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STUDY OF MAGNETITE PARTICLES FROM A FERROFLUID BY AVERAGE DIAMETER CRITERION USING THE MAXWELL DISTRIBUTION AND EXTREME VALUES FUNCTIONS

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The ferrofluid studied in the paper is a biphasic system where liquid phase is the earth-oil, solid phase is constituted of nanometric magnetite particles and the stabilisant is the oleic acid. The hydrocarbon string dissolves in oil and insures the system's stability. The ferrofluid used in technological applications should be stable. Stability depends on the size, shape and distribution of solid particles by size. The particles had heterogeneous forms, so diameters were measured in two perpendicular directions and the average size was calculated for each particle. The objective of this article is to present results of experimental and theoretical study of the distribution of magnetite particles by size diameter using Maxwell and extreme values functions. Also, absolute frequency, arithmetic mean of a group of particles 1227, the dispersion, the mean probable error and the skewness were determined.

INTRODUCTION

Complex liquids are physical systems whose properties are determined by chemical nature, structure and solid nanoparticles dimensions suspended in the dispersant medium.

The size of solid nanoparticles has an influence on the physical properties of complex liquids (as viscosity and especialy stability). Complex liquids are used both in technical applications as magneto-fluidic sealing, in energy industry for solar radiation absorption in very thin layers, in mining for non-ferrous metal separation, in agronomy for stimulating plant growth. The reliability of technical systems requires a good stability of the complex liquids. In this article are studied measures and distributions of magnetite particles in a complex liquid (ferrofluid), which is a solid-liquid biphasic system behaving like a homogeneous enviroment both in the presence of a magnetic field and in his absence.

The role of nanoparticles size in applications with complex fluids is shown in the following examples very used for their role in biology.

In biology, nanomaterials are used to select and transport organic cells or viruses. In this case, the dimension of the magnetic nano-particles is within the range of (5 nm to 100 μm). Magnetic liquids suited for biological applications contain nano-particles similar in size with the biological entities: cells (10 – 100 μm) t, viruses (20 – 450 nm), proteins (5 – 50 nm), and genes (2 nm width and 10 – 100 nm lengh).[1-3]

Knowing the average size of magnetite nanoparticles can be used to predict behavior of complex systems in external magnetic field. Thus in[4] is shown that the saturation magnetization of Ni-Zn ferrite nanoparticles decreases suddenly to size of 6 nm.

In the present paper, the biphasic systems contain nano-particles of Fe_3O_4, with an average size of 11.443 nm, floating into the carrying liquid, which is petroleum mineral oil. Stabilization of the biphasic system needed fat acid use, namely oleic acid, $C_{17}H_{33}$ - COOH.

The polar group, -COOH is adsorbed by the brown spar particles. The hydrocarbon string dissolves in oil, insuring the system's stability.[5]

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The research regarding the absorption of solar radiation through ferrofluids revealed the possibility to use these nano-materials, as thin layers, in thermo-solar conversion.[6, 7] In[8, 9] it is shown that distribution of magnetite particles from ferrofluid can be described with Gauss function.

The objective of this article is to present results of experimental and theoretical study of distribution of magnetite particles by size using other distribution functions.

EXPERIMENTAL

1. Complex liquid preparation

The ferrofluid was prepared using the chemical precipitation method: [4]

$$FeSO_4 + 2FeCl_3 + 8NH_4OH \rightarrow Fe(OH)_2 + 2Fe(OH)_3 + (NH_4)_2SO_4 + 6NH_4Cl$$
$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O. \quad (1)$$

Brown spar density is higher than petroleum's, so that between particles occur dipol-dipol and van der Waals forces. In order to prevent sedimentation and very large aggregations forming, the brown spar particles are covered with a pellicle of oleic acid, by stirring. The pellicle ($C_{17}H_{33}$ – COOH) plays the role of the stabilizer. The polar group — COOH of the oleic acid is absorbed by the brown spar particles and the hydrocarbon string dissolves in petroleum, to which is very much alike as composition.

The salts in solution and in particles porosity are washed away by water at 60-80°C. The exceeding oleic acid breaking of brown spar grains needs an acetone addition. The reaction products disperse in oil heated at 120 °C.

2. The micrography of the brown spar nanoparticles

The micrography was obtained with BS613 transmission with an electron microscope by the voltage U = 100 kV with magnification $M = 6{\cdot}10^4$.

A sample of complex liquid was diluted to 1/1000 of the base fluid and filed as a film on a collodion post with 200 Å thick. The post was then placed on a copper grid electrolytic with 500-800 Mesh. Fig. 1 shows the absolute frequency of occurrence of values for diameters on Ox axis.

The image was fixed on photographic plates, then the film was copied on the film (cartridge) with the magnification $M' = 2.5$. In testing by optical methods, diameters were measured on the Ox and Oy axes.

