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The Spectra of Molecular Light Scattering in High-Viscosity Glycerol-like Liquids

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Abstract—The mechanisms of formation of fine structures in the spectra of the polarized and depolarized components of molecular light scattering in high-viscosity liquids are studied. The temperature dependences of spectral parameters are examined. The results are treated in terms of the concept of a microheterogeneous structure of supercooled high-viscosity liquids.

High viscosity glycerol-like liquids exhibit many nontrivial thermodynamic and kinetic properties [1–3]. These properties manifest themselves in the spectra of molecular light scattering. In particular, the spectra of depolarized molecular light scattering show so-called fine structure (fine structure of the Rayleigh line wing) [4, 5]. In the frequency range $(0, c_{t\infty}, k)$, where $c_{t\infty}$ is the high-frequency transverse sound velocity and k is the wave vector, an intense central component and two side peaks are formed. Qualitatively, the origin of these peaks is known [6–8], but the reasons why central component shapes deviate from Lorentzian contours and why the intensity ratio between the central and side peaks abnormally rapidly increases with decreasing temperature [9, 10] have not been elucidated. Important data on the temperature dependence of Mandelshtam–Brillouin component parameters were obtained in [11, 12] but were not given a satisfactory physical interpretation.

Consider weak points of the concepts used in interpreting the above-mentioned and other special features of the spectra of scattered radiation. One such point is a trivial generalization of the relaxation theories that are used in the low-viscosity region by merely increasing the number of relaxation processes [7, 13, 14] even to an infinite number of relaxation variables [2]. The major difficulty is specifying the physical meaning of the variables introduced. Next, in recent years, a diversity of modifications of the theory of interacting modes have been in wide use [3, 15–17]. This approach makes it possible to reproduce the fractional-power laws of dispersion of viscoelastic parameters in high-viscosity liquids and many spectral effects. However, this is achieved by extending the use of macroscopic characteristics (such as the structure factor) far beyond the scope of their applicability. In addition, this approach does not explain relations with the special features of the behavior of thermodynamic values. Other approaches [18] are of a more fragmentary character.

In this work, we treat the specific features of molecular light scattering in supercooled states of high-viscosity glycerol-like liquids in terms of the concept of their microheterogeneous structure [19, 20]. To describe the behavior of scattered radiation, we use correlation functions obtained by solving the system of hydrodynamic equations suggested by us for the high-viscosity region. The characteristic feature of these equations is that they take into account not only unusual frequency dispersion of kinetic coefficients [20, 21] but also the dependence of the heat capacity of the system on frequency. This dependence has a noticeable influence on the spectral parameters that are determined by thermal modes and even causes the appearance of additional details. In this work, we concentrate on the fine structure of the Rayleigh line wing, the shape of the spectrum of polarized light scattering, and the temperature dependences of spectral parameters.

SPECTRA OF CORRELATION FUNCTIONS

Most of the above-mentioned features of the spectra of molecular light scattering are caused by the low-frequency components of thermal motions of molecules and can be described using hydrodynamics methods. The structure of hydrodynamics equations in the high-viscosity region was discussed in [21]. It was shown that the number and the general form of the equations are the same as in the low-viscosity region, and only the frequency dispersion of viscoelastic moduli changes substantially. Below, we refine the results of [21] by additionally including the frequency dispersion of heat capacities C_p and C_V and explicitly partitioning anisotropy tensor $\xi_{\alpha\beta}(\mathbf{r}, t)$ into the $\xi'_{\alpha\beta}(\mathbf{r}, t)$ and $\tilde{\xi}_{\alpha\beta}(\mathbf{r}, t)$ components which differently change in passage to the high-viscosity region.

The frequency dispersion of the heat capacity of a system depends on the same mechanism of structural relaxation as that responsible for the behavior of shear and volume viscosities in the high-viscosity region. It was shown [22] that the complex heat capacity of the system at a constant volume, $C_V(\omega)$, is described by the equation

$$C_V(\omega) = C_g + c(\pi^2 \chi(i\omega\tau) + i\omega\tau \operatorname{Re} F(i\omega\tau)), \quad (1)$$

where C_g is the heat capacity component obtained by extrapolation of its value in the vitreous state,

$$\chi(\omega\tau) = \operatorname{Re} \frac{1}{u} \left(\operatorname{cth} u - \frac{1}{u} \right), \quad u = \pi(i\omega\tau)^{1/2}, \quad (2)$$

