Materials Physics and Mechanics 39 (2018) 81-86 Received: November 1, 2017

OPTICAL CHARACTERIZATION OF 3D DISPERSE SYSTEMS WITH NANO- AND MICRO- PARTICLES: UNIQUE VECTORS

Alexandra G. Bezrukova*, Olga L. Vlasova

Department of Medical Physics, Peter the Great St. Petersburg Polytechnic University,

Polytekhnicheskaya Street 29, St. Petersburg, 195251, Russian Federation

*e-mail: bezr@PB1097.spb.edu

Abstract. Three classes of parameters can be obtained from the different optical methods for nondestructive testing of 3D disperse systems with nano- and microparticles. These optical methods are refractometry, absorbance, fluorescence, light scattering (integral and differential, static and dynamic, unpolarized and polarized). Each of *3D* disperse system can be characterized by unique vector in the *N*-dimensional space of the second-class optical parameters. The phenomenon can be used for elaboration of on-line control of systems with nano- and / or microparticles in the water or air medium.
Keywords: absorbance, disperse system, fluorescence, light scattering, nanoparticle

1. Introduction

Three-dimensional disperse systems (*3D* DS) [1], the systems of nano- and microparticles (particles as disperse phase) in a dispersive water medium, are often called as dispersions, colloids, suspensions. One of the important tasks of fundamental *3D* DS research is the on-line monitoring of their condition. Optical data in combination with data of other methods can provide valuable information about the processes within *3D* DS (aggregation, sedimentation, flocculation, coalescence, fractal aggregation, etc.) and can help to create means for the control of technological processes and the environment.

2. Materials and methods

In Ref. [2−12] the following *3D* water DS containing nano- and microparticles (with the mean effective diameter from nanometers up to ten micrometers) were studied: proteins (serum albumins, globulins, egg albumin, hemoglobin, lysozyme, chymotrypsin, chymotrypsinogen), serum and plasma of blood, nucleoproteids, lipoproteids, liposomes, influenza virus of different strains, fat emulsions, perfluorocarbon blood substitutes, antibiotics, polyaromatic hydrocarbons, synthetic polymers based on methyl sulfate homo-polymer, cyclodextrins, latexes of different sizes, liquid crystals, bacterial and other biological cells of different strains, shapes and sizes (E. coli, acidophilus rods, thrombocytes, thymocytes, lymphocytes, erythrocyte diagnosticums, Ehrlich ascites carcinoma cells, etc.), metallic powders (iron hydroxides, ruthenium dioxide, colloidal silver), kaolin, kimberlites, fullerenes, zeolites; as well as various mixtures of: proteins and nucleic acids, proteins and polymers, proteins and viruses (vaccine model), liposomes with various substances (radiopaque agents, metal particles, enzymes, viruses, antibiotics), liquid crystals with surface active substances, mixture of E. coli cells with kaolin (water model), mixtures of anthracene with cyclodextrin, samples of oil, petroleum products, food products, samples of natural and tap water, air sediments in water, etc.

http://dx.doi.org/10.18720/MPM.3912018_13

For characterization of the studied *3D* DS, the following compatible non-destructive optical methods are used: refractometry**,** absorption and fluorescence spectroscopy, light scattering (dynamic and static, integral and differential, unpolarized and polarized, single and multiple). They are displayed in Fig. 1.

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy), Raman (inelastic or combinatory scattering), Mandelshtam−Brillouin light scattering, laser-induced breakdown spectroscopy (LIBS) and other methods can be useful for *3D* DS characterization too.

