# SIMPLE SYSTEMS OF FATTY ACIDS UNDER LASER ACTION

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*The paper presents the behavior of some fatty acids –components or forerunner of the biological membrane- in mesomorphic state, under laser action. Experiments are realized with a setup based on diode and argon ions lasers action on the thin film samples of fatty acids, built in our laboratory. Experimental data are computer processed with TC3D program, and a specific nonlinear behavior is emphasized, based on the refractive index modification in laser field. Depending on the laser, this can be obtained or by thermal effect of the laser radiation, either by the molecular reorientation effect in the liquid crystal state of the fatty acids.*

**Keywords**: biological membrane, fatty acids, liquid crystals, laser, nonlinear

## 1. Introduction

Nowadays, biomedicine reported many results [1, 2, 3, 4, 5] concerning the biological membrane operating conditions, and is continuously working for discovering these mechanisms.

As it was shown in some previous works [6], fatty acids (FA) components or forerunner of the biological membrane, present a thermotropic, generally enantiotropic mesomorphic state, during their transition between the solid or gel-like state and the isotropic liquid state, depending many times on the speed of the temperature variation [7]. This liquid crystal (LC) state is maintaining between some temperature values, characteristic for each substance. The LC state is involved in some biological mechanisms, characteristic for the biological membrane [2].

Our works are continuously oriented to the mesomorphic behaviour of some important FA, like unsaturated FA (with double bonds): arachidonic ($C_{20}$:4 *all cis*), elaidic ($C_{18}$:1*trans*), linoleic ($C_{18}$:2*cis*), linolenic ($C_{18}$:3*cis*), - and saturated FA: arachydic ($C_{20}$), myristic ($C_{14}$), lauric ($C_{12}$), caprylic ($C_8$), caproic ($C_6$) [8]. Most natural FA have an even number of carbon atoms. Double bonds in FA are usually in the *cis* configuration. There is free rotation about C-C bonds in a FA, except at a double bond. Each *cis* double bond causes a kink in the chain.

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Rotation about other C-C bonds would permit a more linear structure. In LC state, FA emphasized smectic mesomorphic textures, a dielectric with a small conduction behaviour in electric field ($4x10^4$ V/m), ferroelectricity, optic lens-like effect of He-Ne laser beam, pulse modification of $Nd^{3+}$ laser, depending on the composition of the samples (pure or FA mixtures with other substances, like cholesterol or some drugs), on the temperature, intensity of the electric or optic field, continuous wave (c.w.) or pulsed laser etc. [4, 6].

The paper presents some results obtained by using an experimental setup build in our laboratory for studying thin transparent fatty acids samples under laser treatment, while in the LC state. Experimental results are dealing with the nonlinear answer of the systems of FA with a mesomorphic behavior, useful for modeling a simple biological membrane. The possibility of inducing non-linearity in a biological system, leading to a radical change of its dynamics, is emphasized. A competition between the thermal nonlinearity and the molecular reorientation is evidenced, depending on the characteristics of the used laser.

## 2. Theoretical considerations

Generaly [ 9, 10, 11], the high power density of the optical signal of a laser usually determines a nonlinear all-optical modification of the real part of the refractive index of the material, by the polarization $\boldsymbol{P}$ dependence on the wave electric field intensity $\boldsymbol{E}$ :

$$P = \varepsilon_0 \chi^{(3)} \mid E \mid^2 E \tag{1}$$

where $\chi^{(3)}$ is the third order electric susceptibility [8]. This change is connected with the self phase modulation of the light in materials:

$$\Delta\Phi = \Delta n \omega \frac{l}{c} \tag{2}$$

where:

$$\Delta n = n_2 I \tag{3}$$

$I$ being the intensity of the light, and $n_2$ the nonlinear refractive index.

Absorption - i.e. the change in the imaginary part of the refractive index - limites this mechanism [6, 9].

Another possible nonlinear change of the refractive index is the so-called „thermal nonlinearity”, which is slow [12], since the speed of thermal effect of the radiation is low (μs-ms timescale).

