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Temperature dependence of the Landau-Placzek ratio in liquid water

V. A. Zykova,[1] Y. A. Karpegina,[1,2] V. K. Malinovsky,[1] and N. V. Surovtsev[1,2,*]
[1]*Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk, 630090, Russia*
[2]*Novosibirsk State University, Novosibirsk, 630090, Russia*

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Rayleigh-Brillouin light scattering is studied in liquid water over the range from 249 to 365 K. Experiments are carried out with a high spectral resolution (0.1 GHz), eliminating any contribution of the structural relaxation to the elastic line. The Landau-Placzek ratio is found as the ratio of the Rayleigh and Brillouin intensities. In the whole temperature range, the Landau-Placzek ratio is found to be in good agreement with a prediction of the theory with a pair of independent thermodynamic variables, pressure and entropy. This description is usually used for single-component homogeneous liquids. An excess of the Landau-Placzek ratio above the prediction is expected for inhomogeneous liquids and is observed, for example, in glass-forming liquids below a certain temperature. In contrast to glass-forming liquids, no excess of elastically scattered light increasing at low temperatures is observed for the Landau-Placzek ratio of water. This suggests that the Landau-Placzek ratio of liquid water can be described by a homogeneous structure, and the idea of the water structure consisting of two structural motifs may not be necessary to explain the experimental ratio.

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I. INTRODUCTION

Short-lived directional hydrogen bonds between molecules seem to be responsible for unique properties of water [1–4]. However, the description of the molecular structure of liquid water is still an unsolved problem. A hypothesis that the water structure consists of two structural motifs is very convenient for explaining the peculiar properties of water. That is why the concept of an inhomogeneous structure of water is popular for the description of experimental results [5–8]. Nevertheless this concept still needs unambiguous experimental evidence and is a subject of many studies [8–14].

The study of elastically scattered light has a potential in revealing the inhomogeneous structure of liquids. Usually the Landau-Placzek ratio $R_{\mathrm{LP}}(T)$, being the ratio of the integral intensity of elastically scattered light (Rayleigh peak) to the integrated intensity of the two Brillouin lines provided by scattering from sound waves, is a measure in such kind of experiments. Indeed, $R_{\mathrm{LP}}(T)$ of homogeneous low-viscosity liquids are well described by a theoretical expression of the classical theory, which uses a pair of independent thermodynamic variables [15,16]. An inhomogeneous structure should lead to an additional amount of elastically scattered light by analogy with the effect of concentration fluctuations in binary solutions [17]. The hypothesis of a nanometrically inhomogeneous structure is known for glass-forming liquids. In some works [18–21] peculiar properties of glass-forming liquids were associated with the appearance of local inhomogeneities, which can be described as "locally favored structures" [20,21], at temperatures below a crossover temperature T_A from an Arrhenius-like to a non-Arrhenius behavior for the α-relaxation time temperature dependence. The Landau-Placzek ratio of glass-forming liquids agrees with the theoretical prediction above T_A and significantly exceeds the theoretical prediction below T_A [16,22]. This illustrates the potential of the Landau-Placzek ratio in revealing structural inhomogeneities of liquids.

There are only few studies of the Landau-Placzek temperature dependence in water. In Ref. [23] the Landau-Placzek ratio was found for liquid water in the temperature range from 277 to 323 K. The authors of [23] were not satisfied with agreement between the theoretical prediction and the experimental $R_{\mathrm{LP}}(T)$. In Ref. [24] the Landau-Placzek ratio was first measured in the supercooled water down to 248 K with the use of a grating monochromator. The authors of [24] pointed out that an intense low-frequency Raman wing in the water spectrum is not rejected by a single Fabry-Perot interferometer, and this is a drawback of the interferometric technique. However, the light scattering experiment of [24] is characterized by a low spectral resolution (from Fig. 1 of Ref. [24] it can be seen that the Rayleigh line contour has a full width at half maximum (FWHM) of ≈4 GHz), leading to the ambiguity in the evaluated parameters. Thus the Landau-Placzek ratio of liquid and supercooled water should be revisited. The present work is devoted to this problem. The Landau-Placzek ratio is studied in the temperature range from 249 to 365 K with the use of a tandem Fabry-Perot interferometer [25], combining a high spectral resolution and suppression of high transmission orders.