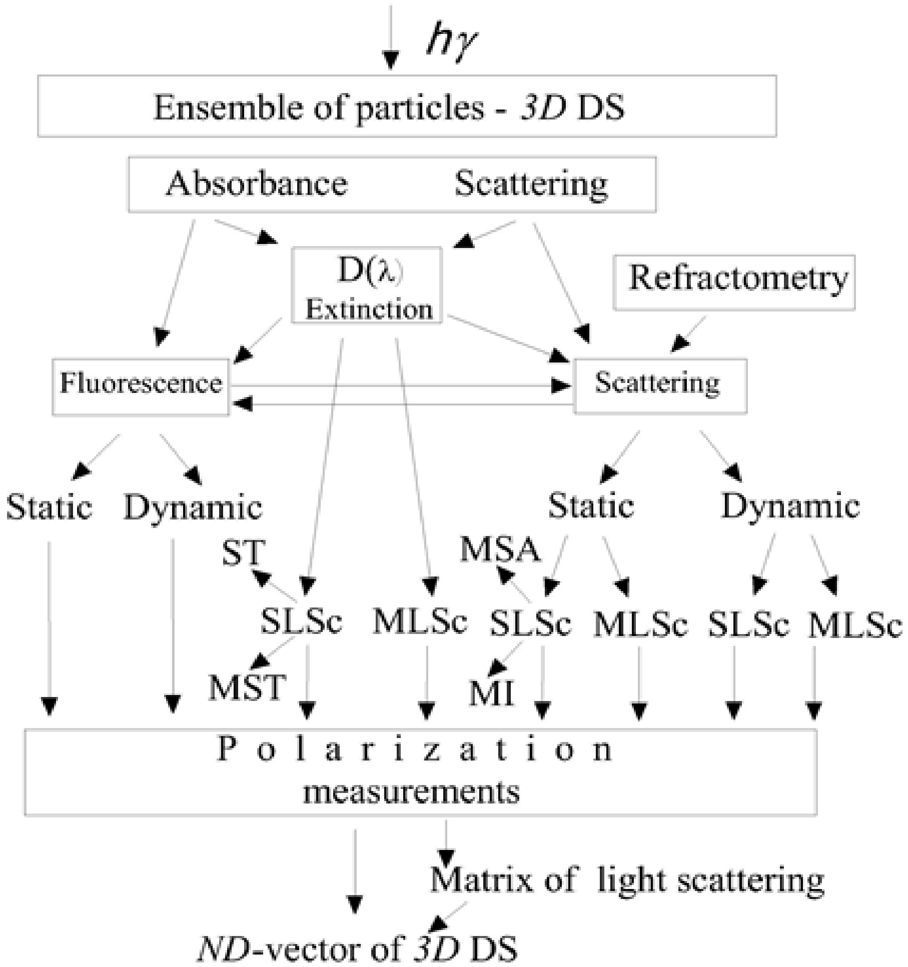

Fig. 1. Scheme of compatible optical methods for *3D* DS characterization; abbreviations: SLSc - singular light scattering, MLSc - multiple light scattering; abbreviations for the methods of solving the inverse optical problem: ST- spectroturbidimetry, MST- method of spectral transparency, MSA- method of small angles, MI- method of indicatrix

Abbe and other types of refractometers were used for determining medium refractive index μ_0. Refractive indexes of particles μ_p were obtained by different methods, they being depending on the content and peculiarities of *3D* DS studied. Light extinction caused by absorbance and integral light scattering was measured with diaphragms at SP-26 (LOMO, St. Petersburg, RF) and at Schimadzu UV 1205 spectrophotometers. For solving the inverse optical problem of integral light scattering, the "turbidity spectrum method" or spectroturbidimetry (ST) [1] was used.

The main characteristic function of ST is so called wave exponent [1]:

$$n(\lambda) = -\frac{\partial \lg \mathrm{D}(\lambda)}{\partial \lg \lambda}, \tag{1}$$

where λ is the wavelength of incident light and D is the optical density (only in the cases when D can be considered as a measure of integral light scattering). Turbidity τ, transmittance of light through a disperse system T and D are determined by the formulas:

$$\tau = 2.3\,\mathrm{D}/l\,, \tag{2}$$

$$\mathrm{D} = -\lg \mathrm{T} = \lg I_0 / I_1, \tag{3}$$

where l is the length of the optical way (length of a cuvette in cm), I_0 is the intensity of incident light and I_1 is the intensity of light transmitted through the cuvette.