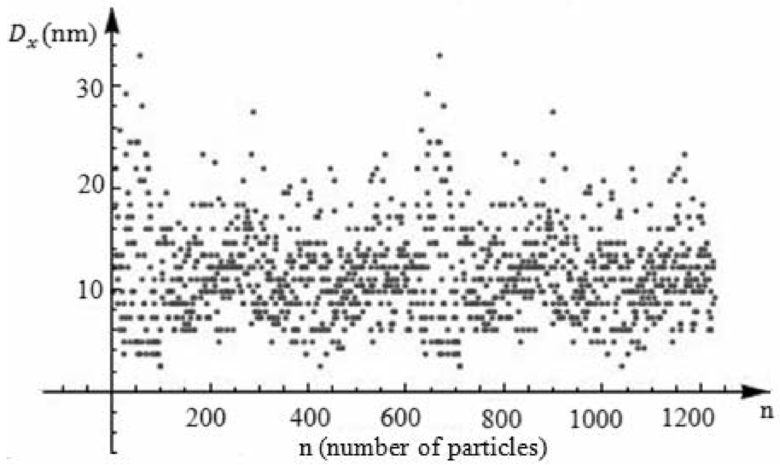

Fig. 1 – The absolute frequency of occurrence of values for diameters on Ox axis.

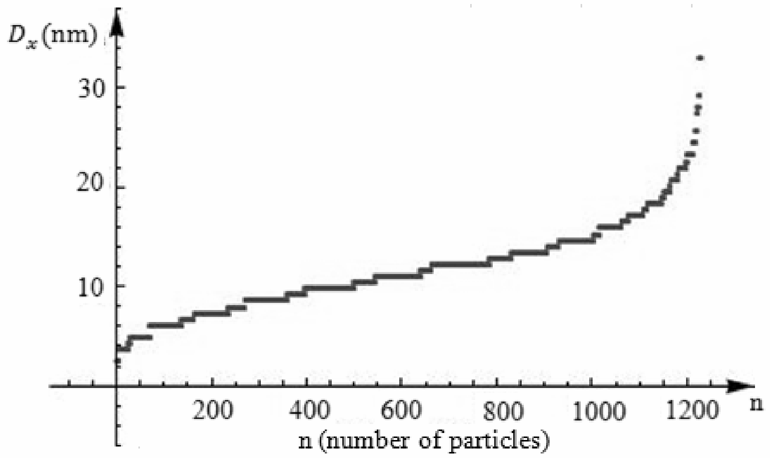

Fig. 2 – The particles size on Ox axis depending on the absolute frequency.

RESULTS

1. Statistical collective

Each magnetite particles is a statistical unit. The set of all magnetite particles forms a statistical collective. The sample size is n = 1227. Geometric feature of the collective is the diameter *D*. Individual values of diameters in two perpendicular axes D_x and D_y, expressed in relative units (r.u.), for the first and last 10 measurements of individual array values are shown in Table 1.

The boundaries of the characteristic interval are: $D_{x,min}$= 2.4478 nm; $D_{x,max}$= 33.0453 nm; $D_{y,min}$=2.4478 nm; $D_{y,max}$ = 36.7170 nm. The amplitudes for the experimental data volume on the two axes are $A_x = D_{x,max} - D_{x,min} = 30.5975$ nm respectively $A_y = D_{y,max} - D_{y,min} =34.2692$ nm. The volume of experimental data was divided into m classes, m_x = 26; m_y = 30. Class width is ΔD=0.846 r.u.

The average values for individual arrays values are: $<D_x>$ = 9.5456 r.u. respectively $<D_y>$ = 9.15403 r.u. The average for the two values is $<D>$ = 11.443 2 nm.

Dispersions are: σ_x= 13.6415 r.u. respectively σ_y = 13.8258 r.u.

In Fig. 3 is shown the experimental histogram on OX axis. In Fig. 4 is shown the experimental histogram on OY axis.

The two histograms suggest an asymmetric distribution of diameters, moved to the left (the "tail" to the right). Asymmetry coefficient of discrete random variables is given by the ratio: $\frac{M_3}{\sqrt{M_2^3}}$ where M_2 and M_3 are respectively centered moments of order 3 and 2. Where studied, the random variables determined by diameters of the particles, the asymmetry coefficients are: 0.845932 for variable diameters parallel to Ox and 1.06731 for the parallel variable diameters Oy.

In Figs. 3 and 4, n represents the absolute frequency values from a class of length equal to unity.

