Original scientific papers UDK 611,84
doi: 10.7251/COM1201055B

MICRO AND NANO LUBRICANT BEHAVIOR OF TEAR FILM AQUEOUS LAYER

B. Bojović[1,], Đ. Koruga[2]*
[1]University of Belgrade, Faculty of Mechanical Engineering, Mechanical Production Engineering Department, Kraljice Marije 16, 11120 Beograd
[2]University of Belgrade, Faculty of Mechanical Engineering, NanoLab, Kraljice Marije 16, 11120 Beograd

Abstract: Tears provide moisture and supply oxygen and other important nutrients to the cornea, mechanically trap and flush out foreign bodies and chemicals and keep the surface of cornea smooth and optically clear. Additionally, during blinking, tear film lubricates the friction area between lids and ocular surface. Tear film contains an aqueous layer that includes water, bacteriostatics, proteins and salt. Contact lens wearers often suffer from dry eyes. These changes in the tear film are caused by contact lens design, surface, material and applied solution for conditioning. In case of application of gas-permeable contact lens, the multi-factorial problem of tear film stability and therefore, maintaining of lubrication are main goals in the ongoing investigation. This paper focuses on applied research of the response of material's surface roughness quality to retain tear film on the micro and nano-level by using a gliding-box method for lacunarity analysis. The topology of contact lens surface with tear film as the lubricant was studied from the point of view of the water as primary consistent in its bulk liquid form, as well as confined water film organized into layers in a nanometer-sized channel. Contact lens surface topology observed on micro and nano-scale indicates different lubrication behavior of aqueous tear layer. As opposed to bulk water as a disordered medium in micro scale that flows very readily, nano-water demonstrates the behavior effectively like some phases of liquid crystals.
Keywords: tears, lacunarity, lubrication.

1. INTRODUCTION

Water is a unique liquid in nature, the most essential of all molecules on Earth, as well as one of the most challenging research problems in science and technology. These words make part of numerous web sites and references available both from public and scholar domains. Of all functions that water has, this paper deals with water as a lubricant. Bulk water flows very readily as a disordered medium, and aware of that, man makes oil-based lubricant systems. Despite that fact, nature prefers water-based lubricant systems [1]. A good example of that is presented by the human eye as a bio system lubricated by water being a prevalent constituent of aqueous layer of tear film in tears.

During blinking, tear film lubricates the friction area between lids and ocular surface. This perfect system is both influenced and disturbed by the presence of any contact lens on the front surface of the eye. Changes in lubrication are influenced by rigid gas permeable contact lens design, surface, material and applied solution for conditioning. Furthermore, contact-lens wearers develop dry eye over the years, which correlates to tear film thickness values that are 3.05±0.20μm and 2.48±0.32μm for normal and dry eye subjects, respectively. These are the recent findings, presented in [2]. An eye with contact lens demands our attention as a multi-faceted problem of tear film stability and therefore, the main goal of the ongoing investigation is how to maintain the lubrication function.

Water-based lubricant systems function well with hydrophilic surfaces. The cornea covered by mucus layer and rigid gas-permeable contact lens coated by conditioning solution are hydrophilic. In case where the motion of the water molecules is strongly restricted by the potential resulting from solid surface (contact lens surface), the properties of the confined water become different from those of the bulk state [3].

* Corresponding author: bbojovic@mas.bg.ac.rs

In biology, nano-confined water plays a vital role in many biological systems such as protein folding and biological channels as well as in geology in rocks and minerals. In nanoscience and nanotechnology, confined water studies can induce development of new nano-devices under aqueous environments [4]. Since 1990s, the experiments have been undertaken that used the surface force apparatus (SFA) and atomic force microscope (AFM) as well as molecular dynamics (MD) simulations to investigate confined water [5].

The existence of confined water between contact lens inner surface and cornea from the one side or contact lens frontal surface and lid from the other side is expected; therefore the topology of contact lens surface with tear film as the lubricant is studied, from the point of view of water as primary consistent in its bulk liquid form, as well as nano-confined water film organized into layers in a nanometer-sized channel.

2. MATERIALS AND METHODS

2.1. Surface Imaging

Our research comprised contact lens surface measurement and analyses of topography images. They are obtained by atomic force microscopy (AFM) that is a scanning probe technique based on point-to-point examination of the specimen made by a sharpened tip probe.

