Depolarized Light Scattering and Dynamic Shear Compliance of Viscoelastic Liquids

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ABSTRACT: We have analyzed the depolarized light scattering (DLS) spectrum of a viscoelastic polymer liquid in which the dielectric constant anisotropy (DCA) is modulated by both chain segmental reorientation and local shear strain fluctuations. Using linear response theory, we have first shown that in the absence of chain segmental reorientation, the DLS spectrum is the imaginary part of the dynamic shear compliance spectrum of the polymer liquid. When both segmental reorientation and shear strain fluctuations are present, the DLS spectrum is complex. In the case that the reorientation rate is fast, we have shown that the DLS spectrum becomes the sum of reorientational and dynamic shear compliance spectra. As part of the DCA is relaxed by molecular reorientation, the DLS spectrum becomes the dynamic shear compliance spectrum associated with the strain fluctuations. Thus, the DLS spectrum of the polymer liquid measured at long times (or low frequency) corresponds to a dynamic shear compliance spectrum. The present work generalizes the results previously presented in which the molecular reorientation is assumed to be slow. The result of the present theoretical analysis thus shows that it is possible to determine the dynamic shear compliance spectra of polymer liquids by using DLS.

I. Introduction

Light scattering occurs as a result of fluctuations in the dielectric constant from its equilibrium value. The isotropic component of the dynamic light scattering spectrum, as detected by the polarized scattering (VV) geometry, is due mainly to the fluctuations of the dielectric constant caused by density fluctuations and by concentration fluctuations (if the scattering medium is a solution). Using fluid mechanics which incorporate linear viscoelasticity, we have related the isotropic component of the dynamic light scattering (DLS) spectrum to the dynamic longitudinal compliance spectrum of the bulk polymer liquid.[1,2] Due to the osmotic stress that exists in a polymer solution, the connection of the isotropic DLS scattering spectrum to the viscoelastic properties of the polymer solution is complex. However, it has been shown that, under some special circumstances, information about the stress modulus of the polymer solution can be extracted from the isotopic DLS.[3,4]

The connection of the depolarized light scattering spectrum of a polymer liquid to the polymer's viscoelastic properties is yet to be clarified. Although the isotropic dynamic light scattering spectrum of a bulk polymer liquid is shown to be proportional to its longitudinal compliance spectrum, as mentioned above,[1,2] it is not clear how the depolarized dynamic light scattering spectrum is related to the dynamic mechanical spectrum of a polymer liquid. Both segmental reorientation and stress (or strain) fluctuations of the polymer liquid contribute to the depolarized light scattering spectral intensity. Is the DLS spectrum of the polymer liquid related to its dynamic shear compliance or shear modulus spectrum? Also, what are the roles of segmental reorientation and polymer stress/strain relaxation in connection with the depolarized spectrum of a polymer liquid? It is necessary to clarify these questions so that the relationship between the DLS spectrum and the dynamic mechanical relaxation spectrum from a polymer liquid can be provided. We have attempted to clarify these issues in this paper.

Depolarized light scattering arises from fluctuations of the anisotropy of the dielectric constant tensor of the medium. Mechanisms concerning the modulation of the dielectric constant anisotropy (DCA) are numerous and have not been clearly delineated.[5] For the dilute solution consisting of a polymer dissolved in a small-molecule solvent, segmental motion of the polymer chain is responsible for modulating the DCA. For a molecular liquid consisting of optically anisotropic molecules at high temperature or low viscosity, molecular reorientation is the main mechanism for modulating the DCA.[5] In associated liquids such as water and alcohols, the dynamics of molecular reorientation is affected by the structure of the hydrogen bond network.[6] In highly optically anisotropic molecules such as CS_2, a collision-induced mechanism also makes a prominent contribution to the modulation of DCA.[7] Other mechanisms that contribute to depolarized light scattering have been extensively discussed in the literature.[8]

Relaxation times as measured by DLS for a number of glass-forming liquids (such as *o*-terphenyl (OTC))[9] and poly(propylene glycols)[10] are found to deviate significantly from the Stokes–Einstein–Debye equation as the temperature of the sample is brought below a characteristic temperature T_s, which is empirically found to be about $1.3T_g$.[11] Here T_g is the glass transition temperature. Recently, Fischer et al.[12] have attempted to provide a rationalization for such a deviation by associating the fluctuation of the DCA with the relaxation of the shear strain. They have equated the strain relaxation time, τ_K, to the mean relaxation time, τ_{DLS}, as determined by depolarizing light scattering.

There is, however, no molecular theory in which the modulation of the DCA is associated with the shear strain, although a phenomenological theory in which the modulation of the DCA is considered to be due to the time evolution of the shear strain has also appeared in the literature.[13] The main difficulty in associating DCA with the shear strain probably arises from the fact that one cannot write down a molecular expression for the

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strain tensor. Moreover, at long times (or low frequency), the molecular liquid cannot sustain a static shear. However, one may argue that the long-time behavior is generally not reached in a viscoelastic polymer liquid because of the effect of chain connectivity. Moreover, at high frequency ($\omega\tau \gg 1$, where τ is the molecular reorientation relaxation time), the molecular liquid behaves as a glassy solid, and one would be able to associate the modulation of the DCA with the shear strain or the shear displacement density.[14] As will be shown below, the connection with the shear displacement density is consistent with the hypothesis of associating the modulation of the DCA with the shear strain fluctuations. Thus, at frequency $\omega \gg \tau^{-1}$, molecular liquids behave like viscoelastic solids. The use of the shear strain as an additional dynamic variable for the DCA in a viscoelastic liquid is hence justified.

In a recent paper,[15] both reorientational dynamics and shear motion were considered in the analysis of the DLS spectrum. However, the analysis given in ref 15 was made on the hypothesis that the DCA is only proportional to the orientational density and the modulation of DCA is due to molecular reorientation. Molecular reorientation is dynamically coupled to the transverse linear momentum density of the liquid because of the anisotropic intermolecular potential acting between molecules. This introduces the shear motion in the depolarized light scattering spectrum. Reference 15 shows that, in the limit of very slow reorientational motion, the depolarized light scattering spectrum reduces to the imaginary part of the dynamic shear compliance spectrum, a result predicted by the Pockels photoelastic law.[16] However, considering the fact that in viscoelastic fluids, such as polymer liquids, molecular or segmental reorientation may not completely relax the DCA, an additional mechanism such as shear strain relaxation should also be considered to relax the remaining DCA. This consideration is important in polymer liquids in which the viscoelastic effect plays an important role in affecting the segmental motion. In this paper, we generalize the theory of ref 15 by including the shear strain density as another component of the DCA. We show here that the conclusion previously obtained in ref 15 remains valid even when molecular reorientational motion is fast. It is believed that the detailed treatment as presented here provides a better description of the nature of the DLS spectra from viscoelastic polymeric liquids. In addition, we also provide for the first time a derivation of the dynamic shear compliance in terms of the time correlation function of the shear strain tensor. This work should facilitate interpretation of the experimental results in regard to the dynamic shear compliance of viscoelastic polymer liquids or solutions. We also show that the theory based upon the shear strain tensor gives a correct limit required by the photoelastic law for the isotropic viscoelastic liquid.[17]

