Determination of vibrational relaxation time of liquids with help of Landau-Placzek ratio

S. V. Lishchuk, N. P. Malomuzh
Dept. of Theor. Phys., Odessa State University, 2 Dvoryanskaya str., Odessa, 270100, Ukraine

Sh. Faizullaev
Dept. of Optics, Samarkand State University, 15 M. Gorkogo str., Samarkand, 703004, Uzbekistan

A new method of determination of the vibrational relaxation time of liquids based on using the Landau-Placzek ratio is proposed. The influence of molecular anisotropy effects is taken into account. The effectiveness of the method is illustrated on the example of substituted benzene.

I. INTRODUCTION

The vibrational relaxation phenomenon in the different types of the molecular gases and liquids is well known [1, 2]. It is manifested most evidently in the frequency dispersion of the absorption coefficient $\alpha(\omega)$ (per wavelength) and longitudinal sound velocity $c_l(\omega)$. In the majority of cases these parameters are measured effectively by acoustical methods and allow one to restore the vibrational relaxation time with high accuracy. However, if the values of the inverse vibrational relaxation time $1/\tau_v$ turn out to be in the hyperacoustical frequency interval $\omega \sim (10^9 \div 10^{10})$ s$^{-1}$, then the inaccuracy of the acoustical experiment increases noticeably. In these cases the use of molecular light scattering [3] is more preferable way of determination of vibrational relaxation time. The existence of vibrational relaxation will affect properly the angular dependence of height and half-width of Mandelshtam-Brillouin peaks, and therefore the angular dependence of the Landau-Placzek ratio. The detailed investigation of this problem for the liquids with quasishotropic molecules was made in works [4–7].

The main purpose of the present work is to attract attention to the expediency of use of the Landau-Placzek ratio $r$ for the experimental determination of the vibrational relaxation time $\tau_v$. It is shown in section II that the data on the scattering on small angles are the most suitable for the liquids with quasishotropic molecules. The relation between $\tau_v$ and $r$ is the most simple in this case. Section III is devoted to the discussion of the dependence of the Landau-Placzek ratio on the parameters describing the relaxation of the molecular anisotropy. The values of the vibrational relaxation time for substituted benzene are calculated.

II. IDEA OF APPROACH

In simple liquids the ratio of the central component intensity $I_c$ in the spectrum of polarized scattering to the total intensity of Mandelshtam-Brillouin components 2$I_{MB}$ is described by the expression [3]

$$r = r_0, \quad r_0 = \gamma - 1, \quad \gamma = \frac{c_p}{c_V}, \quad (1)$$

where $c_p$ and $c_V$ are the specific heat capacities of system at constant values of pressure and volume. The existence of the internal relaxation process leads to deviation of $r$ from $r_0$. The detailed analysis of this situation made in [4–8] showed that

$$r - r_0 = \left\{ r_0 \left[ \frac{1}{\gamma} \left( \frac{c_p^2}{v^2} + v^2 k^2 \right) - Z \right] + \Delta c^2 k^2 - \left( \frac{c_p^2}{v^2} - 1 \right) \left( \frac{c_p^2}{v^2 + c_p^2} + \frac{c_p^2}{v^2 + c_p^2} - \frac{1}{\gamma} \right) \right\} \frac{1}{Z}, \quad (2)$$

$$Z = \left( 1 - \frac{\gamma - 1}{\gamma} \frac{c_p^2}{k^2} \right) \left[ \frac{c_p^2}{v^2 c_p^2} + v^2 k^2 \right] - \Delta c^2 k^2. \quad (3)$$

Here $\tau_v$ is the vibrational relaxation time, $k = |k|$, $k$ is the wave vector of scattering, $\Delta c^2 = c_\infty - c_0$, and $c_\infty$ are the sound velocities on extremely low and high frequencies, $v$ is defined by expression:

$$\left( c k \tau_v \right)^2 = \frac{1}{2} \left( c_\infty k \tau_v \right)^2 - 1 + \sqrt{\left( 1 - c_\infty k^2 \tau_v^2 \right)^2 + 4 c_\infty^2 k^2 \tau_v^2}. \quad (4)$$

The value $\omega_{MB} = v(k)k$ gives the position of the Mandelshtam-Brillouin components and can be measured with high accuracy.