In LC, the nonlinear answer of the material appears both in isotropic and mesomorphic state, being higher in the last one, this behavior having a cooperative feature [4, 6] and the response time usually of the order of ms. The self phase modulation of the light appears by molecular reorientation in LC [4,

13], even at low power laser beams [14]. At such powers, if the thermal nonlinearity is also present, for example for red and infra red (IR) light [5], this thermal effect could be dominant in LC; for other wavelengths of the laser, heating effect of the laser light is weak and the dominant effect might be the molecular reorientation in LC state.

In the case of the thermal nonlinear index induced by laser radiation one can write the temperature dependence of the refractive index [11]:

$$\Delta n = (\frac{dn}{dT})\frac{\alpha I^{\max} R^2}{k} \tag{4}$$

where $I^{max}$ is the laser intensity in the center of the beam of radius $R$, $\alpha$ –the absorption coefficient, $k$ –the thermal conductivity, and:

$$\Delta n = n_2 I^{\max} \tag{5}$$

becomes:

$$n_2 = (\frac{dn}{dT})\frac{\alpha R^2}{k} \tag{6}$$

$\alpha$, $k$, being well known from the transport equation of the heat from the laser light intensity $I$:

$$-k\nabla^2\tilde{T}_1 = \alpha\tilde{I}(r) \tag{7}$$

where $\nabla^2\tilde{T}_1$ are replaced by $-T_1/R^2$, therefore $TI^{max}=\alpha I^{max} R^2/k$. If $dn/dT$ is for example of the order $10^{-5}K^{-1}$, the absorption coefficient $\alpha$ is $100m^{-1}$, $R$ is$10^{-3}$ m, and $k$ -$10^3$W/K, then $n_2$ results $10^{-5}cm^2/W$ [10]. For typical nematics, $n_2$=5x$10^{-7}m^2/W$. The response time $\tau$ is between 1 and 72ns for $T>T^*$.The reason for such a change in refractive index is the fact that fast nonlinearity has an electronic nature – the displacement of electronic cloud confined by the binding potential, which can be that of an atom or a crystal bond. The potential itself is unaffected. Supposing the binding potential between neighboring atom changes, the change of index can be much larger, as happens when the temperature increases and the distance is on the order of a few percent. Thermal nonlinearity is notoriously slow [12], it is often considered only a potential enabling mechanism for ultra-fast all-optical switching. But the intrinsic speed of thermal nonlinearity, i.e. the speed of relative motion of ions is not low. The relative ion motion occurs on the scale of the optical phonon frequency, as fast as few hundred fs. Thermal nonlinearity is slow due to the rate of heat dissipation, typically on the microsecond to millisecond timescale, that happens when the heated region is relatively large, on the micrometer scale.

Electromagnetic signal from the laser is also modified, by interacting with the nonlinear medium [13], a delay being obviously observed and calculated [14], and fluctuations that could act on the membrane stability.

Taking into account the relation between the wavelength λ and the energy of the photons:

$$E = h\upsilon = \frac{hc}{\lambda} \tag{8}$$

where $\upsilon$ is he frequency of the light and $h$ - Planck's constant, it is normal that the molecular reorientation appered at lower $\lambda$ than the thermal refractive index effect.

## 3. Experimental

Thin samples (up to 24μm), having the usual LC sandwich cell geometry were built by us [4] and studied under external stimuli. FA were sandwiched between two glass plates of transparent $SnO_2$ about 2 cm long, with 20μm Mylar spacers at both ends. The liquid samples filled the cells by capillarity; grains of the solid ones filled first the cells and then heated, the unnecessary amount being removed until the required thickness was reached. The temperature (4-150°C) has been controlled. Microscopic aspects revealed during the experiments by the polarizing microscope IOR-MC5 showed smectic C textures for these acids.