$$F(z) = \frac{1}{z} \left\{ 1 + \frac{3}{\pi^2 z} - \frac{3}{\pi z^{1/2}} \operatorname{cth} \pi z^{1/2} \right\}, \quad (3)$$

c is the known coefficient, and τ is the time during which the mass distribution of weakly bound clusters relaxes to the equilibrium distribution. In addition, the frequency dispersion of cluster contributions to shear and volume viscosity is also given by the $F(i\omega\tau)$ function [21]. The behavior of $C_p(\omega)$ was not examined in detail. However clearly, it should be similar in character to that of $C_V(\omega)$. This similarity predetermines the character of variations of the ratio of the heat capacities $\gamma(\omega) = C_p(\omega)/C_V(\omega)$.

The anisotropy tensor component $\xi'_{\alpha\beta}(\mathbf{r}, t)$ is closely related to the frequency dispersion of viscosities, heat capacities, and some other values. This component is determined by processes of partial ordering in the high-viscosity state and changes together with the characteristics of weakly bound clusters. The key relation [21] for the correlator $\langle \xi'_{\alpha\beta}(\mathbf{r}, t) \xi'_{\alpha\beta}(\mathbf{0}, 0) \rangle$ (there is no summation over α and β) has the form

$$\langle \xi' \xi' \rangle_\omega \sim \langle \delta g \delta g \rangle \sim \tau F(i\omega\tau), \quad (4)$$

where δg is the mass change of a weakly bound cluster.

In hydrodynamics equations, parameter $\xi'_{\alpha\beta}$ only operates through frequency dispersions of viscoelastic moduli and heat capacities.

The other anisotropy tensor component ($\tilde{\xi}_{\alpha\beta}(\mathbf{r}, t)$) involves contributions that do not change in passing from the low- to high-viscosity region. Weaker interaction of the $\tilde{\xi}_{\alpha\beta}(\mathbf{r}, t)$ component with the velocity field has the same character as in the low-viscosity region. As a result, the hydrodynamics equations in the high-viscosity region written as Fourier transforms with

respect to spatial coordinates and Laplace transforms with respect to time take the form

$$\begin{aligned} s\rho_1(\mathbf{k}, s) + i\rho_0 k_\alpha v_\alpha(\mathbf{k}, s) &= \rho_1(\mathbf{k}, 0), \\ -\frac{C_p(s) - C_V(s)}{\sigma} s\rho_1(\mathbf{k}, s) &+ \\ &+ \rho_0 C_V(s)(s + \gamma D_T k^2) T_1(\mathbf{k}, s) \\ &= -\frac{C_p(s) - C_V(s)}{\sigma} \rho_1(k, \mathbf{0}) + \rho_0 C_V(s) T_1(k, \mathbf{0}), \\ \frac{ic_0^2 k_\alpha}{\gamma(s)} \rho_1(\mathbf{k}, s) + \frac{ic_0^2 \sigma \rho_0 k_\alpha}{\gamma(s)} T_1(\mathbf{k}, s) & \\ + \left[\rho_0 s \delta_{\alpha\beta} + \eta_c (k^2 \delta_{\alpha\beta} + \frac{1}{3} k_\alpha k_\beta) + \zeta_c k_\alpha k_\beta \right] v_\beta(\mathbf{k}, s) & \\ + \frac{iG_\infty k_\beta}{\gamma_1} \tilde{\xi}_{\alpha\beta}(\mathbf{k}, s) &= \rho_0 v_\alpha(\mathbf{k}, 0), \\ i\gamma_1 (k_\alpha \delta_{\beta\lambda} + k_\beta \delta_{\alpha\lambda} - \frac{2}{3} \delta_{\alpha\beta} k_\lambda) v_\lambda(\mathbf{k}, s) & \\ - (s + \Gamma) \tilde{\xi}_{\alpha\beta}(\mathbf{k}, s) &= -\tilde{\xi}_{\alpha\beta}(\mathbf{k}, 0). \end{aligned} \quad (5)$$

