Fractal Characterization of Heat and Mass Transfer Processes in Nanostructured Materials

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Abstract. The relationship between the fractal self-organization of structural-phase inhomogeneity in nanostructured materials and the processes of heat and mass transfer in them is considered. It is characterized by a non-Euclidean relationship between the rate of increase in the number of the considered elements of the medium and an increase in the scale of their consideration and is described by the transfer equations in fractional derivatives with respect to coordinate and time.

1. Introduction
The use of functional and structural materials with a high content of nanoscale interphase formations ("non-autonomous" phases) of the fractal structure makes it possible to purposefully influence the processes of energy transfer and transformation, their stability and the development of nonlinear regimes with exacerbation. In terms of their physicochemical properties, structure and composition, they differ significantly from the characteristics of continuous phases, causing the effects of local energy concentration, non-uniformity of thermophysical and other characteristics, unusual distribution of temperatures and other physical quantities [1].

The prospect of designing materials and devices at the level of atoms and molecules was first announced by Richard Feynman in his lecture "There's Plenty of Room at the Bottom..." [2]. The term "Nanoscience and nanotechnology" was introduced by the Japanese scientist Taniguchi to designate the field of creating structures with sizes of the order of nanometers [3]. As it turned out, almost all technologies and methods for the synthesis of such materials are characterized by fractal self-organization of their microstructure, similar to that discovered by Benoit Mandelbrot at macroscopic objects when studying the length of the coast of Great Britain [4]. A common feature of all such objects, which he called fractals, is the nondifferentiability (nonsmoothness) of the different-scale structural sets of the object, as well as their metric-statistical self-similarity with a non-Euclidean relation $M \sim \varepsilon^D$ between an increase in the number of considered elements $M$ and an increase in the spatial scale of their consideration $\varepsilon$. Unlike integer indicators of Euclidean geometry objects, the dimensional exponent $D$ of fractal structures is fractional.

For structures with regular fractality, the dimension $D=\ln M / \ln \varepsilon$, introduced by Hausdorff at $\varepsilon = \text{idem}$ and investigated by Bezekovich at $\varepsilon \neq \text{idem}$, can be determined geometrically from the slope of the straight line approximating the experimental data $\ln M(\varepsilon) \sim \varepsilon$ in logarithmic coordinates. In some
cases, for model mathematical sets, it can be determined analytically, for example, for sets of the so-called family of "middle thirds". They are constructed by recursive deletion at each hierarchical level of the average of three parts of a unit length segment and their further self-similar transformations (triad Koch curve $D = \ln 4/\ln 3 = 1.2618$, Sierpinski carpet $D = \ln 8/\ln 3 = 1.8927$, Menger sponge $D = \ln 20/\ln 3 = 2.7268$, etc.). As you can see, the dimension of the fractal turns out to be greater than the topological dimension of the elements used in it, but less than the topological dimension of the space of its embedding [5].

At the same time, the above simple relations are not enough to determine the fractal dimension of nanostructured objects, which is due to the special role of the energy-entropic characteristics of interphase layers ("non-autonomous" phases) and the correlation scale of the phenomena of matter and energy transfer in different-sized macro-, micro- and nano- structural blocks of the material [6]. They require multifractal processing, taking into account the probability of manifestation of irregularity of their structure according to the generalized ratio of informational Renyi entropy of $q$ order [7]:

$$D_{Rq} = \lim_{\varepsilon \to 0} \left[ \frac{1}{q-1} \frac{\ln Z(q, \varepsilon)}{\ln \varepsilon} \right], \quad Z(q, \varepsilon) = \sum_{i=1}^{M(\varepsilon)} p_i^q(e).$$

Here $q = 0$ corresponds to the Kolmogorov entropy and the Hausdorff dimension, $q = 1$ to the Shannon entropy, $q = 2$ to the correlation entropy. The general characteristic of the multifractal spectrum is the function $f(\alpha) = q\alpha - \tau(q)$, where $\tau(q) = (q-1)DRq$, $\alpha = d\tau/dq$, $-\infty < q < + \infty$.

