Lyapunov exponent of the optical radiation scattered by the Brownian particles

Mykhaylo S. Gavrylyak*, Oleksander P. Maksimyak, Peter P. Maksimyak

Department of Correlation Optics, Chernivtsi National University, Chernivtsi 58012, Ukraine

*Corresponding author: mgavrylyak@gmail.com

The computer and physical simulation of light scattering by the system of Brownian particles has been carried out. Temporary fluctuations of field intensity have been found to save chaotic properties of driving particles. Empirical diagnostic links have been retrieved of the largest Lyapunov exponent of fluctuations of field intensity with parameters of the dispersive media.

Keywords: light scattering, Lyapunov exponent, sulfur hydrosols, Brownian particles.

1. Introduction

The light scattering of coherent optical radiation on Brownian particles causes a complicated space–time modulation of field intensity as a result of interference composition of partial waves with random amplitudes and phases. Time correlation of scattered radiation field is defined with the help of particle motion speed and experiment geometry, which is the subject of research in Doppler spectroscopy [1, 2]. Gorelik was the first scientist to propose the method of optical detection in 1947 [3]. Forrester's, Town's, Cummins's, Pike's, and other scientists' experiments being discussed in detail [4] are considered to be the basis of a new trend, *i.e.*, optical mixing spectroscopy which is successfully used in physical and chemical investigation, biology and medicine.

At present the application of optical mixing spectroscopy has a definite critical state. On the one hand, the coefficient determination of translation diffusion of macromolecules, eritrocites, colloid particles, viruses and others has become a standard and rather reliable measuring method [5]. On the other hand, when investigating more complicated systems (polydispersed, with high particle concentration, inhomogeneous) there appear some problems requiring the development of theory and mastering of experimental techniques.

According to modern views Brownian motion of particles is either random or chaotic. Moreover, it possesses fractal properties [6, 7]. That is why one can use the theory of

stochastic and chaotic fluctuations for describing Brownian motion [8]. There arises an important question concerning the character of space-time chaotization of scattered radiation field, quantitative diagnostic of relationship between stochastic characteristic features of medium and field, advantages of stochastic approach in determining structural and dynamic characteristic features of media with Brownian particles.

We will consider the mathematical modeling of Brownian particle motion and calculate the optical radiation field scattered on them. We will carry out experimental investigation of light scattering by sulfur hydrosols. We will use the largest Lyapunov exponent as an example for researching the time chaotization of parameters of light-scattering medium. We will show the possibility of taking into account the errors of defining Brownian particle sizes with the help of measured largest Lyapunov exponent.

2. The modeling of Brownian particle motion

The replacement of Brownian particle along axis OX at time t is given by the normal probability distribution:

$$p(x, \tau) = \frac{1}{\sqrt{4\pi D \tau}} \exp\left(-\frac{x^2}{4 D \tau}\right) \tag{1}$$

The succession of such random values $\{x_i\}$ is a set of independent random numbers with Gaussian distribution and dispersion [9]:

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 p(x, \tau)\mathrm{d}x = 2 D \tau \tag{2}$$

where D – diffusion coefficient, defined by astringent medium resistance. For spherical particles of radius R:

$$D = \frac{kT}{6\pi \mu R} \tag{3}$$

where k – Boltzmann constant, T – absolute temperature, μ – medium ductility.

Particle coordinate at axis x at time moment $t = n\tau$ is as follows:

$$X(t) = \sum_{i=1}^{n} x_i \tag{4}$$

In an extreme case for great n and small τ the set of n random numbers are graded into a random function $X(t)$ [7] having the same properties as the replacement x.

A program for modeling N Brownian particle motion been elaborated. The initial particle motion was given with the help of equiprobable distribution of their coordinates (X, Y, Z) within volume L^3 being investigated. Particles size was given by Gaussian distribution function with an average volume R_0 and size dispersion σ. Particle replacement x, y, z was given under a normal law (1), and the replacement dispersion of particle $(2D\tau)^{1/2}$ depended on particle size as well. Particle coordinates after each replacement step were determined with the help of relationship (4).