where ρ_1 and T_1 are the deviations of density and temperature from their equilibrium values ρ_0 and T ; v is the velocity; σ is the coefficient of thermal expansion; χ is the coefficient of heat conductivity; $D_T = \chi/\rho_0 C_V \gamma$ is the coefficient of temperature conductivity; c_0 is the ultimate low-frequency sound velocity; $\Gamma_a = 1/\tau_a$ is the coefficient of orientation diffusion; γ_1 is the coefficient of dissipative interaction of velocity and anisotropy field modes; $\eta(\omega) = \eta_0 + \eta_c(\omega)$ and $\zeta(\omega) = \zeta_0 + \zeta_v(\omega) + \zeta_c(\omega)$, where η_0 and ζ_0 are the seed values of shear and volume viscosities; $\zeta_v(\omega) = \zeta_v(0)/(1 + i\omega\tau_v)$ is the volume viscosity component related to vibrational relaxation; τ_v is the vibrational relaxation time; $\eta_c(\omega) = \eta_c(0)F(i\omega\tau)/F(0)$; and $\zeta_c(\omega) = \zeta_c(0)F(i\omega\tau)/F(0)$.

It is important that only τ and, consequently, $\eta_c(0)$ and $\zeta_c(0)$ change in order of magnitude with decreasing temperature. One more point that should be taken into account is the applicability range of equations (5). It was shown in [20] that the mechanism of relaxation to equilibrium of mass distribution of weakly bound clusters manifests itself only in the frequency range

$$0 \leq \omega \leq (10-10^2) \frac{1}{\tau}. \quad (6)$$

Another important conclusion follows from consideration of viscoelastic moduli. According to (5), the fre-

quency dispersion of shear $G(\omega)$ and longitudinal $K(\omega)$ elasticity moduli is given by

$$G(\omega) = i\omega [\eta_0 + \eta_a(\omega) + \eta_c(\omega)],$$

$$\eta_a(\omega) = \frac{\eta_a(0)}{1 + i\omega\tau_a}, \quad \eta_a(0) = G_\infty\tau_a, \quad (7)$$

$$K(\omega) = \rho_0 c_0^2 + \frac{4}{3}G(\omega) + i\omega [\zeta_0 + \zeta_a(\omega) + \zeta_c(\omega)].$$

The absence of a noticeable dispersion of transverse $(\text{Re}G/\rho_0)^{1/2}$ and longitudinal $(\text{Re}K/\rho_0)^{1/2}$ sound propagation velocities in the frequency range $\frac{1}{\tau} \ll \omega \ll \frac{1}{\tau_a}$ ($\frac{1}{\tau_v}$)

means that in addition to (4), the following inequalities should be met

$$\frac{\eta_a}{\tau_a} < (\ll) G_c, \quad \frac{\zeta_a}{\tau_a} < (\ll) M_c, \quad (8)$$

where $G_c = \eta_c(0)/\tau$, $M_c = \zeta_c(0)/\tau$.

The spectra of correlation functions can conveniently be obtained using vector \mathbf{u} with components $(\rho_1, T_1, v_x, v_y, v_z, \tilde{\xi}_{xx}, \tilde{\xi}_{xy}, \dots, \tilde{\xi}_{zz})$. System (5) then takes the form

$$M_{\alpha\beta}(\mathbf{k}, z)u_\beta(\mathbf{k}, z) = u_\alpha(\mathbf{k}, 0) \quad (9)$$

or

$$u_\alpha(\mathbf{k}, z) = (M^{-1})_{\alpha\beta}u_\beta(\mathbf{k}, 0). \quad (9')$$

As the simultaneous values of vector \mathbf{u} components are mutually orthogonal,

$$\langle u_\alpha^*(\mathbf{k}, 0)u_\beta(\mathbf{k}, 0) \rangle = \langle |u_\alpha(\mathbf{k}, 0)|^2 \rangle \delta_{\alpha\beta}, \quad (10)$$

we obtain the spectral density of hydrodynamic variables in the form

$$\langle u_\alpha(\mathbf{r}, t)u_\beta(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega} = \text{Re}(M^{-1})_{\alpha\beta} \langle |u_\beta(\mathbf{k}, 0)|^2 \rangle. \quad (11)$$

In conformity with the foregoing, the correlation function of the anisotropy tensor components is given by the sum

$$\langle \xi_{\alpha\beta}(\mathbf{r}, t)\xi_{\alpha\beta}(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega} = \langle \xi'_{\alpha\beta}(\mathbf{r}, t)\xi'_{\alpha\beta}(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega} + \langle \tilde{\xi}_{\alpha\beta}(\mathbf{r}, t)\tilde{\xi}_{\alpha\beta}(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega}.$$

