Doppler shifts in spectral bands of scattered light and their application to the physics and mechanics of polymers

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Two new investigation techniques based on the phenomenon of Doppler shifts in light scattered by moving scattering centers, are described. When applied to displacements of scattering centers associated with the rotation of a solid sample in an incident laser beam or with the structural relaxation following uniaxial compression, the phenomenon is shown to be fairly informative of the structure and mechanical behavior of the samples. In the first case the the informaton is provided in the form of statistical parameters of a randomly microinhomogeneous medium. In the second, the kinetics of the structural reorganization in the mode of the stress relaxation can be measured.

Key words: light scattering, Doppler shift, statistics, random media, holographic interferometry.

When light scattering occurs on a moving object, a Doppler shift is seen both in the spectral band of the scattered light and in the spectrum of its intensity fluctuations. Pecora[1] was the first who applied this phenomenon to polymer solutions and demonstrated that the spectral broadening of light scattered by brownian particles is proportional to the rate constant of equilibrium diffusion. From that time on, Doppler broadening has provided the basis for the familiar method of photon correlation, which became a conventional technique for measuring not only the rate constants of equilibrium processes, but also the speed distribution in turbulent and laminar fluxes, biological motion, *etc.*[2]

Here we discuss two novel techniques making use of the shape of the band in the spectrum of intensity fluctuations of scattered light: (i) for optically testing solid transparent media for microhomogeneity and (ii) for studying the kinetics of structural relaxation in mechanical tests in the mode of strain relaxation. The first case deals with light scattering by a rigid transparent sample moving in a laser beam using the known law. In this case, the frequency of the light scattered by moving scattering centers is somewhat shifted with respect to the frequency of the incident light, and, if the speed vectors of the scattering centers are different, the spectral band in the spectrum of the intensity fluctuations broadens, and its shape reflects the distribution of the scattering centers within the moving object. In the second case, the process setting the scattering centers in motion is relaxational structural rearrangement in a macroscopically motionless sample.

According to the approach proposed by Debye,[3] the scattering centers in rigid transparent media are microfluctuations of the electron density Δ_i. The most convenient description of the structure of such media containing randomly distributed microfluctuations ("random media") is a statistical one expressed in terms of correlation functions of polarizability fluctuations

$$\gamma(r_{ij}) = \langle\Delta_i\Delta_j\rangle,$$

where r_{ij} is the distance between the scattering centers. The limit behavior of the function: $\gamma(0) = \langle\Delta^2\rangle$, $\gamma(\infty) = \langle\Delta\rangle^2 = 0$.

As a rule, both $\gamma(r_{ij})$ and its normalized counterpart $\langle\Delta_i\Delta_j\rangle/\langle\Delta^2\rangle$ have an exponential form[3]. The possibility that the density fluctuations in polymers are gaussian correlation function has also been discussed.[4]

Debye also suggested a way to experimentally determine the $\gamma(r_{ij})$ correlation function: namely, the Fourier-transform of the angular dependence of the scattered light intensity. Using this operation one obtains the mean square amplitude of fluctuation $\langle\Delta^2\rangle$ and the correlation length r_c (Fig. 1). This approach has provided the basis for the concept of small angle light scattering (SALS). However, the essential shortcoming of this description (and therefore of SALS as an investigation technique) is its ambiguity, because, taken alone, an averaged statistical characteristic of a medium is not sufficient to ensure an adequate description of the latter. To improve the statistical description, one should have at his disposal another similar characteristic, with a different order of averaging. In this case, it can be the correlation function of the same fluctuations squared

