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STUDY OF DYNAMICS OF DRYING PROCESSES IN Fe_2O_3 AND SiO_2 NANOCOLLOID DROPLETS

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ABSTRACT

This work is devoted to comparison of changes in geometry and in light transmittance of evaporating drop of nanocolloid deposited on flat surface. One of the focuses of paper is aimed at differentiation of drying process into separate stages, each being characterized by particular behavior of suspension nanoparticles inside the droplet, the last of which ends by forming of ring-shaped patterns (known as "coffee ring effect") that appear after all the fluid has evaporated. Dynamics of colloids` evaporation was studied according to two observing techniques. The first one was based on spectrometric measuring of light transmitted through droplets. The second method was based on registering of geometrical properties of drying puddles that were changing in time due to evaporation. Patterns left by droplets of nanocolloids were alike in general – collars were formed along the perimeter of initial droplet. According to coffee ring effect a major part of suspended particles assembled in these collars though a thin film of suspended substance deposited within initial drop perimeter. The results of drying dynamics experiments carried out in two different techniques appeared to be also different. The second (geometrical) method showed a uniform decrease of drop height while the first (spectrometric) method showed non-uniform changing of parameters. The time of drying according to the second technique was less than the time of drying received in experiments undertaken with the first technique.

INTRODUCTION

Researches in the field of hydrodynamics of colloid solutions are very important for fluid mechanics. By itself this topic is very extensive being a whole branch of science. This work focuses on drying processes in droplets of specific suspensions (with SiO_2 and Fe_2O_3 nanoparticles).

In many areas of modern thermal energetics liquids with microparticles suspended in it due to some causes (functional or as a result of contamination) are being used. It can be advisable to know possible consequences of these liquids being dried on effective areas of heat exchangers and other devices.

In nanotechnologies colloids with nanoscale particles of different substances are one of main subjects of inquiry. Possible applications of mesoscopic drops vary from optics, where they can be used as dynamic and controllable lenses, to different cooling machines. Using colloid solutions instead of simple liquids without any additions can be explained by better thermal conduction of firsts. In this case specific computations supported by divine experiments must be undertaken.

Experiments carried out in this work showed that particles of the suspension do not evaporate with the liquid but deposit on the surface. The character of deposition is not uniform. Particles precipitate mainly around the circumference of initial droplet. This phenomenon matches so called coffee ring effect. The coffee ring effect is responsible for forming of a capillary-forces-caused pattern left after the droplet of solution with suspended particles has fully dried [1]. In everyday life it can be observed for coffee and red wine.

METHODS AND MATERIALS

Equipment and instruments

The main idea of the work consisted in measuring of the light intensity, transmitted through drying droplets. For this purpose spectrometer AvaSpec-2048XL-RS-USB2 was used. It is equipped with 500 μm CCD detector and diffraction grating. This device covers all wavelengths of visible light, long-wave UV and some part of short-wave IR. Halogen and deuterium light-sources were used.

The second part of investigation consisted in measuring of drying times of identical volumes of concerned liquids along with fixation of dynamically changing geometrical parameters of drops. For these purposes KRÜSS EasyDrop DSA20 was used. This laboratory setup provides ability to measure interfacial angles, surface tension and free surface energy.

EasyDrop DSA20 is equipped with a system of automatic dispensing and videocamera.

Thereby, experimental part of this work consisted in combining of lateral profile observation with spectrometric measuring of intensity of light, transmitted in the perpendicular to the substrate plane. Similar combination of experimental methods is presented in [2] but that paper emphasizes on the transport processes visualization of the solute polymer inside the drying droplet whereas this paper focuses on non-visual but spectrometric analysis of the transmitted light intensity being changed due, as it was considered, to height decreasing. Also there is a difference in liquids.

Liquids

Experiments defined above were undertaken on two different suspensions of nanoparticles. The first one was colloid of Fe_2O_3 nanoparticle concentrate with 9% NaCl physical solution as a basis of colloid. Its concentration was 1 g/l. Average diameter of nanoparticles was around 4 nm (Figure 1). Volume of drops was 4 ml, metered by automatic batcher.