As above, the sums over α and β are not taken. The simultaneous correlators of hydrodynamic variables are described by the equations

$$\langle |\rho(\mathbf{k}, 0)|^2 \rangle = \rho^2 kT\beta_t, \quad \langle |T(\mathbf{k}, 0)|^2 \rangle = kT^2/\rho C_p, \quad (12)$$

$$\langle |\mathbf{v}(\mathbf{k}, 0)|^2 \rangle = kT/\rho, \quad \langle |\xi(\mathbf{k}, 0)|^2 \rangle = kT/\alpha,$$

where

$$\beta_t = \rho \left[-\frac{1}{C_l^2 \rho^2} + \left(\frac{1}{C_l^2 \rho_l^2} - \frac{1}{C_g^2 \rho_g^2} \right) \Phi + \left(\frac{1}{\rho_g} - \frac{1}{\rho_l} \right) \frac{\partial \Phi}{\partial \rho} \Big|_T \right]$$

is the isothermal compressibility [22] and α is the coefficient in the expansion of free energy $\delta F = \frac{\alpha}{2} \int \tilde{\xi}_{\alpha\beta}(\mathbf{r}, t)dV + \dots$. Formulas (11) and (12) give an unambiguous solution to the problem of determining the spectra of correlation functions in the high-viscosity region.

DEPOLARIZED LIGHT SCATTERING

Let the incident light beam propagate along axis y and be polarized along axis z , and let the scattered light beam lie in plane (x, y) and make angle θ with axis y . The geometry of the experiment is described by the following expression for depolarized light scattering intensity:

$$I^{\text{VH}} \sim \sin^2 \frac{\theta}{2} K_2(\mathbf{k}, \omega) + \cos^2 \frac{\theta}{2} K_3(\mathbf{k}, \omega), \quad (13)$$

$$I^{\text{HH}}(\theta = 90^\circ) \sim \frac{1}{2} K_4(\mathbf{k}, \omega) \quad (14)$$

$$+ \frac{1}{4} [K_1(\mathbf{k}, \omega) + 2K_2(\mathbf{k}, \omega)].$$

Here,

$$K_1 = t_{MM, NN}(\mathbf{k}, \omega), \quad K_2 = t_{MN, MN}(\mathbf{k}, \omega), \quad (15)$$

$$K_3 = t_{ML, ML}(\mathbf{k}, \omega), \quad K_4 = t_{LL, LL}(\mathbf{k}, \omega)$$

are the components of the anisotropic part of the tensor of scattering and

$$t_{iklm} = \langle \delta\varepsilon_{ik}^{(0)}(\mathbf{r}, t)\delta\varepsilon_{lm}^{(0)}(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega}, \quad (16)$$

where $\delta\varepsilon_{ik}^{(0)}(\mathbf{k}, t)$ are the anisotropic components of the fluctuation dielectric constant tensor in the (MNL) coordinate system whose L and M axes lie in the xy plane, axis L is aligned with scattering vector \mathbf{k} , and the axis perpendicular to L is formed by turning axis L counterclockwise through $\pi/2$. Axis N coincides with the z axis of the laboratory coordinate system.

It is assumed that

$$\delta\varepsilon_{ik}^{(0)} = c_a \xi_{ik}. \quad (17)$$

The c_a coefficient value is on the order of unity and does not change substantially on passing to the high-viscosity region (see [21]).

The explicit form of the K_1, K_2, K_3 , and K_4 functions is as follows:

$$K_1(\mathbf{k}, \omega) = K_2(\mathbf{k}, \omega) = c_a^2 \operatorname{Re} \left\{ a\tau F(i\omega\tau) + \frac{k_B T}{\alpha} \frac{1}{i\omega + 1/\tau_a} \right\}, \quad (18)$$

$$K_3(\mathbf{k}, \omega) = c_a^2 \operatorname{Re} \left\{ a\tau F(i\omega\tau) + \frac{k_B T}{\alpha} \left[i\omega + \frac{1}{\tau_a} + \frac{G_a k^2}{\rho(i\omega + (v_0 + v_c(\omega)) q^2)} \right]^{-1} \right\},$$

