Aerogel structures in a gas

A. A. Lushnikov, A. E. Negin, A. V. Pakhomov, and B. M. Smirnov

L. Ya. Karpov Physicochemical Institute, Moscow
Institute of High Temperatures, Academy of Sciences of the USSR, Moscow
(Submitted 1 October 1990)
Usp. Fiz. Nauk **161**, 113–123 (February 1991)

Fractal filaments, which are fractal structures formed as a result of relaxation of a plasma evaporated from the surface of a metal in an external electric field, are considered. The physical properties of systems of this kind, their formation under natural conditions, and potential applications are discussed.

The growth of science changes the nature of propositions representing the content of a given science. As new experiments accumulate, some statements cease to be categorical because practice reveals exceptions from general rules. This is true also of the physics of the state of matter. From the beginning of physics to our century it has been assumed that matter is in three states: gaseous and two condensed (liquid and solid). Plasma is said to be the fourth state of matter. In fact, it fits within the framework of the three states. In fact, an ideal plasma is a gas with a long-range interaction between the particles and a nonideal plasma is equivalent to a condensed state of matter. Thus, at this stage it is sufficient to use the three states of matter to describe plasma.

However, modern physics gives a number of examples which do not fit this simple framework. By way of such an example we shall consider a gas containing clusters which consist of up to hundreds of atoms or molecules. Such a system is not disperse, i.e., it is not a gas which contains macroparticles. In fact, clusters are not macroparticles,[1)] so that the system does not belong to any of the three states of matter or their mixture.

Another example is a porous substance. As long as pores represent a small fraction of a substance, it is natural to regard it as condensed. However, if the fraction of the condensed substance represents only a small proportion of the volume of a porous body, it is difficult to consider it within the framework of the three states of matter.

Such highly porous materials include a thoroughly investigated class of aerogels.[1,2] The first stages of preparation and investigation of aerogels date back to the thirties[3] and considerable experimental data have been accumulated on the properties and behavior of aerogels. These data show that there is approximately a dozen oxides which can form aerogels. These oxides are characterized by the strongest chemical interaction and form the most thermally stable solid substances in the form of ceramics. The strong chemical interaction between the oxide molecules accounts for the stability of the aerogels of which they consist.

Aerogels are formed as follows. A chemical process occurs in a solution and is followed by hydrolysis which produces oxides in the form of macroparticles of the nanometer size. These particles combine with one another forming macrostructures and these are known as aerogels. If the process occurs at low temperatures and pressures, then the molecules of the solution accumulate in the pores of an aerogel. These molecules disturb stability of the aerogel and cannot be extracted from the pores because of the high energies of interaction with the aerogel particles. This is avoided by performing the process at high temperatures and pressures of the solvent, which exceed certain critical values. For these reasons the technology of manufacture of aerogels is complex and expensive. Since the pressure in an autoclave where an aerogel is formed is high, the density of the resultant aerogel cannot be too low. In practice it cannot be less than 10 g/liter.

It would seem that the difficulties encountered in the making of aerogels and the conditions of their formation would make these substances exotic. However, there is a different method of formation of such structures which takes place in the gaseous phase (including atmospheric air) when a plasma, formed as a result of evaporation of a part of a surface, escapes into space. Clearly, such a process must frequently occur in nature. We shall consider structures of the aerogel type formed in the gaseous phase. Such structures are of general physical interest as systems with unusual properties. They are objects with a highly developed surface and, from the point of view of the state of matter, they cannot be classified as any one of the classical free states or their mixture, although in an analysis of some of their properties we can use the model of a disperse substance. Structures of the aerogel type formed in the gaseous phase have special properties. Some of them will be discussed below.

Macroscopic structures of the aerogel type were prepared in the Laboratory of the Physics of Aerodisperse Systems at the Karpov Institute of Physical Chemistry in 1989 (Refs. 4 and 5) as a result of irradiation of metallic surfaces with laser radiation pulses.[2)] Figures 1–3 show photographs of such structures, which were obtained employing an electron microscope. Systems of this kind are formed using different metallic surfaces and different buffer gases. This is evidence of the universality of the process.