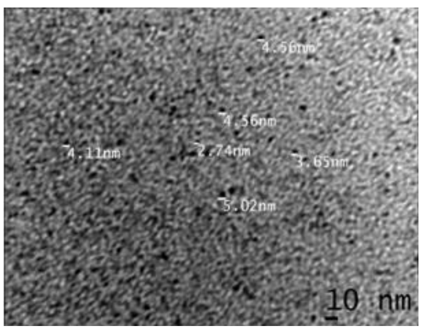


Figure 1. Transmission electron microscopy of Fe_2O_3 nanoparticles deposited on polymer mesh

The second colloid solution was based on distilled water with addition of 200 g/l SiO_2 nanoparticle concentrate in proportion 20 to 1. SiO_2 concentrate was extracted from wells of Mutnovskaya geothermal power plant and aged for some time [3]. Size spread is shown on Figure 2. The volume of drops was 4 ml.

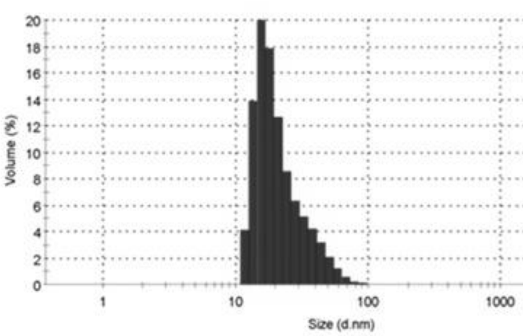


Figure 2. Size spread of SiO_2 nanoparticles [2]

Substrates

Drops of fluids described hereinbefore were deposited on 2x2 cm^2 glass substrates (thickness 1,5mm) covered with 190 nm thin layer of TiO_2. A graph of its spectral transmission coefficient is shown on Figure 3.

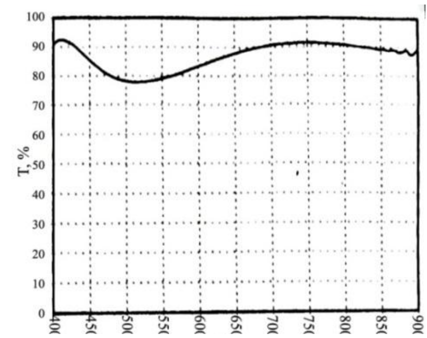


Figure 3. Spectral transmittance of glass wafer with 190 nm TiO_2 layer

Experiment

The first step of experimental investigation was measuring drying times for both fluids. Figure 4 shows story board of process development. Pictures were taken by KRÜSS EasyDrop DSA20.

a)

b)

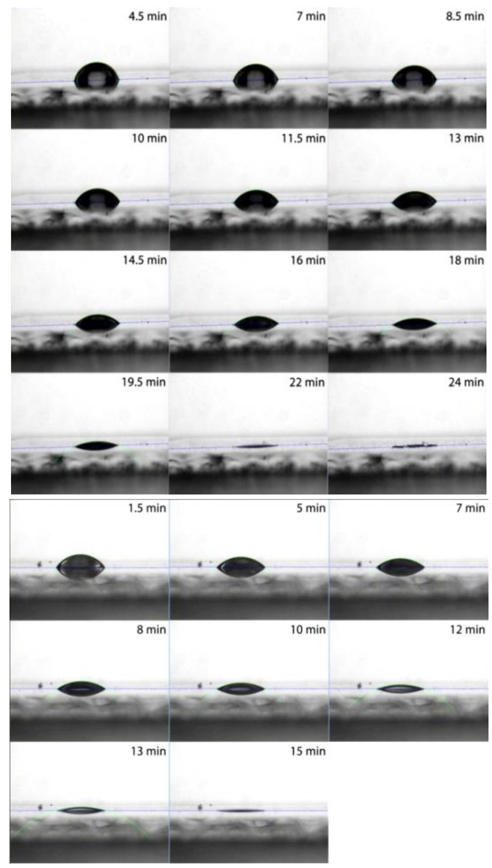


Figure 4. Story board for drying dynamics of drops: a) Fe_2O_3; b) SiO_2

After all the liquid from drops had fully evaporated sediments left after them were examined by the use of optical microscope. Both of liquids left ring-shaped patterns composed of material of suspension among which there also were nanoparticles. Micrographs of patterns are shown on Figure 5 and Figure 6.

