Studies of the rotation-translational coupling and bulk-viscosity relaxation of liquids composed of anisotropic molecules by Rayleigh-Brillouin scattering

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Abstract – Effects of the rotation-translational coupling on the spectra of the longitudinal and transverse (sheer) acoustic phonons in molecular liquids have been analysed. Experimental results, supporting theory, are presented.

Modern development in optical technology has made the Rayleigh-Brillouin light scattering technique very useful in studying translation and rotational motions of molecular liquids in the GHz (10^9 Hz) frequency range. The spectrum in this frequency range consist of a central component and a pair of shifted sidebands. In general, the central Rayleigh components in polarized and depolarized spectrum arise from the overdamped translational and rotational diffusive motion; the shifted sidebands are due to scattering of the incident light from the thermally induced sound waves in the medium.

At the 90° scattering angle, the scattered light observed in the polarized (VV) scattering configuration is a superposition of the isotropic (due to density fluctuations) and aniso-tropic (due to orientational fluctuations) components in the combination:

$$I_{VV}(q,\omega) = I_{iso}(q,\omega) + \frac{4}{3} I_{ani}(q,\omega) \tag{1}$$

On the other hand, the scattered light observed in the depolarized (VH) scattering configuration is only due to orientational fluctuations:

$$I_{VH}(q,\omega) = I_{ani}(\underset{\sim}{q},\omega) \tag{2}$$

Thus by measuring both the VV and VH scattering spectral components, it is possible to separate the isotropic and anisotropic components from the VV spectrum. Here the quantity q which appears in Eqs. (1) and (2) is equal to $q = (\underset{\sim}{q}) = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2}$, where λ is the wave-length of the incident light in vacuum, n is the refractive index, and θ is the scattering angle.

The combination known as the longitudinal stress modulus $M(t) + \frac{4}{3} G(t)$. However, the anisotropic component of the scattering spectrum is closely associated with the relaxation behavior of the shear modulus G.

In this paper, we shall give a hydrodynamic description of the effect of the rotation-trans-lational coupling on the spectra of density fluctuations and orientational fluctuations of molecular liquids composed of anisotropic molecules. Experimental results confirming the theory will be presented at the conference.

Although analysis of the experimental spectra was previously provided using microscopic theory,[1,2] we shall present the analysis here using the method of continuum mechanics. This is possible because the fluctuating wavelength involved in light scattering is long compared with the inter-molecular distance. Consider first the general formulation.

The intensity distribution of the isotropic component of the dynamic light scattering spectrum detected at the scattering angle θ is proportional to the Fourier transform of the time correlation function of the density fluctuation $C(q,t)$ given by

$$C(\underset{\sim}{q},t) = \langle \delta\rho(\underset{\sim}{q},t)\delta\rho^*(\underset{\sim}{q})\rangle \tag{3}$$

where $\delta\rho(\underset{\sim}{q},t)$ is the spatial Fourier transform of the fluctuation of the number density from the equilibrium value ρ_0 within scattering volume.

In continuum mechanics, the connection between force and deformation is formulated in terms of the stress-strain relation (i.e. the constitutive equation). The general constitutive equation for the linear stress-strain relation incorporating the rotation-translation coupling appropriate for describing the light scattering spectrum from an isotropic system

is given by

$$\sigma_{ij}(t) = -p\delta_{ij} + \int_0^t dt'\{K(t-t')\dot{\gamma}_{kk}(t')\delta_{ij} + 2G(t-t')[\dot{\gamma}_{ij}(t') - \frac{1}{3}\dot{\gamma}_{kk}(t')\delta_{ij}]\}$$

$$+ \mu\dot{\beta}_{ij}(t) \tag{4}$$

where p is the hydrostative pressure, $K(t)$ is the bulk modulus, $G(t)$ is the shear modulus, μ is a parameter introduced to account for the coupling of the stress tensor σ_{ij} to the polarizability anisotropy $\beta_{ij} = (\alpha_{ij} - \frac{1}{3}\alpha_{kk}\delta_{ij})$, designating the orientational fluctuation. α_{ij} is the polarizability tensor and γ_{ij} is the rate of the strain tensor given by $(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i})/z$. Here V_i is the ith component of the velocity. The Einstein summation convention is implied in Eq. (4). The quantities σ_{ij}, γ_{ij} and β_{ij} depend on the spatial coordinates, although they are not explicitly written out. The dots above γ_{ij} and β_{ij} denote taking the time derivative.