The outline of this paper is as follows: In section II we discuss various types of motion that contribute to depolarized light scattering. In section III we use linear response theory and express the dynamic shear compliance in terms of the time correlation function of the shear strain. In the absence of molecular reorientation, we show that the DLS spectrum of a viscoelastic medium is equivalent to its dynamic shear compliance spectrum. In section IV we generalize the work of ref 15 and formulate a three-variable generalized hydrodynamic theory for the depolarized spectrum. We first derive an expression for the correlation function of the shear strain and obtain a microscopic expression for the shear compliance. We then show that when both molecular reorientation and shear strain are present, the expression for the depolarized spectrum consists of two terms, one corresponding to the molecular reorientation spectrum and the other to the shear compliance spectrum. As molecular reorientation rapidly relaxes, the shear creep compliance becomes the remaining part of the depolarized spectrum in the low-frequency region.

II. Depolarized Light Scattering Spectral Densities

Using the scattering geometry with the incident light propagating along the x axis and polarized along the y axis of the laboratory coordinate system, it can be shown that the depolarized light scattering spectrum arising from fluctuations of the DCA (dielectric constant anisotropy, $\delta\epsilon_{ij}$, $i \neq j$) is given by[18]

$$I_{\mathrm{VH}}(\mathbf{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}t\,\exp(-i\omega t)\Big[\langle\delta\epsilon_{yz}(\mathbf{q},t)\delta\epsilon_{yz}^{*}(\mathbf{q})\rangle \times \cos^2\frac{\theta}{2} + \langle\delta\epsilon_{yx}(\mathbf{q},t)\delta\epsilon_{yx}^{*}(\mathbf{q})\rangle\sin^2\frac{\theta}{2}\Big] \equiv I_{yz}(\mathbf{q},\omega)\cos^2\frac{\theta}{2} + I_{yx}(\mathbf{q},\omega)\sin^2\frac{\theta}{2} \quad (1)$$

where in eq 1 the scattering vector $\mathbf{q}$ is along the z axis. θ is the scattering angle. The polarization of the incident wave is perpendicular to the scattering plane (the xz plane). The angular brackets indicate an ensemble average. $I_{yz}(\mathbf{q},\omega)$ and $I_{yx}(\mathbf{q},\omega)$ are spectral power densities defined according to eq 1.

In order to construct a molecular theory for the spectral densities $I_{yz}(\mathbf{q},\omega)$ and $I_{yx}(\mathbf{q},\omega)$, we need to consider the types of molecular motion that modulate $\delta\epsilon_{ij}(\mathbf{r},t)$ at position $\mathbf{r}$ and time t. Unlike the assumption introduced in ref 15, we assume that the DCA is modulated by two dynamic variables Q_1 and Q_3 by the equation

$$\delta\epsilon_{ij}(\mathbf{r},t) = \left(\frac{\partial\epsilon_{ij}}{\partial Q_1}\right)_0 Q_1(\mathbf{r},t) + \left(\frac{\partial\epsilon_{ij}}{\partial Q_3}\right)_0 Q_3(\mathbf{r},t) \quad (2)$$

where we shall designate $Q_1(\mathbf{r})$ as the orientational density variable, which, for $\delta\epsilon_{yz}(\mathbf{r})$, is designated as

$$Q_1(\mathbf{r}) = \left(\frac{1}{6}\right)^{1/2}\sum_j[D_{10}^{(2)}(\Omega_j) + D_{-10}^{(2)}(\Omega_j)]\delta(\mathbf{r}-\mathbf{r}_j) \quad (3)$$

and for $\delta\epsilon_{yx}(\mathbf{r})$ as

$$Q_1(\mathbf{r}) = \left(\frac{1}{6}\right)^{1/2}\sum_j[D_{10}^{(2)}(\Omega_j) - D_{-10}^{(2)}(\Omega_j)]\delta(\mathbf{r}-\mathbf{r}_j) \quad (4)$$

Here $D_{mn}^{(2)}(\Omega_j)$ are second-rank Wigner functions of the Euler angles Ω_j specifying the orientation of the jth segment at position $\mathbf{r}_j$. Summation index j is to include segments in all polymer chains in the liquid. As molecules translate and reorient, Q_1 becomes a function of time.

$Q_3(\mathbf{r},t)$ is a variable associated with shear waves. If the shear wave propagates along the z direction, $\delta\epsilon_{yx}(\mathbf{r},t)$ cannot couple to shear waves because of wrong symmetry. Thus the coefficient $(\partial\epsilon_{yx}/\partial Q_3)_0$ must vanish. Furthermore, because of rotational isotropy of the medium, we also have $(\partial\epsilon_{yz}/\partial Q_1)_0 = (\partial\epsilon_{yx}/\partial Q_1)_0$. Here, the subscript 0 in the coefficients $(\partial\epsilon_{ij}/\partial Q_k)_0$, $k = 1,3$, denotes that those quantities are evaluated at equilibrium. Thus, after taking the Fourier transform of the spatial coordinate, we obtain from eq 2

$$\begin{aligned}\delta\epsilon_{yz}(\mathbf{q},t) &= \int_V \mathrm{d}^3r\, \delta\epsilon_{yz}(\mathbf{r},t)e^{i\mathbf{q}\cdot\mathbf{r}} \\ &= AQ_1(\mathbf{q},t) + BQ_3(\mathbf{q},t)\end{aligned} \tag{5}$$

and

$$\delta\epsilon_{yx}(\mathbf{q},t) = AQ_1(\mathbf{q},t) \tag{6}$$

where $A = (\partial\epsilon_{yz}/\partial Q_1)_0$ and $B = (\partial\epsilon_{yx}/\partial Q_3)_0$. The shear mode does not contribute to the $I_{yx}(\mathbf{q},\omega)$ spectrum. For an isotropic medium, the physical property depends only on the amplitude and not on the direction of **q**; thus, we shall henceforth omit the vector sign and simply write the scattering vector as q.