For calculating scattered radiation field distribution the Rayleigh–Gans–Debye light scattering model was chosen [10]. For monodisperse ensemble such particles scatter the intensity, which is proportional to R [6] at the same angle. The field amplitude at an arbitrary point of space (z_0, ξ, ζ) is defined as a sum of complex field amplitudes scattered by all Brownian particles:

$$U(\xi, \zeta, z_0) \;=\; \frac{4\pi^2 I_0}{\lambda^2}\left[\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2}\right]\sum_{i=1}^{N}\frac{R_i^3 \exp\left[-ik(r_i + z_0)\right]}{r_i} \tag{5}$$

where $r_i = [(z_i - z_0)^2 + (x_i - \xi)^2 + (y_i - \zeta)^2]^{1/2}$ is the distance from i-Brownian particle to the point in the observation plane; z_0 – the distance between the plane where there is a scattering volume and observation plane, $x_i, y_i, z_i, \xi, \zeta, z_0$ – rectangular coordinates in object plane and observation plane, respectively; $k = 2\pi/\lambda$ – a wave number, where λ is a wavelength.

The complex field amplitude was calculated and written down in the form of $U = \mathrm{Re}\,U + i\,\mathrm{Im}\,U$. It was used for determining amplitude A, phase φ and field intensity I.

3. Objects of experimental investigation

Sulfur hydrosols were chosen for physical modeling objects [11]. They are obtained by mixing l – normal solutions of hydrochloric acid and sodium thiosulfate. Then, molecularly dispersion sulfur is condensed in the form of the drops of overcooled sulfur, which are equally increased in size with the rate of sol deterioration. Sulfur refraction index is equal to 1.44 relative to water. In the absence of extraneous nuclei of condensation the drops are formed after gaining the definite solution supersaturation. Then, their initial radii will be of the order of 0.01 μm.

When using sulfur hydrosols in physical experiment they have to be calibrated, *i.e.*, the definite particle size is to be brought to correspondence with the definite time of sol growth. Assuming that particle sizes of sulfur hydrosols (0.01–2 μm) correspond to Rayleigh–Gans–Debye particles, we used light scattering tables edited by Shifrin for their calibration [12]. The essence of calibration consists in comparing scattering indicatrices, measured experimentally, to theoretical ones, obtained from the tables,
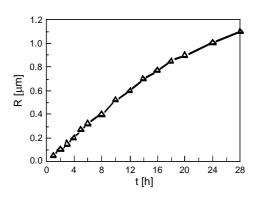
Fig. 1. Calibrated dependence of particle sizes of sulfur hydrosols on their growth time.

for the definite parameters of sulfur particles. The main criterion of the comparative estimation was the coincidence of diffraction extremes in scattering indicatrices.

Figure 1 shows the calibrated dependence of particle sizes of sulfur hydrosols on their growth time. Under inclination of environment temperature ±5 °C it leads to the inclination of hydrosol sizes not greater than 10%.

4. Definition of Brownian particle sizes

The correlation function of radiation field scattered by Brownian particle system once is as follows [13]:

$$F_S(u, t) = \exp(-u^2 D_T t) \tag{6}$$

where the light scattering vector $u = |k - k_R| = \dfrac{4\pi}{\lambda} n \sin\left(\dfrac{\theta}{2}\right)$.

For Gaussian distribution spectral density of scattered radiation is determined as follows [4]:

$$S(u, \omega) = N|A|^2 \frac{u^2 D_T / \pi}{(\omega_R - \omega)^2 + \left(u^2 D_T\right)^2} \tag{7}$$

Laurents's counter with a halfwidth $\Delta\omega_{1/2} = u^2 D_T$ and center $\omega = \omega_R$ is described by means of this expression.

According to (6) and (7) for Gaussian distribution one has [4]:

$$K_R^{(2)}(t) = 1 + \exp(-2u^2 D_T t) \tag{8}$$

Measuring the inclination angle of line $\ln\left|K_R^{(2)}(t) - 1\right|$ (in linear approximation) to axis t we found the values of diffusion coefficient and particle size.

Experimental investigation of sulfur hydrosols was carried out for the growth time from 2 to 25 hours. This corresponded to sizes of sulfur particles from 0.01 to 1 μm as one can see in the calibrated diagram of Fig. 1. The values of initial concentration
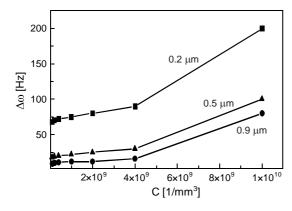
Fig. 2. Dependence $\Delta\omega$ on particle concentration for sulfur hydrosols of three sizes.

of condensed sulfur particles in forming the hydrosols in various sources are different [14], being of the order of 3×10^9–10^{10} particles per 1 mm^3. We decreased the initial concentration a hundred times. The smallest concentration under study was approximately 5×10^7 particles per 1 mm^3, and it was defined by photoelectronic multiplier capability to register weak scattered streams. However, this limit corresponds to sulfur particles less than 0.2 µm only, as the intensity of light scattering increases as R with the particle radius growth R^6.