The AFM system used in this study is JSPM-5200, JEOL, Japan. The cantilever is produced by MikroMasch (Estonia) by trade name NCS18 Co-Cr. AFM probe is a silicon etched probe tip of conical shape. It is coated with Co and Cr layers, so the resulting tip radius with the coating is 90nm. Full tip cone angle is 40°. Samples are taken from contact lenses that are manufactured from fluorosilicone acrylate doped poly methyl methacrylate PMMA material (Boston EO). All samples are imaged in tapping mode and in ambient air.

2.2. Lacunarity Analysis

Mandelbrot introduced the term lacunarity from the Latin word “lacuna” that is related to English “lake” [6]. Lacunarity analysis is a multi-scaled method for describing patterns of spatial dispersion. Surface lacunarity analysis, as part of ongoing project activities, is based on “gliding box” method proposed by Voss in [7] and Plotnic [8].

This method considers the gliding box as a window systematically moving through the binary image. Binary images represent a section of surface topography images that are sliced on levels by planes starting from the top and all the way down. For each section the pixels that belong to a surface are colored white and considered as binary 1. The rest of the surface image belongs to valleys, so they represent an empty space that is supposed to be filled with lubricant. Those pixels are colored black and are considered as binary 0. For a particular level the binary image represents the distribution of lubricant’s lacuna (Figure 1, left side).

Box mass value *m* is determined for each of the gliding boxes as a number of black pixels occupied by the gliding box. The gliding box size *r* is a variable and can take values of 2^n pixels length. The in-house made procedures for lacunarity value determination of engineering surfaces are developed in Matlab software. All necessary image processing is performed in Matlab also.

According to Plotnic [8] lacunarity L(r) is defined by the following equation:

$$L(r)=\frac{M_2(r)}{M_1^2(r)}, \qquad (1)$$

where $M_1(r)$ and $M_2(r)$ are first and second moment of distribution of black pixels in gliding box. Moments are defined by equations:

$$M_1(r)=\sum_{m=1}^{r^2} m \cdot P(m,r); \qquad (2)$$

$$M_2(r)=\sum_{m=1}^{r^2} m^2 \cdot P(m,r)\cdot \qquad (3)$$

Probability $P(m,r)$ that the gliding box of size *r* contains *m* black pixel is defined by the equation:

$$P(m,r)=\frac{n(m,r)}{N(r)}, \qquad (4)$$

where $n(m, r)$ is the number of box size *r* with mass *m*, and $N(r)$ is the total number of boxes of size *r.*

When the double logarithmic plot of points *(L, r)* is fitted by polynomial line (Figure 1, middle), the line slope *p*, as a numerical value for every section made by slicing the engineering surface image, are presented in Figure 1-right as a dot.

Lacunarity analysis is used to investigate the lubricant distribution on engineering surface. The distribution of tear film and its stability, for a contact lens surface, are analyzed in next sections.

3. RESULTS AND DISCUSSION

The surface topography images, gathered by AFM, are considered as matrix filled by surface height in each pixel. Such matrix represents an intensity image type with greyscale map. Imaging size is 256x256 pixels and images area are

10μm×10μm and 1μm×1μm for investigation of contact lens surface lubricant behavior in micro and nano scope. Sixteen contact lenses are imaged and forty images with the size of 10μm×10μm and thirteen images with the size of 1μm×1μm are studied using the "gliding box" method. Lacunarity analysis provides a diagram that presents the slope value *p* vs. cutting level *n*.

3.1. Tears lubrication in micro range

Forty *p*-diagrams are being observed and they are selected in two groups for micro scope behavior explanation. The first group represents *p*-diagrams with three line slopes and we label them as slanted *p*-diagrams and show some representatives in Figure 2-up. Opposing to them is a second group that consists of contorted *p*-diagrams with four slopes in Figure 2-down. The images related to specific group diagrams demonstrate the same surface topology. The contorted *p*-diagrams present a topology with distinctive high hills. The slanted *p*-diagrams present topology with uniformly distributed lower hills. In Figure 2-right, 3D topography images that refer to a particular group are presented.