The process occurs under certain irradiation conditions, when the specific power of the radiation is 10^6–10^7 W/cm^2. In this case there is no laser breakdown (because the radiation power is insufficient) and no splashing of the sur-

 0038-5670/91/020160-07$01.00

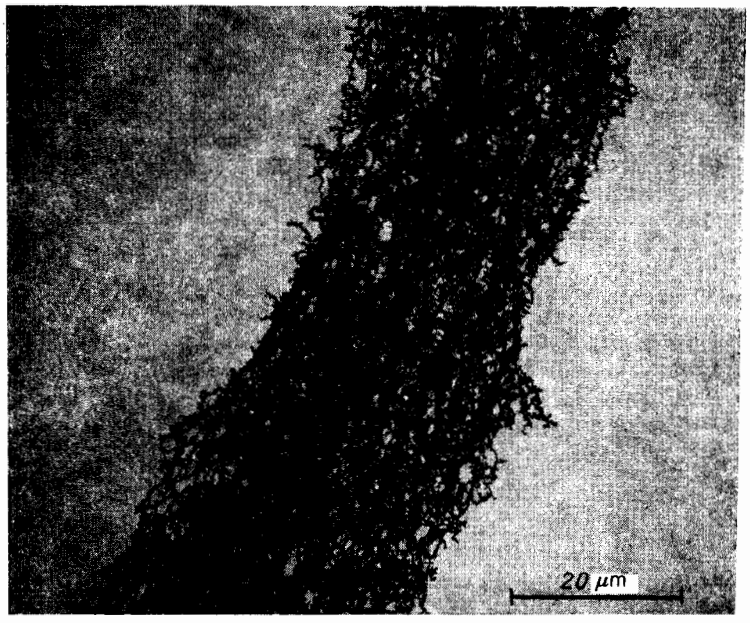

FIG. 1. Photograph of a fractal filament.

face converted into the liquid state. The situation represents evaporation of a weakly ionized vapor from the surface. This is followed by a chain of processes with characteristic times listed in Table I (Ref. 7). We shall now make some brief comments about these processes.

The evaporated atoms and ions exhibit a semi-Maxwellian distribution of the velocities considered as a function of the temperature of the heated surface. At a distance of the order of several mean free paths from the surface the evaporated atoms form a hydrodynamic beam. If the pressure of the evaporated vapor exceeds greatly the pressure of the surrounding buffer gas, the beam travels at the velocity of sound. Naturally, the temperature of the atoms in the beam differs from the temperature of the surface. A typical temperature of the surface is several thousands of degrees and the evaporated vapor pressure amounts to hundreds of atmospheres.

In the course of propagation in the buffer gas the hydrodynamic beam cools and expands. At some stage of the beam expansion the gas pressure becomes identical with the saturated vapor pressure at a given temperature. At this stage we can expect condensation and the nuclei of such condensation are ions. It is important to note that, because of the rapid cooling of the plasma, the density of the ions in the plasma is

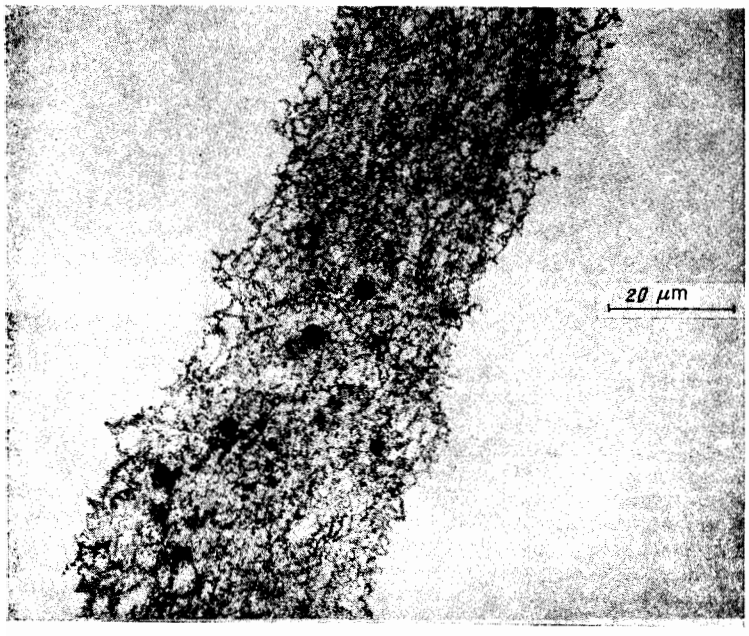

FIG. 2. Fractal filament.