In principle, the formula (2) allows to determine the value $\tau_v$ through $r$, $r_0$, $c_p$, $c_\infty$, $\gamma$, and $k$ that are known. But the using of it is much more expedient if $(c_0 k \tau_v)^2 \ll 1$. In this case

$$r - r_0 = c_p^2 k^2 \delta^4 \left[ \left( \frac{\Delta c^2}{c_0^2} \right) \frac{1 + \gamma \Delta c^2}{c_0^2} \right], \quad (4)$$

so the value of $\tau_v$ can be found in more direct way. Expressing in addition $\Delta c^2 / c_0^2$ in terms of the ratio of the heat capacities [9]:

$$\frac{\Delta c^2}{c_0^2} = \frac{\gamma - 1}{\gamma} \frac{c_i}{c_V - c_i}, \quad (5)$$

where $c_i$ is the vibrational part of the heat capacity, the formula for determination of $\tau_v$ can be presented in form:

$$\tau_v = \frac{1}{\omega_{MB}} \left[ \frac{r - r_0}{\lambda(1 + \lambda)} \right]^{1/4}. \quad (5)$$
Here:
\[ \lambda = (\gamma - 1) \frac{c_1}{c_{V_0} - c_1} = (\gamma - 1) \frac{c_1}{c_{V_\infty}} \] (6)

Formula (5) can be used for liquids and scattering angles satisfying the inequality
\[ \frac{r - r_0}{\lambda(1 + \lambda)} \ll 1. \] (7)

Here only \( r = r(k) \) depends on the scattering angle and decreasing the last one can satisfy the inequality (7) in many cases.

The vibrational part of heat capacity \( c_i \) can be estimated with high accuracy with help of Planck-Einstein formula [10]:
\[ c_i = R \sum_i g_i \left( \frac{\hbar \omega_i}{kT} \right)^2 \exp \left( \frac{\hbar \omega_i}{kT} \right) \left[ 1 - \exp \left( - \frac{\hbar \omega_i}{kT} \right) \right]^{-2} \] (8)

where \( \omega_i \) is the \( i \)-th vibrational mode frequency, \( g_i \) is the degeneracy of \( i \)-th frequency, \( h \) is the Planck's constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature. The values of vibrational normal modes frequencies \( \omega_i \) for liquids, considered by us, can be taken from [11].

If in experimental conditions the inequality opposite to (7) takes place, the vibrational relaxation time \( \tau_v \) can be determined by the expression
\[ \tau_v = \frac{1}{\omega_{MB}} \sqrt{\frac{2 - \lambda}{r_\infty - r} \left[ 1 - \frac{1}{2} \lambda \left( 1 + \frac{1}{r_\infty + 1} \right) \right]} \] (9)

where
\[ r_\infty = r_0 + \lambda. \]

It is important to note, that formulas (5) and (9) are correct if the coefficient
\[ L = \left( \frac{d^2L}{d\eta^2} \right) \frac{1}{p} \left( \frac{d^2p}{d\eta^2} \right) \frac{1}{S} \]

where \( \eta \) is the refraction index, \( p \) is the mass density, \( \sigma \) is the thermal expansion coefficient, is equal to unity. In other cases one must substitute \( r' = r/L \) instead of \( r \).

The application of the formulas (5) and (9) for the case of substituted benzyl is demonstrated with help of the Table I. Besides the relaxation time, the values of all the used parameters are indicated. The closeness of the values of \( \tau_v \) obtained with a help of Landau-Placzek ratio, to that, obtained by the acoustic methods, testifies the effectiveness of the proposed method.