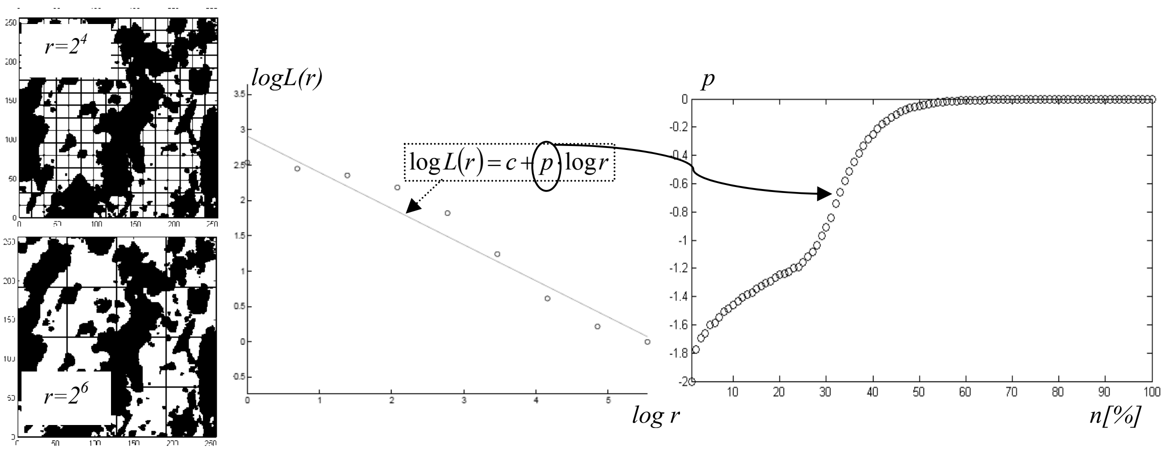

Figure 1. Plot of natural logarithms of L(r) against r (middle) for cutting level 35% of engineering surface (left) and slope value p vs. cutting level n (right)

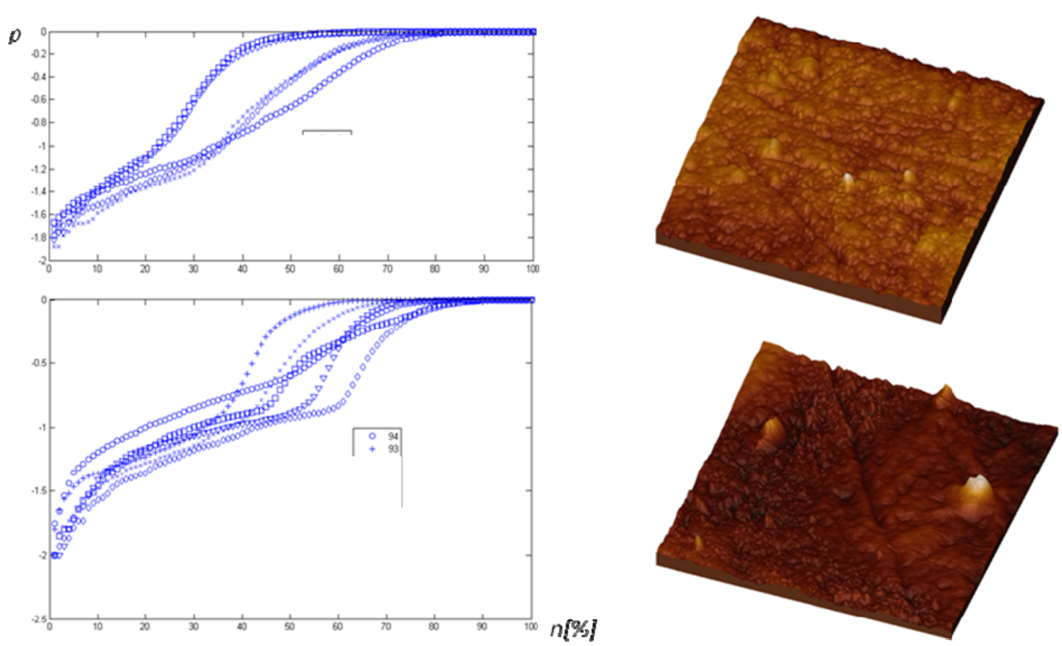

Figure 2. Slanted (up) and contorted (down) p-diagrams for AFM images of sample area size 10μm×10μm with representatives

For slanted *p*-diagram three characteristic slopes are distinct. The first slope refers to the range of upper quarter, the second scope to the range of quarter to half and the third refers to the rest of the cutting levels. This implies a simple conclusion that the engineering surface can be considered as an object with different properties along the asperity height. These three slopes coincide with real matter, because the surface includes large regions of space in the top quarter of maximal height. Also, lacunarity is different in the second quarter and it is caused by space reduction in favour of material accumulation. The surface includes large regions of material in the bottom half of maximal height, which makes the object very dense and lacunarity obtains a constant value.

