

Rayleigh-Brillouin light-scattering study of a simple glass former: Evidence of locally favored structures

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The Rayleigh-Brillouin light scattering is studied in the glass-forming picoline with emphasis to the temperature dependence of the Landau-Placzek ratio. It was found that the Landau-Placzek ratio is in good agreement with the theoretical prediction at $T > T_A$, where T_A is the temperature of transition from an Arrhenius-like to a non-Arrhenius behavior for the α -relaxation time dependence on temperature. Below T_A the Landau-Placzek ratio exceeds significantly the theoretical prediction. The finding is interpreted as the evidence of the locally favored structures, which presence in an equilibrium glass-forming liquid below T_A .

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I. INTRODUCTION

When a liquid is cooled from a low-viscous state two radically different scenarios can occur. One is the transition to a crystal, characterized by a particular temperature T_m (melting temperature). Some of substances, usually called as glass formers, can cross T_m during cooling without crystallization. Increasing viscosity of these substances reaches a very high level of 10^{12} Pa s at the temperature of glass transition T_g , indicating that for the most of experiments the substance behaves as a solid state (glassy state). The temperature range around T_g is rich for different interesting dynamical (and other) phenomena, which are extensively studied in numerous experimental and theoretical works.

Studies of glass transition are mainly focused in different aspects of the relaxational behavior [1–7]. There are few particular temperatures, which are important for the description of the relaxational behavior of glass-forming liquids. One of them is T_c —the critical temperature in framework of mode-coupling theory, being above T_g . In spite that T_c is defined within the theory, some experiments demonstrate the model-independent evidence of the “peculiarity” of T_c for the relaxational response of a glass former (for example, the fast relaxation intensity at T_c [8]). Another important temperature is T_0 , serving for the description of the temperature dependence of α relaxation time (or viscosity) near and above T_g via Vogel-Fulcher-Tammann expression

$$\tau_\alpha = \tau_0 \exp\left(\frac{B}{T - T_0}\right). \quad (1)$$

Also, T_0 often serves as an estimation for temperature of an “ideal glass transition.”

While the majority of glass transition studies are devoted to the relaxation behavior, less attention is focused to why and how a liquid pass T_m without crystallization. Recently this problem was addressed in the works of Tanaka [9–11]. In this approach it is stressed the importance of the appearance of the local structures in a glass-forming liquid during

cooling. The locally favored structures can be energetically favored, but not consistent with the long crystalline order [10], so preventing the crystallization process. The role of the locally favored structures for the glass-forming ability was also recognized in a number of previous works ([12] and references therein).

Among partisans of the locally favored structures there are different opinions about the temperature at which the locally favored structures appear. Sometimes this temperature is associated with T_m [13], sometimes with a temperature of a narrowly avoided phase transition T^* above T_m [14]. Recent study for the temperature dependence of inhomogeneous broadening of a Raman line of a glass-former was found to be in favor that the locally favored structures appear at $T \sim T_A$ and are absent at higher temperatures [15]. Here, T_A is the temperature of the transition from an Arrhenius-like to a non-Arrhenius behavior for the α -relaxation time dependence on temperature. Following the experimental results of [15], namely T_A is the temperature of the locally favored structures appearance. Moreover, it was shown that for good glass-formers $T_A > T_m$, while for poor glass-formers the estimation of T_A is about T_m or lower [16].

Recently, it was shown that the number of dynamically correlated molecules in a liquid becomes constant and consistent with the value of unity above $\sim T_A$ [17]. This result is interpreted as the transition to intermolecularly noncooperative relaxation [17] and is in line with the view that T_A is the temperature of the locally favored structures disappearance, as the temperature increases. Also, within the random first-order transition theory T_A is described as the temperature delimiting collisional and energy landscape-dominated transport, following the appearance of persistent local liquid structures [18].

The question is how one could visualize the locally favored structures? If the appearance of the locally favored structures were not followed by atomic number fluctuations, it would be hardly possible to reveal them by usual structural methods. Alternative experimental technique would be sensitive to the existence of local clusters (or cohesive domains in other words). These clusters should be able to contribute to the elastic scattering of visible light, increasing the Landau-Placzek ratio R_{LP} , which is defined as the ratio be-

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tween the integral intensity of the central Rayleigh peak I_C to the integrated intensity of the two Brillouin lines I_B . Unfortunately, previous studies of the Landau-Placzek ratio in the glass-forming liquids were devoted either to the low-viscous state only or focused to the temperature range below T_A (e.g., [19]). The goal of the present work is to study experimentally the temperature dependence of the Landau-Placzek ratio for a good glass-former picoline, widely studied in a number of previous works (e.g., [15,20,21] and references therein). It was found that the Landau-Placzek ratio clearly depicts the peculiarity at $T \sim T_A$, indicating the appearance of additional fluctuations, which are interpreted as the locally favored structures.