Having a halfwidth of power spectrum, according to relation (7), we defined the coefficient of translation diffusion D_T, which we used for calculating particle radius.

Figure 2 represents the dependence of halfwidth of power spectrum $\Delta\omega$ on particle concentration for sulfur hydrosols of three sizes ($R = 0.2$, 0.5 and 0.9 µm) with the following parameters of the experiment: $d = 0.1$ mm, $\theta = 0.02$, $z_0 = 100$ mm, $\omega = 0.001$.

At small concentrations of sulfur particles spectrum halfwidth cannot be practically changed, and at big concentrations it increases. Obviously, this is connected with the appearance of multiple scattering effects and the appropriate spectrum widening. From rectilinear parts of concentration dependence of power spectrum halfwidth we defined Brownian particle size. It was equal to 0.31, 0.72 and 1.15 µm, respectively, and it exceeded by 35% the values obtained when calibrating the process of hydrosol growth. The reason for that may be the error of experimental measurements, temperature instability of hydrosol growth. However, the main reason can be the increase of a real size of sulfur particles at the expense of the formation of the transitional layer of water molecules [15]. Hydrodynamic radius at light scattering is impossible to be studied, and the real movability of particles increases.

A more complicated situation is observed when investigating the concentration of particles greater than 5×10^9 per 1 mm^3. Figure 2 shows that halfwidth of power spectrum $\Delta\omega$ increases abruptly. This is connected with the chaotization growth of scattered radiation field upon the growth of scattering multiplicity. For qualitative estimation of chaotization degree of scattered radiation intensity we used the largest Lyapunov exponent [8].

5. Investigation of the largest Lyapunov exponent
of radiation field scattered by Brownian particles

Lyapunov exponents play an important role in studying dynamic systems. They characterize the average velocity of exponential divergence of close phase trajectories. Taking the initial distance d_0 between two initial points of phase trajectories, the distance between trajectories, coming off these points, at time t will be as follows:

$$d(t) = d_0\exp(\lambda t) \tag{9}$$

The value λ is called Lyapunov exponent [8]. Each dynamic system is characterized by Lyapunov exponent spectrum λ_i ($i = 1, 2, ..., n$), where n – quantity of differential equations which are necessary for system description. For experimental data, obtained at observing dynamic systems, the availability of positive Lyapunov exponent can be the proof of chaos existence in the system. Generally speaking, chaotic system is characterized by the divergence of phase trajectories in similar directions and their convergence in others, *i.e.*, there are both positive and negative Lyapunov exponents in chaotic system. The sum of all the indices is negative, *i.e.*, the trajectory convergence degree exceeds that of divergence. If this condition is not met, dynamic system is instable, and the behavior of such a system is recognized easily. Thus, in most cases, it is sufficient to calculate the largest Lyapunov exponent only. The positive value of the largest Lyapunov exponent gives the possibility of chaos existing in the system, and the value of this index characterizes chaoticness intensity.

Most algorithms for calculating the largest Lyapunov exponent have some disadvantages. For example, a great quantity of experimental data is required, there is a relative complexity of algorithm program realization, and numerous calculations are time consuming [8]. Using theoretical conclusion, described in paper [15], we have elaborated the algorithm and calculation program of the largest Lyapunov exponent, which is free of the above-mentioned disadvantages.

The first step of the algorithm consists in reconstructing the phase trajectory. The latter is represented in the form of matrix X, each column of which is a vector in phase space:

$$X = \begin{bmatrix} \mathbf{X_1} & \mathbf{X_4} & ... & \mathbf{X_M} \end{bmatrix}^T$$

where $\mathbf{X_i}$ – system condition at time moment i. For a series of N measurements $\{x_1, x_2, ..., x_N\}$ any X is defined as follows:

$$\mathbf{X_i} = \begin{bmatrix} x_i & x_{i+J} & ... & x_{i+(m-1)J} \end{bmatrix}$$

where J – time delay (reconstruction delay), m – embedding dimension.

Embedding dimension is usually estimated based on Takens' theorem, according to which $m > 2n$, where n is the system order. However, the method described enables obtaining correct result at lesser value m. Reconstruction delay is chosen as being equal to time at which autocorrelation function decreases by $1-1/e$ compared to its initial value.