3. Results and discussion

Three classes of parameters can be obtained due to different optical methods for nondestructive testing of *3D* disperse systems with nano- and microparticles [2−4, 6]. As the result of our research [2−12], the new phenomenon has emerged that consists in the existence of unique characteristic for any of *3D* DS in the multidimensional space (*ND* space) of the so-called "second class" optical parameters (obtained after experimental data processing without invoking any data about the dispersed phase particles). In another word, the characteristic of any *3D* DS can be represented as the unique *N*-dimensional vector (*ND* vector, a set of second class parameters) in the *ND* space of second class optical parameters. There are second class parameters in each of compatible optical methods. The classical examples of the second class parameters are wave exponent *n (λ)* [1] and elements of light scattering matrix [11].

In Figure 2 *4D* vectors are presented as the points on a plane for different *3D* DS mainly with nano-particles. Here the number near a vector point corresponds to dispersion number. Point 1 shows *4D*-vector **P** {P_1, P_2, P_3, P_4} for latex dispersion with d =150 nm [8]. Points 2−11 characterize the inclusion of anthracene in cyclodextrin cavity [8].

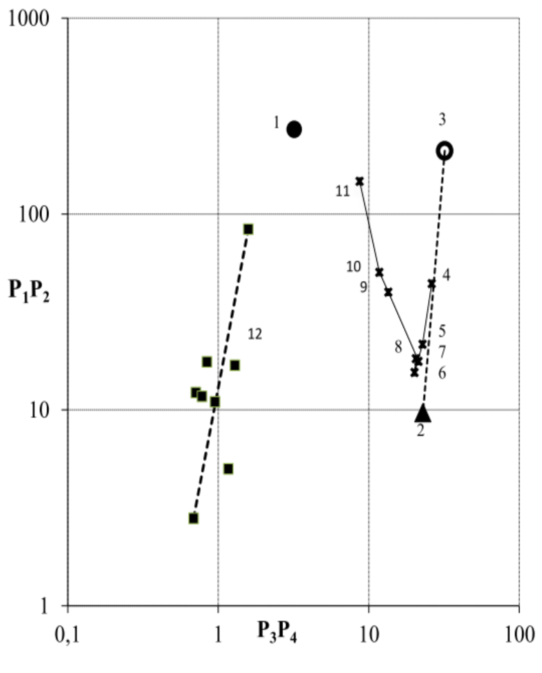

Fig. 2. Bilogarithmic presentation of vectors **P** {P_1, P_2, P_3, P_4} on a plane.
1= latex dispersion: d = 150 nm, n *(500)* = 3.2;
2= nanoparticle dispersion of anthracene, concentration 1.4 x 10^{-4} M/l;
3= β-cyclodextrin, concentration 8.75 x 10^{-3} M/l.
4-11= points corresponding to mixtures of anthracene of concentration 1.4 x 10^{-4} M/l and β-cyclodextrin with different concentrations (in M/l), here:
4 = 1.75 x 10^{-6}; 5 = 8.75 x 10^{-6};
6 = 1.75 x 10^{-5}; 7 = 8.75 x 10^{-5};
8 = 1.75 x 10^{-4}; 9 = 8.75 x 10^{-4};
10 = 1.75 x 10^{-3}; 11 = 8.75 x 10^{-3}
12 = bovine serum albumin dispersions with different particle aggregation.
Relative errors are about 7%

The group of points 12 are the points for bovine serum albumin (Reachim) dispersions with different aggregation of particles (molecules) from “less aggregated” (point 1.6; 83.6) to “more aggregated” (point 0.7; 2.8).

Similar to Fig. 2, *4D* vectors are presented in Fig. 3 as the points on a plane for different *3D* DS with mainly micro-particles having the mean effective diameter *d* up to 10 micrometers.