Thus, the spectral power densities, $I_{yz}(q,\omega)$ and $I_{yx}(q,\omega)$, are given by

$$I_{yz}(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}[A^2\langle Q_1(q,t)Q_1^*(q)\rangle + B^2\langle Q_3(q,t)Q_3^*(q)\rangle]e^{-i\omega t}\,\mathrm{d}t \tag{7}$$

and

$$I_{yx}(q,\omega) = \frac{A^2}{2\pi}\int_{-\infty}^{\infty}\langle Q_1(\mathbf{q},t)Q_1^*(q)\rangle e^{-i\omega t}\,\mathrm{d}t \tag{8}$$

III. Linear Response Theory for Shear Strain

Consider first that rotational motion is extremely slow and the fluctuation of DCA is completely due to strain. Thus, we set $A = 0$ and write

$$\delta\epsilon_{yz} = BQ_3(q,t) = B'\gamma_{yz}(q,t) \tag{9}$$

and

$$\delta\epsilon_{yx} = 0 \tag{10}$$

where $B' = n_0^4S$, n_0 being the mean refractive index and S the photoelastic constant.[16]

In this case, the depolarized light scattering spectrum is equal to

$$I_{VH}(q,t) = \frac{B'}{2\pi}\cos^2(\theta/2)\int_{-\infty}^{\infty}\langle\gamma_{yz}(q,t)\gamma_{yz}^*(q)\rangle e^{-i\omega t}\,\mathrm{d}t \tag{11}$$

According to eq 11, it is clear that the shear component is absent at $\theta = 180°$ (the back scattering geometry).

We now use linear response theory to relate the correlation function of the shear strain to the shear creep compliance. The shear strain correlation function is given by

$$G_{yz}(q,t) = \langle\gamma_{yz}(q,t)\gamma_{yz}^*(q)\rangle \tag{12}$$

In linear response theory, one deals with a set of dynamic variables A_1, A_2, ..., A_n. Each of these is coupled to external force fields F_1, F_2, ..., F_n. The most general type of Hamiltonian describing the coupling of various dynamic variables is given by

$$H_{\text{ext}}(t) = -\sum_j\int_V \mathrm{d}^3r\int_{-\infty}^{t}\mathrm{d}t'\,\dot{A}_j(r,t')F_j(r,t') \tag{13}$$

where the dot above variable A_j indicates taking the time derivative. The space integration is over the volume of interest.

Following a series of steps introduced in linear response theory, we find that the linear response of A_i in (q,ω) is simply given by[19]

$$\langle\delta A_i(q,\omega)\rangle = \sum_j\chi_{ij}(q,\omega)F_j(q,\omega) \tag{14}$$

where the angular brackets denote average over the equilibrium distribution function; $\chi_{ij}(q,\omega)$ is the generalized susceptibility tensor and has real and imaginary parts.

$$\chi_{ij}(q,\omega) = \chi'(q,\omega) - i\chi''(q,\omega) \tag{15}$$

Here $\chi'(q,\omega)$ and $\chi''(q,\omega)$ are the real and imaginary parts, respectively.

In eq 14, $\delta A_i(q,\omega)$ is given by

$$\delta A_i(q,\omega) = \int \mathrm{d}^3r\int_0^{\infty}\mathrm{d}t\,\exp\{i(\mathbf{q}\cdot\mathbf{r} - \omega t)\}\delta A_i(\mathbf{r},t) \tag{16}$$

where $\delta A_i(\mathbf{r},t)$ is the fluctuation of A_i from the equilibrium value. Likewise, the force $F_j(q,\omega)$ is given by the Fourier–Laplace transform of $F_j(\mathbf{r},t)$:

$$F_j(q,\omega) = \int \mathrm{d}^3r\int_0^{\infty}\mathrm{d}t\,\exp\{i(\mathbf{q}\cdot\mathbf{r} - \omega t)\}F_j(\mathbf{r},t) \tag{17}$$

The fluctuation–dissipation theorem gives a relationship connecting the imaginary part of $\chi_{ij}(q,\omega)$ to the Fourier transform of the time correlation function of variables A_i and A_j. For the classical system, the theorem is given by[19]

$$\chi_{ij}''(q,\omega) = \frac{\omega}{kT}\int_{-\infty}^{\infty}\mathrm{d}t\,e^{-i\omega t}\langle A_i(q,t)A_j^*(q)\rangle \tag{18}$$

Consider a quiescent fluid system not subject to a macroscopic flow. The rate of energy dissipation due to shear stress tensor σ_{yz} is given by[20]

$$\dot{E} = -\int\sigma_{yz}\dot{\gamma}_{yz}\,\mathrm{d}^3r \tag{19}$$

where dots denote taking time derivatives. Thus, if we identify A_i to the shear strain γ_{yz}, and F_j to the shear stress σ_{yz}, then the Hamiltonian is given specifically by

$$H_{\text{ext}} = -\int\mathrm{d}^3r\int\mathrm{d}t'\,\sigma_{yz}(\mathbf{r},t')\dot{\gamma}_{yz}(\mathbf{r},t') \tag{20}$$

and eq 14 becomes

$$\delta\gamma_{yz}(q,\omega) = \chi_{yz}(q,\omega)\sigma_{yz}(q,\omega) \tag{21}$$

which, in time representation, can be written as

$$\delta\gamma_{yz}(q,t) = \frac{1}{kT}\int_0^t\mathrm{d}t'\,\langle\gamma_{yz}(q,t)\dot{\gamma}_{yz}(q,t')\rangle\sigma_{yz}(q,t') \tag{22}$$

In eqs 21 and 22, we omit the angular brackets associated with $\delta\gamma_{yz}$ for brevity. By carrying out the integration by parts, we reduce the above equation to

$$\delta\gamma_{yz}(q,t)\frac{1}{kT}\langle|\gamma_{yz}(q,t)|^2\rangle\sigma_{yz}(q,t) - \frac{1}{kT}\int_0^t\mathrm{d}t'\,\langle\gamma_{yz}(q,t)\gamma_{yz}^*(q,t')\rangle\dot{\sigma}_{yz}(q,t') \tag{23}$$

We next assume that the macroscopic stress tensor involved in a mechanical experiment is identical to the stress tensor σ_{yz} given above. We next consider a mechanical experiment in which the external field (the stress tensor) is applied at time 0 and then maintained constant thereafter; i.e., we set

$$\sigma_{yz}(q,t) = \sigma_0(q)\theta(t) \tag{24}$$

where $\theta(t)$ equals 0 for $t \leq 0$ and equals 1 for $t > 0$. Thus,

$$\dot{\sigma}_{yz}(q,t) = \sigma_0(q)\delta(t) \tag{25}$$

where $\delta(t)$ is the Dirac delta function. By substituting eqs 24 and 25 into eq 23, we obtain for $t > 0$

$$\delta\gamma_{yz}(q,t) = \gamma(q,t) = \frac{1}{kT}\langle|\gamma_{yz}(q,t)|^2\rangle\sigma_0(q) - \frac{1}{kT}\langle\gamma_{yz}(q,t)\gamma_{yz}{}^*(q)\rangle\sigma_0(q) \tag{26}$$

The corresponding equation defining the shear creep compliance in a spatially homogeneous sample is

$$\gamma_{zy}(r,t) = \int_0^t \mathrm{d}t'\, J(r-r')\dot{\sigma}_{yz}(r,t') = J(t)\sigma_0(r) \tag{27}$$

For a spatially inhomogeneous sample, one can generalize the above equation and define a q-dependent shear compliance $J(q,t)$ as

$$\gamma_{zy}(q,t) = \int_0^t \mathrm{d}t'\, J(q,t-t')\dot{\sigma}_{yz}(q,t') = J(q,t)\sigma_0(q) \tag{28}$$