$$K_4(\mathbf{k}, \omega) = c_a^2 \operatorname{Re} \left\{ a\tau F(i\omega\tau) + \frac{k_B T}{\alpha} \times \left[i\omega + \frac{1}{\tau_a} + \frac{v_0(0)k^2}{i\omega + \left(\frac{4}{3}v_0 + \zeta'(\omega) + (c_0^2/i\omega)\right)k^2} \right]^{-1} \right\},$$

where $v_i = \eta_i/\rho$, $i = 0, c$, $\zeta' = \zeta/\rho$, a is the proportionality factor between $\langle \xi' \xi' \rangle$ and $F(i\omega\tau)$ in (4). Substituting (18) into (13) gives the spectrum of depolarized scattering in the form

$$I^{\text{VH}}(\mathbf{k}, \omega) \sim c_a^2 \left\{ a\tau F(i\omega\tau) + \frac{k_B T}{\alpha} \left[\frac{1/\tau_a}{\omega^2 + (1/\tau_a^2)} \sin^2 \frac{\theta}{2} + \cos^2 \frac{\theta}{2} \right] \times \operatorname{Re} \left(i\omega + \frac{1}{\tau_a} + \frac{G_a k^2}{\rho(i\omega + (v_0 + v_c(\omega)) k^2)} \right)^{-1} \right\}. \quad (19)$$

By virtue of the inequality $1/\tau \ll 1/\tau_a$, the relaxation processes in the high-viscosity region determine the special features of the spectrum only in the frequency range $(0, 10/\tau)$. In addition, taking into account that in (19), $k_B T/\alpha \approx a$, we obtain

$$I^{\text{VH}}(\mathbf{k}, \omega) \sim c_a^2 a\tau \operatorname{Re} F(i\omega\tau), \quad \omega \in (0, 10/\tau). \quad (20)$$

It follows that the shape of the central component is essentially non-Lorentzian. As temperature decreases, the height of the central component $I^{\text{VH}}(\mathbf{k}, 0)$ increases in proportion to τ or, in other words, to viscosity η . In the frequency range $1/\tau \ll \omega \leq 1/\tau_a$, side components are formed:

$$I^{\text{VH}}(\mathbf{k}, \omega) \sim c_a^2 \frac{k_B T}{\alpha} \left[\frac{1/\tau_a}{\omega^2 + 1/\tau_a^2} \sin^2 \frac{\theta}{2} + \sum_{\pm} \frac{1/\tau_a}{(\omega \pm c_{t\infty} k)^2 + 1/\tau_a^2} \cos^2 \frac{\theta}{2} \right]. \quad (21)$$

Here, $c_{t\infty} = (G_c/\rho + G_a/\rho)^{1/2} \approx (G_c/\rho)^{1/2}$ is the transverse sound propagation velocity. The first term in (21) corresponds to a slowly [in comparison with (20)] varying contribution to the central component.

Note that the integrated intensities of the narrow central component and side peaks have comparable values. However, in contrast to the rapidly narrowing central component, the parameters (height and half-width proportional to $1/\tau_a$) of the side peaks change only slightly.

The observed patterns are strongly affected by instrumental effects. For simplicity, we assume that the instrument response function $A(\omega)$ in the equation

$$J^{\text{VH}}(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} I^{\text{VH}}(\mathbf{k}, \omega') A(\omega - \omega') d\omega' \quad (22)$$

has a Lorentzian shape, that is $A(\omega) = \frac{1}{\pi} \frac{\Gamma_A}{\omega^2 + \Gamma_A^2}$, and

that $I^{\text{VH}}(\mathbf{k}, \omega)$ is given by (19). The observed signal, $J^{\text{VH}}(\mathbf{k}, \omega)$, is then given by

$$J^{\text{VH}}(\mathbf{k}, \omega) \sim c_a^2 \left\{ a\tau \operatorname{Re} F[i\tau(\omega - \Gamma_A)] + \frac{k_B T}{\alpha} \times \tau_a \left[\frac{1}{1 + (\omega\tau_a)^2} \sin^2 \frac{\theta}{2} + \sum_{\pm} \frac{1}{\tau_a^2 (\omega - c_{t\infty} k)^2 + 1} \cos^2 \frac{\theta}{2} \right] \right\}. \quad (23)$$

