlation spectroscopy (PCS) measurements of the I_{VH} component of scattered light gave a correlation function with the same features of the I_{VV} component. The depolarization ratio I_{VH}/I_{VV} was about 0.15, an evidence of the fact that the fluctuations of the dielectric tensor give rise to an anisotropic component in the scattering light. Generally speaking, anisotropic light scattering[13] arises from reorientation of scatterers, while isotropic scattering arises only from motion of the center of mass of scatterers. This motion can originate in a translational diffusion and/or a structural relaxation of the local environment. The experimental Φ_{VH} spectrum is essentially due to the optical anisotropy, while Φ_{VV} takes into account the isotropic contribution as well as the anisotropic one,

$$(\Phi_{VV}=\Phi_{\text{iso}}+\tfrac{4}{3}\Phi_{VH}) .$$

In our case the fact that the behavior of Φ_{VH} and Φ_{VV} is essentially the same implies that there is a strong coupling between orientational and translational dynamics. Similar results were obtained in other PCS investigations of liquids near the glass transition.[11,12] Moreover the k independence of our PCS spectra suggests that the observed Φ_{VH} is not due to a coupling between a collective motion, as shear wave in fluids, and the reorientational dynamics; therefore the fact that the isotropic and anisotropic spectra are identical could be due to the reorientational dynamics of the scatterers that induces a motion of their center of mass. This motion, which produces the structural relaxation, gives rise to the dominant contribution in Φ_{VV}.

Figure 3 shows Arrhenius plots of $\langle \tau_s \rangle T$ and $\tau_L T$ versus $1/T$, together with the shear viscosity η_s of the molten SbCl$_3$. The data of shear viscosity[14] reported in the plot refer only to the temperature range above the melting point $T_m = 73.3$ °C. As it can be seen, the behavior of $\ln(\langle \tau_s \rangle T)$ versus $1/T$ is linear with a slope (4.78 kcal/mol) almost identical, within the experimental uncertainty, to the slope found for $\ln(\tau_L T)$ (4.93 kcal/mol). Therefore, we think that both relaxation processes are triggered by the same physical mechanism.

The leading idea in our interpretation of experimental results is that the sample behaves as an associated liquid in which chains of several molecules, linked by chlorine bridges, are more or less connected together by weak van der Waals forces. At the thermodynamical equilibrium there are fluctuations of local configuration due to the breaking and reforming of these bonds. The dynamics of the breaking of chlorine bridges is faster than interchain dynamics falling in a temporal scale that has been investigated by means of Rayleigh-Wing measurements.[3] The process of breaking and reforming interchain bonds leads to the presence, in the melt, of clusters which continuously change their configurational environment with a time constant proportional to the square of dimensions L of the clusters and inversely proportional to the diffusion coefficient of the chains $\tau = L^2/4D$.[15] The dimensions of these clusters may vary and consequently it is natural that the dynamics of this system of correlated clusters is characterized by a distribution of relaxation times. In this frame the Williams-Watt function, which fits the low-time region of the experimental spectra, assumes a well-defined role, and the parameter β is related to the distribution of the dimensions of the local structured clusters. In Fig. 4 we report the behavior of β versus temperature. As it can be seen, β decreases smoothly from a value of about 1 above the melting point to a value of 0.8 in the supercooled region. This behavior suggests that, in the normal liquid phase, the structured clusters are nearly monodispersed and these density fluctuations decay with an almost single relaxation time. When the metastable phase is approached, the dynamics of fluc-

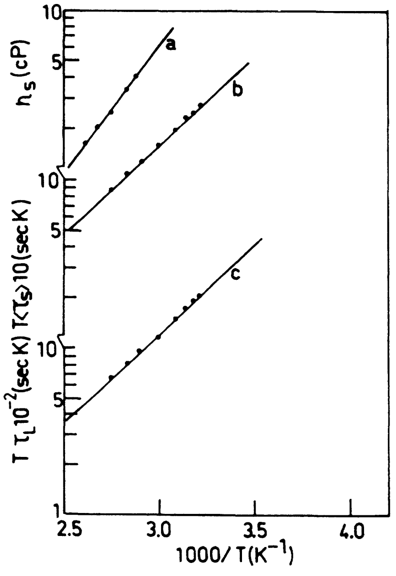

FIG. 3. Arrhenius-type plots of $\langle \tau_s \rangle$, τ_L, and η_s.

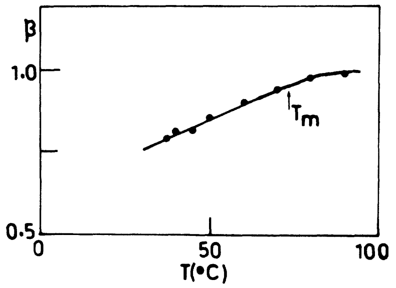

FIG. 4. Temperature dependence of the Williams-Watt parameter β. The arrow indicates the melting temperature.

tuations is more hindered than in the normal phase and this increases the polydispersity in the dimensions of the clusters and therefore produces a wider distribution of relaxation times than in the normal phase. This picture is confirmed by the temperature dependence of β. The observed phenomenon is anomalous with respect to those discussed in molten salts literature[16] in the supercooled region because it happens in a liquid with very low viscosity. In fact, if we try to put the relaxation time observed in our previous work[4] by hypersound measurements in the nanosecond scale and that observed in the present work in the same plot versus $1/T$, we see that they fall on different temporal scales in the same temperature region, and this allows us to assert that the two connected processes are different in character.