II. THEORETICAL BACKGROUND

The thermodynamic consideration leads to the following expression for the Landau-Placzek ratio [22,23]:

$$R_{LP} = \frac{\beta_T - \beta_S}{\beta_S}, \quad (2)$$

where β_T and β_S are the isothermal and adiabatic compressibilities, respectively. Equation (2) is written for the case of the isotropic light scattering caused by isotropic fluctuations of the dielectric constant ε , which are determined by the pair of independent thermodynamic variables pressure P and entropy S . In the derivation of Eq. (2) it is assumed that the change of ε with temperature at constant density ρ is negligible

$$\left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \ll \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T, \quad (3)$$

and effects of dispersion (dependences of variables on frequency) are ignored [22,23].

Since in the light scattering the Rayleigh (central) and Brillouin lines are placed on different frequencies, in some cases the effects of dispersion should be taken into account. Labeling by “static” for the typical frequencies of the Rayleigh scattering and by “hs” for the frequencies of the Brillouin peaks, Eq. (2) is rewritten [23] in the form

$$R_{LP} = \frac{[(\rho \partial \varepsilon / \partial \rho)_T (\beta_T - \beta_S)]_{STATIC}}{[(\rho \partial \varepsilon / \partial \rho)_T \beta_S]_{HS}}. \quad (4)$$

Ratio

$$a = \frac{[(\rho \partial \varepsilon / \partial \rho)_T]_{STATIC}}{[(\rho \partial \varepsilon / \partial \rho)_T]_{HS}} \quad (5)$$

is difficult to be determined. The estimation made in [24] for a number of liquids provides $a = 1.2 \pm 0.15$ [23].

It is convenient to write Eq. (4) by use the known thermodynamic relations $\beta_T - \beta_S = \alpha^2 T / \rho C_P$, where $\alpha = (\frac{1}{\rho} \frac{\partial \rho}{\partial T})_P$ is the thermal expansion coefficient, C_P is the specific heat at constant pressure; and $\beta_S^{-1} = \rho c^2$, where c is the longitudinal sound velocity. Then [22,23],

$$R_{LP} = a \frac{\alpha^2 T c^2 (\nu_B)}{C_P}. \quad (6)$$

In Eq. (6) the sound velocity should be taken for the frequency of the Brillouin line position ν_B .

Expression (6) can be used for the comparison with experimental data. Fabelinsky also tried to take into account the contribution of the change of ε with temperature at constant density ρ . He has shown [22] that in this case R_{LP} is multiplied by the factor L

$$L = \frac{(\alpha^{-1} \partial \varepsilon / \partial T)_P^2}{(\rho \partial \varepsilon / \partial \rho)_S^2}, \quad (7)$$

which is estimated from 1 to 1.5 for different liquids [22]. Finally, the theoretical Landau-Placzek ratio takes form

$$R_{LP} = La \frac{\alpha^2 T c^2 (\nu_B)}{C_P}. \quad (8)$$

Taking $L = 1.25 \pm 0.25$ the product $L \cdot a = 1.5 \pm 0.5$ can be estimated.

Deviations from Eq. (8) are expected for the cases when the pair of two thermodynamic variables (P and S) is not enough to characterize the state of a liquid. This is well known, for example, for the case of solutions, where the concentration fluctuations contribute to the Rayleigh line intensity [22], increasing R_{LP} .

In our experiments we also expected that appearance of the locally favored structures will lead to the insufficiency of two variables P and S . Following [19] let's assume a third order parameter $z(\rho, T)$ responsible for the description of the locally favored structures. In this case the excess scattering intensity is described by

$$I_{exc} \propto \left(\frac{\partial \varepsilon}{\partial z} \right)^2 \langle \delta z^2 \rangle, \quad (9)$$

where the mean square fluctuation of order parameter $\langle \delta z^2 \rangle$ is described by

$$\langle \delta z^2 \rangle = k_B T \left(\frac{\partial \mu}{\partial z} \right)^{-1}_{\rho, T, A}. \quad (10)$$

In Eq. (10) μ is the chemical potential and A is the thermodynamically conjugated variable. By comparison with Eq. (4) and by use $\beta_S^{-1} = \rho c^2$ one can find the expectation for the excess of the Landau-Placzek ratio ΔR_{LP} above the value predicted by Eq. (8):

$$\Delta R_{LP} \propto \frac{(\partial \varepsilon / \partial z)^2 (\partial \mu / \partial z)^{-1}}{(\rho \partial \varepsilon / \partial \rho)_T^2 [\rho c^2 (\nu_B)]^{-1}} \quad (11)$$

