

Non-resolved problems of theoretical and applied plasma chemistry

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Abstract

The main problems of the foundation of theoretical and applied unequilibrium plasma chemical reactions and processes are considered. Up-to-date state and perspectives of the plasma chemical evolution (gasphase and multiphase processes and phase transitions) are analysed.

Approximately twenty years ago took place first international Symposium on plasma chemistry; the number of participants was seventy nine. The tenth Symposium in 1991 had four hundred eighteen participants. It is interesting to analyse now these years plasma chemistry evolution. The first decade of this period was dedicated mainly to the investigation of gaseous (one phase) plasma chemical processes and the second - to two-phaseous- gas- solid- and transitions between these phases in various types of plasmas.

I want at the beginning to remind you the results of experimental and theoretical study of plasma chemical reactions and the processes in gaseous phase. What are the general specific features of plasma chemical systems? A plasma chemical system is open, unequilibrium, nonstationary, and the processes (particularly chemical reactions) in such a system are non-linear. The open character of plasma chemical systems and their unequilibrium structure are especially important.

One hundred twenty years ago Darwin created the theory of evolution from simple to complicated structures, and Boltzman created the theory of vice versa evolution from complicated to simple structures and finally to chaos (Wärmetod). Darwin's theory was founded on many (biological) data, Boltzmann's theory was founded on principles of physical and mathematical analyses. Why does such a contradiction exist? The answer is clear. Darwin's theory supposes the interaction of the investigated system with the surroundings (an open system); Boltzmann's theory describes a closed system. The situation principally changes if Boltzmann's thermodynamical theory is applied to open system.

Entropy flux out of and into the open system may have various signs and the sum of changes of inner production and outer entropy flux may be positive or negative. But the last case is the formation of order or strictly speaking new structures - the so named process of self-organisation. The thermodynamically forbidden processes can take place in such an open unequilibrium system. The characteristic features of plasma chemical processes are:

- a) high energy density (volume and surface)
- b) unequilibrium (nonmaxwellian, nonboltzmannian distribution functions of particles for the translatory energy and the population of quantum levels)
- c) the leading role of electrons, excited molecules, ions, radicals in chemical processes
- d) multichannel type of processes in reacting systems.

Plasma chemical reactions (in electrical discharges particularly) as a rule proved to occur under non-equilibrium conditions and to create non-equilibrium themselves. Reactions of charged particles and electronically, vibrationally and rotationally excited molecules and their fractions play a very important if not principal role; chemical reactions under plasma conditions result in particles which have non-equilibrium distributions, are "hot" or have "strange" valency correlations etc.

Detailed studies show us that:

1. Relaxation of population distributions by vibrational levels of the ground electronic state for example of $X^1\Sigma_g^+$ of the molecule N_2 under the process (e-V) is non-equilibrium in character and proceeds through a sequence of quasi-Boltzmann distributions.
2. The kinetics of vibrational relaxation over various levels and molecular dissociation, accounting for (e-V), (V-V), (V-T) processes, can be calculated by a direct solution of the system of kinetic equations.
3. It was shown that dissociation can essentially affect the population distributions of the upper vibrational levels of the molecule.
4. Velocity ratios for (e-V), (V-V), (V-T) processes under the constant values of T_e and T_g depend on level population and vary with time during the relaxation process. For these processes it is necessary to give the full description of gas plasma chemical reactions. This description can be deterministic or stochastic. For the first we have the Pauli or Boltzmann equations, and the Langevin equation for the second one. Pauli equation variables are concentrations of reagents and products - macroscopical quantities which are measured in chemical kinetical experiments. The variables of the Boltzmann equation as is well known are functions of molecular distributions upon the velocities (energy) and space (coordinates). The Pauli equation is one from the so named "master equations". Pauli equation for the change of concentrations on level i with time:

$$\frac{dn_i}{dt} = \sum \omega_{ij} P_{ij} n_j(t) - \sum \omega_{ji} P_{ji} n_i(t) - k_i n_i(t) + R_i(t)$$

flux on level i from all other levels	flux from level i an all other levels	chemical reaction from i -level	velocity of i -level excitation
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There are various program packets for solutions of this equation on computer in complicated cases.