The results of surface lacunarity analysis confirm sample surface state as belonging to either group adequate (slanted *p*-diagram) or inadequate (contorted *p*-diagram) roughness concerning the tear film maintenance in lacunas region.

Contact lens surface topology analysis on micro scale reveals features lower that 200nm. Tear film has thickness no less than 2000nm, even for dry eye wearers confirmed in [9], and compared to surface topology observations; there is no problem of aqueous layer lubrication. In reality, dry air, wind, high temperature, non-frequent blinking, staring at a screen, etc. influence tear film instability, especially in case of dry eye and cause discomfort for contact lens wearing.

There is no simple solution to a contact lens lubrication problem, and lacunarity analysis of contact lens surface could provide some insight in lubrication behavior, not only in micro but in nano range, too. A solution could be hidden in nano range and therefore, a lacunarity analysis is performed on 1µm×1µm images area.

3.2. Tears lubrication in micro range

Since the width of water molecule is about 0.25nm, according to [10], lacunas on contact lens surface size of 1µm×1µm (Figure 3-a) are filled by water molecules as cobble stone pattern. In that way defined cutting levels *n* present water layers only 0.25 nm thick. In Figure 3-b, *p*-diagram presents a very slanted shape and according to the analysis that is established in the previous chapter, three distinctive behaviors can be determined. In range 1-40 layers, the binary image in Figure 3-c includes large regions of lacunas. In range 40-80 layers in Figure 3-d there is a space reduction of lacunas in favour of material accumulation.

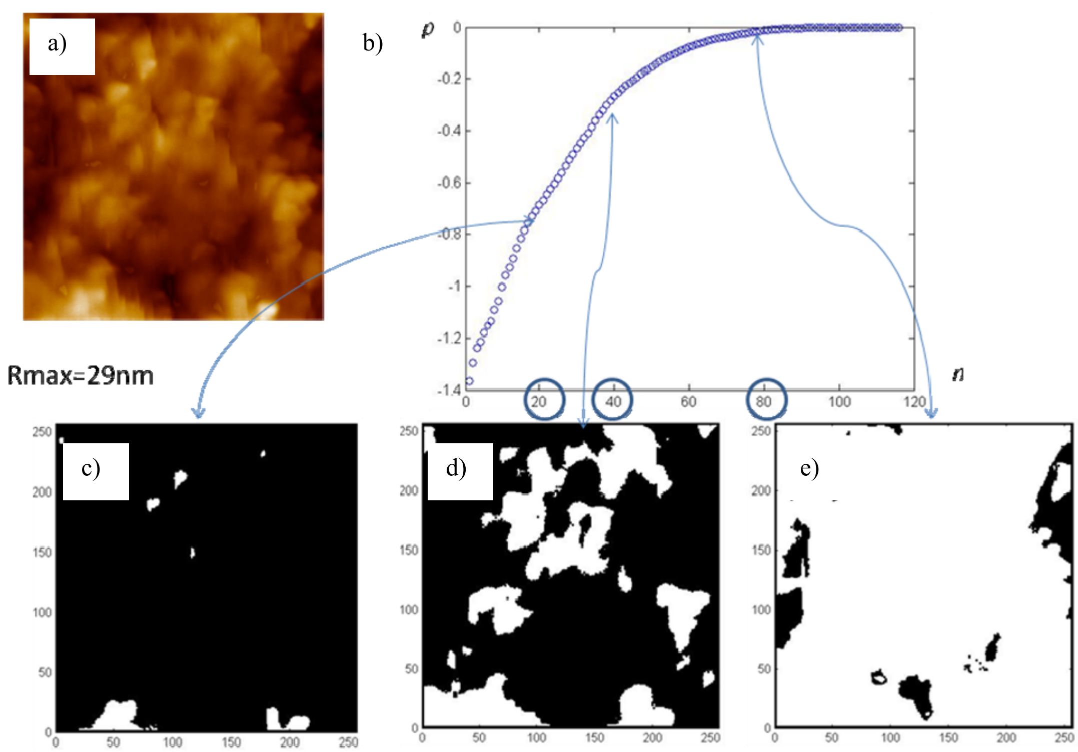

Figure 3. a) AFM topography image size of 1µm×1µm, b) p-diagram with 120 water layers, c) binary image for 20th level, d) binary image for 40th level, e) binary image for 80th level