The second relaxation time τ_L is originated by a relaxation process slower than the first one, and is about three orders of magnitude larger than $\langle \tau_s \rangle$. Therefore this dynamics falls in a time scale (1–10 s), in which digital clipped correlators are in the limit of their performance. In fact the values of τ_L are obtained as results of a fitting procedure, taking into account the theoretical value of the dc term of the correlation function. This procedure can lead to possible errors in the correct determination of long correlation time making us unable to decide if the long-time tail is better fitted by another Williams-Watt function or with a single relaxation time. Therefore, although the presence of such a long-time tail is quite evident, an accurate analysis of the results on long-time dynamics cannot be performed. For this reason we have preferred to fit the long-time tail with a single exponential function rather than with a WW function. It is worthwhile to note that such an indetermination on the long-time behavior of the correlation function does not appreciably affect the results of the fit in the short-time part of the spectra. A long-time tail in the correlation function has been found by other authors in different systems.[5,17] In any case, independent of the fit function selected, the spectra seem well separated into two different regions: the short-time region and the long-time one. The identity in the behavior of the long-time tail in *VV* and *VH* polarization leads us to treat the second (longer) relaxation time in a similar manner. Tentatively, we can try to give an explanation of the long-time behavior of the correlation function, by associating to this time a process of structural relaxation of a hierarchy of topologically more extended structures. More research is in progress in our laboratory to study this process by means of a full correlator that allows us to extend the temporal window of the clipped correlator to sampling times of several seconds.

In order to have more information about the origin of the observed relaxation we have used an Einstein-Stokes-Debye equation $\tau T = V\eta_s / k_B$ to relate the observed relaxation time τ_s to the shear viscosity of the liquid. In Fig. 3 we have plotted also the macroscopic shear viscosity versus $1/T$. As it can be seen, the viscosity data above the melting point can be fitted according to the Arrhenius law, and the fit yields an activation energy of 7.0 kcal/mol that is higher than the activation energy found for the structural relaxation times τ_x and τ_L, which are 4.78 and 4.93 kcal/mol, respectively. This result shows that the processes implied in the configurational relaxation are not directly connected with the macroscopic shear viscosity (similar results have been found also for liquid 2,4-pentanediol[11,18] by Fytas and Dorfmuller). We think that this behavior is due to the fact that when the system is viewed on a magnitude scale of the light wavelength, the "viscosity," observed by local structures (diffusing, or undergoing rotation), is lower than the viscosity measured with a macroscopic method (Ubbelhode, rotating cylinder, etc.) and furthermore the temperature dependence of related relaxation time can be generally different. In our case, the decay of the clusters is caused by diffusive and/or rotational motions of the chains in a medium of apparent viscosity $\eta_s'(T)$. The last one and its temperature dependence are different from the corresponding quantities of the macroscope viscosity $\eta_s(T)$, which must take into account the presence of at least two hierarchies of clusters with their dynamics.[11] This can clarify the different temperature behavior between the viscosity $\eta_s(T)$ and the relaxation times. Therefore, the comparison of $\langle \tau_s \rangle$ and τ_L with η_s confirms our hypothesis that liquid $SbCl_3$ behaves as a strongly associated liquid in which the concept of local structure imposed by a bond connectivity takes an important role in determining the macroscopic transport and thermodynamical properties.

CONCLUDING REMARKS

In this paper we have discussed PCS measurements in molten and supercooled antimony trichloride. The experimental results yield correlation functions which present contributions in two different time regions. The first one, analyzed with a WW function, has been related to a structural relaxation induced by a scattered center-of-mass motion. The second contribution falls in the time scale which is three orders of magnitude higher than the first one. Moreover polarization analysis, together with the evidence of a k-independent behavior of the correlation function, suggest that the first relaxation is structural in character and is related to the change of the local configuration due to the breaking and reforming of the bonds between chains. Using a Debye-Einstein-Stokes formula or using the formula $\tau = L^2/4D$, it is possible to find a dimension for these dynamical clusters, due to bond connectivity, that is about 1 μm. Preliminary experiments of small-angle neutron scattering (SANS) performed at Rutherford Appleton Laboratory showed an increase of the forward scattering of supercooled with respect to molten $SbCl_3$. This preliminary result confirms the hypothesis of the presence, in the molten state, of such clusters whose dynamics become more hindered and slow as the molten state approaches the supercooled state. The dynamics of bond connectivity perhaps affects larger regions, whose temporal fluctuations originate the second contribution in the long-time tail of the correlation function. This analysis confirms the idea that molten $SbCl_3$ behaves as an associated liquid rather than a molten salt.

As far as the temperature behavior of the spectra is concerned, we found that the mean relaxation time $\langle \tau_s \rangle$ together with the long-time τ_L do not behave like the shear viscosity. Moreover, the parameter β decreases in the supercooled region, showing that in this region the dynamics of the breaking of interchain bonds is more hindered than in the normal phase. The temperature dependence of τ_L and $\langle \tau_s \rangle$, at least in the frame of this experimental investigation, shows an apparent activation energy lower than η_s. Tentatively, we have given a qualitative interpretation of this difference in terms of modes contributing to the shear viscosity, whose behavior depends on the topological scale in which the phenomenon is observed. More research is in progress in order to better clarify the origin of this discrepancy and the nature of the slow response dynamics.

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