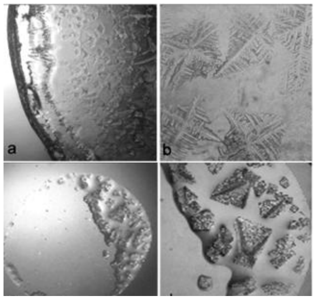


Figure 5. Micrographs of depositions made by optical microscope: a) Fe_2O_3 colloid, 4x/0.10; b) Fe_2O_3 colloid, 40x/0.65; c) NaCl 4x/0.10; d) NaCl, 10x/0.25.

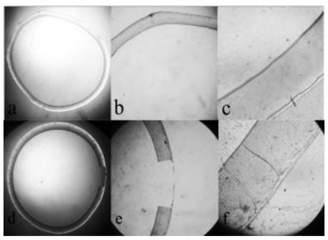


Figure 6. Micrographs of SiO_2 patterns: a,d) magnification 4x/0.10; b,e) magnification 10x/25; c,f,) magnification 40x/0.65

Density of deposition was higher near periphery of circumference thereby collars made of nanoparticles had formed. All signs conformed to coffee ring effect. This effect is a characteristic behavior of colloids' evaporation with the assumption of pinned contact line [4, 5].

On Figure 5a, 5b specific dendritic crystals can be observed. General color of deposition is rust just like the color of initial colloid solution. It is well seen that collars are well-defined and the area within circumference is covered with NaCl crystals fully. After comparing with patterns left by pure NaCl solution (Figure 5c, 5d) a deduction can be made that Fe_2O_3 nanoparticles made an influence on character of pattern left after complete evaporation of liquid. Deposition of pure NaCl solution tied into localized field and the NaCl crystals had a pyramidal shape (or truncated parallelepiped shape). But pattern of nanocolloid consisting of NaCl crystals and nanoparticles filled all the area within perimeter of initial puddle.

According to Figure 6 forming of distinctive ring-shaped collar is characteristic for SiO_2 nanocolloid solution also. Besides it is clearly obvious that the ring was divided into arches. This division was probably caused by the power of shrinking that appear in exsiccant liquid. The area inside of ring is not empty. It is filled with before-mentioned thin film and depositing particles of initial solution (compare with [6]).

Pattern left after complete evaporation of liquid and corresponding to coffee ring effect arose as a result of difference in evaporation rate along the surface. It is higher near the border of a droplet and that's why a directed flow of fluid from center of drop to periphery takes place. This flow causes a transfer of particles. In ideal case of coffee ring effect all the suspended particles would transfer to a border. It was not observed in these experiments. It means that stirring processes took place that caused some particles to transfer back to the area within perimeter of initial droplet.

Simultaneously drops of the same size placed on the same substrates were tested on transmittance of light. Spectra of relative transmittance intensity in different moments of time were measured. Schematic diagram of experiment is shown on Figure 7.

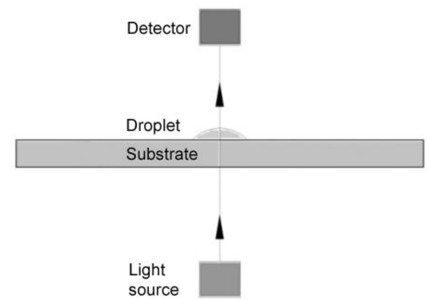


Figure 7. Schematic diagram of spectrometric experiment

A glass substrate was fixed horizontally. On both sides of perpendicular held to the substrate two fiber-optic cables with lenses on their ends were attached. The top one led to spectrometer, the lower one – from the light source. Then a drop of certain volume was dosed onto substrate right in the spot where the light beam emerged from glass.

On Figure 8 spectra of light intensity in different drying times are shown. This figure is for SiO_2 nanocolloid solution. It lacks representativeness so that's why only one plot is shown.

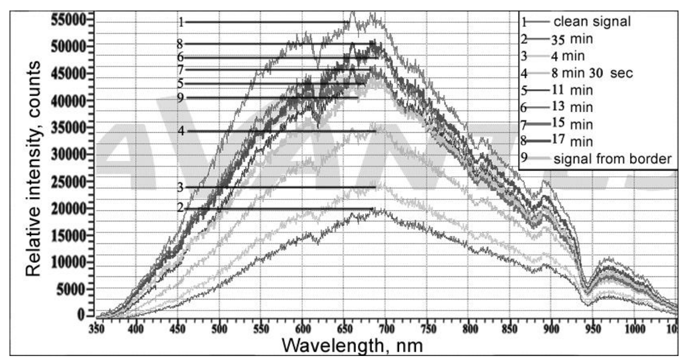


Figure 8. Spectra of relative intensity of light transmitted through drying droplet of SiO_2 colloid after indicated periods of time.