The coefficient of chemical reaction rate k_i in the third term of Pauli equation depends on σ_i -cross-section, and f_i -function on energy distribution. For the simple case: dissociation of two atomic molecules in gaseous thermostate, with taken into account only the vibrational degrees of freedom for the i -th vibrational level is

$$k_i = \int \sigma_i v f_i d^3v.$$

From the physical point of view an essential difference between k_i and k is emphasized. k_i is a fundamental quantity describing any given molecular chemical reaction through the cross section $\sigma_i(E)$. Strictly, k_i depends upon the molecular interaction potential defined for given quantum states and energy distribution functions. k_i is the only rate factor for the elementary chemical reaction. The rate factor k , as measured in a chemical experiment, is always a complex parameter depending on σ_i and f_i and upon level populations, and may coincide with k_i only very rarely. Such occasions are most likely under low temperature conditions and for slow reactions (particularly thermoneutral). In general, k depends upon the level populations, for example, upon concentration of molecules in given quantum states. These concentrations vary widely. Evidently k changes with temperature (even under Maxwell-Boltzmann distribution conditions) because of changes of various k_i contributions into k .

Plasma chemical reactions in the gas phase are characterized by the following:

Non-elastic collisions are more important in "hot" gases than in ordinary gases, the properties of which are described well by the kinetic theory based upon the consideration of only elastic collisions.

The difference between the characteristic times of various physical and chemical processes decrease; consequently:

Chemical kinetics can not be considered independently of physical kinetics.

Multichannel processes should be considered in plasma chemical kinetics.

Non-equilibrium effects may be observed in systems initially in equilibrium if all processes are occurring with a finite rate within the system.

Taking into account chemical reactions, the equilibrium establishment process becomes still more complex because of endothermicity or exothermicity of reactions involved and variations in particle densities (due to association and dissociation) in every element of the space. To study the mechanisms and kinetics of a chemical reaction under non-equilibrium conditions, it is necessary to know cross-sections of all the processes, their dependence on the energy of the reacting particles, the energy distributions of these particles and the evolution of such distributions with time.

There are well known conditions in which translational, vibrational and rotational temperatures differ and/or various components of a system (electrons, ions and excited neutral molecules, for instance) have different energies (temperatures) and/or a system can not be described at all using the concept of temperature (non-equilibrium, stationary and relaxing systems). Strictly speaking, Arrhenius-type kinetics can not be used in these cases and the ordinary expression for the rate of a chemical reaction is inapplicable.

Multichannel processes should be considered in plasma chemical kinetics. From the quantum mechanical point of view (we shall consider only two channels for simplicity), in a certain energy range two pairs of particles (A_1, B_1) and (A_2, B_2) can exist, so that there are two independent wave functions which satisfy boundary conditions for a given system. It is known that in one channel problems the S-matrix contains all the information about interaction properties of the system, while in a multichannel case a similar theorem has not yet been proved. Moreover, in order to compose the Hamiltonian using the results of scattering all components of the S-matrix should be known for all energies.

In glow discharges (in the region of the positive column) the following conditions are realized: stationary distributions of electrons and heavy particles with energies are set, but in this case the average energies of electrons exceed by one or more orders of magnitude those of the heavy particles. The effect of the electron distribution on the velocity of a chemical reaction was obtained from the analysis of numerous experiments.

Formation of stationary non-equilibrium conditions in reacting multicomponent systems usually takes place in glow and analogous discharges (under low pressure). A commonly used way to explore non-equilibrium plasma chemical systems consists of manipulations with electrical discharges of direct (DC) and alternating (AC) current with various geometries, high (HF) or radio (RF) frequency discharges, ultra high or microwave (MW) discharges, complex systems with so called removed and hybrid plasma, UV and IR irradiation. New methods which are perspective for industrial purposes are non-equilibrium MW discharges in large volume under atmospheric pressure (USSR), quasi glow AC atmospheric discharges in a small gap in helium gas buffer (Japan), complex systems including simultaneously lasers, gaseous plasmas of different types and non-equilibrium surfaces and systems with a controllable electron beam.

The main source of the non-equilibrium appears to be an energy flux penetrating the system. This flux, branching into multichannel due to an intrinsic structure of components and particles compiling the system, creates all the complication of physical and chemical interactions. The final result of the evolution of a system depends not only on the magnitude but also on the method of energy supply. The distinction of plasma chemical systems consists of the use of electrical fields as an energy transfer method.