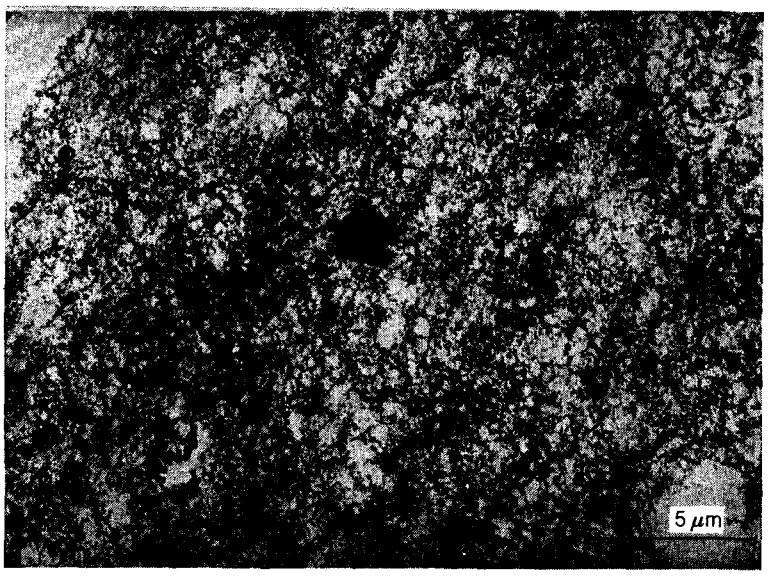

FIG. 3. Internal structure of a filament.

much higher than the equilibrium value corresponding to the plasma temperature. The ionization nonequilibrium of the plasma is responsible for the fast condensation, so that in the course of the subsequent cooling the vapor pressure is equal to the saturation value and the excess vapor becomes condensed.

Such condensation produces singly charged liquid droplets. The subsequent condensation is accompanied by coagulation: liquid droplets combine with one another and become neutralized. This goes on as long as the temperature of the vapor exceeds the melting point of the material. The droplets then become solid particles and they combine to form a fractal cluster. These stages of the process have been investigated thoroughly in the eighties and fractal clusters have been produced by a variety of methods, such as electrical explosion of wires,[8] laser evaporation of metals,[9] heating of a wire in a special furnace,[10] and explosion of a material.[11] An example of a fractal cluster[9] is shown in Fig. 4. The size of particles in a cluster formed from a laser plasma is typically of the order of 10 nm.

The average density of matter in a fractal cluster falls as it grows. This is accompanied by a reduction in its stability.[12] Therefore, the dimensions of a fractal cluster are limited. Usually they amount to microns and a fractal cluster contains 10^3–10^4 particles.

Such fractal clusters may combine with one another to form aerogel-like structures. In the gaseous phase this occurs under different conditions than in a solution, because the density of the material in a gas is much less than in a solution. As structures grow, the time needed for the subsequent coalescence of the components of the structure increases greatly, so that it is unrealistic to expect formation of macroscopic aerogel-like structures in a gas as a result of mutual approach and coagulation of fractal clusters and of their components. However, the process is accelerated by an external electric field. Such a field induces dipole moments in the components of the structure, so that the two components of the structure moving in a gas approach and combine because of the interaction between the induced dipole moments. Since an induced dipole moment increases with the size of a component, the process of coagulation of the components to form a macroscopic structure becomes accelerated on increase in the size of the components. The process of formation of fractal filaments develops in the interior (Fig. 5) and then the filaments become attached to the electrodes. Under the conditions in the reported experiments up to a hundred of individual fractal filaments may form.

Since aerogel-like structures in a gas are formed in an external electric field, they have one special property which is absent in the case of aerogels formed in solutions. An elec-

TABLE I. Duration of the processes in a laser plasma (size of the irradiated surface ~1 mm, power density of the radiation 10^7 W/cm^2).