Comparing eq 28 with eq 26, we obtain

$$J(q,t) = \frac{1}{kT}\{\langle|\gamma_{yz}(q,t)|^2\rangle - \langle\gamma_{yz}(q,t)\gamma_{yz}{}^*(q)\rangle\} \tag{29}$$

Since the steady-state compliance is given by

$$J_{\mathrm{e}}(q) = \lim_{t\to\infty} J(q,t) = \frac{1}{kT}\langle|\gamma_{yz}(q)^*|^2\rangle \tag{30}$$

we obtain

$$\langle\gamma_{zy}(q,t)\gamma_{zy}(q)\rangle = kT\{J_{\mathrm{e}}(q) - J(q,t)\} \tag{31}$$

The real and imaginary parts of the dynamic shear compliance are therefore given by

$$J'(q,\omega) = \omega\int_0^\infty \mathrm{d}t\, \langle\gamma_{zy}(q,t)\gamma_{zy}{}^*(q)\rangle \sin \omega t \tag{32}$$

and

$$J''(q,\omega) = \omega\int_0^\infty \mathrm{d}t\, \langle\gamma_{zy}(q,t)\gamma_{zy}{}^*(q)\rangle \cos \omega t \tag{33}$$

Incorporating eq 31 into eq 11, we obtain that in the absence of reorientational motion, the VH spectrum is proportional to the compliance spectrum, provided that the photoelastic law is applicable. We discuss in Appendix I in more detail the q-dependent compliance spectrum and the compliance spectrum defined in a different coordinate system.

IV. Three-Variable Theory for the Coupled System

To include both reorientation and shear strain, we need to construct a three-variable theory to calculate the $I_{yz}(q,\omega)$ spectrum. For this we use a vector variable $A(q,t)$ consisting of three dynamic variables, Q_1, Q_2, and Q_3. As described in section II, Q_1 is the orientational density, Q_3 is the shear strain density, and Q_2 is the shear velocity density given by

$$Q_2(q,t) = \sum_j \left(\frac{\pi_y{}^{(j)}}{m_j}\right) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j} \tag{34}$$

Here $\pi_y{}^{(j)}$ is the y component of the linear momentum of segment j. m_j is its mass. For brevity, the time dependence in $\pi_y{}^{(j)}$ and $\mathbf{r}_j$ are not explicitly written out.

In order to calculate the DLS spectrum, we need to obtain equations for the correlation functions $\langle Q_1(q,t)\cdot Q_1{}^*(q)\rangle$ and $\langle Q_3(q,t)Q_3{}^*(q)\rangle$.

Having chosen the vector variable $A(q,t)$ as

$$\mathbf{A}(q,t) = \begin{bmatrix} Q_1(q,t) \\ Q_2(q,t) \\ Q_3(q,t) \end{bmatrix} \tag{35}$$

we use the Zwanzig–Mori technique to obtain the generalized Langevin equation of motion for $A(q,t)$ as[21]

$$\frac{\partial}{\partial t}\mathbf{A}(q,t) = \mathrm{i}\mathbf{\Omega}(q)\cdot\mathbf{A}(q,t) - \int_0^t \mathbf{K}(q,\tau)\cdot\mathbf{A}(q,t-\tau)\, \mathrm{d}\tau + \mathbf{F}(q,t) \tag{36}$$

where $\mathbf{\Omega}(q)$ and $\mathbf{K}(q,t)$ are the frequency and the relaxation matrix, respectively. $\mathbf{F}(q,t)$ is the random force.

From eq 36, we write explicitly the kinetic equations for the component of $\mathbf{A}$ as

$$\frac{\partial}{\partial t}Q_1 = -K_{11}{}^*Q_1 - K_{12}{}^*Q_2 - K_{13}{}^*Q_3 \tag{37a}$$

$$\frac{\partial}{\partial t}Q_2 = -K_{21}{}^*Q_1 - K_{22}{}^*Q_2 + \mathrm{i}\Omega_{23}Q_3 - K_{23}{}^*Q_3 \tag{37b}$$

$$\frac{\partial}{\partial t}Q_3 = -K_{31}{}^*Q_1 + \mathrm{i}\Omega_{32}Q_2 - K_{32}{}^*Q_2 - K_{33}{}^*Q_3 \tag{37c}$$

where $K_{ij}{}^*Q_j$ denotes the convolution of K_{ij} and Q_j, given by

$$K_{ij}{}^*Q_j = \int_0^t \mathrm{d}\tau\, K_{ij}(\tau)Q_j(t-\tau) \tag{38}$$

To proceed, we shall need to evaluate the elements of the frequency matrix and the relaxation matrix. We now identify variable Q_3 as the strain density. The other case of considering Q_3 as shear stress density is given in Appendix II.

For a solid, the Fourier component of the displacement is a well-defined quantity; it is given by

$$U_\alpha(q) = \sum_j x_\alpha{}^{(j)} \exp(\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j) \tag{39}$$

where $x_\alpha{}^{(j)}$ is the αth component of the local displacement vector of segment j located at the position $\mathbf{r}_j$ at the lattice point, which has the periodicity of the crystal lattice. For a polymer liquid, on the other hand, $\mathbf{r}_j$ is a slowly varying quantity as the position of the center of mass of the segment moves randomly due to translational diffusion and the long-range translational symmetry is broken in the liquid. However, if the deformation of a viscoelastic liquid can be described in terms of a pseudolattice, then one can define a local deformation tensor by[22]

$$\gamma_{\alpha\beta}(\mathbf{r},t) = \frac{1}{2}\left(\frac{\partial U_\alpha(\mathbf{r},t)}{\partial x_\beta} + \frac{\partial U_\beta(\mathbf{r},t)}{\partial x_\alpha}\right) \tag{40}$$

From eq 40, one finds that the yz component of the Fourier transform of the shear strain tensor with $\mathbf{q}$ along the z axis is given by

$$\begin{aligned}\gamma_{yz}(q,t) &= \int \gamma_{yz}(\mathbf{r},t)\,\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\,\mathrm{d}^3r \\ &= -\frac{\mathrm{i}}{2}qU_y(\mathbf{q},t)\end{aligned} \tag{41}$$

Thus, in Fourier space, the strain tensor is proportional to the displacement density. Choosing $U_y(\mathbf{q},t)$ as Q_3, Wang has developed a theory of depolarized Rayleigh–Brillouin scattering spectra for isotropic molecular solids.[23] In this section, we use a similar approach by specifying Q_3 as

$$Q_3 = U_y = \sum_j y^{(j)} \exp(\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j) \tag{42}$$

and proceed to evaluate the components of the frequency and relaxation matrices. The main difference is that we also let r_j depend on time.