Equation (11) allows one to rationalize the expected excess of the Landau-Placzek ratio in the terms of temperature dependence of some parameters. In particular, if we suppose in Eq. (11) the weak temperature dependences of derivatives of ε , then

$$\frac{\partial \mu}{\partial z} \propto \frac{c^2 (\nu_B)}{\Delta R_{LP}}. \quad (12)$$

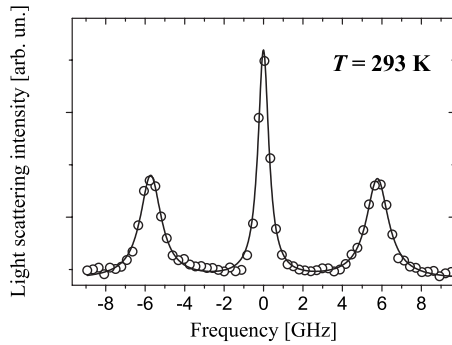


FIG. 1. Example of a scan of the Rayleigh-Brillouin spectrum in picoline at room temperature.

III. EXPERIMENT

The sample of molecular glass former α -picoline was prepared by sealing it in a glass tube under vacuum after few cycles of degassing. The right-angle polarized Rayleigh-Brillouin spectra were recorded by a home-made pressure scanned plane Fabry-Perot interferometer. Light scattering was excited by a solid-state laser (Excelsior, Spectra Physics) with wavelength 532.1 nm and a power of 100 mW. A free spectral range of 18.5 GHz was used in our experiments. The experimental finesse of the optical interferometer was about 30. A home-made liquid nitrogen flowing cryostat was used for measuring of Rayleigh-Brillouin spectra at different temperatures. The temperature range 160–372 K was studied. Below 160 K our sample crystallized during the measurement.

The isotropic component of the Rayleigh-Brillouin spectrum was calculated through $I_{ISO}(\nu) = I_{VV}(\nu) - 4/3 I_{VH}(\nu)$, where I_{VV} and I_{VH} depict polarized and depolarized light scattering, respectively. Note that this correction was small for the most part of the temperature range studied. The apparent depolarization ratio at zero frequency ρ has a low value at $T > 200$ K, as it is expected for a low-viscous liquid [22]. Also, note that in the temperature range studied we had no notable contribution of the longitudinal Brillouin component to depolarized I_{VH} spectrum. This means that in whole temperature range the sample had a good optical quality.

IV. RESULTS AND DISCUSSION

An example of the experimental scans of the Rayleigh-Brillouin spectrum is shown in Fig. 1 with a fit of the spectrum by the sum of three Lorentz contours. From the experimental Rayleigh-Brillouin spectra the shift of Brillouin peak ν_B and the ratio between the integral intensity of central Rayleigh peak I_C to the integrated intensity of the two Brillouin lines I_B

$$R_{LP} = \frac{I_C}{2I_B}$$

were found. For each temperature about 20 raw spectra like in Fig. 1 were used to obtain the accurate evaluation of the Landau-Placzek ratio.

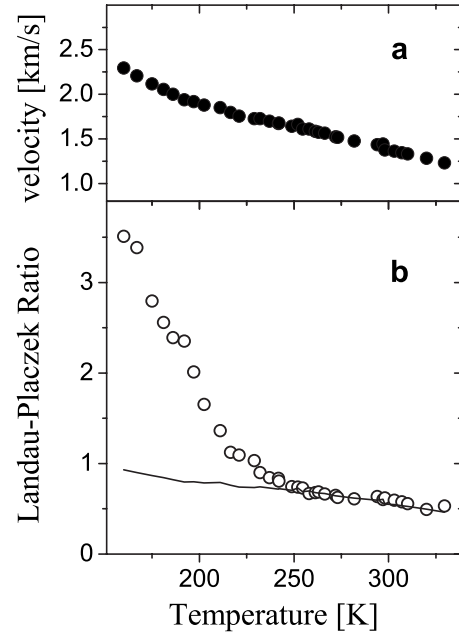


FIG. 2. Temperature dependence of the parameters of the Rayleigh-Brillouin spectrum in picoline: sound velocity (a) and the Landau-Placzek ratio (b). Line corresponds to the theoretical estimation for the Landau-Placzek ratio from Eq. (8).