Process	Time, s
1. Formation of beam	10^{-9}
2. Cooling to onset of condensation	10^{-7}
3. Condensation of atoms on ions and coagulation	10^{-5}
4. Formation of fractal clusters	10^{-2}
5. Formation of aerogel-like structures	10^{2}

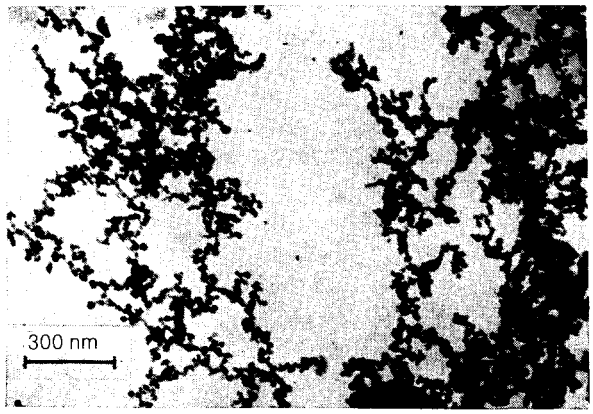

FIG. 4. Fractal cluster of titanium formed by laser evaporation of titanium. Particle size in the structure 20 nm.

tric field induces an anisotropy of the structure growth. This gives rise to filaments whose radius is considerably greater than the size of fractal clusters from which they are formed. For example, under the conditions used to form the structure in Fig. 1 (energy of laser radiation pulses 100 J, width of the irradiated spot 1 mm, external electric field intensity 300 V/cm), the diameter of a filament is approximately 30 μm and its length is of the order of 1 cm, whereas the size of the initial fractal cluster (and, consequently, the size of the pores in the structure) is of the order of 1 μm, and the diameter of the particles in the cluster is 20 nm.

Under natural conditions such filaments may become detached from the surface and intertwined. The result is a complex structure which, when large, resembles a ball of intertwined thread, and when small is fractal. This is the structure of the framework of ball lightning and the nature of formation of this structure suggests similar processes occurring in nature.

We shall now consider the properties of aerogel-like filamentary structures. When they are small, their properties are fractal. This means that if from a filamentary structure we cut a sphere of radius r with one of the particles of the structure at the center, the number of individual particles inside this sphere is

$$n(r) = \left(\frac{r}{a}\right)^D, \tag{1}$$

where a is the radius of a single particle, D is the fractal dimensionality. This relationship is valid in the range

$$R \gg r \gg a, \tag{2}$$

where R is the radius of a fractal cluster or the maximum radius of the pores in the structure. In the case of such structures the fractal dimensionality is $D = 1.8$–1.9 (Ref. 9). It should be pointed out that the fractal dimensionality of structures in aerogels is somewhat higher and amounts to about 2.1 (Ref. 1).

It follows from Eq. (1) that the ratio of the average density of the material $\bar{\rho}$ in a structure to the density of the same material in the condensed phase ρ_0 is $\bar{\rho}/\rho_0 = (a/R)^{3-D}$.