In deriving (23), it was taken into account that renormalization of side components can be neglected at typical Γ_A values of 10^8 Hz, which satisfy the inequality $1/\tau < \Gamma_A \ll 1/\tau_a$. Evidently, for not too deep supercooling, when $\Gamma_A \tau < 1$,

$$J^{\text{VH}}(\mathbf{k}, 0) \sim \tau, \quad \frac{J^{\text{VH}}(\mathbf{k}, 0)}{J^{\text{VH}}(\mathbf{k}, c_{t\infty} k)} \sim \frac{\tau}{\tau_a}. \quad (24)$$

In the other limiting case, when $\Gamma_A \tau > 1$,

$$J^{\text{VH}}(\mathbf{k}, 0) \sim \frac{1}{\Gamma_A}, \quad \frac{J^{\text{VH}}(\mathbf{k}, 0)}{J^{\text{VH}}(\mathbf{k}, c_{t\infty} k)} \sim \frac{1}{\Gamma_A \tau_a}, \quad (25)$$

i.e., at temperatures $T \approx T_0$, when $\Gamma_A \tau(T_0) \sim 1$, the height ratio between the central and side peaks is stabilized but is still far above unity.

In passing to the low-viscosity region, the obtained results are transformed to the well-known ones [14].

Next, let us briefly consider the special features of depolarized scattering $I^{\text{HH}}(\theta = 90^\circ)$. Similarly to depolarized VH scattering, there are central and side HH

scattering components. It directly follows from (14), (15), and (19) that

$$I^{\text{HH}}(\theta = 90^\circ) \sim \frac{5}{4} c_a^2 a \tau \text{Re} F(i\omega\tau), \quad \omega \in (0, 10/\tau), \quad (26)$$

$$I^{\text{HH}}(\theta = 90^\circ) \sim \frac{k_B T}{4\alpha} c_a^2 \left[3 \frac{1/\tau_a}{\omega^2 + 1/\tau_a^2} + \text{Re} \sum_{\pm} \frac{1/\tau_a}{(\omega - c_{l\infty} k)^2 + (1/\tau_a^2)} \right]. \quad (27)$$

Here, $c_{l\infty} = \left(c_0^2 + \frac{4}{3} c_{l\infty}^2 + M_c \right)^{1/2}$ is the high-frequency

longitudinal sound velocity. Note that $v_0 k^2, \zeta_0 k^2 \ll 1/\tau_a$, and the half-width of side components is largely determined by anisotropy relaxation time. The influence of instrument effects on I^{HH} is the same as with VH scattering.

POLARIZED LIGHT SCATTERING

Polarized light scattering intensity I^{VV} (with a vertical orientation of polarization unit vectors) is described by the equation [21]

$$I^{\text{VV}}(\mathbf{k}, \omega) \sim \langle \delta\epsilon(\mathbf{r}, t) \delta\epsilon(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega} + t_{NN, NN}(\mathbf{k}, \omega), \quad (28)$$

where

$$\delta\epsilon(\mathbf{r}, t) = c_\rho \delta\rho + c_T \delta T + \dots \quad (29)$$

is the isotropic component of the fluctuation dielectric constant tensor and $\delta\rho$ and δT are the density and temperature fluctuations, respectively.

At a constant density, temperature fluctuations are largely determined by the degrees of freedom that do not affect the structure and special features of the high-viscosity state. The correlator $\langle \delta T \delta T \rangle_{\mathbf{k}\omega}$ value is the same as for the low-viscosity and vitreous regions. The contribution of temperature fluctuations is relatively small in this region, and we will therefore ignore it.

The contribution of anisotropy fluctuations does not exceed 10^{-2} of the contribution of density fluctuations [6]. Therefore,

$$I^{\text{VV}}(\mathbf{k}, \omega) \sim c_\rho^2 \langle \delta\rho(\mathbf{r}, t) \delta\rho(\mathbf{0}, 0) \rangle_{\mathbf{k}\omega}. \quad (30)$$

For supercooled states of high-viscosity liquids with microheterogeneous structures, optomechanical coefficient c_ρ is given by [23]

$$c_\rho = \left[\frac{\epsilon_{\text{eff}}}{\epsilon_l} - \frac{9\epsilon_g \epsilon_l}{[\epsilon_g + 2\epsilon_l - (\epsilon_g - \epsilon_l)\phi]^2 \phi} \right] \frac{\partial \epsilon_\rho}{\partial \rho_l}, \quad (31)$$

where ϵ_{eff} satisfies the equation

$$\frac{\epsilon_{\text{eff}} - \epsilon_l}{\epsilon_{\text{eff}} + 2\epsilon_l} = \frac{\epsilon_g - \epsilon_l}{\epsilon_g + 2\epsilon_l} \phi,$$

ϵ_l and ϵ_g are the dielectric constants of the system in the low-viscosity and vitreous states extrapolated to the high-viscosity state, and ϕ is the specific volume occupied by strongly bound clusters.