The variety of reasonable and potential methods of energy supply through the electrical fields creates a multiplicity of discharge types for practical applications.

The self-consistency of electrical fields and charges (and more complicated physical-chemical self-consistency) restricts the extent of the potential variation of the intrinsic discharge parameters in every particular reactor and discharge. So the way to disrupt these limitations consists always in the development of new reactors with more precise control of intrinsic discharge parameters. Experimental kinetic investigations based on diagnostics and modelling of the kinetics and the mechanisms of the processes carried out in discharge systems can give the direction for that development.

Mathematical modelling kinetics of physical-chemical processes in glow discharges was investigated in the pressure range of 0,1 - 4,0 torr, the energy range 10^{-3} - 10^{-1} w/cm³, in mixtures of Ar +2,90 vol% CH₄, C₂H₆ and other hydrocarbons. The diameter of the reactor was 5 scm. Collision electron-heavy particles: excited molecules and atoms, new electrons and positive ions, hydrocarbon radicals, H-atoms. In reactions of the products of decomposition and of plasma molecules are originated gase phaseous products, and in reactions of active particles at surfaces of the reactor and electrodes-polymer film. For the description of such processes we have a program packet and algorithms: 1) Definition of the function of the electron energy distribution from stationary Boltzmann's equation with e-e collisions, and collisions of second type and its momentums (mean electron energy, coefficients of chemical reaction rate and another); 2) Description of kinetics of active plasma particles; 3) Modelling kinetics of chemical reactions: dissociation and formation of various products polymer film and gaseous, adsorbtion and reaction (heterogeneous) at the surfaces of the reactor walls.

A new method of self-consistent modelling is developed: correlation of processes of physical kinetics (ionisation, transfer of charged particles in plasma, reaction of out discharges chain on kinetics of electrons etc.) and chemical kinetics. Results of such new method of modelling give us the possibility to connect external and inner parameters of a reacting unequilibrium plasma. If we know the external parameters of a discharge (pressure, power, running time, reactors size etc.) it is possible to obtain kinetic curves for the concentrations of neutral and charged particles, deposition rates of polymer film growth, its elemental composition, coefficients of chemical reaction rates under electron attack. The coincidence of this calculation with experimental data is sufficiently good.

There exist two types of plasma chemical reactions in thermal plasmas:

- a) Processes in which end products are final at high temperatures and thermodynamically allowed under equilibrium conditions. Examples: formation of NO in air plasma jet, TiN from tetrachlorid titanium.
- b) Processes in which end products are intermediate products of chemical reactions. Examples: production of acetylene from hydrocarbons (especially methane), tetrafluor-ethylene from tetrafluormethane.

For processes of this type, a study of the reaction kinetics, as well as the determination of reaction time, are of great importance: quenching requirements follow from the kinetic processes. Not only the quenching rate, but also the time of quenching imposed, are of decisive importance.

But in cases when the methods of chemical kinetics can be thought to be applicable, the studies on chemical kinetics of the system present difficulties in that the rather high velocities of chemical reactions at the temperatures under consideration can depend to a considerable extent on velocities of physical processes such as the diffusion (molecular) and turbulent transfer, the microscopic mixing of the reacting systems' components.

Hence plasma chemical kinetics include without exception a study of the mixing of the reacting gases. To study this problem combined equations of hydrodynamics and chemical kinetics should be solved, using similarity theory methods as well.

Plasma chemical processes hold particular promise for the industrial realization of chemical reactions possessing the following characteristics: 1. new unique structures and properties of solid materials, especially surface properties are obtained (for examples ultra dispersed powder films, ion implantation, surface modification) under substantially non-equilibrium conditions.

2. equilibrium is shifted to high temperatures and reaction rates are sharply increased with temperature increase.
3. widely accessible and low-cost raw materials, unstable in composition, are used. There are great promises in the field of obtaining pure and super-pure (e.g. conductors) materials, since purity of products during plasma chemical processes in high-frequency and microwave plasmas is determined by the purity of source materials only and even purity can be increased during the process without any additional expenses.