In practice this ratio is of the order of 10^{-3}, i.e., a typi-

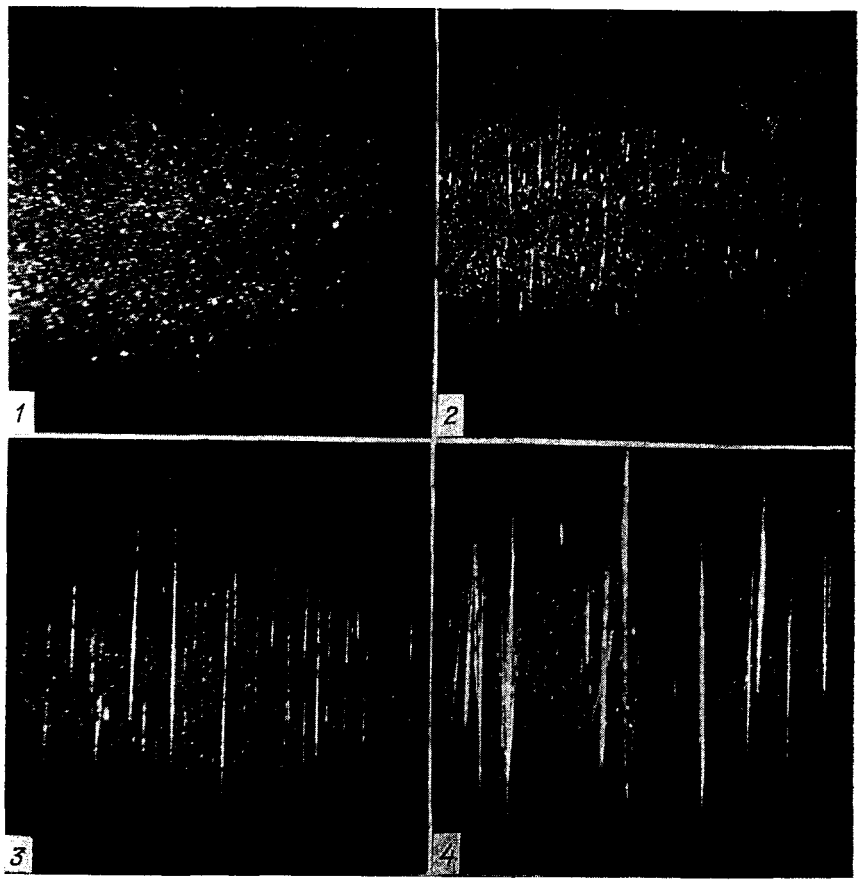

FIG. 5. Formation of fractal filaments in the bulk.

cal density of the material in the filaments is of the order of 10 g/liter, which is comparable with the specific gravity of atmospheric air.

We shall now estimate the strength of such a filament. We shall assume that it is cut by two adjacent planes. In an element formed by such planes a fraction $\bar{\rho}/\rho_0$ is occupied by matter. This means that, on the average, a fraction $\bar{\rho}/\rho_0$ of the cross section is occupied in this way. If the ends of a filament are subjected to a force, this force is transmitted by the filament material and the load is $\rho_0/\bar{\rho}$ times higher than in the case of a continuous condensed phase. Consequently, the strength of a filament is $\bar{\rho}/\rho_0$ times less than the same material in the condensed phase. In particular, in the case shown in Fig. 1 the strength of a filament is 10^3 times less than that of the condensed material. In this case the strength is an important parameter of the structure, because it determines the existence of the object.

In the above estimate we assumed that the cross section of a single component of the structure is approximately the same at different points. This is true if we model the simplest component of a structure by a cylindrical filament. Since the structure in question forms by coagulation of spherical particles, it is necessary to introduce some corrections. The area of contact between the particles is in this case s_0 and a reduction in the strength includes an additional factor $s_0/(\pi a^2)$. For example, if the radius of a "neck" is one-third of the particle radius, the strength decreases additionally by an order of magnitude.

The conductivity of the structure varies in a similar manner. Also the strength and the conductivity of the structure depend on its chemical composition. Experience shows that oxides represent a definite fraction in the chemical composition of such a structure. They are responsible for the strong binding in the structures. On the other hand, formation of the oxides corresponds to a fall in conductivity. These parameters should be investigated in a comprehensive manner.

The radiative properties of such filaments are of interest. The maximum absorption can be expected at the wavelengths comparable with the pore size. Therefore, filaments of this kind with an aerogel-like structure can be used as infrared radiation detectors. These detectors should be highly sensitive and should have a short relaxation time ($\sim 10^{-5}$ s).

We shall consider one other aspect of the preparation of such structures. The process is initiated by heating of the surface with laser radiation and the result is the evaporation of atoms from the surface. The question arises whether it is possible to achieve the same effect by some other surface treatment, for example, by bombardment with an electron or an ion beam, a gas discharge, etc. It is not yet possible to answer this question unequivocally. It is possible that other methods of the interaction with the surface can create a flux of a weakly ionized atomic vapor at the surface, but this must be investigated specially. The nature of the interaction of high energy fluxes with the surface of a solid may vary, as will be demonstrated by our analysis of the interaction of laser radiation with matter given below.