In the last range 80-120 layers in Figure 3-e there is asymptotic look of dots, and there is a potential appearance of isolated lacunas appropriate for confined water. This asymptotic region is additionally observed and analyzed in last ten water layers (Figure 4-a) because the confined water usually contains only 6-10 molecule layers, which is confirmed in [5].

The research focuses on the detection of nano gaps in surface topography using lacunarity analysis. In Figure 4 a *p*-diagram is presented for last ten water layer (b) and binary images for 96th (c), 101st (d), and 113th (e) layer. The form of dots represents distribution of confined water lacunas assemblies along the depth of ten water molecules layer. In Figure 4-c, three lacunas assemblies can be observed on binary image. At just about 101st level one of them is vanishing and *p*-diagram shows a slope distinction in a particular dot. The binary image in Figure 4-d represents 101st level. There are two lacunas assemblies that cannot be observed in Figure 4-e, because one of them vanishes again and in *p*-diagram a particular dot arises.

A different form of *p*-diagram is presented in Figure 5-a. Smooth curve without any abruption adequately represents topography that exhibits single lacuna region at the ten lower levels. It is opposite to *p*-diagrams in Figure 4-a. The existence of either dot or dots that are prominent compared to the smooth path followed by the rest of dots, indicates several region of lacunas.

In Figure 6-the *p*-diagram with two abruptions in layer 250 and 255 is presented. According to the previous analyses in reference to Figure 4 and Figure 5, it can be concluded, in advance, that there are three lacunas region on 247th layer and they are vanishing subsequently around 250th and 255th layer. Binary images in Figure 6-c confirm the existence of three, Figure 6-d of two, and Figure 6-e the existence of a single lacuna region. Both, Figure 4 and Figure 6 reveal several lacuna regions on topography of contact lens and changes in *p*-diagrams provide information about that.