Table 1

Some values of individual array values

Particle's number, *i*	D_x (r.u.)	D_y (r.u.)	Particle's number, *i*	D_x (r.u.)	D_y (r.u.)
1	2	2	1218	14	15.5
2	3	2.5	1219	15.5	16
3	4	3	1220	17	17
4	5	3.5	1221	17.5	18
5	6	4	1222	18	19
6	7	4.5	1223	19	20
7	8	5	1224	21	21
8	9	6	1225	22.5	22
9	10	6.5	126	23.5	22.5
10	11	7	127	24	27

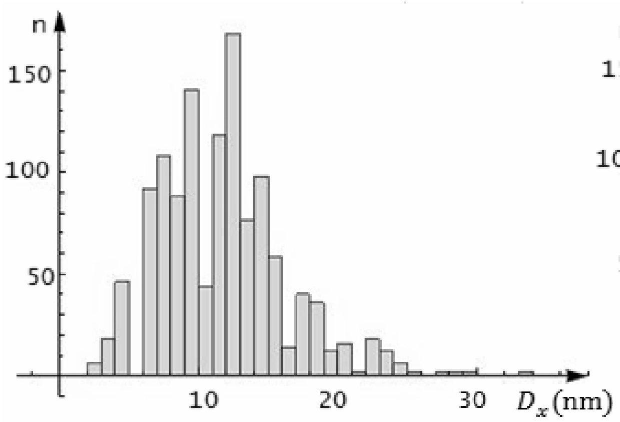

Fig. 3 – The histogram on Ox axis.

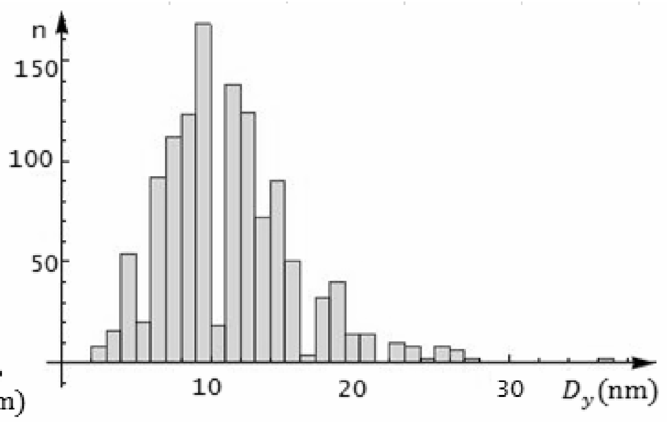

Fig. 4 – The histogram on Oy axis.

2. Functions and distribution curves

Below we present the distribution functions that have been corrected for theoretical determination of the distribution of magnetite particles by diameter characteristic. For each function were mapped distribution curves compared with experimental histogram on the two axes. The number of particles contained in the sample studied was 1227. The theoretical results obtained on this sample were validated by comparison with results on a control sample with a volume of 430 particles.

2.1. Extreme value distribution

The expression for extreme value distribution is

$$f_E(x,\mu,\sigma)=\frac{1}{\beta}\exp\left(-e^{\frac{\alpha-x}{\beta}}+\frac{\alpha-x}{\beta}\right) \qquad (2)$$

with parameters α and β determined by relations:

$$\alpha+\gamma\cdot\beta=\mu\,; \qquad (3)$$

$$\beta^2=\frac{6}{\pi^2}\cdot\Delta \qquad (4)$$

where $\gamma=0.577216...$ is Euler's constant and μ respectively σ^2 are the mean and dispersion of variable X. The coefficient of asymmetry of distribution of outliers is constant and therefore independent of the parameters considered, ie average and dispersion, having the value: $\frac{12\sqrt{6}\ (3)}{3}$ 1.13955...

Where the number $\varsigma(3)$ represents the value of zeta Riemann function in the point s=3.

$$\varsigma(s)=1+\frac{1}{2^s}+\cdots+\frac{1}{n^s}+\cdots \quad (\mathrm{Re}(s)>1)$$

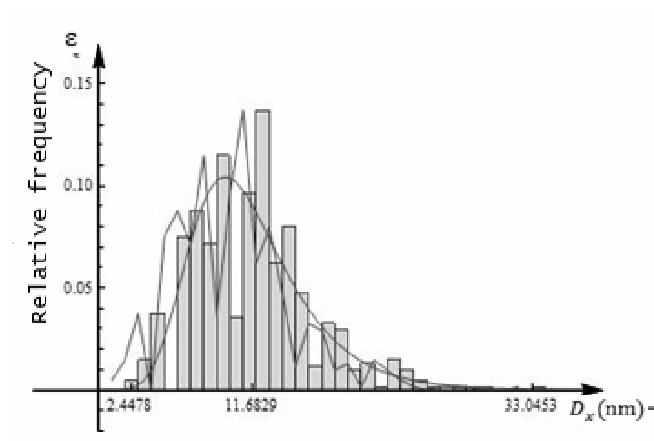

Fig. 5 – Extreme value distribution vs. histogram on Ox axis.