II. EXPERIMENT

Commercially available vials of distilled dust-free water of high purity (water for injections of medical grade) were purchased and used in the light scattering experiment without opening the vials. Light scattering was excited by a solid-state laser (Quantum Torus 750) with a wavelength of 532.1 nm and power of 200 mW. The right-angle Rayleigh-Brillouin spectra were recorded with a $3+3$-pass Sandercock tandem Fabry-Perot interferometer [25]. A single scan with a free spectral range of 10 GHz was used. The sample was placed in a home-made nitrogen flowing cryostat for measurements at different temperatures. The spectral resolution, determined through the description of the elastic line component of the water spectrum by a Gaussian contour, was 0.1 GHz (FWHM). According to

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[*] lab21@iae.nsk.su

[26] the width of the structural relaxation peak of water is wider than 2 GHz for $T \geqslant 260$ K; hence the spectral resolution 0.1 GHz excludes any contribution of the structural relaxation to the narrow central line for the temperature range studied.

Efforts were made to exclude the stray light contribution from elements of the experimental setup, but some extra elastic scattering from the cryostat window, the vials, and dust or bubbles in water cannot be avoided. Low intensity of the elastic line in water demands a hardly achievable purity of the water sample. For a Brillouin experiment with quick light registration the contribution of the residual particles of dust can be seen as temporally resolved spikes [15]. We adapted the temporal discrimination of the dust contribution [15] in the following way. For each experimental condition (certain vial and temperature) 50 spectra with 10 s accumulation were measured. The Landau-Placzek ratio was evaluated for every spectrum. Quality of a single spectrum, reflected in the signal-to-noise and Stokes-to-anti-Stokes ratios, ensured the evaluation of the Landau-Placzek ratio with precision better than 15%. Variation in the dust contribution leads to a data spread of the Landau-Placzek ratio for different spectra. The lowest values of the Landau-Placzek ratio correspond to the spectra, which have a minimum of the dust contribution. An example of the distribution of different Landau-Placzek ratios over the 50 spectra is shown in the file "distribution.pdf" of Supplemental Material [27]. We calculated the value of the Landau-Placzek ratio within the 15% interval from the lowest edge of the distribution.

To reveal the reproducibility of the experimental results, several series of experiments with different vials were performed.

III. RESULTS

Rayleigh-Brillouin spectra of water at three representative temperatures—significantly above the melting point (324 K), near the melting point (272 K), and in the supercooled state (249 K)—are shown in Fig. 1. Each spectrum in the figure is an average over the spectra selected for evaluation of the Landau-Placzek ratio, as described in the Experiment section. Data for other temperatures are available in Supplemental Material [27] as the files sample1.dat, sample2.dat, and sample3.dat. The central line in the spectra of Fig. 1 is the Rayleigh peak due to elastic scattering. The lines near ±5 GHz are the Brillouin lines corresponding to inelastic scattering by sound waves. Due to the high spectral resolution of the experiment the elastic line contribution is clearly separated from the rest of the spectrum. There is no ambiguity in the evaluation of its parameters from the experimental spectrum. To evaluate the integral intensity of the Rayleigh peak I_C and of the Brillouin line I_B the experimental triplet was fitted by a sum of three Voigt contours. From Fig. 1 it can be seen that the fit works well in the temperature range studied.