$$f(r_{ij}) = \langle\Delta_i^2\Delta_j^2\rangle.$$

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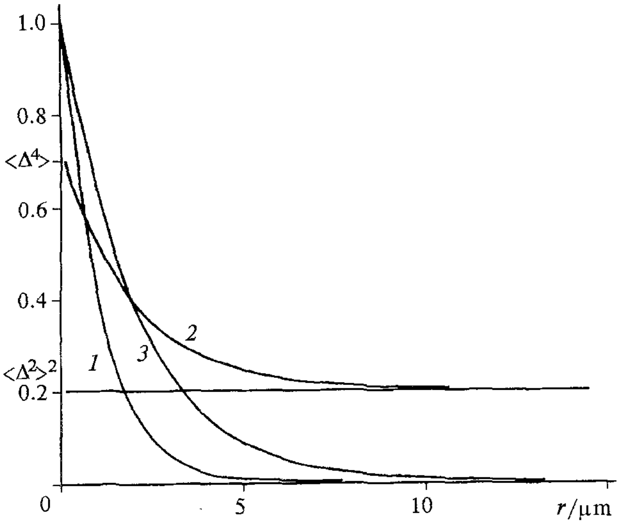

Fig. 1. Correlation functions of electron density fluctuations of various orders of averaging (for randomly inhomogeneous media): *1*, normalized pair correlation function $\gamma(r) = \langle\Delta_i\Delta_j\rangle/\langle\Delta^2\rangle$; *2*, pair correlation function of the squared fluctuations $f(r_{ij}) = \langle\Delta_i^2\Delta_j^2\rangle$; *3*, normalized correlation function of the squared fluctuations. The functions are calculated with the assumption that the random medium is described by the Gaussian Markov process: $\gamma(r) = \exp(-r/a)$; $h(r) = \exp(-2r/a)$.

The limit behavior of the function: $f(0) = \langle\Delta^4\rangle$, $f(\infty) = \langle\Delta^2\rangle^2$ (Fig. 1).

This function makes it possible to define the averaged fourth order of the intensity of fluctuations and the corresponding correlation length, r_c, which, in general, differs from Debye's correlation radius. In order to record this higher order correlation function it is necessary to carry out yet another experiment related to the other type of averaging with respect to the intensity of scattered light. The other type of averaging can be found, for example, by studying the shape of the spectral band of the intensity fluctuations in the field of scattered light, using the Wiener—Hinchin theorem,[5] which relates the frequency spectrum to the time correlation of scattered light intensities $\langle I_iI_j\rangle$ rather than to a single averaged intensity.

One relevant experiment is to detect the Doppler broadening in the spectral band of fluctuations in light scattered by a moving sample when the detector remains fixed and I_i and I_j are the intensities of light thrown upon the detector at some sequential instants of time, *i.e.*, $I_i(t)$ and $I_j(t+\tau)$. The correlation fucntion that can thus be measured is:

$$G(\tau) = \langle I(t) + I(t+\tau)\rangle$$

The shape of the spectral lines can be obtained by the transform

$$S(w) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G(\tau)\exp[i\omega\tau]d\tau$$

The sample employed in our experiments was a rigid transparent disc that rotated at some constant angular speed in a laser light beam. In this case, the tangential speed of every scattering center can be determined from its coordinates r using Euler's law:

$$dr/dt = [r\cdot\Omega]$$

The photocurrent generated by the detector is modulated by a moving scattered field that exhibits an apparent interferential ("speckle") pattern. The corresponding fluctuations of the photocurrent are analyzed by a spectroanalyzer. The Doppler shift on the scattering centers, whose velocities are different due to their different positions with respect to the rotation center of the sample, is responsible for the broadening of the thus-recorded spectral line. Its shape reflects the spatial distribution of the centers in the material studied.