The formulas (2), (5) and (9) for determination of the vibrational relaxation time are correct only in the case when one can neglect the influence of the molecular anisotropy on the evolution of density fluctuations. This condition does not take place for the majority of the molecular liquids. The liquids, listed in Table I, also require more correct consideration.

<table>
<thead>
<tr>
<th>Substance</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tr>
<td>( r ) [16]</td>
<td>0.68</td>
<td>0.58</td>
<td>0.53</td>
<td>0.58</td>
<td>0.47</td>
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<td>( \omega_{MB} ), GHz [16]</td>
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<td>26.0</td>
<td>25.2</td>
<td>26.0</td>
<td>26.0</td>
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<td>( c_{v_{\infty}} ), J/(mol·K) [16]</td>
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<td>115</td>
<td>119</td>
<td>111</td>
<td>125</td>
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<tr>
<td>( \omega_{v_\infty} ), J/(mol·K) [16]</td>
<td>60</td>
<td>74</td>
<td>77</td>
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<td>83</td>
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<tr>
<td>( c_i ), J/(mol·K) [16]</td>
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<td>76</td>
<td>63</td>
<td>63</td>
<td>68</td>
</tr>
<tr>
<td>( \tau_v ), ps [17]</td>
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<td>120</td>
<td>120</td>
<td>124</td>
<td>1275</td>
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<tr>
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<td>0.95</td>
<td>0.85</td>
<td>0.81</td>
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<td>( \rho_s ), g/cm³ [17]</td>
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<td>1.2681</td>
<td>1.2508</td>
<td>1.2571</td>
<td>0.9974</td>
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Table I: Vibrational relaxation time for substituted benzene at 293 K. 1 — para-difluorobenzene, 2 — orthofluorochlorobenzene, 3 — metafluorochlorobenzene, 4 — para-fluorochlorobenzene, 5 — metaflurotoxene.

III. ANISOTROPY EFFECTS

Let us consider the structure of the Landau-Placzek ratio for the molecular liquids in which the anisotropy effects play an important role together with the vibrational relaxation. Here it is very essential that the anisotropy effects influence more considerably the character of the spectral distribution than the total intensity of the light scattering.

In the discussed case the set of variables \( \rho_1, T, \) and \( \nu \), describing the state of the system, must be completed with the traceless tensor of anisotropy \( \xi_{ik} \): \( \sum_{i=1}^{3} \xi_{ii} = 0 \). The last can be identified, for example, with the density of molecular inertia tensor. Extended in such a way the system of hydrodynamical equations has a standard structure (see [12, 13]). The densities of the free energy and of the dissipative function in the quadratic approximation are equal to:

\[ F = \frac{1}{2} \rho_1^2 \xi_{ik}^2 + \frac{1}{2} \xi_{ik} \left( \text{div} \ \nu \right)^2 + \frac{1}{2} \xi_{ik} \left( \nabla \xi_{ik} \right)^2 + \ldots, \]

\[ R = \frac{1}{2} \rho_1^2 \xi_{ik}^2 + \rho_1 \xi_{ik} \left( \text{div} \ \nu \right)^2 + \frac{1}{2} \xi_{ik} \left( \nabla \xi_{ik} \right)^2 - \rho_1 g_{ik} \xi_{ik} + \ldots, \]

where \( g_{ik} = \nabla_k v_i + \nabla_i v_k - \frac{2}{3} \delta_{ik} \text{div} \ \nu \).

Note, that the interaction between modes of anisotropy tensor and the velocity field can be described by including the respective contributions into the dissipative function only. The contribution \( \lambda_1 g_{ik} \xi_{ik} \) into \( R \) must be negative because the interaction of different modes leads to the lowering of the entropy production. The condition \( R > 0 \) gives the inequality for dissipative coefficients: \( \eta \lambda > \lambda_0^2 \).