Having specified the dynamic variables Q_1, Q_2, and Q_3, we use the prescription given by the Zwanzig–Mori technique and find that the random force $\mathbf{F}$ of eq 36 is given by

$$F = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \end{pmatrix} \tag{43}$$

where

$$f_1 = \mathrm{i}\mathcal{L}Q_1(q) = \dot{\alpha}_{yz}(q) \tag{44a}$$

$$f_2 = \dot{P}_y(q) + \frac{NkTM(q)}{m}Q_3(q) \tag{44b}$$

$$f_3 = \mathrm{i}q\sum_j y^{(j)}\pi_z^{(j)}/m_j \exp(\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j) \tag{44c}$$

Here, $M(q) = 1/\langle|Q_3(q)|^2\rangle$. In contrast to the case of isotropic solids as described in ref 23, f_3 is not zero but has a contribution arising from the diffusive motion of the center of mass, due to the time dependence of r_j. Such diffusive motion gives rise to relaxation of the local strain variable Q_3.

As shown in Appendix B of ref 14, at small q, $M(q)$ is proportional to q^2. Furthermore, according to Newton's law $\dot{P}_y(\mathbf{q}) = \mathrm{i}q\sigma_{yz}(q)$, where $\sigma_{yz}(q)$ is the yz component of the stress tensor. Thus, in the $q \to 0$ limit, f_1 is independent of q, and both f_2 and f_3 are linear in q. Therefore, various elements of the relaxation matrix may be written as

$$\mathbf{K}(q,t) = \begin{bmatrix} \Gamma_{11} & q\Gamma_{12} & q\Gamma_{13} \\ q\Gamma_{21} & q^2\Gamma_{22} & q^2\Gamma_{23} \\ q\Gamma_{31} & q^2\Gamma_{32} & q^2\Gamma_{33} \end{bmatrix} \tag{45}$$

where at small q, Γ_{ij}'s are independent of q. The quantity that is related to the shear modulus is Γ_{22}; it is given by

$$\Gamma_{22}(q,t) = \frac{1}{VkT}\langle\sigma_{yz}(q,t)\sigma_{yz}^*(q)\rangle \tag{46}$$

where $\sigma_{yz}(\mathbf{q},t)$ is the yz component of the local molecular shear stress tensor and is independent of q as $q \to 0$. Γ_{11} is associated with the relaxation of the orientation density, Γ_{12} (or Γ_{21}) is associated with the coupling between orientation and shear stress, Γ_{13} (or Γ_{31}) is associated with the coupling between orientation and the motion of the local center of mass, Γ_{23} (or Γ_{32}) is due to coupling between the molecular stress and the motion of the local center of mass and, finally, Γ_{33} is related to the relaxation of shear strain arising from the slow diffusion of the local center of mass.

To compare the present result with that of linear response theory given in section III, we assume that molecular reorientation is extremely slow and the strain variable Q_3 is proportional to the DCA (dielectric constant anisotropy). Thus, in this case Q_1 will not be involved in the theory. This is equivalent to setting in eq 45 $\Gamma_{11} = \Gamma_{12} = \Gamma_{21} = \Gamma_{13} = \Gamma_{31} = 0$. In this simplification, eqs 37 reduce to two coupled equations. Using the Laplace transform technique, the coupled equations (eqs 37b and 37c), can be converted to a two by two algebraic matrix equation, given by

$$\begin{bmatrix} (s + q^2\hat{\Gamma}_{22}) & q^2\hat{\Gamma}_{23} \\ q^2\hat{\Gamma}_{32} & s + q^2\hat{\Gamma}_{33} \end{bmatrix}\begin{bmatrix} \hat{Q}_2 \\ \hat{Q}_3 \end{bmatrix} = \begin{bmatrix} Q_2(q) \\ Q_3(q) \end{bmatrix} \tag{47}$$

where $Q_2(q)$ and $Q_3(q)$ are the initial values of $Q_2(q,t)$ and $Q_3(q,t)$, respectively. We have used carets to denote Laplace transforms of the quantities. Namely

$$\hat{Q}_i \equiv \hat{Q}_i(q,s) = \int_0^\infty Q_i(q,t)\mathrm{e}^{-st}\,\mathrm{d}t \tag{48}$$

$$\hat{\Gamma}_{ij} \equiv \hat{\Gamma}_{ij}(q,t) = \int_0^\infty \Gamma_{ij}(q,t)\mathrm{e}^{-st}\,\mathrm{d}t \tag{49}$$

Solution of eq 46 yields the correlation functions of $\hat{Q}_2$ and $\hat{Q}_3$ as

$$\langle\hat{Q}_2(q,s)Q_2^*(q)\rangle = \frac{\langle|Q_2(q)|^2\rangle}{(s + q^2\hat{\Gamma}_{22}) + q^4|\hat{\Gamma}_{23}|^2/(s + q^2\hat{\Gamma}_{33})} \tag{50}$$

$$\langle\hat{Q}_3(q,s)Q_3^*(q)\rangle = \frac{\langle|Q_3(q)|^2\rangle}{(s + q^2\hat{\Gamma}_{33}) + q^4|\hat{\Gamma}_{23}|^2/(s + q^2\hat{\Gamma}_{22})} \tag{51}$$

There is no cross correlation between Q_2 and Q_3, due to opposite time reversal symmetry. In accordance with eqs 33a and 33b we can identify eq 51 as the dynamic shear compliance

$$\begin{aligned}J^*(q,\omega) = sq^2\langle\hat{Q}_3(q,s)Q_3^*(q)\rangle|_{s=\mathrm{i}\omega} &= \\ \mathrm{i}\omega\int_0^\infty \mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}\langle\gamma_{yz}(q,t)\gamma_{zy}^*(q)\rangle &= \\ \mathrm{i}\omega q^2\int_0^\infty \mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}\langle Q_3(q,t)Q_3^*(q)\rangle& \end{aligned} \tag{52}$$

Furthermore, from the limiting hydrodynamic result, we have[24]

$$\lim_{s\to 0}\langle\hat{Q}_2(q,s)Q_2^*(q)\rangle = \lim_{s\to 0}\langle\hat{V}_y(q,s)V_y^*(q)\rangle = \frac{1}{(q^2/\varrho_\mathrm{m})\eta_\mathrm{s}}\langle|Q_2(q)|^2\rangle \tag{53}$$

where ϱ_m is the mass density and η_s is the macroscopic shear viscosity. Thus, taking the $s \to 0$ limit in eq 50, we obtain

$$\eta_s/\varrho_m = \lim_{\substack{q\to 0\\ s\to 0}}\{\hat{\Gamma}_{22}(q,s) + |\hat{\Gamma}_{23}(q,s)|^2/\hat{\Gamma}_{33}(q,s)\} \quad (54)$$

We consider next the other case in which the rate of reorientation is fast and the coupling between reorientation and stress is weak, so that only the coupling between the local strain and center of mass diffusion is important. The kinetic equations appropriate for such a case are

$$\frac{\partial}{\partial t}Q_1 = -\Gamma_{11}{*}Q_1 - q\Gamma_{13}{*}Q_3 \quad (55a)$$

$$\frac{\partial}{\partial t}Q_2 = -q^2\Gamma_{22}{*}Q_2 - q^2\Gamma_{23}'{*}Q_3 \quad (55b)$$

$$\frac{\partial}{\partial t}Q_3 = -q\Gamma_{31}{*}Q_1 - q^2\Gamma_{32}'{*}Q_2 - q^2\Gamma_{33}{*}Q_3 \quad (55c)$$

Equations 55a–c are obtained from eqs 37a–c by setting $K_{12} = K_{21} = 0$. The element $q^2\Gamma_{23}'$ is given by

$$q^2\Gamma_{23}' = K_{23} - \Omega_{23} \quad (56)$$

Similarly, $q^2\Gamma_{32}' = K_{32} - \Omega_{32}$. The frequency matrix elements Ω_{ij} can be evaluated by using the dynamic variables Q_2 and Q_3 as given by eqs 34 and 42, respectively.