1. Shape of spectral band of intensity fluctuations in the light scattered by a rotating object and its relation to the microscopic structure of the scattering medium

The analysis of the shape of a spectral band showed that the spectrum of intensity fluctuations of scattered light is a superposition of two components (Fig. 2):

$$S(\omega) = S_1(\omega) + S_2(\omega).$$

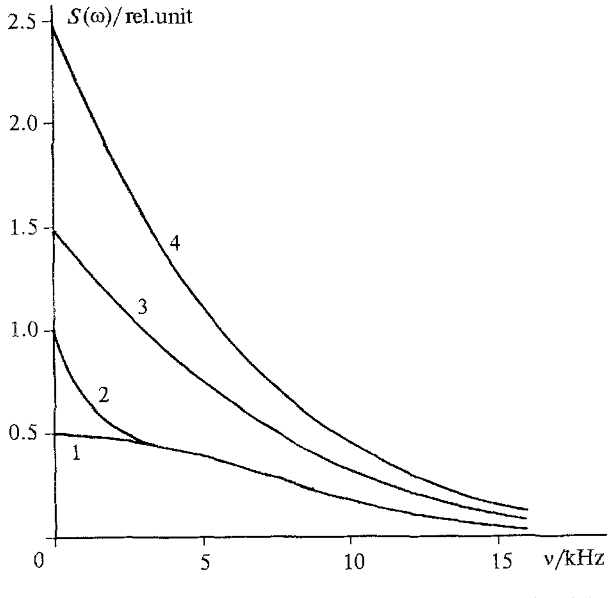

Fig. 2. Theoretical spectra of intensity fluctuations in the light scattered by rotating samples of media with different widths of amplitude distributions of fluctuations. The distribution width is characteried by its dispersity $D = \langle\Delta^4\rangle/\langle\Delta^2\rangle^2$: *1*, D = 0 — the spread function $S_2(\omega)$; *2*, D = 50; *3*, D = 100; *4*, D = 200. The calculations are performed for a sample shaped as a plane-parallel disc illuminated by a laser beam with a Gaussian radial intensity distribution at the ratio between the beam and the correlation dimensions $\sigma_{\mathrm{beam}}/r_c = 10$.

The spatial distribution of the scattering centers within the medium studied accounts only for the first component $S_1(\omega)$, while the second one, $S_2(\omega)$, is the spread function. The latter depends on the shape, the value and position of the scattering volume with respect to the rotation axis, the distribution of the incident light intensity within the scattering volume, and $<\Delta^2>$ and $<\Delta^4>$, the mean characteristics of the scattering medium. The rotation speed and scattering angle affect both components in the same manner. The experimental problem consists of isolating the informative component $S_1(\omega)$, *i.e.*, separating $S_2(\omega)$, the spread function. One of the possible techniques for this separation is described in Ref 6. The explicit relation of the informative component $S_1(\omega)$ to the normalized form of the wanted spatial correlation function of density fluctuations was obtained in Ref. 8:

$$h(r) = -\frac{A}{\omega}\frac{dS_1(\omega)}{d(\omega)},$$

where $h(r) = \dfrac{f(r) - f(\infty)}{f(0) - f(\infty)}$ is the normalized form of $f(r)$, (Fig. 3). $S(w)$ is the frequency spectrum of intensity fluctuations in scattered light that makes it possible to obtain the explicit form of the $h(r)$ correlation function. The modulus of a vector **q** that we introduced for describing scattering by rotating samples, serves as a coefficient to transform frequency units (Hz) into units of length (cm). This vector can be considered as the "rotational" counterpart of the familiar wave vector **K** of scattered light introduced for describing scattering by "immobile" objects:

$$\mathbf{q} = [\mathbf{K}\cdot\Omega],\ r = \frac{\omega}{\mathbf{q}}.$$

To compare the behavior of the correlation functions $\gamma(r)$, $f(r)$ and $h(r)$, one can write their limit values:

$$\gamma(0) = <\Delta^2>,\ \gamma(\infty) = <\Delta>^2 = 0$$
$$f(0) = <\Delta^4>, f(\infty) = <\Delta^2>^2$$
$$h(0) = 1,\ h(\infty) = 0,$$

The interconnection between these functions on one hand, and the microscopic structure of the scattering medium on the other are analyzed in Ref. 7.

