Theoretical Model of Polymer Plasma Laser Ablation

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Polymer plasma laser ablation has been investigated theoretically. An elegant mathematical tool using the fractal structure of space-time was developed. The model was verified with good accuracy on the existing experimental results.

Keywords: polymer, laser ablation, fractal space-time theory

Obtaining new materials or developing special techniques [1] for processing and increasing materials performance are well known common practices in contemporary scientific research.

The achievement of high-quality thin films is important in many applications ranging from material reinforcement to molecular electronics. In this sense, the laser ablation - a technique widely used to deposit a variety of inorganic materials - can be used as a versatile method for forming thin polymer films [2]. Also, the application of soft polymers laser ablation, for the creation of micron-sized containers of alkali metal in light-induced atom desorption experiments, becomes an accessible technique.

If ultraviolet radiation of a laser pulse interactions with the organic polymer surface, the material surface is spontaneously etched away to a depth of 0.1 to several micrometers. In particular, the depth of etching is controlled by the width of the pulse and the fluence of the laser, and there is no detectable thermal damage to the substrate [3].

In this study a theoretical investigation of polymer laser ablation was performed. The model developed here describes only the dynamics [4-5] of a polymer plasma plume generated by laser ablation and not the chemical transformations that occur during the treatment.

Experimental part

Mathematical model

Let us suppose that the motion of the particles takes place on continuous but non-differentiable curves, *i.e.* on fractals [6]. The "non-differentiability" in the topological dimension D_F implies the replacement of the standard time derivative d/dt by a new complex operator $\partial/\partial t$ (for details see [7-9]),

$$\frac{\hat{\partial}}{\partial t}=\frac{\partial}{\partial t}+V\cdot\nabla-i\frac{\lambda^2}{2\tau}\left(\frac{dt}{\tau}\right)^{\left(\frac{2}{D_F}\right)-1}\Delta \qquad (1)$$

where V is the complex speed field, dt is a time resolution, τ is a fractal – non-fractal transition time and λ a characteristic length scale. Unlike the classic manner [10-11], we are now able to write the conservation law of a fractal function ε in a fractal space-time under its covariant form:

$$\frac{\hat{d}\varepsilon}{dt}=\frac{\partial\varepsilon}{\partial t}+V\cdot\nabla\varepsilon-i\frac{\lambda^2}{2\tau}\left(\frac{dt}{\tau}\right)^{\left(\frac{2}{D_F}\right)-1}\Delta\varepsilon=0 \qquad (2)$$

or more, by separating the real and imaginary parts,

$$\frac{\partial\varepsilon}{\partial t}+V\cdot\nabla\varepsilon=0\ ,\quad -U\cdot\nabla\varepsilon=\frac{\lambda^2}{\tau}\left(\frac{dt}{\tau}\right)^{\left(\frac{2}{D_F}\right)-1}\Delta\varepsilon \qquad (3a,b)$$

Consequently, at the differentiable scale the local temporal variation, $\partial\varepsilon/\partial t$, and the term $V\cdot\nabla\varepsilon$ are equal, while at the non-differentiable scale, the terms $U\cdot\nabla\varepsilon$ and $\Delta\varepsilon$ compensate each other.

Particularly, for $V=U$ (*i.e.* "synchronal" movements at differentiable and fractal scales), from (3a, b) we get the diffusion type equation,

$$\frac{\partial\varepsilon}{\partial t}=\frac{\lambda^2}{\tau}\left(\frac{dt}{\tau}\right)^{\left(\frac{2}{D_F}\right)-1}\Delta\varepsilon \qquad (4)$$

Such an equation is implied by the Fourier type law

$$j(\varepsilon)=\frac{\lambda^2}{\tau}\left(\frac{dt}{\tau}\right)^{\left(\frac{2}{D_F}\right)-1}\nabla\varepsilon \qquad (5)$$

with a current density $j(\varepsilon)$. Therefore, eqs. (4) and (5) describe the fractal fluid of conductive type behavior.