Figure 2(a) shows the temperature dependence of the sound velocity c found from ν_B through the known expression for the right angle scattering

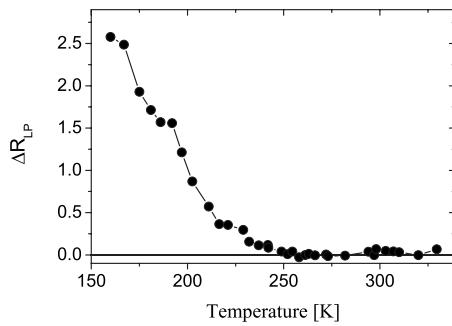
$$c = \frac{\nu_B \lambda}{\sqrt{2n}}, \quad (13)$$

where ν_B is measured in hertz, λ is the laser wavelength in vacuum, n is the refractive index of the sample. The temperature dependence for n of α -picoline was extrapolated from the data at two temperatures found in [25] as $n(T) = 1.515 - 5.1 \times 10^{-4} T / ^\circ\text{C}$.

Figure 2(b) demonstrates the temperature dependence of the Landau-Placzek ratio. It is noticeable the different behaviors of the temperature dependence of the sound velocity and the Landau-Placzek ratio. The former parameter increases rather gradually as the temperature decreases. The later parameter depicts the clear peculiarity near 250 K, which is T_A for α -picoline [15]. The strong increase of the Landau-Placzek ratio below T_A is expected from the assumption of the appearance of the locally favored structures at T_A . Thus, the simple qualitative view of Fig. 2(b) is in favor of the appearance of the locally favored structures at T_A .

Let's compare the experimental Landau-Placzek ratio with the prediction from Eq. (8). Data for specific heat were taken from [26], interpolated for the temperatures of our experiment. Few temperatures below 200 K were extrapolated by a polynomial fit. Thermal expansion was taken $0.99 \times 10^{-3} \text{ K}^{-1}$ according to the data, presented in [25]. Product $L \cdot a$ in Eq. (8) was taken 1.7.

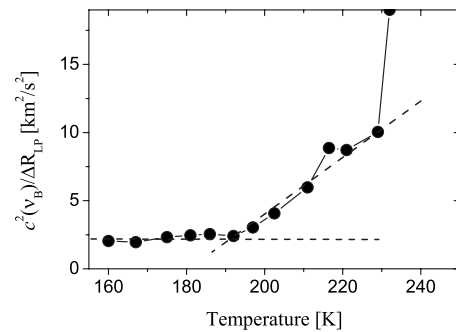
From Fig. 2(b) it is seen that the theoretical expression provides a very good description of the experimental Landau-Placzek ratio at $T > 250$ K. The difference between

FIG. 3. Temperature dependence of ΔR_{LP} .

the experimental data and the theoretical estimation, ΔR_{LP} , versus temperature is shown in Fig. 3. Above 250 K ΔR_{LP} is about zero. Below this temperature the noticeable divergence of the experimental data and theory is found. This disagreement are expected if below $T_A=250$ K the locally favored structures do appear in the glass former picoline. Thus, our investigation of the Landau-Placzek ratio supports the view of the appearance the locally favored structures in glass-formers below T_A [16]. This outcome is in the agreement with the conclusion from Raman scattering analysis in [15].

We used Eq. (12) and the Landau-Placzek data to check whether the effective chemical potential obeys a critical behavior. Early the critical behavior was suggested in the work [19] with the critical temperature near T_0 (below T_g). Figure 4 presents the parameter $c^2(\nu_B)/\Delta R_{LP}$ versus temperature. There is no obvious critical behavior. Instead of this two temperature ranges can be identified. The parameter decreases as the temperature decreases from 250 K to ~ 190 K and for lower temperatures it seems to be temperature independent.

It is interesting that the temperature of the change of temperature dependence of $c^2(\nu_B)/\Delta R_{LP}$ is close to crossover temperature T_X (180 K for picoline) estimated in [20] as a temperature where first deviations from MCT predictions appears. Moreover, Fig. 5 in [20] evidences that the estimated

FIG. 4. Parameter $c^2(\nu_B)/\Delta R_{LP}$ versus temperature. Dashed lines are guides to eyes.

nonergodicity parameter changes its behavior in the range 190–200 K. Our finding in Fig. 4 hypothesizes that T_X can be interrelated also with the statistics of the locally favored structures.

V. CONCLUSION

Study of the Rayleigh-Brillouin scattering in a glass-former picoline was done and it was shown that the Landau-Placzek ratio has the peculiarity at the temperature T_A (250 K). Above this temperature the ratio is well predicted from the theory, while below the significant excess of elastic scattering was found. This result supports the view that at $T=T_A$ the locally favored structures are appeared in the glass formers. The temperature dependence of an effective chemical potential for these structure can be extracted from the light scattering data. The potential is temperature independent below ~ 190 K and increases at higher temperatures.

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