The **K** and **q** vectors make it possible to determine the phase difference $\Delta\phi$ of beams scattered by two different scattering centers and undergoing interference at the observation point on the detector photocathode. One has $\Delta\phi_{ij} = \mathbf{K}r_{ij}$ in the conventional case and $\Delta\phi_{ij} = \mathbf{q}r_{ij}\tau$ for a rotating sample.

In the latter case the phase difference, $\Delta\phi_{ij}$, experiences cyclic changes with time; this difference changes with the frequency at which the sample is rotated.

The spectrum of intensity fluctuations in scattered light is proportional to the power spectrum of photocurrent fluctuations and thus can be recorded using a spectroanalyzer. On the other hand, it can be inferred from the correlation function of electron density fluctuations similarly to Debye's calculations of angular dependencies of the scattered light intensity (indicatrices) for an immobile sample.[3] According to the Wiener—Hinchin theorem, the correlation function of intensity fluctuation can be transformed to the frequency spectrum $S(\omega)$ by a Fourier-transform.[2] The detailed calculations of the correlation function of intensity fluctuations, its transform into the spectrum, and a way of obtaining $h(r)$, the normalized spatial correlation function of the squared polarizability fluctuations, from the shape of the specrtal band are given in Refs. 6 and 8. To improve the statistical reliability of the results, the spectrum was taken several times and from various areas of the sample. This was performed by a special technique using an optical-mechanical sweep across the sample in the laser beam.[9] This information, coupled with the SALS results, $\gamma(r_{ij})$, gives an estimate of the width of the amplitude distribution of electron density fluctuations in terms of the ratio of its different moments $<\Delta^4>/<\Delta^2>^2$, similarly to the polydispersity coefficient M_v/M_n in polymer chemistry. The ratio between the correlation lengths corresponding to the $\gamma(r)$ and $h(r)$ correlation functions is also indicative of the structure of the scattering medium.[7]

Thus, the combination of SALS with the spectral study of the intensity fluctuation in light scattered by a rotating sample is a natural development of SALS that significantly improves the adequacy of the statistical description of random microinhomogeneous media in terms of correlation functions.[9]

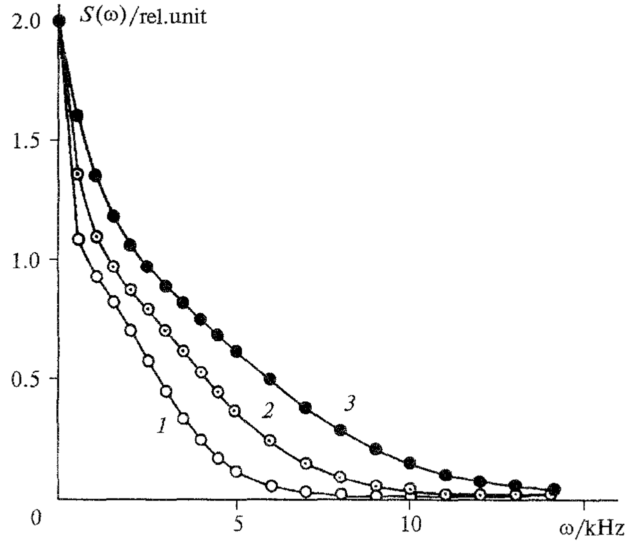

Fig. 3. Experimental spectra of intensity fluctuations in the light scattered by microinhomogeneous samples (opalescent glass MC-19, National Optical Institute) rotating at a frequency of 50 Hz at various scattering angles: 5.5°(*1*); 11.3°(*2*); 27.4°(*3*). The dotted line indicates the separated spread functions. The incident beam is focused on the sample with Gaussian intensity distribution in the focal plane, σ = 150 Mm.

The technique of the relevant experiment and some examples of its application to the physical chemistry of polymers are described in Refs. 6 and 10 (Fig. 3).