The laser radiation power density in the process of evaporation of an atomic vapor from the surface is 10^6–10^7 W/cm^2. An increase in this value creates a new regime resulting in breakdown of the evaporated gas when all the deposited energy is absorbed by a plasma created from the first batch of the evaporated substance.

However, even in the absence of laser breakdown the evaporation of atoms from the surface is not always uniform. Since the temperature of the surface is several thousand degrees, it liquefies and splashing out of droplets is possible. Figure 6 shows a time scan of an element of the surface region in the process of irradiation. We can see that in addition to a plasma jet, the final stage of irradiation produces a droplet. The velocity of this droplet is considerably less than the plasma propagation velocity, so that in a scan the path of a luminous drop is oriented at a small angle to the abscissa. Figure 7 shows a photograph obtained employing a long exposure time. It shows paths of a number of luminous drops.

It should be pointed out that the splashing out of drops from a heated surface occurs also in the cathode spot of an

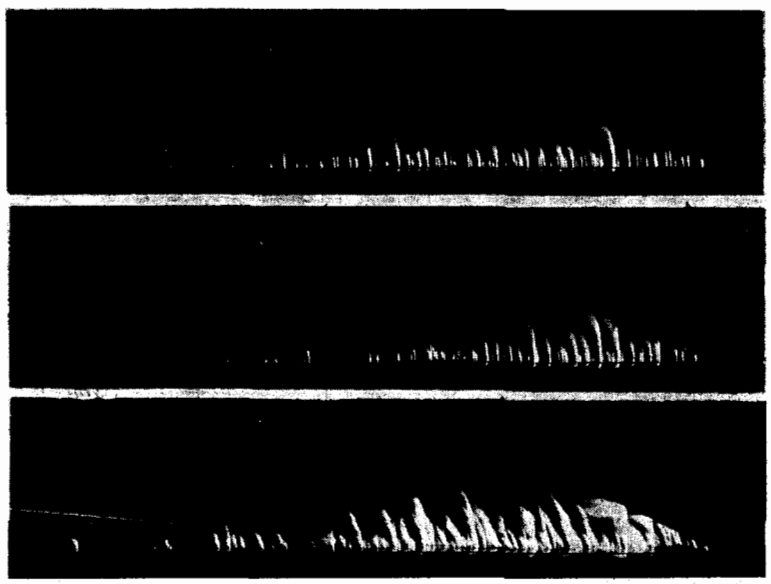

FIG. 6. Time resolved photographs of a plasma jet formed as a result of laser irradiation of a metal.

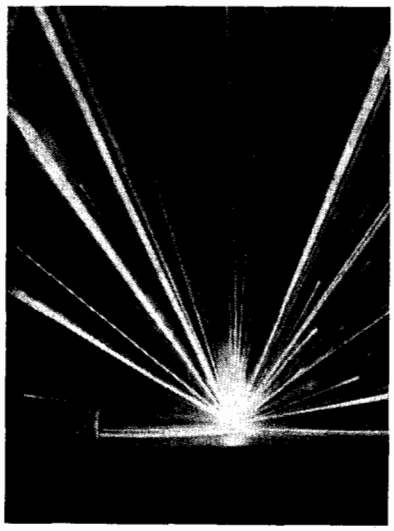

FIG. 7. Radiation emitted by liquid particles in a plasma jet recorded in the course of long exposure.

electric arc. All this is evidence of the complexity of the nature of the interaction of high energy fluxes with the surface and of the general relationships that apply when different methods are used.