RESULTS AND DISCUSSION

Time dependence of droplet's height was measured according to Figure 4. Measuring was conducted by comparing droplet's height with the length of contact line that stayed nearly constant and was computed by EasyDrop's software. So long as incumbent droplet geometrically is a spherical segment a dynamical dependence of drop's volume and mass from height and length of base line (that is the same as contact line) can be computed. Fluid's density was taken equal to water's density (0,9982 g/cm^2) under condition that all particles had deposited on substrate. Results of computation are combined in Table 1 and Table 2.

Table 1. Experimentally measured time dependence of geometrical parameters of Fe_2O_3 drops

Time, min:sec	Contact angle, °	Diameter of drop base, mm	Surface area, mm^2	Height, mm	Volume, mm^3	Mass, mg
4:30	75,5	2,29	6,59	0,87	2,14	2,13
7:00	68,6	2,29	6,07	0,80	1,93	1,93
8:30	64,5	2,29	5,77	0,73	1,72	1,72
10:00	59,9	2,29	5,48	0,66	1,52	1,52
11:30	55,0	2,28	5,21	0,59	1,33	1,33
13:00	48,7	2,28	4,94	0,50	1,10	1,10
14:30	43,7	2,28	4,75	0,43	0,93	0,93
16:00	37,8	2,27	4,54	0,39	0,82	0,82
18:00	28,7	2,25	4,25	0,30	0,61	0,61
19:30	22,1	2,23	4,07	0,22	0,43	0,43
21:00	14,7	2,18	3,81	0,21	0,39	0,39
22:30	-	2,18	3,75	0,10	0,19	0,19

Table 2. Experimentally measured time dependence of geometrical parameters of SiO_2 drops

Time, min:sec	Contact angle, °	Diameter of drop base, mm	Surface area, mm^2	Height, mm	Volume, mm^3	Mass, mg
0:00	58,9	2,47	6,34	0,73	1,97	1,96
1:30	54,9	2,47	6,09	0,70	1,84	1,84
3:40	48,9	2,47	5,76	0,60	1,57	1,57
5:00	45,1	2,46	5,57	0,56	1,43	1,42
7:00	39,0	2,45	5,32	0,48	1,20	1,20
8:33	34,0	2,44	5,12	0,40	0,97	0,97
10:15	27,4	2,44	4,89	0,32	0,76	0,76
12:08	19,8	2,42	4,75	0,24	0,56	0,56
13:00	15,5	2,50	5,00	0,19	0,46	0,46

Graphs showing time dependences of droplet's height were made (Figure 9) predicated by tables 1 and 2.

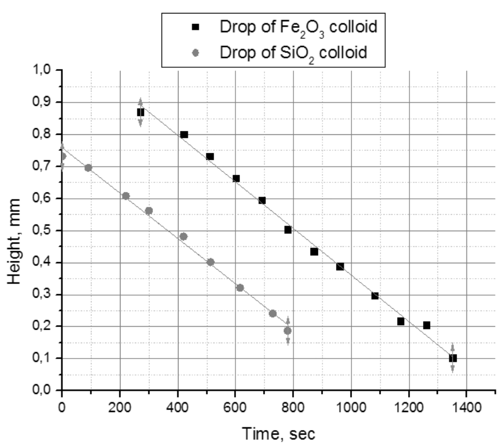


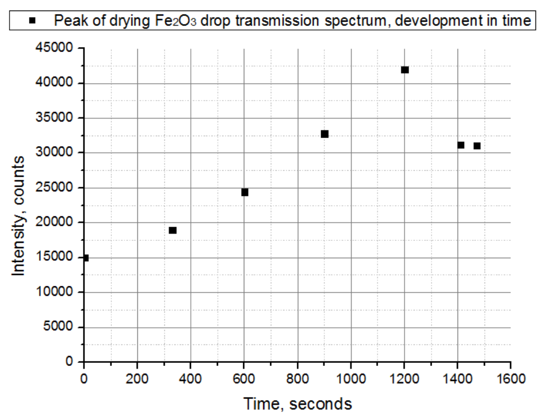
Figure 9. Dynamics of drop height changes

Visual control of droplet drying (Figure 9) showed a uniform decrease of drop's height. It is notable that curve slope is similar in both cases. It can be described by the assumption that it is a solvent being the evaporating substance. Similar conclusions were made in [2, 7], but they were achieved by the use of other experimental methodics.