The linearized system of hydrodynamical equations is presented and solved in the Appendix. As it is proposed in [4], the vibrational part of the shear viscosity is given by the equation:

\[ \eta_v(\omega) = \frac{b_v}{1 + i\omega \tau_v} \]
The final expression for the Landau-Placzek ratio is rather cumbersome and inconvenient for using. It becomes relatively more simple only in the limit case $(c_0 k \tau_v)^2 \ll 1$. Here

\[ r - r_0 = \gamma^2 \beta^2 + \gamma \beta (b_v - b_0) k^2 \tau_a + \gamma^2 \beta^2 (\tau_v^2 - \tau_v \tau_a + \tau_a^2) + 2 \gamma \beta c_0 k^2 \tau_v \tau_a \beta, \tag{12} \]

where

\[ \beta = b_v k^2 \tau_v + b_b k^2 \tau_a. \]

One can easily see that at $\tau_a = 0$ formula (12) turns into (4). The value of $b_v/\tau_v$ is connected with the heat capacities at constant volume and pressure and their vibrational part $c_i$ by the expression [9]:

\[ \frac{b_v}{\tau_v} = \frac{(c_p - c_v) c_i}{(c_v - c_i) c_p} \tag{13} \]

and $c_\infty$ can be found from the condition

\[ \frac{c_\infty^2}{c_0^2} = \frac{b_v}{\tau_v} + \frac{4 \nu - \nu_0}{3 \tau_a} \approx \frac{c_0^2}{c_0^2} \left( 1 + \frac{1}{\gamma} \right) + \frac{4 \nu}{3 \tau_a} \tag{14} \]

where $\nu = \eta/\rho$, $\nu_0 = \eta_0/\rho$, $\eta$ is the total shear viscosity, $\eta_0$ its static value. In the limiting case of $(c_0 k \tau_v)^2 \ll 1$ the value $\omega_{MB}$ can be substituted for $c_0 k$. The value $\tau_v$ can be obtained from the experiments on depolarized light scattering [15]. As a result, all auxiliary values in the equation for $\tau_v$

\[ r - r_0 = \gamma^2 \beta^2 + \gamma \beta \left[ \frac{\lambda}{\gamma} \omega_{MB}^2 \tau_v \tau_a - \frac{4}{3} \nu k^2 \tau_a \right] + \gamma \beta \omega_{MB}^2 \left( \tau_v^2 - \tau_v \tau_a + \tau_a^2 \right) + 2 \omega_{MB}^2 \tau_v \tau_a \beta, \tag{15} \]

where

\[ \beta = \frac{\lambda}{\gamma} \omega_{MB}^2 \tau_v + \frac{4}{3} \nu k^2 \tau_a. \]

and $\lambda$ is determined by formula (6), can be measured experimentally. If the influence of the anisotropy is small, formula (15) is considerably simplified:

\[ \tau_v = \tau_{v0} + \left[ \frac{2 \gamma \lambda + \gamma - \lambda \nu k^2}{3 \lambda (\lambda + 1) \omega_{MB}^2 \tau_{v0}} + \frac{2 + \lambda - \gamma}{4 (\lambda + 1)} \right] \tau_a, \tag{16} \]

where $\tau_{v0}$ is given by the expression (5).

In the other limiting case $((c_0 k \tau_v)^2 \gg 1)$ the expression for $r - r_0$ becomes considerably more cumbersome and its explicit form will not be given. It is always possible to satisfy the inequality $(c_0 k \tau_v)^2 \ll 1$ by changing the scattering angle.