Since the formation of these fractal filaments represents a universal process, they may form in technical devices and in nature. We shall consider briefly one problem when this may be important, i.e., the problem of ball lightning. Ball lightning has a rigid framework[13,14] and an aerogel is a suitable physical model of the lightning.[2] However, if the framework of the ball lightning represents an isotropic gel of the kind obtained from solutions, then a more detailed analysis leads to the following conflict. The radiation emitted by the ball lightning is concentrated in spots[14,15] and this means that many small hot spots can coexist (the temperature in a spot is 2000 K and its size is of the order of 0.1–1 mm) and they emit radiation. Such hot spots appear as a result of propagation of chemical reaction waves in a medium[14,15] and in particular these spots can cause coalescence of the aerogel particles and release of surface energy (of the order of ~ 1 kJ/g). The conflict is this: in the case of an isotropic gel, we cannot find the size of the luminous region and this means that in further analysis the process should extend over the whole volume of the aerogel. If we represent the ball lightning framework as an intertwined ball of fractal filaments, then the chemical reaction waves may propagate along individual filaments so that the conflict is removed. Moreover, such a model of the ball lightning framework fits better the nature of its formation in atmospheric air. Then, since the density of the material in the ball lightning is $\sim 10^{-4}$ g/cm^3, whereas the density of the material in the filaments is $\sim 10^{-2}$ g/cm^3, the filaments themselves occupy only a small fraction of the volume inside the ball lightning. We can see that the framework of the ball lightning is essentially a clump of spiders' webs and each web has a complex internal structure.

This model is a development of the aerogel model of ball lightning, but it is more complex and it may have additional properties. In particular, it can account for the observation[27] that a ribbon-like or a rod-like ball lightning can be transformed into a spherical one and vice versa. However, this shows that a better understanding of the processes that occur in this case may provide a deeper insight into the observed phenomena.

We shall now establish the relationship between the processes that occur in the formation of fractal filaments with the laboratory ball lightning usually called a fire ball. There are three ways in which this object can form when during much of its existence the external source is switched off.

In the first method[16–20] an individual fire ball is formed by a discharge of batteries which contain an accumulated energy of the order of 1 MJ. When the electric arc formed in this case is blown away, a luminous region of about 10 cm in size may exist in the atmosphere for about 1 s. Another method[21–25] utilizes an electric spark in atmospheric air containing a fuel or a chemically active impurity. The electrical energy deposited in a spark is of the order of several hundreds of joules, the size of the luminous sphere is of the order of 1 cm, and the lifetime is about 1 s. The third method, used at the beginning of this century by Tesla and being developed at present,[26] is fundamentally an rf discharge. An electrical breakdown in air creates long weakly luminous sparks. Spherical formations with a radius of the order of 1 cm and a lifetime of the order of 1 s are sometimes created by such sparks.

In all the cases discussed above the conditions necessary for the formation of the investigated structures are favorable. Firstly, there is a strong interaction with an electrode resulting in the evaporation of a metal vapor. Secondly, the electric fields in such systems tend to form macroscopic structures. One should mention here a low reproducibility of the experiments designed to produce luminous structures in the atmosphere. This is evidence of the close relationships between the various processes.

We shall conclude by noting that aerogel structures formed in a gas represent a characteristic class of physical objects with special properties. These properties make the structures of considerable physical and practical interest. The nature of formation of objects with an aerogel structure shows that they should be easily available and they may appear under natural conditions. This accounts for the interest in these objects and demonstrates the need for further investigations.

[1)] The individual parameters of a macroparticle consisting of atoms and molecules of a definite kind vary monotonically on addition of new atoms and molecules. This is not true of clusters which consist of up to hundreds of atoms and molecules.

[2)] It is possible that such structures have been observed on many previous occasions. For example, it is reported in Ref. 6 that electrical explosions of thin metal wires produce web-like low-density systems, with the size of the components of the order of 10 nm, which become attached to the walls of the vacuum chamber and can exist in this state for days. However, the diagnostics of earlier experiments has not been sufficiently detailed to judge the properties of the resultant structures.

[1] J. Fricke (ed.), Aerogels, Springer Verlag, Berlin (1986); Sci. Am. **258**(5), 68 (1988).
[2] B. M. Smirnov, Usp. Fiz. Nauk **152**, 133 (1987) [Sov. Phys. Usp. **30**, 420 (1987)]; Phys. Rep. **188**, 1 (1990).
[3] S. S. Kistler, J. Phys. Chem. **36**, 52 (1932); J. Phys. Chem. **39**, 79 (1935).
[4] A. A. Lushnikov, A. E. Negin, and A. V. Pakhomov, *Ball Lightning* (ed. by B. M. Smirnov) [in Russian], Institute of High Temperatures, Academy of Sciences of the USSR, M., 1990, p. 11.