To provide the calculation of $C(q,t)$, we also need the equation of continuity

$$\dot{\rho} = -\frac{\partial}{\partial x_i}(\rho V_i) \tag{5}$$

and Newton's equation

$$\rho_m \frac{d}{dt} V_i = \rho_m (\frac{\partial}{\partial t} V_i + V_i \frac{\partial}{\partial x_j} V_j) = \frac{\partial}{\partial x_j} \sigma_{ij} \tag{6}$$

where ρ_m is the mass density equal to $m\rho$.

To calculate the light scattering spectrum, it suffices to linearize Eqs. (5) and (6). This amounts to neglecting the $V_i \frac{\partial}{\partial x_j} V_j$ term in Eq. (6) and the $\frac{\partial}{\partial t}(\delta\rho V_i)$ in Eq. (5). Here $\delta\rho$ denotes the density fluctuation from the equilibrium density ρ_0, $\rho = \rho_0 + \delta\rho$.

The hydrostatic pressure term in Eq. (4) is affected by the density and temperature fluctuations. Formally it is straightforward to include both contributions in the calculation. For simplicity, we shall neglect the temperature fluctuating contribution and write $p = p_0 + \delta p$, $\delta p = \delta\rho/\rho_0 \chi_T$. This amounts to neglecting the effect of thermal diffusivity and assuming that the sound wave propagates with an isothermal velocity rather than the correct adiabatic one.

Substituting Eq. (4) into Eq. (6), we obtain

$$\rho_m^0 \frac{\partial}{\partial t} V_i = -\frac{1}{\rho_0\chi_T}(\frac{\partial}{\partial x_i}) + \int_0^t dt'\{[K(t-t') + \frac{1}{3} G(t-t')] \frac{\partial}{\partial x_i} \nabla\cdot\underset{\sim}{V}(t')$$

$$+ G(t-t') \nabla^2 V_i(t')\} + \mu \frac{\partial}{\partial x_j} \dot{\beta}_{ij} \tag{7}$$

To complete the description, we shall also need a kinetic equation for the polarizability anisotropy tensor β_{ij},

$$\dot{\beta}_{ij} = -\Gamma\beta_{ij} + \mu'\dot{\gamma}_{ij} \tag{8}$$

where Γ is the relaxation rate of β_{ij} and is assumed to be equal to the collective rate of molecular reorientation. μ' is a rotation-translational coupling coefficient which is related to μ.

Equations (5), (7) and (8) constitute a set of coupled equations that are needed to calculate the polarized and the depolarized components of the scattered light in an isotropic linear viscoelastic medium.

Consider first the depolarized component. For this, we shall use a coordinate system with the y-axis indicating the polarization of the incident light. The scattered light is polarized in the x-z plane and the scattering vector $\underset{\sim}{q}$ lies along the z-axis. In this coordinate system the depolarized spectrum is given by[3]

$$I_{VH}(\underset{\sim}{q},\omega) = I_{yz}(\underset{\sim}{q},\omega) \cos^2 \frac{\theta}{2} + I_{yx}(\underset{\sim}{q},\omega) \sin^2 \frac{\theta}{2} \tag{9}$$

where $I_{yz}(q,\omega)$ and $I_{yx}(q,\omega)$ are the Fourier transforms of the polarizability correlation functions, $\sim <\alpha_{yz}(q,t)\alpha_{yz}^*(q)>$ and $<\alpha_{yx}(q,t)\alpha_{yx}^*(q)>$, respectively.

Symmetry consideration (reflection planes containing q and each of the three Cartesian axes) show that $\alpha_{yz}(q)$ has the same reflection symmetry property as the transverse velocity $V_y(q)$, whereas $\tilde{\alpha}_{yx}(q)$ does not transform as any of the three components of the velocity. Thus, α_{yz} can couple to the transverse velocity $V_y(q)$, and α_{yx} cannot. The coupling of α_{yz} to $V_y(q)$ is the rotation-translational coupling. The rotation-translational coupling has the effect of relaxing the shear modulus which gives rise to the appearance of the shear wave central dip or the shear wave sideband in the VH spectrum at the low temperature.[4,5]

The transverse component of Eq. (7) is

$$\rho_m^o \; \dot{V}_y(q,t) = - q^2 \int_0^t dt' \; G(t-t')V_y(q,t') + iq\mu\dot{\alpha}_{yz}(q,t) \tag{10}$$

The equation for $\alpha_{yz}(q,t)$ is obtained from Eq. (8) as

$$\dot{\alpha}_{yz}(q,t) = - \Gamma \; \alpha_{yz}(q,t) + \frac{i}{2} \; q\mu'V_y(q,t) \tag{11}$$

In Eqs. (10) and (11), $V_y(q,t)$ and $\alpha_{yz}(q,t)$ are the spatial Fourier transforms of $V_y(r,t)$ and $\alpha_{yz}(r,t)$, respectively.