### IV. CONCLUSION

The use of the Landau-Placzek ratio is the convenient way to determine the vibrational relaxation time. We have determined in this way the values of $\tau_v$ for substituted benzene, for which the acoustical data are absent. The obtained values of $\tau_v$ are close to the value of the vibrational relaxation time for benzene. The agreement of the obtained results with data on angular dependence of Mandelshtam-Brillouin components half-width could prove their correctness more consecutively. Th independent estimation for $\tau_v$ can be obtained by substitution $\tau_a$ determined from data on depolarized molecular light scattering into (20). The more accurate is the determined angular dependence of $\Gamma(k)/k^2$, the more accurate will be the results of calculations. The use of Landau-Placzek ratio is preferable from this point of view, because one can confine to the measuring of the parameters of spectra for one scattering angle only. Note that the values of the vibrational relaxation time mentioned in the Table 1 match the corresponding values of half-width of Mandelshtam-Brillouin components.

### Appendix

In accordance with (10,11) the system of linearized equations for the state variables has the form:

\[ \begin{align*}
\frac{\partial p}{\partial t} + \rho_0 \text{div} \mathbf{v} &= 0, \\
\rho_0 c_V \frac{\partial T_1}{\partial t} - \frac{c_v (\gamma - 1)}{\sigma} \frac{\partial \rho_1}{\partial t} &= -\kappa \Delta T_1, \\
\rho_0 \frac{\partial v_3}{\partial t} &= -\frac{c_0^2}{c_0^2} \nabla \rho_1 - \frac{c_0^2 \sigma \rho_0}{c_0} \nabla T_1 + \eta \Delta v_3 + \left( \frac{\zeta + 1}{3 \eta} \right) \nabla \eta \text{div} \mathbf{v} + \\
&+ \int_0^t \eta (t - t') \nabla \eta \text{div} \mathbf{v}(t') dt' - \lambda_1 \nabla \beta \frac{\partial \xi_{\alpha \beta}}{\partial t},
\end{align*} \tag{17} \]

Here $\rho_1$, $T_1$ are the deflections of the density and the temperature from their equilibrium values, $c_V$ is the specific heat capacity at constant volume, $\kappa$ is the heat conductivity coefficient, $\eta$ and $\zeta$ are the static values of shear and bulk viscosities, $\eta_0$ is the vibrational part of the shear viscosity, $\tau_a = \lambda/\sigma$ is the anisotropy relaxation time, $\gamma_1 = \lambda/\lambda_1$. Total shear viscosity is determined by the expression

\[ \eta = \lambda_1 \gamma_1 + \eta_0, \]

in which $\eta_0 \ll \lambda_1 \gamma_1$ for the majority of molecular liquids (see also [13]). It is evident that the equations for the heat conductivity and the mechanism of the vibrational relaxation do not change in the linear approximation.

The roots of a dispersion equation, corresponding to the hydrodynamic equations (17), up to $D_T k/c_0 \ll 1$, $D_V k/c_0 \ll 1$ are equal to

\[ s_1 = -D_T k^2, \]
Here $v = v(k)$ satisfies the equation
\[ -\omega^2 + \frac{c_0^2 k^2}{1 + \omega^2 v^2} + \frac{b_v k^2 v^2 \tau_v}{(\tau_v + \tau_a)} = 0, \quad \omega = vk, \quad (19) \]
in which $b_v = \rho \eta_v(0)$, $b_a = 4\nu^3/3$, $\nu = \lambda_1\gamma_1/\rho_0$ is the kinematic orientational viscosity. The value of $\Gamma$ is given by the expression
\[ \frac{\Gamma(k)}{k^2} = D_T k^2 + \left( \gamma - \frac{c_0^2}{v^2} \right) D_T k^2 + \frac{1 - \gamma D_T k^2 v}{1 + v^2 k^2 v^2} \tau_v k^4 \]
\[ + \left( \frac{v^2 k^2 v^2}{\tau_a} + \tau_a \right) \frac{b_v}{\tau_v} \left( \gamma D_T + v^2 \tau_v \right) k^4 + \gamma D_T (D_T + b_a) k^4 - (v^2 - c_0^2) k^2 \]. \quad (20)