The fit provides also the values of the Brillouin shift $\nu_B(T)$ shown in Fig. 2. For the right-angle scattering the sound velocity of water $c(T)$ is extracted from the experimental curve $\nu_B(T)$ as

$$c(T) = \frac{\nu_B(T)\lambda}{\sqrt{2}n}, \qquad (1)$$

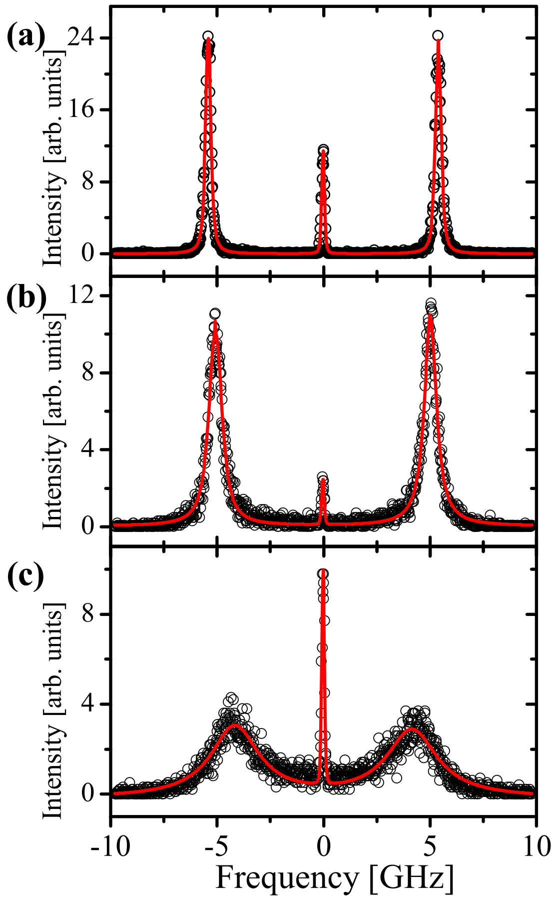

FIG. 1. Rayleigh-Brillouin spectrum of water at three representative temperatures (circles): $T = 324$ K (a); $T = 272$ K (b); $T = 249$ K (c). The lines are the fits by the sum of three Voigt contours.

where λ is the laser wavelength and n is the water refractive index. The extracted values of $c(T)$ were used for theoretical predictions of the Landau-Placzek ratio.

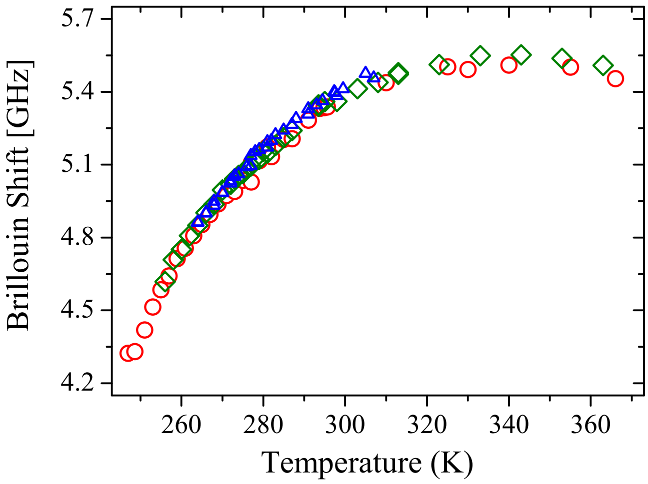

FIG. 2. Temperature dependence of the Brillouin shift for right-angle scattering. Different symbols correspond to different experimental series.