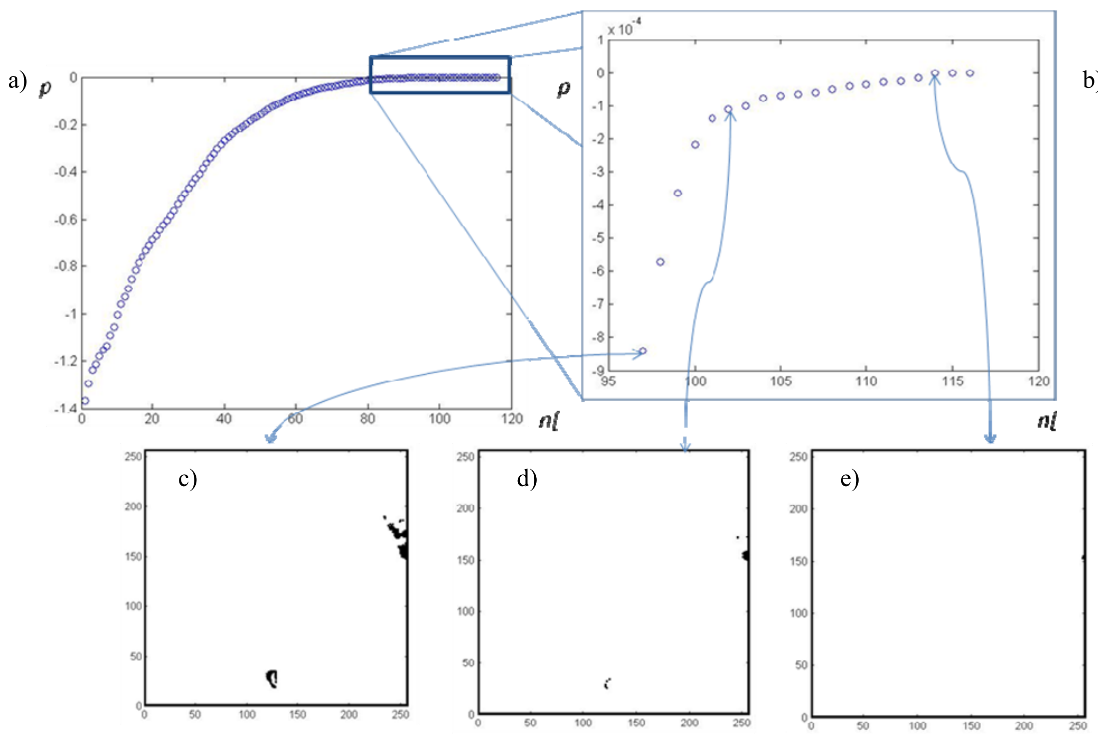

Figure 4. a) p-diagram with 120 water layers, b) p-diagram with last 10 water layers, c) binary image for 96th level, d) binary image for 101st level, e) binary image for 113th level

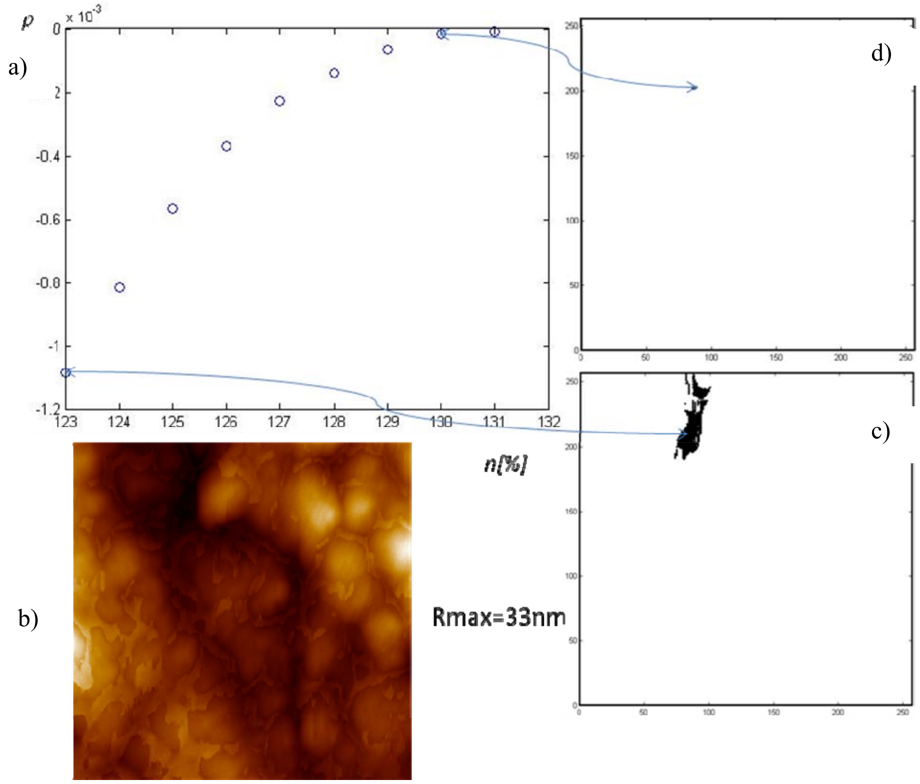

Figure 5. a) p-diagram with last 10 water layers of 132 water layers, b) AFM topography image size of 1 μm×1 μm, c) binary image for 123rd level, d) binary image for 130th level