2. Dynamic holography in scattered light and its application to the study of slow structural rearrangements

Another promising way of using the Doppler shift in light scattered by mobile particles is its application to the kinetic study of slow and superslow internal rearrangements during mechanical testing of solid polymers in the regime of strain relaxation. These processes are known to be associated with very slow internal movements, and hence, with extremely small frequency shifts. Therefore, it is more convenient to describe them in terms of the time correlation function of the scattered field rather then in terms of the spectral band shape.[2] The registration of these slow displacements requires a basically different experimental technique.

Among the possible solutions of this experimental problem, recording the time correlations in the scatterd light field by holographic correlational spectroscopy[11] seems to be particularly inviting due to the fact that the technique operates in real time. The scattering pattern of the sample is fixed on a hologram (glass photoplate) at some initial instant of time. A special technique of hologram treatment makes possible its rapid development *in situ.*[11] The light scattered by a sample undergoing structural relaxation is viewed by a photomultiplier through the hologram. The difference between the initial (fixed on the hologram) and the current scattering patterns results in a decline in the contrast of the pattern formed by their superposition. The contrast measurement is performed by phase hunting in a supporting a laser beam. The alternating component of the photocurrent is proportional to the contrast of the pattern formed by the superposition of the real and holographic scattering patterns and to the modulus of the correlation function in the scattered light field.[11] Once the hologram is developed, the correlation function can be recorded directly with any a.c. recording technique.

Thus recorded, the time correlation function of the scattered light field corresponds to averaging over the sum of the scattering centers fixed on the hologram rather than over some time period (as takes place in the photon correlation technique). Therefore, this variant of holographic correlational spectroscopy can be employed to investigate slow nonstationary processes like structural relaxation in polymers.

We studied the usefulness of the correlation function of a scattered light field recorded during mechanical testing of a polymer in the mode of strain relaxation. The correlation functions were recorded using a holographic correlational spectrometer that had been developed at the former All-Union Research Institute of Optical Physical Measurements.[11] The essence of the experiment was the holographic monitoring of structural rearrangements in the polymer following rapid axial compression imposed on a cylindrical sample. The kinetics of the microscopic structural displacements in the macroscopically immobile sample in the course of strain relaxation was studied. The details of the experiment can be found in Ref. 12.

The interpretation of the recorded correlation function and the search for its relation to the kinetic parameters of the relaxation process require some definite model for the movement of the scattering centers in the sample in the course of the structural relaxation. In terms of the affine expansion-contraction of a polymeric material, for the movement of any stuructural elements, one can write:

$$r_j(t) = r_j(0)[1 + \varepsilon(t)],$$

where r_j designates the coordinates of the j-th structural element, and $\varepsilon(t) = \Delta r_j(t)/r_j(0)$ is the temporal dependence of relative deformation. In this case, the normalized correlation function of the scattered light field can be calculated as:[12]

$$g(t) = \frac{1}{V}\int_V \exp[i\mathbf{K}r\varepsilon(t)]\,\mathrm{d}V,$$

where V is the scattering volume.

The results of integration over the scattering volume V depend on its shape and orientation with respect to the scattering vector, **K**.

The experimental correlation functions, which reflect the displacements of structural units in a sample experiencing relaxational rearrangements, are in a good agreement with the theoretical results[13] (Fig. 4). To significantly improve the usefulness of the correlation functions, optical heterodinynation, *i.e.*, the superposition of the beam scattered from the bulk of the sample at a 23° scattering angle with one scattered from its surface at 155°, was used. The high accuracy of the registration of the relative deformation (10^{-3}) made it possible for us to reveal two modes of the relaxation process that develop simultaneously within the sample. One of them is an elastic response of the system to the strain imposed, and the other is a plastic response.[14] The characteristic relaxation times in a viscous medium made it possible to determine the sizes of the relaxing centers. The details of the holographic experiment and its application to the study of creep in solid epoxide polymers are described in Ref. 12.