This installation is realized for a low cost and rapid study of transparent samples, by means of a diode laser, working in red/infrared (IR) domain. We used a beam of $\lambda$=650nm, at the $P_{max}$=5mW. A bias voltage source is used and a reliable voltage of 1.6-3V was applied to the laser. Emitted light acts by filters (for absorbing the light background from the environment) on the reflectorizing room of a light photo-resistive sensor, is amplified and reaches a calibrated powermetter, which displays the power of the emitted signal. The sample is placed on a mobile support. Usual measuring apparatus (voltmeter V and ampermetter A) are included in the installation.

Laser applied voltage $U$ being between 2V and 3 V, and current between 18.8mA and 63 mA, the command of the laser is realized by the current. Depending on the goal of the experiment, the work temperature can be monitored and kept constant, in order to not create undesirable parasite effects. This was performed by a digital thermostat, attached to the sample, designed and realized in our laboratory. This thermostat is based on the Atmega128 microcontroller, following these guidelines: interior and exterior temperature measuring using two temperature sensors; display of these two temperatures using two ±XX.X format displays; setting of interior temperature in 0.1°C increments. During temperature setting phase the exterior temperature display switches to requested temperature display. A cooling or heating output is turned on if measured temperature is greater or less than the requested temperature by 0.5°C. Power is supplied by standard power grid (220V/50Hz). After the computer layout was made, the layered circuits were printed. Advantages of this system are the scalability, stability and low cost. Temperature acquisition operation comprises calibration,

the voltage-temperature variation characteristic, voltage necessary conversions for obtaining a [0,1]V output interval corresponding to the -50°C ... +50°C temperature interval, and a 25mV/°C sensibility at the output of the temperature acquisition system, and also sets temperature quantization in 0.1°C increments.

Under the laser light action, no longer than 300s, the temperature of the samples increased with almost 10°C, depending on the substance, and textures changed like in Fig.1, (at the polarizing microscope), showing a refractive index modification:

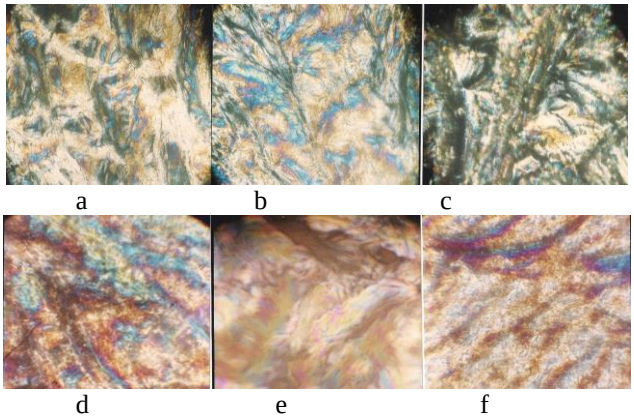


Fig.1. Elaidic acid. a) before laser action; b) after laser action, 48°C; c) after relaxation
Lauric acid. d) before laser action; e) after laser action 42°C; f) after relaxation

When an accordable $Ar^+$ ions (c.w.) laser was used, the temperature of the samples did not increase under laser beam, but a nonlinear feature of the dependencies of the emergent power versus incident power was evidenced, that showed the domination of the molecular reorientation mechanism in the refractive index modifications.The laser maximum power was 100mW, and the used wavelength 4880Å. Optical polarizing microscope evidenced a finely "chopped up" texture of the samples (Fig.2).

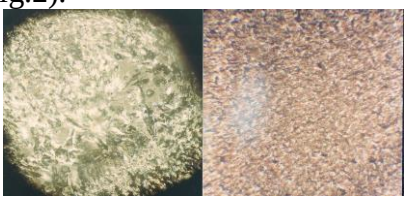

Fig.2. Microscopic aspects of the elaidic (left) and, respectively, lauric acids (right), under $Ar^+$ laser action

In all cases the incident/emergent optical powers were registered. Similar results were obtained for other wavelengths of the $Ar^+$ ions laser (5145 Å, 4765 Å).

## 4. Results and discussions

Experimental data were processed with TableCurve3D program for modeling experimental setup behavior.