Let us pass to the determination of the Landau-Placzek ratio. We use the following assumption about the evident form of the dielectric permittivity:
\[ \delta \varepsilon_{\alpha\beta} = \left[ \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \rho_1 + \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho T_1 \right] \delta_{\alpha\beta} + C \xi_{\alpha\beta}. \quad (21) \]

In accordance with (21) the spectrum of the polarized part of the scattered light intensity is equal to
\[ I_{VV}(k, \omega) \sim \left( \frac{\partial \varepsilon}{\partial \rho} \right)^2_T \left( \rho_1(r, t) \rho_1(0, 0) \right)_{\omega k} + \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \left( T_1(r, t) T_1(0, 0) \right)_{\omega k} + C^2 (\xi_{zz}(r, t) \xi_{zz}(0, 0))_{\omega k}. \quad (22) \]

As in [4-7], the contribution of the temperature fluctuations is omitted. The relative value of the contribution, given by the fluctuations of anisotropy, does not exceed a few percents [14]. So, we will hold only the first term further. Take into account that
\[ \int_{-\infty}^{\infty} \langle \rho_1(r, t) \rho_1(0, 0) \rangle_{\omega k} d\omega = \sum \text{poles } L(s), \quad (23) \]
where $L(s)$ is determined by the equation
\[ \rho_1(k, s) = L(s) \rho_1(k, 0) \]
and is equal to
\[ L(s) = \frac{\rho_0^3 \varepsilon V F(s)}{\tau_0 (1 + \tau_v s) \det M(k, s)}, \]

\[ F(s) = \tau_v \tau_a s^4 \left( \tau_v + \tau_a - \tau_v b_a k^2 \right) s^3 + \left( 1 + \frac{\gamma - 1}{\gamma} \right) \tau_v k^2 \left( \tau_v + \tau_a \right) + b_a k^2 \right) s^2 + \left( \frac{\gamma - 1}{\gamma} \right) \tau_v k^2 \left( \tau_v + \tau_a \right) + b_a k^2 \right) s + \frac{\gamma - 1}{\gamma} c_0^2 k^2. \]

We get from the expressions for the roots that the intensity $I_c$ of the central component is stipulated by the contributions of the roots $s_1$, $s_2$, and $s_3$ only. Therefore we get from (23):
\[ I_c \sim \left( \frac{\partial \varepsilon}{\partial \rho} \right)^2_T (M_1 + M_2 + M_3), \quad (24) \]
where
\[ M_1 = \frac{F(s_1)}{\tau_0 \tau_a} \frac{1}{(s_1 - s_2)(s_1 - s_3)(s_1 - s_4)(s_1 - s_5)}, \]
\[ M_2 = \frac{F(s_1)}{\tau_0 \tau_a} \frac{1}{(s_2 - s_1)(s_2 - s_3)(s_2 - s_4)(s_2 - s_5)}, \]
\[ M_3 = \frac{F(s_1)}{\tau_0 \tau_a} \frac{1}{(s_3 - s_1)(s_3 - s_2)(s_3 - s_4)(s_3 - s_5)}. \]
The integral intensity of the Mandelehtam-Brillouin components is determined by the roots $s_4$ and $s_5$ and, in accordance with (23), it is equal to
\[ 2I_{MB} \sim \left( \frac{\partial \varepsilon}{\partial \rho} \right)^2_T \frac{1}{\tau_0 \tau_a} \frac{1}{(s_4 - s_5)} \times \left\{ \begin{array}{l} F(s_4) \left( (s_4 - s_1)(s_4 - s_2)(s_4 - s_3) \right) \quad \text{if} \quad s_4 > s_5
\end{array} \right. \]
\[ - \left. \frac{F(s_5)}{(s_5 - s_1)(s_5 - s_2)(s_5 - s_3)} \right\}. \quad (25) \]
The expressions (24) and (25) allow us to determine the Landau-Placzek ratio $\tau = I_c/2I_{MB}$. 