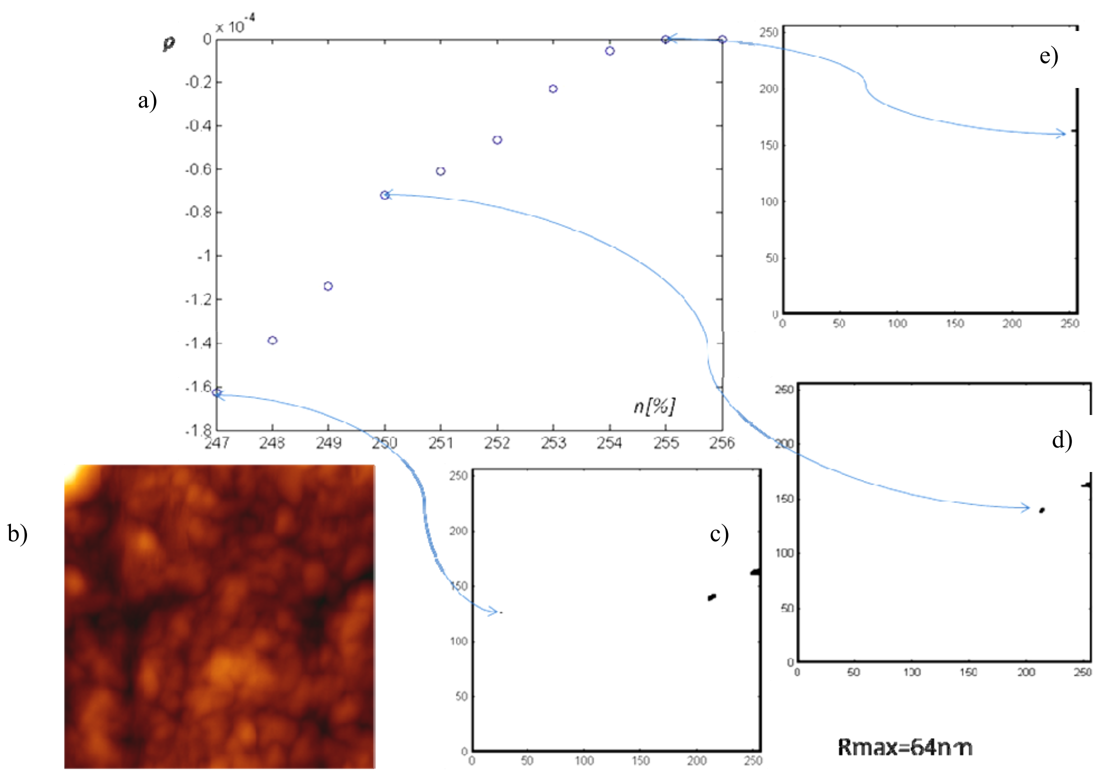

Figure 6. a) p-diagram with last 10 water layers of 256 water layers, b) AFM topography image size of 1 μm×1 μm, c) binary image for 247th level, d) binary image for 250th level, e) binary image for 255th level

It can be concluded that *p*-diagram in nano scale application could provide explicit information about surface lacunarity, and therefore possibilities for water accumulations in it. Thus, the restrained water between solid walls is known as confined water [11]. Due to a decreased mobility of molecules, the following properties of confined water were reported in [3-5]:

- the oscillation of the average local density near the solid walls with the distance normal to the boundaries,
- prolonged molecular relaxation time,
- reduced diffusion coefficient,
- increased effective shear viscosity and
- two different responses during transition to solidification.

As a result of different properties, confined water behaves effectively like liquid crystals and exhibits good lubricant behavior in nano scale. Good lubricant behavior is reported for specific conditions, like pure (sterile) water that was used for experiments, along with the atomic flat surfaces of solid walls. In the eye lubricated by the water that contains proteins and salts, between contact lens rough surface of polymer, as a solid wall from the one side and tissue as real non-solid wall from the other side, the existence of aqueous tear layer in the role of confined water should be confirmed in experimental way.

5. CONCLUSION

AFM images of contact lens surface are studied using the “gliding box” method for lacunarity analysis, which provides a diagram that presents slope value *p* vs. cutting level *n*. Based on *p*-diagram shape and slopes changes along it, it can be concluded that the engineering surface can be considered as an object with different properties along the asperity height. Therefore, an explanation about the surface lubrication behaviour can be given with certainty.

The results of surface lacunarity analysis in micro domain confirm contact lens surface state as belonging to either a group of adequate (slanted *p*-diagram) or inadequate (contorted *p*-diagram) roughness concerning tear film stability.

The research of nano domain is related to the detection of nano gaps in surface topography using lacunarity analysis for last ten molecular layers. A smooth curve of *p*-diagram without any abruption, adequate represents topography that exhibits single lacuna region at the ten lower levels. It is opposite to existence of prominent dots that indicates several regions of lacunas. Potential appearance of gaps presents isolated regions of lacunas that are appropriate for confined water existence.