To proceed, we take the Laplace transform of eqs 55a–c, and after rearranging, we obtain the matrix equation

$$\begin{bmatrix} s + \hat{\Gamma}_{11} & 0 & q\hat{\Gamma}_{13} \\ 0 & s + q^2\hat{\Gamma}_{22} & q^2\hat{\Gamma}_{23}' \\ q\hat{\Gamma}_{31} & q^2\hat{\Gamma}_{32}' & s + q^2\hat{\Gamma}_{33} \end{bmatrix} \begin{bmatrix} \hat{Q}_1 \\ \hat{Q}_2 \\ \hat{Q}_3 \end{bmatrix} = \begin{bmatrix} Q_1(q) \\ Q_2(q) \\ Q_3(q) \end{bmatrix} \quad (57)$$

where, as before, $\hat{Q}_i$ and $\hat{\Gamma}_{ij}$ denote the Laplace transform of $Q_i(q,t)$ and $\Gamma_{ij}(q,t)$, respectively.

To obtain the correlation functions, we invert eq 57 to obtain the solutions for $\hat{Q}_i$. Afterward, we multiply $\hat{Q}_i(q,s)$ by its initial value and then take the ensemble average. The results for three autocorrelation functions are

$$\hat{C}_{11}(q,s) = \langle \hat{Q}_1(q,s)Q_1{}^*(q)\rangle = \frac{(s + q^2\hat{\Gamma}_{33})(s + q^2\hat{\Gamma}_{22}) + (q^2\hat{\Gamma}_{23}')(q^2\hat{\Gamma}_{32}')}{(s + \hat{\Gamma}_{11})\Delta}\langle |Q_1(q)|^2\rangle \quad (58a)$$

$$\hat{C}_{22}(q,s) = \langle \hat{Q}_2(q,s)Q_2{}^*(q)\rangle = \frac{s + q^2\hat{\Gamma}_{33} - q^2|\hat{\Gamma}_{13}|^2/(s + \hat{\Gamma}_{11})}{\Delta}\langle |Q_2(q)|^2\rangle \quad (58b)$$

$$\hat{C}_{33}(q,s) = \langle \hat{Q}_3(q,s)\hat{Q}_3{}^*(q)\rangle = \frac{s + q^2\hat{\Gamma}_{22}}{\Delta}\langle |Q_3(q)|^2\rangle \quad (58c)$$

where Δ is the dispersion function given by

$$\Delta = \left(s + q^2\hat{\Gamma}_{33} - \frac{q^2|\hat{\Gamma}_{13}|^2}{s + \hat{\Gamma}_{11}}\right)(s + q^2\hat{\Gamma}_{22}) + (q^2\hat{\Gamma}_{23}')(q^2\hat{\Gamma}_{32}') \quad (59)$$

Again, consider first the limiting hydrodynamic result for all molecular fluids:

$$\lim_{s\to 0} \hat{C}_{22}(q,s) = \lim_{s\to 0}\langle \hat{V}_y(q,s)V_y{}^*(q)\rangle = \frac{1}{(q^2/\varrho_m)\eta_s}\langle |V_y(q)|^2\rangle \quad (60)$$

where ϱ_m is the mass density and η_s is the macroscopic shear viscosity equal to[25]

$$\eta_s = \lim_{\omega\to 0}[G''(\omega)/\omega] \quad (61)$$

We next take the $s \to 0$ and $q \to 0$ limit in eq 58b and obtain

$$\eta_s = \eta_{22} + \frac{|\eta_{23}|^2}{\eta_{33} - |\eta_{13}|^2/\eta_{11}} \quad (62)$$

where we have defined η_{ij} as

$$\eta_{ij} = \varrho_m \lim_{\substack{s\to 0\\ q\to 0}} \hat{\Gamma}_{ij}(q,s) \quad (63)$$

Equation 63 relates the macroscopic shear viscosity η_s to the various η_{ij} elements. One notes that η_s differs from that given in eq 54 due to the coupling coefficient Γ_{13}.

To proceed, we define a coupling viscosity $\hat{\zeta}$ by

$$\frac{\hat{\zeta}}{\varrho_m} = \frac{|\hat{\Gamma}_{32}'|^2\hat{\Gamma}_{11}}{\hat{\Gamma}_{11}\hat{\Gamma}_{33} - |\hat{\Gamma}_{31}|^2} \quad (64)$$

In addition, we define an effective relaxation rate $\hat{\Gamma}$ as

$$\frac{1}{\hat{\Gamma}} = \frac{\hat{\Gamma}_{11}}{\hat{\Gamma}_{11}\hat{\Gamma}_{33} - |\hat{\Gamma}_{13}|^2} \quad (65)$$

Thus, we have

$$|\Gamma_{13}|^2 = \hat{\Gamma}_{11}(\hat{\Gamma}_{33} - \hat{\Gamma}) \quad (66a)$$

and

$$|\Gamma_{23}|^2 = \hat{\zeta}\hat{\Gamma}/\varrho_m \quad (66b)$$

and the dispersion function Δ can then be written as

$$\Delta = \left(s + q^2\hat{\Gamma}_{33} - \frac{q^2\hat{\Gamma}_{11}(\hat{\Gamma}_{33} - \hat{\Gamma})}{s + \hat{\Gamma}_{11}}\right)(s + \hat{\Gamma}_{22}) + \frac{q^4}{\varrho_m}\hat{\zeta}\hat{\Gamma} \quad (67)$$

and since we have assumed that the Q_1 mode (the reorientation variable) fastly relaxes, we set $\hat{\Gamma}_{11} \gg s$. As a result, the dispersion function becomes

$$\Delta \simeq (s + q^2\hat{\Gamma})(s + q^2\hat{\Gamma}_{22}) + \frac{q^4}{\varrho_m}\hat{\zeta}\Gamma \quad (68)$$

On the account of eq 68, we can rewrite eq 58c as

$$\hat{C}_{33}(q,s) = \frac{1}{s + q^2\hat{\Gamma} + (q^4\zeta/\varrho_m)/(s + q^2\hat{\Gamma}_{22})}\langle|Q_3(q)|^2\rangle \tag{69}$$

If we set $s = i\omega$, we then find that the functional form of eq 69 is identical to eq 51, provided that $\hat{\Gamma}_{33}$ is replaced by $\hat{\Gamma}$ and $|\hat{\Gamma}_{23}|^2$ by ζ/ϱ_m. Since we assume that the orientational relaxation is fast, Γ is effectively equal to the diffusion rate of the center of mass of the pseudolattice. Furthermore, according to eq 64 the coupling viscosity ζ has an additional viscosity due to the coupling of the relaxation of the orientational variable to the strain.