An explicit form of the correlator can be found from equations (9'), (11), and (12). The special features of its behavior are determined by the roots of the equation

$$\det(M_{\alpha\beta}) = 0. \quad (32)$$

Relaxation of heat capacities $C_V(\omega)$ and $C_p(\omega)$ and the $\gamma(\omega)$ ratio in (5) complicates the problem substantially. However, in the limits of

$$(a) D_T k^2 \ll 1/\tau \ll c_0 k, \quad (33)$$

$$(b) 1/\tau \ll D_T k^2 \ll c_0 k, \quad (34)$$

and on the additional assumption

$$1/\tau_a, 1/\tau_v \sim c_0 k \text{ (for not too low } k \text{ values),}$$

the roots are more easy to determine. It is obvious that the roots that describe thermal and sound modes are

$$\omega_h^{(a)} = -\frac{i\chi}{\rho_0 c_{p0}} \equiv -ix_0^{(a)}, \quad (35)$$

$$\omega_{1,2}^{(a)} = -\frac{i}{2} \Gamma k^2 \pm ck \equiv -ix_1 \pm x_2,$$

$$\omega_h^{(b)} = -\frac{i\chi}{\rho_0 c_{p\infty}} \equiv -ix_0^{(b)}, \quad (36)$$

$$\omega_{1,2}^{(b)} = -\frac{i}{2} \Gamma k^2 \pm ck,$$

where

$$c_{p0} = c_p \left(\omega \ll \frac{1}{\tau} \right), \quad c_{p\infty} = c_p \left(\frac{1}{\tau} \ll \omega \ll \frac{1}{\tau_a} \right),$$

$$c^2 = c_0^2 + \frac{1}{\rho_0} \left(\frac{4}{3} G_c + M_c \right),$$

$$\Gamma = \left[\frac{4\eta_0 + \eta_a(\omega_k)}{3\rho_0} \right. \quad (37)$$

$$\left. + \frac{\zeta_0 + \zeta_v(\omega_k)}{\rho_0} + \frac{\chi}{\rho_0 c_{p\infty}} (\gamma_b - 1) \right],$$

$$\omega_k = ck, \quad \gamma_a = \gamma \left(\omega \ll \frac{1}{\tau} \right), \quad \gamma_b = \gamma \left(\frac{1}{\tau} \ll \omega \ll \frac{1}{\tau_a} \right).$$

The spectral density of the intensity of molecular light scattering corresponding to (35) and (36) has the form (see [24]):

$$I^{(a,b)}(k, \omega) \sim \left(1 - \frac{1}{\gamma_{a,b}} \right) \frac{x_0^{(a,b)}}{\omega^2 + x_0^{(a,b)2}} + \frac{x_1}{2\gamma_b} \left[\frac{1}{(\omega - x_2)^2 + x_1^2} + \frac{1}{(\omega + x_2)^2 + x_1^2} \right] \quad (38)$$

$$-\frac{x_1}{2\gamma_b x_2} \left[\frac{\omega - x_2}{(\omega - x_2)^2 + x_1^2} - \frac{\omega + x_2}{(\omega + x_2)^2 + x_1^2} \right].$$

Note that there is one more root in case (b):

$$\omega_c \approx -\frac{i\gamma_a}{\gamma_b \tau}. \quad (39)$$

The narrow central peak that corresponds to (39) has a relatively low integrated intensity. The ratio of this intensity to that of the thermal peak is

$$\frac{I_c}{I_h} \approx \frac{\gamma_b - \gamma_a}{\gamma_b(\gamma_b - 1)D_T} \frac{c^2 c_0^2 + \gamma_b(c^2 - c_0^2)}{k^2 \tau c_0^2} \quad (40)$$

This ratio decreases rapidly as temperature lowers. The peak can, however, be detected by correlation spectroscopy methods [24].