Future research activities of aqueous layer of tear film by AFM should be predominantly directed toward experimental verification of confined water role as a lubricant. We have cast some light on water as a lubricant, using lacunarity analysis but we want to fully understand it, explain it and finally, be able to apply it.

6. ACKNOWLEDGEMENT

This paper is a part of the research financed by The Serbian Government, The Ministry of Science and Technological Development. Project title: Functionalization of nanomaterials for manufacturing new sort of contact lenses and early diagnostics of diabetes (III45009).

7. REFERENCES

[1] M. Urbakh, J. Klafter, D. Gourdon, J. Israelachvili, *The nonlinear nature of friction,* Nature, 430 (2004) 525−528.

[2] K. Azartash, J. Kwan, J. R. Paugh, A. L. Nguyen, J. V. Jester, E. Gratton, *Pre-corneal tear film thickness in humans measured with a novel technique*, Molecular Vision, 17 (2011) 756−767.

[3] A. V. Khomenko, N. V. Prodanov, *Molecular dynamics simulations of ultrathin water film confined between flat diamond plates*, Condensed Matter Physics, 11−4(56), (2008) 615−626.

[4] H. Kyakuno, K. Matsuda, H. Yahiro, et al., *Confined water inside single-walled carbon nanotubes: Global phase diagram and effect of finite length,* The Journal of Chemical Physics, 134 (2011) 244501(1)−(14).

[5] F.Wang, Y.Zhao, *Tehnique properties of the solid-like confined liquid films: A large scalemolecular dynamics simulation approach*, Acta Mechanica Solida Sinica, 24−2 (2011) 101−116.

[6] B. Mandelbrot, *The Fractal Geometry of Nature*, W.H. Freeman and Co, New York, 1982.

[7] R. Voss, *Random fractals: characterization and measurement*, Scaling phenomena in disordered systems, 10−1 (1986) 51–61.

[8] Plotnick, R. E, Gardner, R. H, Hargrove, W. W, Prestegaard, K, Perlmutter, M, *Lacunarity analysis: A general technique for the analysis of spatial patterns,* Physical review E, 5461−5468, 1996.

[9] K. Azartash, J. Kwan, J. R. Paugh, A. L. Nguyen, J. V. Jester, E. Gratton, *Pre-corneal tear film thickness in humans measured with a novel technique*, Molecular Vision, 17 (2011) 756−767.

[10] http://wiki.answers.com/Q/Width_of_a_water_molecule#ixzz1T8WDNrE4.

[11] http://www.btinternet.com/~martin.chaplin/interfac2.html.

ПОНАШАЊЕ ВОДЕНОГ СЛОЈА СУЗНОГ ФИЛМА
КАО СРЕДСТВА ЗА ПОДМАЗИВАЊЕ У МИКРО И НАНО ПОДРУЧЈУ

Сажетак: Сузе обезбеђују влажност и снабдевају кисеоником и осталим важним састојцима рожњачу, механички уклањају страна тела и хемикалије и одржавају је глатком и оптички провидном. Додатно, током трептања, сузни филм подмазује тарне површине између капака и ока. Сузни филм се састоји од воденог слоја који садржи још и бактериостатике, протеине и соли. Носиоци контактних сочива често пате од сувог ока. На те промене у стабилности сузног филма утичу дизајн, површина и материјал контактног сочива, као и раствори за одржавање. Основни циљеви тренутног истраживања су више факторијални проблем стабилности сузног филма и самим тим и одржавање функције подмазивања код гас-пропусних контактних сочива. Овај рад се бави примењеним истраживањима способности храпаве површине контактног сочива да задржи сузни филм у микро и нано подручју, и то коришћењем методе клизних прозора за анализу лагунарности. Топологија контактних сочива са сузним филмом као средством за подмазивање испитани су са аспекта воде као доминантног флуида, као и стишњеног слојевитог воденог филма у нанометарским процепима. Топологија контактних сочива посматрана у микро и нано скали указује на различито понашање сузног филма у улози средства за подмазивање. Супротно од воде која је у свом макроокружењу лош лубрикант, јер је флуид који лако тече, нановода се понаша као течни кристал.

Кључне речи: сузе, лагунарност, подмазивање.