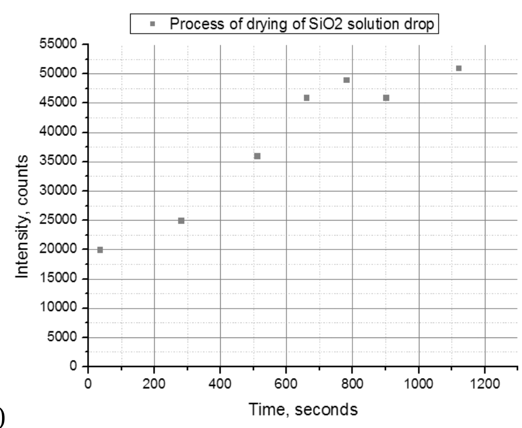
Time dependences of intensity of light transmitted through the system droplet/substrate are shown on Figure 8. But it is not an obvious representation. That's why it was decided to take intensity's value for peak (wavelength ~ 685 nm) and plot its dependence (Figure 10).

In both cases dynamics of drying process could be divided into three stages. The first stage could be characterized by uniform increase of transmittance. The second stage probably could be called as a critical one for drying because light once got into a thin layer of drop, characterized by high density of nanoparticles, is being reflected, absorbed and dispersed by them. All these inner processes forced intensity of transmitted light got into analyzer to decline.

The third stage differs for Fe_2O_3 and SiO_2 colloids. For liquid with iron oxide nanoparticles the intensity of transmitted light stayed the same as for second stage because of deposited NaCl crystals that filled all the area within initial drop perimeter. In case of SiO_2 colloid the third stage can be described by slight increase of transmittance intensity. During this last stage liquid lasting in thin layer of colloid with high density of nanoparticles had finally evaporated and semitransparent film deposited on substrate. An assumption can be made that at the very last moments of drying a bigger part of nanoparticles suspended in thin film transferred to the border.



a)



b)

Figure 10. Dynamics of changes of transmitted light intensity: a) Fe_2O_3; б) SiO_2

CONCLUSION

The comparison of two different methods of drop drying investigation showed that spectrometric technique gives bigger times than technique based on measuring of contact angles. This difference is caused by forming of thin film of liquid with higher density of nanoparticles within circumference of initial droplet that at a certain point of process stops being received as a drop by the KRÜSS instrument and its software, though the evaporation hadn't stopped yet. The fact that evaporation keeps on proceeding impacts on the intensity of transmitting light so that spectrometric method allows to register drying up to the end. The experiment showed that spectrometric method can be considered as a technique to detect the evaporation of liquids. Also it can be applied as an alternative way to measure concentration of colloid solutions.

In general patterns left by droplets of two observed suspensions are alike: the majority of suspended nanoparticles undergo ring dispersion assembling on periphery of initial droplet and forming collars along its circumference. It matches coffee ring effect though a thin film of suspended substance deposits within initial drop perimeter. Fe_2O_3 colloid can be characterized by formation of saline crystals inside the ring of collars with nanoparticles deposited on it. As it is claimed in [8-9] coffee ring effect can be applied as a method of molecular self-assembling.

A sharp increase of transmitting light intensity was observed for SiO_2 colloid within last few seconds. It occurred because particles left in thin film inside the collar ring absorbed abruptly into collars and so the density of particles inside "coffee ring" decreased. As a consequence transmittance of the whole construction increased.

Analysis of Figure 10 allows making a recap that the process of drying of observed suspensions is non-monotonous. Three stages of it can be distinguished: a steady drying of a large volume of liquid; almost total evaporation of liquid, formation of thin film characterized by high density of nanoparticles; complete evaporation of all the liquid.

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