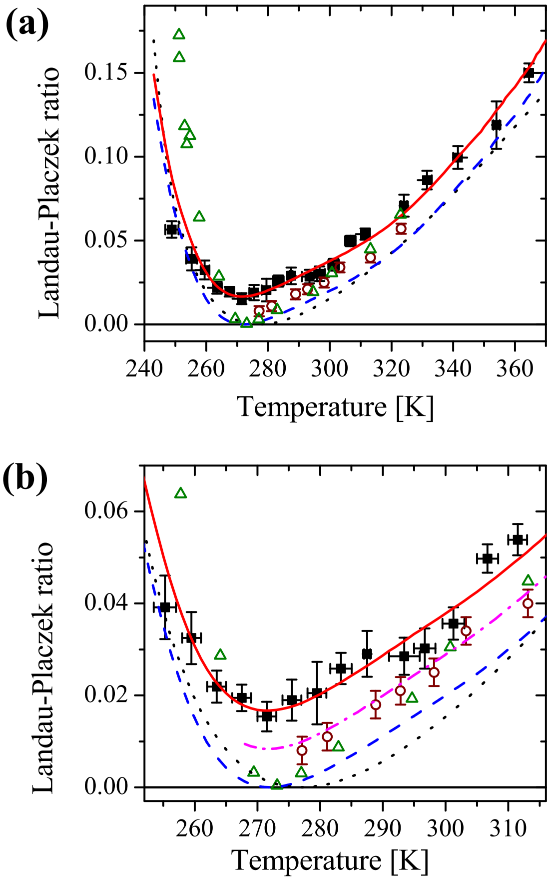

FIG. 3. Temperature dependence of the Landau-Placzek ratio of water. The squares are the experimental values of the present work, circles from [23], triangles from [24]. Panel (a) shows the whole temperature range, panel (b) near the minimum. The lines are model predictions: the dotted line from Eq. (2), the dashed line from Eq. (3); the solid and dash-dotted lines fit the squares and circles, respectively, by Eq. (5).

The Landau-Placzek ratio $R_{\rm LP} = I_C/(2I_B)$ was calculated as described in the Experiment section for each experimental condition. The values of $R_{\rm LP}$ from different series of the experiments were averaged within the temperature intervals shown in Fig. 3 by temperature error bars. The scatter of the $R_{\rm LP}$ data within the interval served to estimate the error. The temperature dependence of $R_{\rm LP}$ is shown in Fig. 3(a). The absolute values of $R_{\rm LP}$ are significantly lower than those of most other liquids, whose typical values of $R_{\rm LP}$ are about ~0.5 in the low-viscosity state [15,16]. The experimental values of $R_{\rm LP}$ for water demonstrate a minimum near the melting point (273 K), reaching a value of $R_{\rm LP} = 0.015$ at $T = 271.5$ K in our experiment. The behavior of $R_{\rm LP}$ near the minimum is shown in Fig. 3(b) in detail.

The data of $R_{\rm LP}$ from the previous studies [23,24] are also shown in Fig. 3. It is seen that our data demonstrate the same temperature dependence as $R_{\rm LP}(T)$ of [23] measured in the temperature range from 277 to 323 K. On the average our data are shifted up by ~0.008 from $R_{\rm LP}(T)$ of [23]. The most probable reason for the shift is additional parasitic elastic scattering in our experiment. Nevertheless, the agreement for the temperature-dependent part of $R_{\rm LP}(T)$ from [23] and our data is very good, while the temperature-independent shift can be easily taken into account.

Worse agreement is observed between our data and $R_{\rm LP}$ of [24]. $R_{\rm LP}(T)$ of [24] demonstrate a similar behavior as our data or the data of [23] above the room temperature, go to significantly lower values below room temperature, and demonstrate higher $R_{\rm LP}$ values for supercooled water, being three to five times higher than our $R_{\rm LP}$ near 250 K [the last point $R_{\rm LP}(T = 250\ {\rm K}) \approx 0.26$ from [24] is out of the frame in Fig. 3(a)]. We attributed this discrepancy to the low spectral resolution in the experiment of [24], which leads to significant ambiguity of the extracted parameters (compare Fig. 1 of [24] and our Fig. 1]).