Particularly, for movements on fractal curves of the Peano's type, *i.e* in the fractal dimension, $DF\equiv 2$ (for details see [12-17]), the equations (4) and (5) take the standard forms

$$\frac{\partial\varepsilon}{\partial t}=\frac{\lambda^2}{\tau}\Delta\varepsilon \qquad (6)$$

and respectively

$$j(\varepsilon)=\frac{\lambda^2}{\tau}\nabla\varepsilon \qquad (7)$$

If ε is identified with the transient ionic current, I, then equation (6) becomes:

$$\frac{\partial I}{\partial t}=\alpha\Delta I\ ,\ \alpha=\frac{\lambda^2}{\tau} \qquad (8a,b)$$

In the one-dimensional case, the general solution can be written in the form:

$$I=A+Bx+e^{i\omega t}\left[Ce^{(1+i)\sqrt{\frac{\omega}{2\alpha}}x}+De^{-(1+i)\sqrt{\frac{\omega}{2\alpha}}x}\right] \qquad (9)$$

For establishing the values of the constants A, B and C is necessary that I to be finite for $x=\infty$. In this case, $B=C=0$ and $A=T_\infty=T_0$.

Making the following notations:

$$\sqrt{\frac{2\alpha}{\omega}}=\delta\ ,\ \sqrt{2\alpha\omega}=\nu\ ,\ D=\tilde{T} \qquad (10a,c)$$

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we obtain finally

$$T = T_0 + \tilde{T} e^{-\frac{x}{\delta}} \cos\left(t - \frac{x}{v}\right) \quad (11)$$

and in the plane $x = 0$, in which the perturbation occurs,

$$T(0) = T_0 + \tilde{T}' \cos\omega t \quad (12)$$

From relation (11) it results that the amplitude T of these waves decreases exponentially with the distance.

Since the plasma is quasineutral, the fractal force [18-20]

$$\boldsymbol{F} = -\nabla Q \quad (13)$$

where Q is the fractal potential

$$\tilde{Q} = -m\frac{\boldsymbol{U}^2}{2} - m\frac{\lambda^2}{2\tau}\nabla\cdot\boldsymbol{U} \quad (14)$$

must be null.

In such context, $x=ct$ and the solution (11) describes waves whose amplitude is exponentially decreasing with time [21].

Results and discussions

An excellent experimental investigation of the laser-ablation modification of diblock copolymer films having nano-scale microdomain structures has recently been made [22]. The authors used a thin diblock copolymer, polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP), film doped selectively with tetrakis(4-carboxyphenyl)porphine (TCPP) into the nanoscale spherical domains of P4VP as a target polymer film. As expected the transient ionic current recorded by the Langmuir probe has multi-peak structure.

In figure 1 the ionic currents oscillations, experimental points and theoretical curve on a single graph, are shown.

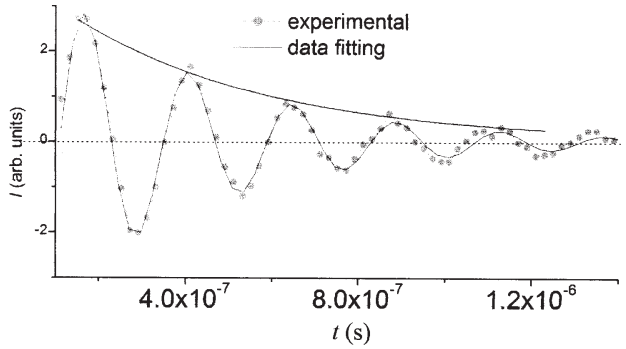

Fig. 1. The temporal ion current oscillations

The velocity of the plasma formation has been calculated by measuring the position of the maximum emissivity at different times. For the plasma structure it amounts $v_i = 4.66 \cdot 10^4$ m/s.

According to our experimental data, the amplitude exponential decay factor is $\delta(t) = (4.16 \pm 0.34)$MHz (fig. 2) and the oscillations period is $T = 1 / \delta(t) = 240$ ns. The velocity calculated of the polymer plasma plume, for $\alpha = 46 m^2/s$, is $v = \sqrt{4\pi\alpha\delta(t)} \approx 5\cdot 10^4\, m/s$.

Therefore, the present theoretical model is fitting very well the experimental data.

Conclusions

The laser ablation of the polymers is theoretically investigated. A mathematical model is elaborated using the fractal space-time theory.

Also, the experimental results of the laser-ablation modification of diblock copolymer films having nano-scale microdomain structures were analyzed.

A good correlation between the experimental data and the theoretical model was highlighted.

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