If inequality (34) is not fulfilled, the spectrum has a more complex form. This is especially true of the component corresponding to the thermal mode. The parameters of this component will take on intermediate values. The Landau–Placzek relationship changes accordingly:

$$R = \begin{cases} \frac{\gamma_\infty}{\gamma_0}(\gamma_0 - 1), & \text{case a} \\ \gamma_\infty - 1, & \text{case b.} \end{cases} \quad (41)$$

Consider the temperature dependence of the Mandelshtam–Brillouin component width. According to (37),

$$\Gamma(T) \approx \left[\frac{4}{3} \left(v_0 + \frac{c_{1a}^2 \tau_a}{1 + c_{l\infty}^2 \tau_a^2 k^2} \right) + \left(\zeta_0' + \frac{c_{1v}^2 \tau_v}{1 + c_{l\infty}^2 \tau_v^2 k^2} \right) + \frac{\chi}{\rho_0 c_{p\infty}} (\gamma_b - 1) \right] k^2. \quad (42)$$

The temperature dependence of parameter Γ can be described if it is taken into account that relaxation times τ_a and τ_* decrease slowly as temperature lowers. For simplicity, consider the situation when viscosity formation is dominated by one mechanism. Put

$$\Gamma(T) \approx \frac{4}{3} \left(v_0 + \frac{c_{1a}^2 \tau_a}{1 + c_{l\infty}^2 \tau_a^2 k^2} \right) k^2. \quad (43)$$

At $T > T_*$, where T_* is defined as

$$c_{l\infty}^2(T_*) \tau_a^2(T_*) k^2 = 1, \quad (44)$$

the $\Gamma(T) \approx \frac{4}{3} (v_0 + c_{1a}^2 \tau_a) k^2$ value decreases with increasing temperature. If $T < T_*$ and temperature

decreases, then

$$\Gamma(T) \approx \frac{4}{3} \left[v_0 k^2 + \frac{1}{\tau_a} \right]$$

also decreases. It follows that at $T \sim T_*$, the Mandelshtam–Brillouin component width is a maximum. This conclusion is in complete agreement with experiment [11, 12].

Absorption per wave length at Mandelshtam–Brillouin frequencies is related to half-width Γ of side component as

$$(\alpha\lambda) = \frac{\pi}{\rho c k} \Gamma.$$

For comparison, we give equations for sound velocity and the coefficient of sound absorption ($\alpha\lambda$):

$$c_l^{-1}(\omega) = \left(\frac{\rho}{2} \right)^{1/2} \frac{(|L| + L')^{1/2}}{|L|}, \quad (45)$$

$$(\alpha\lambda)(\omega) = 2\pi \left(\frac{|L| - L'}{|L| + L'} \right)^{1/2}, \quad (46)$$

where

$$L(\omega) \approx \rho [c_0^2 + (c_\infty^2 - c_0^2) i\omega\tau F(i\omega\tau)]. \quad (47)$$

It follows from (47) that the frequency dependences of $c_l(\omega)$ and $(\alpha\lambda)(\omega)$ at a constant temperature and the dependences of these values on relaxation time at a constant frequency are described by similar curves. In other words, there exists scaling in the frequency range

$$0 < \omega \leq 10/\tau \ll 1/\tau_a. \quad (48)$$

CONCLUSIONS

The principal results of this work are in qualitative agreement with the available experimental data. Because of inaccuracy of these data, detailed verification of the theory is, however, impossible. Indeed, none of high-viscosity glycerol-like liquids was studied by the methods of acoustic, molecular, and dielectric spectroscopy in the same temperature range. This seriously impedes checking consistency of various theoretical approaches and revealing their potentialities.

Attention should be given to thorough examination of two integral characteristics of polarized molecular light scattering, the integrated intensity and the Landau–Placzek relation. The degree of nonlinearity of integrated intensity variations with temperature is closely related to the formation of weakly bound clusters and can be used as a sensitive test for their presence. A nonlinear temperature behavior of the Landau–Placzek relation in some temperature range gives information about structural relaxation contributions to system's heat capacity and compressibility. Note also the importance of comprehensive studies of the behavior of

liquids in the region of intermediate viscosities, for in this region, various physical mechanisms can be identified more accurately.

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