On the account of eqs 51 and 52, $\hat{C}_{33}(q,s)$ given in eq 69 can be identified as the dynamic shear compliance. Namely

$$I_{33}(q,\omega) = \mathrm{Re}\,\hat{C}_{33}(q,s)|_{s=i\omega} = \frac{1}{q^2}\,\mathrm{Re}\,\frac{J^*(q,\omega)}{i\omega} = \frac{1}{q^2}\frac{J''(q,\omega)}{\omega} \tag{70}$$

where in eq 70 the expression is divided by q^2 due to the factor that Q_3 is defined in terms of the local displacement, which is related to strain $\gamma_{yz}(q,t)$ by $\gamma_{yz}(q,t) = -iqQ_3/2$ (eq 41).

We have obtained the spectral density due to the modulation of the dielectric constant tensor by Q_3. We next consider the spectral density associated with Q_1, the orientational density. We rewrite eq 58a as

$$C_{11}(q,s) = \langle|Q_1|^2\rangle/\left\{(s + \hat{\Gamma}_{11}) - \frac{q^2\hat{\Gamma}_{11}(\hat{\Gamma}_{33} - \hat{\Gamma})}{s + q^2\hat{\Gamma}_{33} + (q^2\hat{\zeta}/\varrho_m)(q^2\hat{\Gamma})/[s + q^2/\varrho_m(\hat{G} - \hat{\zeta})]}\right\} \tag{71}$$

Since $\hat{\Gamma}_{11}$ is large, one has $\hat{\Gamma} \approx \hat{\Gamma}_{33}$, and the second term in the denominator vanishes. As a result, eq 71 reduces to

$$C_{11}(q,s) = \frac{\langle|Q_1|^2\rangle}{s + \hat{\Gamma}_{11}} \tag{72}$$

If the dispersion of $\hat{\Gamma}_{11}$ is neglected, we obtain the orientational spectrum as a Lorentzian function given by

$$I_{11}(q,\omega) = \mathrm{Re}\left[\frac{\langle|Q_1|^2\rangle}{i\omega + \Gamma_{or}}\right] = \langle|Q_1|^2\rangle\frac{\Gamma_{or}}{\omega_2 + \Gamma_{or}} \tag{73}$$

where Γ_{or} is the reorientational rate constant given by

$$\Gamma_{or} = \hat{\Gamma}_{11}(s{=}0) = \int_0^\infty \Gamma_{11}(t)\,dt \tag{74}$$

After substituting $I_{11}(q,\omega)$ and $I_{33}(q,\omega)$ in eq 7 and also substituting $I_{11}(q,\omega)$ in eq 8, we obtain a simple expression for the VH spectral density as

$$I_{VH}(q,\omega) = \frac{A^2}{\pi}\left(\frac{\Gamma_{or}}{\omega^2 + {\Gamma_{or}}^2}\right) + \frac{(B')^2}{\pi}\cos^2(\theta/2)\frac{J''(q,\omega)}{\omega} \tag{75}$$

which is of the same form as that given in ref 15 in the slow rotation limit.

In terms of the time variable, eq 78 becomes

$$I_{VH}(q,t) = A^2 e^{-\Gamma_{o4}t} + (B')^2\cos^2(\theta/2)kT\{J_e(q) - J(q,t)\} \tag{76}$$

Equation 75 or 76 shows that the depolarized light scattering spectrum contains two components: one is associated with orientation, and the other with the imaginary part of the dynamic shear compliance. Although this result is similar to that previously obtained in ref 15 (eq 28 of ref 15), using a two-variable theory, the major difference between the present and the earlier results is that the earlier version deals with the case of slow reorientation, whereas the present one considers also the fast reorientation case. One notes that while the second term in eq 76 contains a factor of $\cos^2(\theta/2)$, an explicit angular calculation carried out by using a different coordinate system removes this factor. This is shown in Appendix I.

Segmental reorientation in the viscoelastic polymer liquid may remain to be fast, and the DCA may not be completely relaxed by the reorientational mechanism; thus the strain fluctuation of the molecular strain remains as the mechanism to relax the DCA. Consequently, one expects that the depolarized light scattering spectrum measured at long times (such as using the photon correlation technique in the dynamic range between 10^{-1} and 10^{-6} s) corresponds to the dynamic compliance spectrum, as given by the second term in eq 75 or 76. This conclusion is consistent with that recently arrived by Fischer et al.[11]

In summary, we have investigated the depolarized light scattering spectrum of a polymer liquid consisting of an optically anisotropic segment in which reorientation is dynamically coupled to shear motion. By assuming that the modulation of the dielectric constant anisotropy is due to shear strain, we have first shown using linear response theory that the depolarized light scattering spectrum is equivalent to the imaginary part of the dynamic shear spectrum. At higher temperature, the situation becomes more complex as the dielectric constant anisotropy is modulated by both molecular reorientation and shear strain. Using a generalized hydrodynamic approach involving three dynamic variables, we have shown in this case that the depolarized light scattering spectrum consists of reorientational and shear components. In the situation when segmental reorientation is fast, we have found that the dynamic light scattering spectrum becomes the sum of the reorientational and the dynamic compliance spectra. As part of the DCA quickly relaxes by molecular reorientation, the remaining DCA is slowly relaxed by the shear strain relaxation, and the depolarized light scattering spectrum in the low-frequency region (or at long times in the case of the time correlation function) becomes proportional to the shear compliance spectrum. Thus, it is possible to determine the dynamic shear compliance spectra of polymer liquids by using DLS.

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Appendix I. Depolarized Light Scattering and Shear Compliance in a Spatially Inhomogeneous System

In section III we have shown that in the absence of molecular reorientation, the depolarized light scattering spectrum is related to the shear creep compliance by

$$I_{\mathrm{VH}}(q,t) = \frac{(B')^2 kT}{2\pi} \cos^2(\theta/2)[J_e(q) - J(q,t)] \quad \text{(I-1)}$$

where $J(q,t)$ is given by

$$J(q,t) = \frac{1}{kT}\langle \gamma_{yz}(q,t)\gamma_{yz}{}^*(q)\rangle \quad \text{(I-2)}$$

and $J_e(q)$ is the steady-state creep compliance, equal to $\lim_{t\to\infty} J(q,t)$. Here the direction of q is along the z axis of the laboratory coordinate system.