The diode laser efficiency $\eta$ is:

$$\eta = P / IU(100\%) \tag{8}$$

where $P$ is the light emergent power (Fig.2). After adding the sample, the efficiency $\eta'$ has similar feature (Fig.3), but the attenuation $A$ of the radiation emerging from the sample:

$$A = (P_1 - P) / P(100\%) \tag{9}$$

($P_1$ being the emergent power in this case), decreased, when laser power increased (Fig.4). Therefore, substance becomes "more transparent" that leads to the mechanism of thermal nonlinearity consideration, as being dominant in this case. The efficiency saturated in both situations, i.e. the sample is not responsible for this saturation and we cannot increase the efficiency by increasing $U$ and $I$.

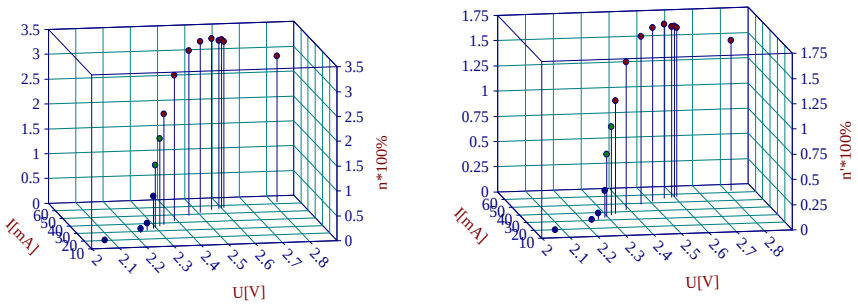


Fig.3 Laser efficiency $\eta$ versus applied voltage $U$ and current intensity $I$ and installation efficiency $\eta'$ versus applied voltage $U$ and current intensity

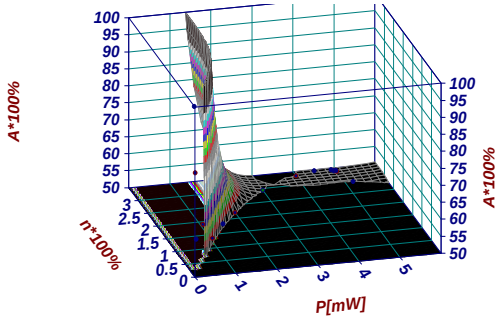


Fig.4 Attenuation $A$ versus efficiency $\eta$ and optic power $P$, in presence of the sample

The dependence between the optical output laser power and input one, experimentally applied on the samples of FA, is obtained by processing the experimental data with the computer program TC3D. This program can simply

provide a 3D graph of the required dependencies (similar with Fig.3), or also provide the most appropriate nonlinear equation which models the experimental behavior. Other useful amounts when fitting experimental data- standard deviation, residuals etc., are provided by this program, and give the possibility to appreciate and choose the most appropriate experimental conditions in terms of the future experiments requirements. An example is illustrated in Fig.5 for arachidonic acid, under diode laser action. T

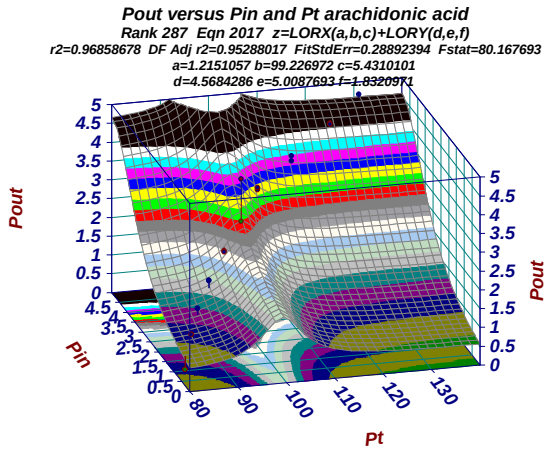


Fig.5 Emergent optical power $P_{out}$ versus incident optical power $P_{in}$ and theoretical power $P_t=UI$

The nonlinear equation is

$$z=LORX(a,b,c)+LORY(d,e,f) \quad (10)$$

where *a, b, c, d, e, f* are indicated on the figure.