At present, the low-temperature plasma affords the possibility of conducting chemical processes at temperatures up to $15\,000^{\circ}\text{K}$, electron energy 0,5 - 10 eV, pressures ranging from 10^{-4} to 10^3 atm, under both equilibrium and non-equilibrium conditions. Low-temperature plasma can be used in chemical reactions as

1. A source of extremely concentrated specific energy, in other words, of heat content at high temperatures;
2. A source of positive and negative ions, potential precursors for ion-electron and ion-molecule reactions;
3. A source of luminous radiation for photochemical reactions.

Now I want to give a more detailed description of two phaseous plasma chemical reactions, the study of which were chief fundamental problems in the last decade and their applications in ultra dispersed pulvers, coactings, films. They are widely spread in industry, medicine and various other practical problems.

Principally new in plasma chemistry theory was the investigation (experimental and calculative) of problems of two phaseous plasma jets (gas + solid) and plasma chemical heterogenous reactions on the surfaces of solid macroscopic particles in plasma streams and at the walls of reactors and at electrodes.

Interaction between charged and neutral particles and macroscopic surfaces-adsorption, excitation, desorption, chemical reaction, lateral diffusion - is a complicated complex of various mutually influencing physical-chemical processes, especially in electromagnetic fields. Kinetics and mechanisms of physical-chemical processes in low temperature reacting plasma with dispersed phases are investigated from theoretical and practical points of view.

A new model was developed which describes simultaneously occuring processes of the initial decay, nucleation, surface growth and coagulation of macro-particles of various sizes. The model permits to find the size distribution of "primary" macroparticles up to sizes of 30-40 nm, using a relatively small set of equations. The computed time dependence of macroparticles concentration and size distribution agrees satisfactorily with available experimental date. The existence of two limiting stages of macroparticle formation is revealed.

The structure and properties of ultradispersed particles are so specific that many authors propose to name them fifth aggregate state of matter (gas, fluid, solid, plasma, ultra-dispersed particles).

Although random Brownian motion is supposed to be the simplest collision mechanism for ultradispersed particles, the conditions in thermal plasma reactors may influence the other factors, which would essentially increase the collision rates and specifically the electric charges action, London - van-der-Waals forces actions, the actions of thermo-diffusion and diffusion, causing the transversal gradients. A thorough description of these effects requires more detailed exploration of the powder plasma synthesis.

The detailed description of physical and chemical processes taking place in a homogeneous plasma is recently workable only for some comparatively simple cases. The presence of surfaces contacting the plasma brings about an appearance of a series of new phenomena and a further complication of the general picture.

During the plasma-surface interaction the most essential factors are of two phase nature of interaction and of discharge structures, properties of near-surface layers of both plasma and substrate. The overall interaction of plasma processes, including excitation and quenching, appearance and losses of charged and neutral particles, chemical reactions and so on with surface processes, including practically all possible phenomena taking place in liquids and solids and at their interfaces, create much more complicated systems.

That mentioned above prescribes a practically available general approach for studying those systems. The approach consists of discriminating the most important factors and the phenomena determining the kinetics of the overall processes, and the use of achievements and experimental data obtained in adjacent fields of plasma chemistry.

A comparative analysis of some phenomena assigned to such plasma chemical processes as the synthesis of ultradispersed powders and inorganic films in thermal and non-equilibrium plasmas, etching of different materials, plasma or gas discharge polymerization and so on allows a more clear understanding of the mechanisms of deposition in various systems under a wide range of intrinsic conditions.

There are correlated surface phenomena in the kinetics of film growth and etching - adsorption and desorption, sputtering and condensation, polymerization and ablation. The relative role of each of them depends on the relative role of such surface characteristics as lateral diffusion, rate constants of chemical reactions, the rate of neutralization of electrically charged sites etc. In general, plasma chemical inorganic coatings and powder formation have three possible ways to convert a gas phase into the condensed one:

1) homogeneous nucleation; 2) condensation of existing particles; 3) heterogeneous nucleation on surfaces.

The combination of fast high temperature (high energy) reactions with rapid quenching being realized usually under plasma conditions promotes an implementation of the homogeneous nucleation. The beginning of particles or films growth may occur through the mechanisms 2) and 3) or a coagulation. A chemical generation (or a consumption) of initial compounds may be included as a source term into the kinetic equation of the process (compare with the equation for photochemical aerosols).