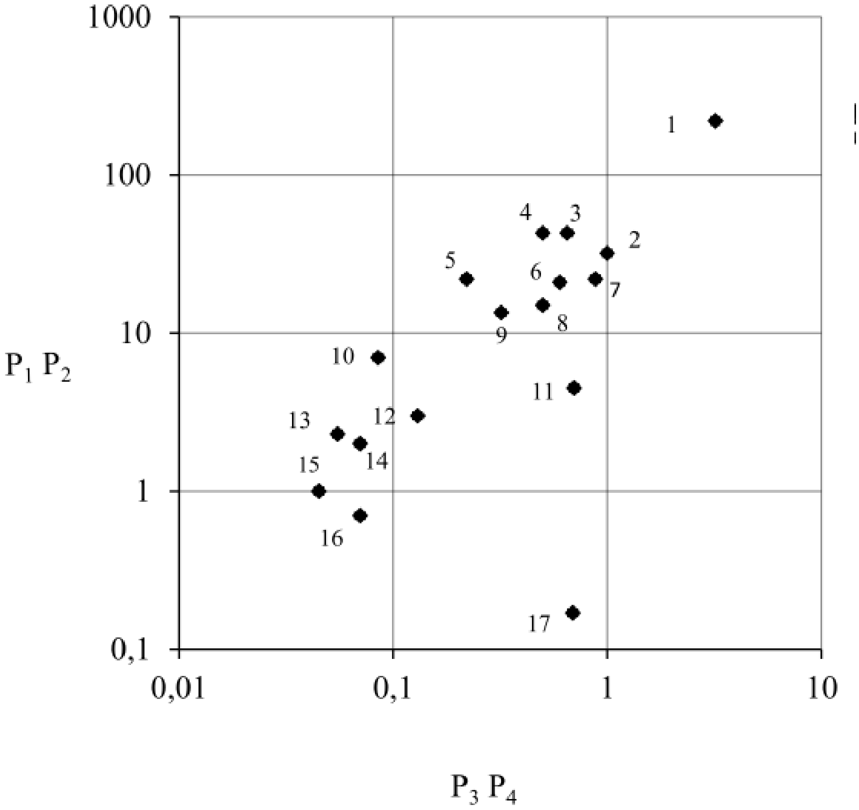

Fig. 3. Bilogarithmic presentation of experimental data as vectors **P {P_1, P_2, P_3, P_4}** for different dispersions. The numbers near the points correspond to optical data for *3D* DS: 1 = latex dispersion with *d* = 150 nm, *n (500)* = 3.2; 2 = iron hydroxides, 3 = zeolites, 4 = liquid crystals with surface active agents, 5 = sodium dodecyl sulfate aggregates, 6 = sample of kaolin dispersion with *n (500)* =1.5 [12], 7 = blood platelets, 8 = nucleoproteids, 9 = sample of kaolin dispersion with *n (500)* = 0.2 [12], 10 = ruthenium dioxide, 11 = E. coli, 12 = crude oil, 13 = erythrocyte diagnosticums, 14 = thymus lymphocytes, 15 = liquid crystals, 16 = yeast cells, 17 = Ehrlich ascites carcinoma cells approximated by spheres of *d* = 12 micrometers. Relative errors are about 7%

The inverse optical problem solution for polycomponent polymodal 3D DS meets with difficulties due to necessity of a priori information about the component content and the nature of components. ND-vector approach to 3D DS characterization can overcome this difficulty without any a priori information (without introducing any models of particle structures and particle size distributions). It can be seen in Fig. 3 that different 3D DS have different positions even in 4D space of second class optical parameters. For example, 2D-vectors, 4D-vectors, and 6D-vectors can characterize the aggregation bovine serum albumin molecules. In Ref. [11] 16D-vectors allow differentiate for about four orders the positions of influenza virus (strain A1-H1N1) and E. coli (strain K-802) dispersions in the 16D space of second class parameters from integral and differential static light scattering and from angular dependence of light scattering matrix elements. For differentiation of *3D* DS constituents in mixtures [12] the dimension of vectors can be enlarged due to the involvement into consideration different measurement conditions such as wavelengths, angles and apertures of measurements, polarization, etc. For each particular *3D* DS, the preliminary search of informative parameters can help to organize the particles of interest on-line control.

4. Conclusions

Based on the modern technique, it is possible to manage simultaneous on-line measurements of *3D* DS first class parameters and after on-line processing to obtain parameters of the second class. For example, from the measurements of integral light scattering in the region of wavelengths, where is no absorbance (imaginary part of particle refractive index is about zero), one can obtain the first class parameter D (λ) and then calculate the second class parameter $n\ (\lambda)$.