Conclusions

1. The Doppler broadening of a band in a photocurrent power spectrum that has been earlier used in dynamic light scattering for the study of diffusion processes is shown to be fairly informative when associated

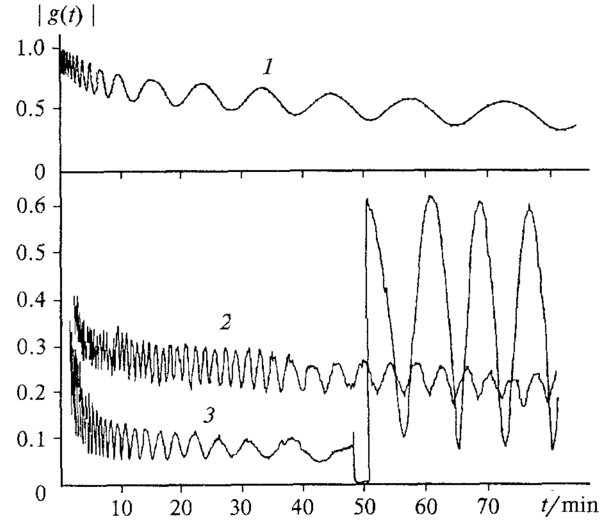

Fig. 4. Theoretical (*1*) and experimental (*2* and *3*) time dependences $|\gamma(t)|$ for the field of light scattered in the bulk and on the surface of the sample: *1*, correlation function calculated with the assumption of two characteristic relaxation times τ_1 = 3 min and τ_2 = 80 min; *2* and *3*, experimental $|\gamma(t)|$ curves recorded at T = 130 °C (*2*) and T = 135 °C (*3*).

both with the motion of the scattering centers according to Euler's law (rotation of a rigid microinhomogeneous sample in a laser beam), and with that obeying the affine expansion-contraction model (in mechanical testing of solid polymers in a laser beam in a strain relaxation regimen). The first case offers information on a sample's microstucture in terms of the correlation function of electron density fluctuations $f(r_{ij}) = \langle\Delta_i^2\Delta_j^2\rangle$, while in the second case the kinetics of structural relaxation in terms of $\varepsilon = \langle r(t)/r(0)\rangle$, relative deformation averaged over the scattering volume, is acquired.

2. The shape of the spectral band in the photocurrent power spectrum (spectrum of intensity fluctuations in the scattered light) is calculated for the case of scattering from a transparent rigid microinhomogeneous disc rotating in a laser beam at a constant angular speed Ω. To perform the calculations, a rotational counterpart of the scattering vector **K** was introduced $\mathbf{q} = [\mathbf{K}\cdot\Omega]$.

3. The analytic interrelation of the thus-calculated shape of the spectral band with the spatial correlation function of the intensity fluctuations is inferred:

$$h(r_{ij}) \approx -\frac{1}{\omega}\frac{dS}{d\omega}$$

4. $h(r_{ij})$ coupled with Debye's correlation function $\gamma(r_{ij}) = \langle\Delta_i\Delta_j\rangle$ offers an estimate of the width of the amplitude distribution of the electron density fluctuations in a random medium in terms of the ratio of the moments $\langle\Delta^4\rangle/\langle\Delta^2\rangle^2$ similarly to the MWD width of polymers in terms of the M_v/M_n ratio.

5. An alternative technique to photon correlation based on holography is developed that makes it possible to directly measure correlation functions in a scattered light field. The use of holographic correlation spectroscopy makes it possible to extend the dynamic range of detectable Doppler shifts by three orders of magnitude in the direction of slower processes that have been inaccessible by conventional photon correlation techniques. This makes possibile kinetic studies of structural relaxation during the testing of glassy polymers in a strain relaxation regimen and other slow processes in highly viscous media with characteristic times below 10^{-5}sec.

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