The correlation function $<\alpha_{yz}(q,s)\alpha_{yz}^*(q)>$ can be obtained by first solving $\hat{\alpha}_{yz}(q,s)$ from Eqs. (10) and (11) and then multiplying $\alpha_{yz}^*(q)$, followed by an ensemble average. The result is

$$<\hat{\alpha}_{yz}(q,s)\alpha_{yz}^*(q)> = (\frac{kTX_\alpha}{\pi}) \; [\frac{s + q^2\overline{G}(s)/\rho_m^o}{(s+\Gamma)(s+q^2\overline{G}(s)/\rho_m^o)+RTn_sq^2/\rho_m^o} \tag{12}$$

where $\hat{\alpha}_{yz}(q,s)$ is the Laplace transform of $\alpha_{yz}(q,t)$, and

$$\overline{G}(s) = \int_0^\infty dt \; e^{-st} \; [G(t) + \mu\mu'\delta(t)] = \hat{G}(s) - Rn_s \tag{13}$$

Here $R(= - \mu\mu')$ is the rotation-translational coupling coefficient. n_s is the zero frequency shear viscosity. $\hat{G}(s)$ is the Laplace transform of the shear modulus; kTX_α is equal to $<|\alpha_{yz}(q)|^2>$.

Using Eq. (8), we also find

$$<\alpha_{yx}(qs)\alpha_{yx}^*(q)> = \frac{kTX_\alpha}{s+\Gamma} \tag{14}$$

In Eq. (14), we have assumed $<|\alpha_{yx}(q)|^2> = <|\alpha_{yz}(q)|^2>$ because of rotational isotropy of the medium.

Substituting Eqs. (12) and (14) into Eq. (9), we obtain

$$I_{VH}(q,\omega) = \frac{kTX_\alpha}{\pi} \; Re \; \{\frac{1}{s+\Gamma} \; sin^2(\theta/2)$$

$$+ \frac{s + q^2 \; \overline{G}(s)/\rho_m}{(s+\Gamma)(s+q^2\overline{G}(s)/\rho_m) + R\Gamma n_s q^2/\rho_m} \; cos^2 \; (\frac{\theta}{2})\}_{s=i\omega} \tag{15}$$

The quantity $\hat{G}(s=i\omega)$ plays the role of dynamic shear viscosity; it can be written as

$$\eta^*(\omega) = \hat{G}(s=i\omega) = \eta'(\omega) - i \; \eta''(\omega) \tag{16}$$

Assuming the amplitude of $\eta^*(\omega)$ to be n_s, it can be shown that $\lim_{\omega \to 0} \eta^*(\omega) = n_s$.

Three parameters play an important role in affecting the VH spectrum. They are: Γ (the collective molecular reorientation rate), n_s and q (the amplitude of the scattering vector). At high temperature such that $\Gamma >> q^2n_s/\rho_m$, we find that the profile of the VH spectrum displays a fine structure with a dip at the center of the central component. At the temperature such that $\Gamma \approx q^2n_s/\rho_m$, the central dip disappears and the spectral lineshape is non-Lorentzian. At low temperature where $\Gamma << q^2n_s/\rho_m$, the VH spectrum consists of a pair of

shifted sidebands of very weak intensity, accompanied by an intense yet very narrow central component.

For several molecular systems so far studied in this laboratory, we have found that the lineshapes of the VH spectra over a wide range of temperature can be accounted for by assuming that $\eta^*(\omega)$ is given by

$$\eta^*(\omega) = \eta_V - i\frac{G_V}{\omega} \tag{17}$$

Equation (17) shows that in the GHz range, the liquid behaves as a viscoelastic solid. The study of VH spectra of molecular liquids in the GHz range thus provide an unique technique for obtaining information about the high frequency behavior of the dynamic shear viscosity.