One of the promising directions for studying the information content of various optical parameters for determining the component composition of *3D* DS mixtures and natural *3D* DS is the information-statistical theory of observation interpretation [13, 14]. The algorithms and programs developed on the base of this theory can allow identifying the components which presence in *3D* DS is the most probable [7]. The peculiarity of the input data set is that the probability of the component presence is determined from the experimental quantitative values of the optical parameters of an unknown *3D* DS. To determine these probabilities, it is necessary to have the representative so-called “training data” in the knowledge bank for each of the possible components of *3D* DS. On investigating a model mixed *3D* DS, it is possible to analyze the algorithm efficiency even against the background of strong interactions of components and with various physical and chemical effects on the system. With increasing the component number in a complex *3D* DS, the parameter number should also increase. It should be noted that a uniform representation of the input and output data provides the ability to add new parameters to those obtained earlier. Judgment about the reliability of the results allows the most informative unique parameters to be selected.

Unique *ND*-vectors can reflect implicitly all *3D* DS features: the structure and shape of the particles, the refractive index of the particles matter, the distribution functions of the number and mass of particles in size, etc. Due to the fusion of various optical data and by information-statistical methodology, it is possible to find the unique *ND*-vector for *3D* DS control and for technology optimization by feedback.

Acknowledgments. *The authors would like to thank Prof. Vitaly J. Klenin, Prof. Sergei Ya. Frenkel, Prof. Vladimir O. Samoilov, Dr. Yolande Hendrikx, Prof. Bertrand Deloche, Prof. Ewa Rogalska for the help in research and useful discussions.*

References

[1] V. Klenin, *Thermodynamics of Systems Containing Flexible Chain Polymers* (Elsevier, 1999).

[2] A.G. Bezrukova, Development of multiparametric optical analysis for on-line environmental control // *Proceedings of SPIE* **3107** (1997) 298.

[3] A.G. Bezrukova, Perspectives of multiparametric optical analysis of natural disperse systems (Conception of on-line control of water and air) // *Newsletter of St. Petersburg Division of RANS* **2(2)** (1998) 157.

[4] A.G. Bezrukova, Characteristics of biomedical and natural disperse systems in the multidimensional space of optical parameters // *Scientific and technical bulletins of SPbPU* **2-3(12-13)** (1998) 157. (In Russian)

[5] O.L. Vlasova, A.G. Bezrukova, Laser control of natural disperse systems // *Proceedings of*

SPIE **5127** (2003) 154.

[6] A. Bezrukova, Nondestructive testing of *3D* disperse systems with micro- and nano-particles: *N*-dimensional space of optical parameters // *Proceedings of SPIE* **6253** (2006) 62530C-1.

[7] A.G. Bezrukova, Statistical approaches to the inverse optical problem solution for biomedical and natural systems of micro- and nanoparticles // *Scientific and technical bulletins of SPbPU* **2(50)** (2007) 114.

[8] A.G. Bezrukova, Nanoparticle interactions: improvement of experimental optical data analysis // *Proceedings of SPIE* **7377** (2009) 73770B-1.

[9] O.L. Vlasova, Multiparametric approach to the optical analysis of model dispersions of bovine serum albumin // *Scientific and technical bulletins of SPbPU, Physics and mathematics* **2(77)** (2009) 39.

[10] O.L. Vlasova, P.V. Plotnikova, A.G. Bezrukova, Algorithm for the realization of experimental-parametric data for the optical analysis the states of biodispersions // *Scientific and technical bulletins of SPbPU, Physics and mathematics* **1(189)** (2014) 91.

[11] A.G. Bezrukova, O.L. Vlasova, Optical characterization of *3D* disperse systems with nano- and micro-particles: Light scattering matrix elements // *Materials Physics and Mechanics* **20(2)** (2014) 124.

[12] A.G. Bezrukova, O.L. Vlasova, Mixtures of 3D disperse systems with nano- and micro-particles: Optical characterization // *St. Petersburg Polytechnical University Journal: Physics and Mathematics* **4(253)** (2016) 121.

[13] F.M. Goltsman, *Physical Experiment and Statistical Conclusions* (Leningrad University Publishing House, Leningrad, 1982).

[14] D.F. Kalinin, *Information and Statistical Prediction of Mineral Resources* (Geological Exploration Group Publishing House, St. Petersburg, 2011).