The thermal nonlinear feature is similar for the other samples, both saturated and unsaturated.

By using a laser beam from a c.w. $Ar^+$ions laser, and processing the data, we obtained for both saturated and unsaturated FA some nonlinear dependencies of the emergent optical power $P_{out}$ versus the incident laser power $P_{in}$, in terms of the carbon atoms number. These graphs have different forms for the saturated (Fig.6) and unsaturated FA (Fig.7), in agreement with the different behaviour of the samples.

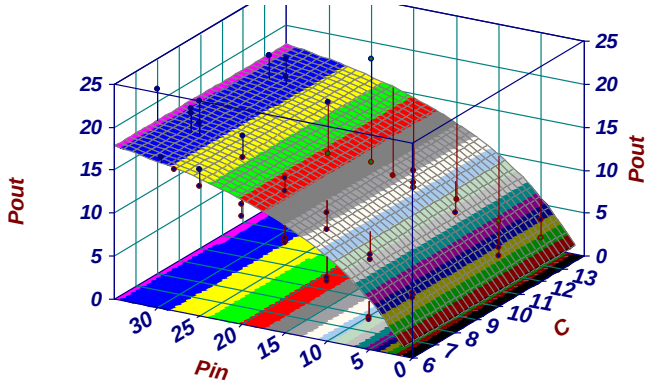


Fig.6 Nonlinear Gauss beams behaviour in terms of emergent optical power $P_{out}$ versus incident optical power $P_{in}$ and carbon atoms number $C$. Saturated acids

The equation is:

$$Z=a+GAUSSX(b,c,d)+LOGNORMY(e,f,g)+GAUSSX(h,c,d)*LOGNORMY(1,f,g) \quad (11)$$

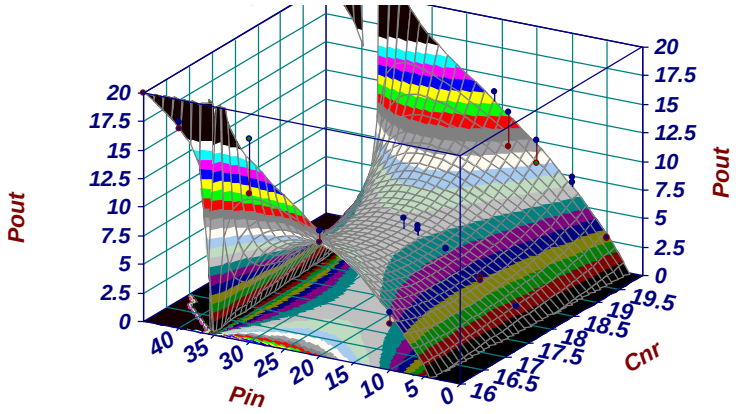


Fig.7 Emergent optical power $P_{out}$ versus incident optical power $P_{in}$. Unsaturated acids

In this case, the equation describing this feature is:

$$z = (a + b\ln x + cy + dy^2)/(1 + e\ln x + f\ln^2 x + gy + hy^2 + iy^3) \quad (12)$$

For instance, at a big number of carbons in saturated acids, a rigid microscopic texture was experimentally evidenced; on the contrary, in the case of the unsaturated acids, we found a more rigid texture at small C atoms number, evidenced also by the form of the graph.

We believe that the double bonds are in fact responsible for this difference [15] therefore the result is quite important for our purposes. It is known that, when

fatty acids are part of a phospholipid in a lipid bilayer, *cis* bonds limit the ability of fatty acids to be closely packed, and therefore could affect the melting temperature of the membrane. The more double bonds the chain has in the *cis* configuration, the less flexibility it has.