Usually the Landau-Placzek ratio of liquids is described by a theory with a pair of independent thermodynamic variables, e.g., pressure and entropy [15]. This implies that there are no locally favored structures or clusters in the liquid structure, because such local nanometric inhomogeneities should lead to additional fluctuations described by a third thermodynamic variable (order parameter). The change of the dielectric constant ε with temperature at constant density ρ being neglected, the Landau-Placzek ratio is predicted by the expression [15,16]

$$R_{\rm LP} = a\frac{\alpha^2 T c^2}{C_P}, \tag{2}$$

where α is the thermal expansion coefficient, C_P is the specific heat at constant pressure, a is a constant of the order of unity, and c is the longitudinal sound velocity, which corresponds to the Brillouin line position. The estimation of a made for a number of liquids yields $a = 1.2 \pm 0.15$ [15].

The model prediction from Eq. (2) for $R_{\rm LP}(T)$ of water is shown in Fig. 3. The data of [28,29] for evaluation of $\alpha(T)$, the data of [30] for $C_P(T)$, $a = 1.2$, and the experimental $c(T)$ are used in the calculation. It is seen that Eq. (2) correctly catches the temperature dependence of $R_{\rm LP}(T)$ of water, being shifted down by a constant from our data and the data of [23]. The drawbacks of Eq. (2) are a somehow higher curvature of the temperature dependence of $R_{\rm LP}(T)$ in the range 275–305 K and the minimum at $T \approx 277$ K instead of the minimum near 271–273 K in the experimental data.

In Ref. [15] an expression for the Landau-Placzek ratio is presented,

$$R_{\rm LP} = \frac{\left[(\partial\varepsilon/\partial T)_P^2\, T/(\rho C_P)\right]_{static}}{\left[(\rho\partial\varepsilon/\partial\rho)_S^2\,\beta_S\right]_{hs}}, \tag{3}$$

which has no restriction of the negligibly small change of the dielectric constant ε with temperature at constant density ρ. In Eq. (3) $\beta_S = 1/(\rho c^2)$ is the adiabatic compressibility, the "*static*" label means the frequencies of the Rayleigh scattering and "*hs*" means the frequencies of the Brillouin peaks. To evaluate the prediction by Eq. (3) we applied the approximations described in [15]

$$\begin{aligned}\left[(\rho\partial\varepsilon/\partial\rho)_S^2\right]_{hs} &\approx \left[(\rho\partial\varepsilon/\partial\rho)_T^2\right]_{hs} = a^{-1}\left[(\rho\partial\varepsilon/\partial\rho)_T^2\right]_{static}\\ &= (\varepsilon-1)^2/a,\end{aligned} \tag{4}$$

and $(\partial\varepsilon/\partial T)_P = 2n(\partial n/\partial T)_P$, where n is the refractive index. The model prediction from Eqs. (3) and (4) for $R_{\rm LP}(T)$ of water is shown in Fig. 3. The data of $n(T)$ presented in [6,31], the data of [30] for $C_P(T)$, $a = 1.2$, and the experimental $c(T)$ are used in the calculation. Expressions (3) and (4) and the experimental $n(T)$ predict a minimum at $T \approx 272$ K in agreement with the experimental $R_{\mathrm{LP}}(T)$.

To take into account a temperature-independent contribution in the experimental $R_{\mathrm{LP}}(T)$, which is likely due to parasitic elastic scattering in the experiment, Eq. (3) can be modified to

$$R_{\mathrm{LP}} = \frac{\left[(\partial\varepsilon/\partial T)_P^2 T/(\rho C_P)\right]_{static}}{\left[(\rho\partial\varepsilon/\partial\rho)_S^2 \beta_S\right]_{hs}} + \frac{B}{\left[(\rho\partial\varepsilon/\partial\rho)_S^2 T\beta_S\right]_{hs}}, \tag{5}$$

where B is a fitting constant. Equation (5) with the help of Eq. (4) is used in Fig. 3 to fit the experimental $R_{\mathrm{LP}}(T)$ of the present work and of [23]. This fit provides excellent agreement between the experimental $R_{\mathrm{LP}}(T)$ and the model prediction.