The effect of the rotation-translation coupling also affects the isotropic Rayleigh-Brillouin spectral component. For non-spherical molecules, the orientational anisotropy can in principle couple to the longitudinal acoustic wave associated with density fluctuations, in analogy to the coupling of the orientation to the transverse waves, as discussed above. To analyze the effect on the isotropic spectrum, we take the longitudinal component of Eq. (7) and obtain

$$\rho_m^o \frac{\partial}{\partial t} V_z(q,t) = - \frac{iq}{\rho_o X_T} \delta\rho(q,t) - q^2 \int_0^t dt' \bar{M}(t-t')V_z(q,t') - i\mu\Gamma q\beta_{zz}(q,t) \tag{18}$$

where $\bar{M}(t) = M(t) - R\eta_s\delta(t)$. Note that the longitudinal modulus is reduced by the rotation-translational coupling.

From Eq. (8), we can obtain the kinetic equation for $\beta_{zz}(q,t)$ as

$$\dot{\beta}_{zz}(q,t) = -\Gamma\beta_{zz}(q,t) + iq\mu'V_z(q,t) \tag{19}$$

Using Eqs. (18) and (19) together with Eq. (5), we obtain the solution for $<\delta\rho(q,s)\delta\rho^*(q)>$ as

$$<\delta\rho(q,s)\delta\rho^*(q)> = \frac{\{s+ \frac{q^2}{\rho_m^o}[\hat{M}(s) - \frac{s}{s+\Gamma} R\eta_s]\}}{\omega_T^2+s\{s+\frac{q^2}{\rho_m^o}[\hat{M}(s) - \frac{s}{s+\Gamma} R\eta_s]\}} <|\delta\rho(q)|^2> \tag{20}$$

where $\hat{M}(s)$ is the Laplace transform of the longitudinal modulus $M(t)$, and ω_T^2 is equal to $q^2/\rho_m^o X_T$.

The isotropic part of the polarized Rayleigh-Brillouin spectrum is obtained from Eq. (20) by setting $s=i\omega$ and then taking the real part of the right hand side of Eq. (20).

If the frequency dependence in the longitudinal modulus is neglected, the $\hat{M}(s)\simeq\eta_V + \frac{4}{3}\eta_s$, where η_V is the bulk viscosity. Setting $s=i\omega$ and taking the real part, we obtain

$$I_{iso}(q,\omega) = \frac{1}{\pi} Re<\delta\rho(q,s)\delta\rho^*(q)>_{s=i\omega}$$

$$= \frac{<|\delta\rho(q)|^2>}{\pi} Re \left\{ \frac{i\omega + \frac{q^2}{\rho_m^o} (\eta_V + \frac{4}{3}\eta_s - \frac{i\omega}{i\omega+\Gamma} R\eta_s)}{\omega_T^2+ i\omega [i\omega+\frac{q^2}{\rho_m^o} (\eta_V + \frac{4}{3}\eta_s - \frac{i\omega}{i\omega+\Gamma} R\eta_s)]} \right\} \tag{21}$$

From Eq. (21), appropriate only for a viscous liquid, we can obtain the dispersion equation of the Brillouin doublet. Assuming that $\omega_T>>\Gamma \sim q^2(\eta_V+\frac{4}{3}\eta_s)/\rho_m^o$, we obtain the roots for the complex frequency having the form

$$\omega\pm = \pm \omega_T(1+\frac{R\Gamma\eta_s}{2\rho_m^o} \frac{q^2}{\Gamma^2+\omega_T^2}) + i \frac{q^2}{2\rho_m^o} [\eta_V+ \frac{4}{3} \eta_s(1- \frac{R}{4} \frac{\Gamma^2+4\omega_T^2}{\Gamma^2+\omega_T^2})] \tag{22}$$

which is the same as the expression obtained by Lipeles and Kivelson using a microscopic theory.[2]

Results of experimental studies of the polarized and depolarized Rayleigh-Brillouin spectra of liquid aniline, p-anisaldehyde and salol show that there is indeed relaxation in the shear viscosity owing to the coupling of orientation to acoustic waves. However, the shear viscosity relaxation appears to play only a minor role in the dispersion of the longitudinal waves. Major contribution to the dispersion and attenuation of the longitudinal wave in the GHz frequency range appears to be dominated by the bulk viscosity relaxation through the translation-vibration energy transfer. Experimental results show that the relaxation of the bulk modulus and hence its frequency dependence cannot be neglected.

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