In view of eq I-1, if $J(q,t)$ is independent of q in the range of q involved in light scattering, then eq I-1 predicts that $I_{\mathrm{VH}}(q,t)$ is proportional to $\cos^2(\theta/2)$. This is, however, not in agreement with the experimental result. It thus suggests that the q dependence introduced in eq I-2 needs to be considered with care.

As shown in eq 41, $\gamma_{yz}(q,t)$ is equal to $-iqU_y(q,t)/2$; thus eq I-1 can be written as

$$I_{\mathrm{VH}}(q,t) = (B')^2\left(\frac{\pi n^2}{2\lambda^2}\right) \sin^2 \theta\{\langle |U_y(q)|^2\rangle - \langle U_y(q,t)U_y{}^*(q)\rangle\} \quad \text{(I-3)}$$

To obtain eq I-3, we have used the expression $q = (4\pi n/\lambda) \sin(\theta/2)$.

We now transform eq I-3 to a coordinate system with the incident light polarized along the z axis and propagating along the x axis. This coordinate system is referred to as scattering geometry II in ref 18. In scattering geometry II eq I-3 can be written as

$$I_{\mathrm{VH}}(q,t) = \frac{(B')^2 kT}{2\pi}[J_e'(q) - J'(q,t)] \quad \text{(I-4)}$$

where the prime associated with J indicates that $\mathbf{q}$ is defined in terms of the new coordinate system given by $\mathbf{q} = (4\pi n/\lambda)[\hat{x}(\cos \theta - 1) + \hat{y} \sin \theta]$. One notes that the $\cos^2(\theta/2)$ factor is absorbed in the definition of scattering vector $\mathbf{q}$. Equation I-4 was derived by Hess using scattering geometry II via linear response theory.[17] Equation I-1 and eq I-4 are thus equivalent. The $\cos^2(\theta/2)$ present in eq I-1 is not explicitly present in eq I-4.

In bulk polymers or neat liquids, the experimentally observed DLS spectra $I_{\mathrm{VH}}(q,t)$ are independent of the scattering angle (or q). This result can be rationalized by employing an argument similar to that employed in ref 12. By assuming that the correlation length l_c is associated with the microscopic strain at two points in space, one can write $J(q,t)$ as

$$J(q,t) = \frac{V}{kT}\int \mathrm{d}^3R\, \langle \gamma_{yz}(t)\gamma_{yz}(0)\rangle \mathrm{e}^{-R/l_c}\mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \quad \text{(I-5)}$$

If $l_c \ll q^{-1}$, then

$$J(q,t) \rightarrow \frac{Vl_c{}^3}{kT}\langle \gamma_{yz}(t)\gamma_{yz}(0)\rangle \quad \text{(I-6)}$$

Thus, if the spatial inhomogeneity is smaller than the wavelength of the scattered light, the q (or angular) dependence of the compliance spectrum is not observed. In this case the depolarized light scattering spectrum is simply proportional to the shear creep compliance spectrum.

Appendix II. Spectral Power Density Calculated Using Shear Stress Density as Q_3

If Q_3 is set to be equal to $\sigma_{yz}(q)$, the shear stress density, then according to Newton's equation, we have

$$\frac{\partial}{\partial t}Py = iq\sigma_{yz}(q) = iqQ_3 \quad \text{(II-1)}$$

The frequency matrix is then given by

$$\mathbf{\Omega} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & q/m \\ 0 & q\mu_\infty/\varrho_0 & 0 \end{bmatrix} \quad \text{(II-2)}$$

where μ_∞ is the shear modulus at infinite frequency (or $t = 0$) equal to $\varrho_0 \langle |\sigma_{yz}|^2\rangle/NkT$. Here ϱ_0 is the number density.

The relaxation matrix is then given by

$$\mathbf{K}(q,t) = \begin{bmatrix} K_{11} & 0 & K_{13} \\ 0 & 0 & 0 \\ K_{31} & 0 & K_{33} \end{bmatrix} \quad \text{(II-3)}$$

The above results form the fact that the random force is given by

$$\mathbf{F} = \begin{bmatrix} f_1 \\ 0 \\ f_2 \end{bmatrix} \quad \text{(II-4)}$$

due to the fact that $f_2 = i(1 - p)\mathcal{L}Q_2 = 0$. Here p is the projection operator defined in accordance with the Zwanzig–Mori technique.

The kinetic equations for the components of **A** are thus given by

$$\frac{\partial}{\partial t}Q_1 = -K_{11}{}^*Q_1 - K_{13}{}^*Q_3 \quad \text{(II-5a)}$$

$$\frac{\partial}{\partial t}Q_2 = iqQ_3/m \quad \text{(II-5b)}$$

$$\frac{\partial}{\partial t}Q_3 = -K_{31}{}^*Q_1 + i(q\mu_\infty/\varrho_0)Q_2 - K_{33}{}^*Q_3 \quad \text{(II-5c)}$$

Solution of the above equations yields the correlation function of $\hat{Q}_1$ and $\hat{Q}_3$ as

$$\langle \hat{Q}_1(q,s)Q_1{}^*(q)\rangle = \frac{\langle |Q_1(q)|^2\rangle}{(s + \hat{K}_{11}) - |K_{13}|^2/[(s + \hat{K}_{33}) + q^2\mu_\infty/\varrho_m s]} \quad \text{(II-6)}$$

and

$$\langle \hat{Q}_3(q,s)Q_3{}^*(q)\rangle = \frac{\langle |Q_3(q)|^2\rangle}{(s + \hat{K}_{33}) + (q^2\mu_\infty/\varrho_m s) - |\hat{K}_{13}|^2/[(s + \hat{K}_{11})]} \quad \text{(II-7)}$$

where $\varrho_m = \varrho_0 m$ is the mass density.

If the reorientational rate is high, one may neglect the last term in the denominator of eq II-7. As a result, eq II-7 becomes identical to the expression previously obtained by Akcasu and Daniels[24] for the shear modulus. One may recall that the relaxation shear modulus is proportional to $\langle \sigma_{yz}(q,t)\sigma_{yz}{}^*(q)\rangle$ (cf. eq 46). Thus, if we set $s = i\omega$ in eq II-6 and then multiply the result by $i\omega$, we obtain the expression of the dynamic shear modulus for fluids consisting of anisotropic molecules.

To obtain the spectral power density for the depolarized light scattering spectrum, one sets $s = i\omega$ in eqs II-6 and II-7 and substitutes the results into eqs 7 and 8. The results would correspond to two parts: one proportional to the rotational spectrum and the other proportional to the imaginary part of the dynamic *shear modulus* spectrum. Thus, by choosing Q_3 to be the shear stress density, the dynamic light scattering spectrum at low frequency becomes the dynamic *shear modulus* spectrum and not the dynamic *shear compliance* spectrum as required by the limiting Pockels photoelastic law for a viscoelastic solid.

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