IV. DISCUSSION

The values of the Landau-Placzek ratio are measured for the liquid and supercooled states of water. The present work extends the temperature range of $R_{\mathrm{LP}}(T)$ to higher temperatures for the liquid state and significantly corrects the previously reported values of $R_{\mathrm{LP}}(T)$ for the supercooled state. The peculiarity of the present work is the high spectral resolution of the light scattering experiment, which excludes the ambiguities in evaluation of the integral intensities of the Rayleigh peak and Brillouin lines. It is found that the temperature-dependent part of $R_{\mathrm{LP}}(T)$ is well described by the theoretical expression Eq. (3), which uses the pair of independent thermodynamic variables, pressure and entropy. A temperature-independent shift between experimental values of $R_{\mathrm{LP}}(T)$ and Eq. (3) is probably due to parasitic elastic scattering, but an extra contribution, which is out of the framework of Eq. (3), cannot be excluded.

The hypotheses of a two-component or nanometrically inhomogeneous structure of water should demand a third thermodynamic variable, whose fluctuations should lead to an excess of elastically scattered light increasing the Landau-Placzek ratio. Indeed a similar effect was observed in glass-forming liquids [16,22], where $R_{\mathrm{LP}}(T)$ was well described by Eq. (2) at high temperatures, but significantly exceeds the theoretical prediction below the Arrhenius crossover temperature $R_{\mathrm{LP}}(T)$ of glass-forming liquids. The difference between the experimental and theoretical $R_{\mathrm{LP}}(T)$'s increases with a temperature decrease [16]. By analogy with glass-forming liquids, one would expect a similar behavior for $R_{\mathrm{LP}}(T)$ in water. However, the experimental results, shown in Fig. 3, contradict this expectation, and there is no evidence for the excess of elastically scattered light increasing with a temperature decrease.

This result provides some restrictions for model hypotheses about the structure of water. Either fluctuations caused by structural inhomogeneities are low (high value of the derivative of the chemical potential with respect to the order parameter [22,32]), or the modulation of ε by these fluctuations is low (low value of the derivative of ε with respect to the order parameter [22,32]). In these cases the inhomogeneous nature of the water structure does not lead to the excess of elastically scattered light. Another possibility is the homogeneous structure of water for temperatures above 250 K.

No evidence of inhomogeneous water structure was found in [10,33], where small-angle x-ray scattering in water was described by number density fluctuations consistent with isothermal compressibility in the homogeneous description of the water structure. Also, recent molecular dynamics simulations of water revealed that the non-Arrhenius behavior of water dynamics [34] and the occurrence of high- and low-density regions [35] can be explained within the framework of a homogeneous structure. On the other hand, thermodynamics of bulk water is usually explained by coexistence of high- and low-density regions in water, and experimental results probing local structure are often described by a heterogeneous picture ([4,8] and reference therein). Thus further investigations of the problem of the water structure are needed, while results of the Landau-Placzek ratio impose certain limitations on characteristics of the water structure.

V. CONCLUSIONS

The Landau-Placzek ratio, being the ratio of intensities of elastically scattered light to the Brillouin components, has been found experimentally for liquid and supercooled water in the temperature range from 249 to 365 K. The values of the Landau-Placzek ratio found previously are corrected for the supercooled state and extended to higher temperatures for the liquid state. We have found that the experimental Landau-Placzek ratio is well described by the theory with a pair of independent thermodynamic variables, pressure and entropy, in the whole temperature range studied, if some temperature-independent contribution is taken into account. No evidence of excess of elastically scattered light increasing at low temperatures is observed in contrast to the case of glass-forming liquids [16,22], where this excess is explained by the additional scattering from locally favored structures. The model descriptions of the water structure as coexisting local clusters of different kinds and increasing of local inhomogeneities in the supercooled state may not be necessary to explain the temperature dependence of the Landau-Placzek ratio.

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