From a general consideration concerning the process of formation of dispersed condensed systems it is clear that the most favourable conditions are the following:

high energy, short time of the process, uniform velocity distribution in a stream or jet. These conditions are valid for the formation of fine microparticles. But they are applicable for some high rate deposition processes as well.

There are a lot of deposition processes realized under low pressure glow discharge type conditions. Several basic problems still exist especially with processes taking place on reactive surfaces. These problems are very close to their elucidation in studies of plasma chemical etching but they are far from being understood especially in plasma polymerization.

Example:

Table 1. Parameters of TiN micro-particles

	<u>Method of formation</u>	
	traditional	plasma chemical
	(1)	(2)
Temperature of reaction	1500 K	4500 K
Time of process	10^4 s	10^{-2} s
Diapason of particle size	10-100 μm	0.01-0.1 μm
Structure and form of particles	polycryst. fragmental	monocryst. cubic
Parameter of crystal lattice	0.4245 nm	0.4237 nm
Critical temperature of superconductivity	4,8 K	5,6 K
Critical magnetic field of superconductivity	1	20-25
Temperature of oxidation beginning	1100 K	600 K
Temperature of recrystallisation	1600 K	600 K
Temperature of fool curdle	2000 K	1300 K

Table 2. Basic reactions occurring in a plasma which control either the deposition or the etching of thin films

1. Electron impact reactions such as	
Excitation R, v, ϵ	$e + A_2 \rightarrow A_2^* + e$
Dissociative attachment	$e + A_2 \rightarrow A^+ + A^- + e$
Dissociation	$e + A_2 \rightarrow 2A + e$
Ionization	$e + A_2 \rightarrow A^+ + 2e$
Dissociative ionization	$e + A_2 \rightarrow A_2^+ + A + 2e$
2. Inelastic collisions between heavy particles (volume reactions)	
3. Heterogenous reactions (S-solid surface in contact with plasma)	
Atom recombination	$S - A + A \rightarrow S + A_2$
Metastable deexcitation	$S + M^* \rightarrow S + M$
Atom abstraction	$S - B + A \rightarrow S + AB$
Sputtering	$S - B + M^* \rightarrow S^+ + B + M$

One of the reasons for these circumstances consists in the lack of experimental approaches and methods of diagnostics specially designed for investigations of these processes and their very fine surface stages and complicated gas phase chemistry.

Some principal results were achieved due to the development of new electrical kinetic probes enabling to discriminate the relative roles of charged and neutral (Italy, Germany) particles and electrical fields in the kinetics of surface stages of thin films processing. It appears that electrical fields in a bulk near surface layer of etching or growing films directly effect films growth rate and hence their structural features.

A gas dynamic and a gas phase plasma chemical kinetics of low pressure electrical discharges are still not under serious consideration. But many difficulties in investigations and in the optimization of plasma chemical processes are common to chemical types of low pressure reactors: neither ideal mixing, nor ideal replacement. An improvement of the geometry and flow characteristics of plasma chemical reactors allows to improve essentially the characteristics of deposition processes.

One example: Plasma-surface interaction was systematically studied under well defined kinetic conditions of a capacitively coupled gas flow type RF discharge to reveal features of plasma polymerization mechanism. Kinetic investigations of gas and surface processes in a wide range of residence times were carried out by means of gas chromatography and chromatomass-spectroscopy, optical emission and IR spectroscopy. It was established that films growth rate does not correlate with the concentrations of stable unsaturated products like as C_2F_4 , C_3F_6 , C_4F_8 , C_5F_{10} etc. Surprisingly it correlates with saturated products like CF_4 , C_2F_6 , C_4F_{10} , which are not the source material for film formation. The residence time does not determine completely gas composition and film-growth rate: both the residence time and the gas flow rate are essential. The gas phase synthesis starts immediately at the gas input (first milliseconds) along with a decomposition of the starting material into light radicals. These radicals (including CF_2) do not play an important role in the surface stages of film formation, as it was usually supposed in literature, but especially in a gas phase radical synthesis of heavy products. An atomic fluorine demonstrates considerable participation in the gas phase chemistry and especially in radical synthesis. The results obtained are sufficiently new and interesting for investigations of plasma-surface interaction during thin films processing under low pressure non-equilibrium plasma conditions.