[5] A. A. Lushnikov, A. E. Negin, and A. V. Pakhomov, Chem. Phys. Lett. (in press).
[6] V. Ya. Aleksandrov, I. P. Borodin, E. V. Kichenko, and I. V. Podmoshenskiĭ, Zh. Tekh. Fiz. **52**, 818 (1982) [Sov. Phys. Tech. Phys. **27**, 527 (1982)].
[7] B. M. Smirnov, *Proc. Eighth Conf. of European Physical Society*, Amsterdam (1990), p. 83.
[8] S. R. Forrest and T. A. Witten Jr, J. Phys. A **12**, L109 (1979).
[9] A. A. Lushnikov, A. V. Pakhomov, and G. A. Chernyaeva, Dokl. Akad. Nauk SSSR **292**, 86 (1987) [Sov. Phys. Dokl. **32**, 45 (1987)].
[10] G. A. Niklasson, A. Torebring, C. Larsson *et al.*, Phys. Rev. Lett. **60**, 1735 (1988).
[11] A. P. Ershov, A. B. Kupershtokh, and V. N. Kolomiĭchuk, Pis'ma Zh. Tekh. Fiz. **16**(2), 42 (1990) [Sov. Tech. Phys. Lett. **16**, 102 (1990)].
[12] Y. Kantor and T. A. Witten, J. Phys. Lett. **45**, L675 (1984).
[13] B. Ya. Aleksandrov, E. M. Golubev, and I. V. Podmoshenskiĭ, Zh. Tekh. Fiz. **52**, 1987 (1982) [Sov. Phys. Tech. Phys. **27**, 1221 (1982)].
[14] B. M. Smirnov, Usp. Fiz. Nauk **149**, 177 (1986) [Sov. Phys. Usp. **29**, 481 (1986)]; *Problem of the Ball Lightning* [in Russian], Nauka, M., 1988.
[15] B. M. Smirnov, Phys. Rep. **152**, 177 (1987).
[16] P. A. Silberg, J. Appl. Phys. **49**, 1110 (1978).
[17] P. A. Silberg, in *Problems of Atmospheric and Space Electricity* (ed. by S. C. Coroniti), Elsevier, Amsterdam, 1965.
[18] R. K. Golka, *Proc. Ninth Intern. Wrocław Symposium on Electromagnetic Compatibility*, Wrocław, 1988, p. 59.
[19] G. C. Dijkhuis, Ned. Tijdschr. Natuurkd. B **51**, 125 (1985).
[20] G. C. Dijkhuis, *Proc. Ninth Intern. Wrocław Symposium on Electromagnetic Compatibility*, Wrocław, 1988, p. 166.
[21] J. D. Barry, J. Atm. Terr. Phys. **30**, 313 (1968).
[22] J. D. Barry, Priroda No. 12, 62 (1968).
[23] J. D. Barry, *Ball Lightning and Bead Lightning: Extreme Forms of Atmospheric Electricity*, Plenum Press, N.Y., [Russ. Transl. Mir, M., 1983].
[24] Y. H. Ohtsuki and H. Ofuruton, *Proc. Ninth Intern. Wrocław Symposium on Electromagnetic Compatibility*, Wrocław, 1988, p. 27.
[25] H. Ofuruton and Y. H. Ohtsuki, in *Science of Ball Lightning* (ed. by Y. H. Ohtsuki), World Scientific, Singapore, 1989, p. 220.
[26] K. L. Corum and J. F. Corum, Paper presented at Third All-Union Seminar on the Ball Lightning, Moscow, 1989, Engl. original in Tesla J. 6–7, pp. 79–87 (1989/1990) [Russ. Transl., Usp. Fiz. Nauk **160**(4), 47 (1990)].
[27] A. I. Grigorjev, I. D. Grigorjeva, and S. O. Shirjaeva, in *Science of Ball Lightning* (ed. by Y. H. Ohtsuki), World Scientific, Singapore, 1989, p. 88.

Translated by A. Tybulewicz