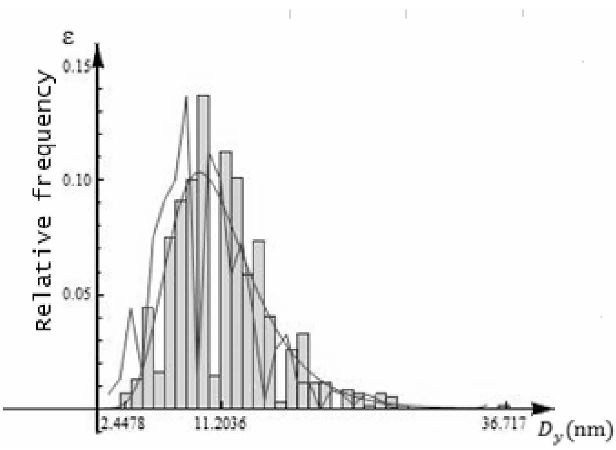

Fig. 6 – Extreme value distribution vs. histogram on Oy axis.

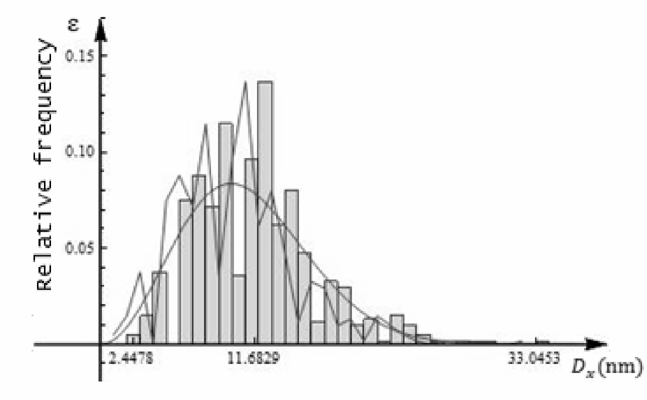

Fig. 7 – Maxwell distribution vs. histogram on Ox axis.

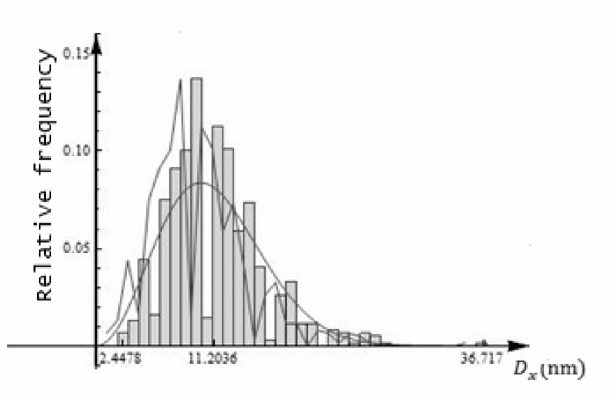

Fig. 8 – Maxwell distribution vs. histogram on Oy axis.

2.2. Maxwell distribution

Maxwell distribution expression associated with a random variable X is:[4]

$$f_M\left(x,\mu,\sigma\right)=\sqrt{\frac{2}{\pi}}\cdot\frac{x^2}{\tau^3}\cdot\exp\left(-\frac{x^2}{2\tau^2}\right) \qquad (5)$$

with parameter τ determined by the relationship:

$$2\sqrt{\frac{2}{\pi}}\cdot\tau=\mu \qquad (6)$$

or equivalently

$$\frac{-8+3\pi}{\pi}\cdot\tau^2=\sigma^2 \qquad (7)$$

where μ and σ^2 are respectively the mean and dispersion of variable X.

Unlike extreme values distribution, Maxwell distribution has one parameter: τ. In determining its average value by using dispersions and then we will see below, very similar results.

The asymmetry coefficient is constant and has value: σ – average standard deviation with values:

$$\frac{2\sqrt{2(16\quad 5\ )}}{\sqrt{(\ 8\quad 3\ )^3}}\qquad 0.485693$$

In Figs. 7 and 8 are shown the distribution curves on the function (5) compares to the histogram envelope on the Ox, respectively Oy axis. In Figs. 5-8 *fr* represents the relative frequency.

CONCLUSIONS

Experimental distribution of magnetite particles in this complex fluid studied, by diameter, is asymmetrical. As a result, the theoretical distribution cannot be described by a symmetric function, as Gauss function is.

In this paper, the theoretical distribution was studied by two distribution functions, namely: the extreme value distribution and Maxwell distribution. The best theoretical approximation is obtained with extreme value distribution. Values of asymmetry coefficients calculated with the extreme value distribution are smaller than those calculated with the Maxwell distribution. The average diameter of the magnetite particles that are suspended in liquid is 11. 443 nm. The complex fluid studied can be used in biology to separate and transport proteins and genes. Experimental data processing and theory of this paper can be used to develop a study on the distribution of magnetite particles by cross-sectional area criterion considering that it is elliptical.

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