Taking into account the presence of both saturated and unsaturated FA in the living matter, the general nonlinear answer of these samples with different carbon atoms number, in the case of the molecular reorientation, could be unitary represented (Fig. 8):

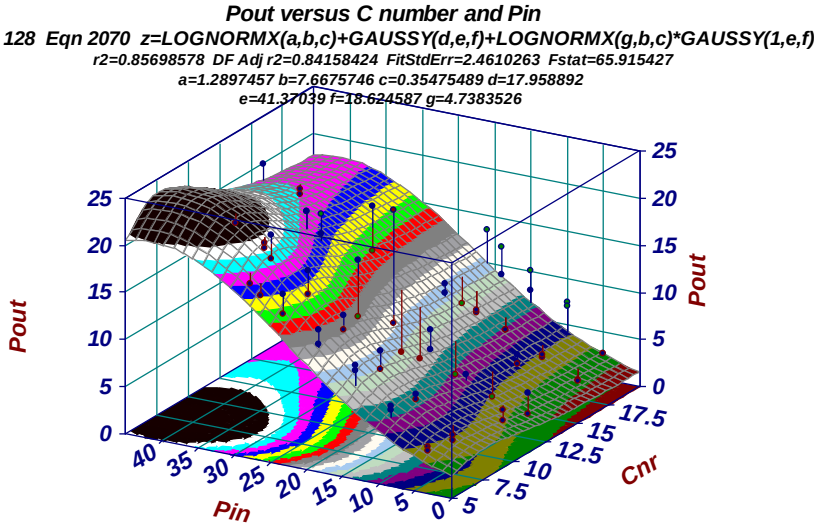


Fig.8 Emergent optical power $P_{out}$ versus incident optical power $P_{in}$ for saturated and unsaturated FA under $Ar^{+}$ laser action

The equation is:

*Z=LOGNORMX(a,b,c)+GAUSSY(d,e,f),+LOGNORMX(g,b,c)*GAUSSY(1,e,f) (11)*

These results, together with the ones obtained for the diode laser actions on FA, confirmed the possibility of inducing a nonlinear answer - based on the refractive index modification in laser field - of our simple membrane models, namely thin transparent sandwich cells of FA. This can be obtained or by thermal effects of the laser radiation, either by the molecular reorientation effect in the LC state of the FA.

## 5 Conclusions

The understanding of the membrane mechanisms, which are implied in various biological processes, can lead to answers to questions on the role of structural elements of the membrane making possible its specific operation;

factors determining the preferential transition selection through the membrane; influence of the environment on the membrane etc. The answer to these questions could lead to the understanding of some operation principles of nature, opening new possibilities in obtaining new materials and smart devices. According to the "fluid mosaic" model, the lipids and proteins constitute a mobile structure and their movement is due to the fluid nature of membrane filamentary surface. The fluidity of the membranes varies from some arrangements with large mobility to almost rigid layers in which molecular motion is limited. The membrane fluidity allows it to perform their functions [16, 17, 18]. Due to this property, connected with its mesomorphic state in some conditions, the biological membrane is a good medium for reaching a nonlinear behaviour. After studying and comparing the results presented in the paper and for other similar ones previously analysed by us, one can conclude:

-The samples of FA, which model a simple biological membrane, act as nonlinear materials, under laser beams action

-The efficiency of the measuring installation is not influenced by sample presence, which simply attenuates the laser light

-The heating of the substance due to the laser beam modifies the samples transmission, therefore the temperature should be computer controlled

- nonlinear optical effects emphasized by us can be evidenced both at low and higher laser optical power

- nonlinearities are in competition, the thermal one being dominant at red/IR laser light; for other smaller wavelengths, the molecular reorientation effect in LC is responsible for the nonlinear refractive index of the samples

- nonlinear effects - all kind of - could be used for leading the membrane composition and functioning

-computer processing emphasized the nonlinear feature of the membrane mechanisms and is useful for forecasting the behaviour of other systems of FA and other membrane models.

Similar and connected reactions in physical fields were reported for some other materials and systems, useful in practice [17, 18, 19, 20, 21, 22, 23, 24].

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