After reconstructing the phase trajectory by the algorithm the search is expected of the nearest "neighbor" for each trajectory point. The point $\mathbf{X_l}$ is considered to be the nearest "neighbor" with minimum distance $d_j(0)$ from it to the basic point $\mathbf{X}_j$:

$$d_j(0) = \min_{\mathbf{X_j}} \| \mathbf{X}_j - \mathbf{X_j} \|$$

A couple of "neighbor" points diverges exponentially in some period of time:

$$d_j(i) \approx C_j \exp(\lambda_1 i \Delta t)$$

where λ_1 – the largest Lyapunov exponent. It can be found as a line inclination defined by the formula:

$$y(i) = \frac{1}{\Delta t} \langle \ln[d_j(i)] \rangle \tag{10}$$

where $\langle \ldots \rangle$ means the average value for all j.

This algorithm was used as a basis for compiling a program in Pascal. For testing program the model and experiment chaotic signals were used. Henon's mapping was regarded as a model signal: $x_{i+1} = 1 - a x_i^2 + y_i$; $y_{i+1} = b x_i$; $a = 1.4$; $b = 0.3$.

The calculation results for Henon's mapping are demonstrated in Fig. 3. Diagram inclination was calculated with the help of the least squares, and there were obtained the values $\lambda_1 = 0.403$. The latter almost corresponds to the theoretical value $\lambda_1 = 0.418$.

Experimental investigation of the largest Lyapunov exponent did not testify to the availability of radiation intensity fluctuations scattered by sulfur hydrosols and did not find its dependence on sulfur particle sizes. This can be explained by that fact
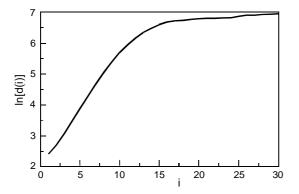

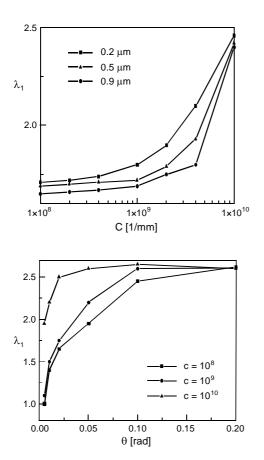Fig. 3. Calculation results $y(i)$ for Henon's mapping.

Fig. 4. Dependence λ_1 on concentration for particles with the sizes of 0.2, 0.5 and 0.9 μm.

Fig. 5. Dependence λ_1 on the angle of scattering θ for three types of concentration: 10^8, 10^9 and 10^{10} particles per mm^3.

that the size change of sulfur monodisperse particles leads to the change of general intensity of scattered radiation field, and not to its distribution. However, the largest Lyapunov exponent depended essentially on particle concentration C and angle of scattering θ.

Figure 4 shows the dependence of the largest Lyapunov exponent on concentration for particle sizes 0.2, 0.5 and 0.9 μm for geometrical experimental parameters corresponding to Fig. 2.

One can observe practically a similar dependence for the above-mentioned size particles. Moreover, the dependences given in Figs. 2 and 4 appear to have similar course. This fact was taken as a basis for increasing the measurement accuracy of Browne's particle sizes with the help of the method of correlation spectroscopy. Dependences, obtained by standardization curves in Fig. 2 for coefficients $\lambda_1/\lambda_1^{max}$, do not practically depend on concentration of Brownian particles and give the values of particle sizes which are closer to real ones: 0.25, 0.59 and 1.04 μm. And these exceed by only 20% the results of optical measurements at calibrating the hydrosol growth process.

The decrease of the angle of scattering influences λ_1 behavior sufficiently. Figure 5 demonstrates dependences of the largest Lyapunov exponent on the angle of scattering θ for three types of concentration: 10^8, 10^9 and 10^{10} particles per mm^3. One can observe λ_1 to increase with θ upon its next saturation. And for great saturation concentrations the process is realized quicker.

Computer modeling enabled us to consider situations which are impossible to realize in a real, physical experiment. It has been found out with the help of computer modeling that the scattering of Brownian particles by sizes has not essential influence on the correlation integral course essentially. The normal distribution dispersion was changed from 0 to 0.1 μm for the average particle size $\overline{R} = 0.3$ μm.

6. Conclusions

The results of carrying out the computer and physical modeling of light scattering by Brownian particle system consist in the fact that temporal intensity fluctuations of scattered radiation field have a chaotic character, as largest Lyapunov exponent is positive.

Stochastic field parameters actually do not depend on particle sizes. The increase of Brownian particle concentration and of the angle of scattering leads to the chaotization increase of temporal intensity fluctuations of scattered radiation field.

There have been determined the empirical diagnostic relationship of largest Lyapunov exponent and the widening of the spectrum of temporal intensity fluctuations. This gave the possibility to widen the concentration range and increase the measurement accuracy of Brownian particle sizes.

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