Plasma deposition is of particular interest since by this technique film deposition can be achieved at low temperatures which are needed to prevent diffusion of shallow functions and interdiffusion of metall. Of the large number of monomers investigated, it appears that the most promising are silicon nitride deposited at about $600^{\circ}K$ for passivation of devices, silicon dioxide deposited at $500^{\circ}K$ for insulation between metall layers or for the masking of multilevel resist structures and amorphous silicon deposited at $320 - 500^{\circ}K$ for solar cells.

The most important raw material for these films is silane. By reaction with ammonia or N_2 it forms silicon nitride, with nitrous oxide it forms silicon dioxide, it decomposes to form amorphous silicon when dopants are added such as diborane or phosphine.

There exist two types of mechanisms for plasma film deposition. A completely conformal coverage is obtained when reactant adsorb and quickly move along the surface before they react. Such rapid migration is found to yield a uniform surface concentration, regardless of topography, and provides a uniform thickness as well.

Another type of coverage takes place when gases adsorb and react without significant migration along the surface.

While the main reason for using the electron kinetic energy in plasma in place of the thermal energy in chemical vapor deposition is to avoid excessive temperatures, there are usually a number of additional benefits in plasma deposition, such as adhesion to substrates which is generally much higher than obtained in chemical vapor deposition, and the ability to dope in fairly quantitative modes and include well-measured comonomers in the feed and the film structure. It is generally observed that one can adjust the composition,

and the physical and electrical properties of films over a considerable range more easily than in any other deposition technique. This is most useful in optics, fiber optics and integrated optics. As example we numerate some applications of plasma films in industrial fields:

Membranes for ion exchange purposes with selective permeability for gases and solutions, biomedical applications for compatibility with biological tissue as protective coating and for delayed release medicinal tablets; optics as coatings for lenses and various substrates for wave guides, integrated optics and optoelectronics; devices in electronics and integrated circuits; detoxification; air and water pollution; contaminant removal; wear and chemical-resistant coating of surfaces; waste conversion; etching; desalination; oxidation; adhesion to metals, polymers, fibers; laser; advanced composites, enhancement of strength and wear; solar energy conversion; ion implantation into metals; passivation of silicon devices; for piezoelectricity; for hardness: high-temperature resistant surfaces; for antistatic magnetic recording tapes; for antireflection; imaging devices; photoresist films; insulating films, etc.

Considerable attention has been paid to plasma polymer films because this technique is feasible and economical and equally important; it provides films which exhibit a high integrity and are generally pin-hole free. Another significant aspect is the relative ease by which such films can be chemically modified and/or doped to impart specific properties. Another common property of plasma-deposited films is their relatively high degree of cross-linking providing high environmental resistance and the general tendency of such films to adhere firmly to their substrates and to be resistant to wear and abrasion.

CONCLUSION

It is, of course, impossible to analyse in this short report all or even most part of non resolved plasma chemical scientific and technological problems. We must and can only shortly mention some more or less important problems, the solution of which is necessary for future plasma chemistry development (end of XX. century).

We can now enumerate some of these problems:

1. The surroundings of open plasma chemical system must be unequilibrium?
2. The correlation of chemical reaction rate and energy of braking relaxation processes?
3. The correlation of outer and inner parameters of plasma chemical system?
4. The prediction of structure and properties of ultra dispersed particles received by phaseous transition in non-equilibrium reacting plasma chemical system?
5. The influence of structure (chemical and energetic) on formation new chemical molecules and solid phase bodies (ultra dispersed particles, films, etc.)?
6. Adsorption and lateral diffusion - "condition sine qua non"?
7. Role of layers near surface in and/or out surface layer?
8. Description of heterogeneous reactions at surfaces of ultra dispersed particles, walls, electrodes?
9. Deviation of plasma chemical processes from the deterministic curve as result of fluctuation characteristics - amplitude and livetime?

One may recall Bellman's well-known remark, which states that when building up the theory one must avoid the desert of oversimplifying and the marsh of overcomplicating. Plasma chemical technology is the technology of to-morrow, but to-day we have only a vague idea of the truly boundless possibilities for utilisation of unequilibrium and quasi-equilibrium low-temperature plasmas in new chemical processes, creation and modification of materials and other applications in various branches of the industry, ecology and medicine. Remember, dear colleagues, that in our cosmos 99,99 % of matter exist in the state of plasma and mankind and universe are of the same entity.

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