When implementing this approach, in order to overcome the difficulties of physically changing the nanoscale of captured images, we have developed a technique for digitally changing the pixelization size of images [8]. As an example of such processing of visualized nanostructures, figure 1 shows micrographs of chips of synthesized thermoelectric nanomaterials with a large proportion of non-autonomous phases for personalized energy systems [9], taken with high-resolution electron microscopes [6].

![Figure 1](image-url)

**Figure 1.** The original micrograph and the sequence of its digital processing.

The effect of structural and phase heterogeneity of materials on the processes of heat and mass transfer under conditions of mass and spatial limitations of media with a high content of nanoscale interfacial formations of a fractal structure with fractional dimension is taken into account by using modified Fick and Fourier laws with fractional derivatives in coordinate and time [10]:

$$\frac{\partial^{\alpha} u}{\partial \tau^{\alpha}} = \Delta^{\beta} u$$

The indicators of fractional derivatives in these ratios can be directly related to the indicators of the fractal dimension of the material, if the thermal conductivity is considered as a random function of the space-time coordinate of such a medium, and its averaging in the transition from derivatives of integer order to derivatives of fractional order is carried out through the integral operator of a certain effective medium [11]:

$$\lambda f = \int_0^1 \int_0^1 K(x-x_1, t-t_1) f(x_1) dx_1 dt.$$
here $K(x-x_1, t-t_1)$ is the kernel of the integral operator, which in a statistically homogeneous medium $\lambda(x)$ is the product of the Green's function $G(x-x_1, t-t_1)$, which satisfies both the original Fick-Fourier problem and the correlation ratio for its averaging

$$\frac{\partial G}{\partial t} - \lambda_0 \frac{\partial^2 G}{\partial x^2} = -\delta(x-x_1)\delta(t-t_1), \quad \lambda_0 = \langle \lambda(x) \rangle = \text{const}, \quad \langle \lambda(x)\cdot\lambda(x) \rangle = r(x-x_1)$$

Taking into account that for media of fractal structure in time and space with the phenomena of spatial correlations, time and space intervals form the Hausdorff-Besicovitch set, we can associate the integral operator of the effective medium with the dimension of the fractal structure of the initial medium:

$$\lambda^* f = \frac{1}{r(\alpha)^\beta} \int f(x, t) \left( (x-x_1, t-t_1) \right)^{\alpha+\beta} dx dt,$$

where $\alpha$ is the fractal dimension of the Hausdorff-Besicovitch set in time, $\beta$ is the fractal dimension of this set in space.

As a result, without resorting to numerical methods, it is possible to obtain analytical solutions to the problems of diffusion and temperature distribution in micro-inhomogeneous bodies of classical shape, using models of regular fractal media. The solutions occupy an intermediate position between relaxation and wave behavior in time and lead to a power-law dependence on spatial arguments. Thus, according to the expressions given in [11], in comparison with the linear temperature distribution in a layer of a homogeneous medium, a nonlinear nature of the temperature distribution with a downward convexity is inherent for a layer of an inhomogeneous fractal medium with a dimension less than one. As for a medium with a dimension greater than one, the convexity is upward (Fig. 2-a). The result of a change in the fractal dimension over a layer of a highly micro-inhomogeneous material can be a large non-uniformity of its thermophysical characteristics, confirmed experimentally in [12] by the wavelike character of the temperature distribution in the TiN-AlN system (Fig. 2-b).

**Figure 2.** The nature of the temperature distribution in the layer with a fractal structure for three media models (a) and the wavelike nature of the thermal conductivity of sintered compositions in the TiN-AlN system with ultradispersed components according to experimental data (b). Explanations are given in the text.

Nanosized pores, slit gaps in layered structures, channels in nanotubes can be used as nanoreactors for chemical and phase transformations of other substances in media inert with respect to reagents and reaction products [13]. In comparison with macro-sized analogs, under conditions of a comparable ratio of the sizes of critical nuclei with the sizes of spatial restrictions of nanophases, the problem of preventing the fusion and growth of solid particles during chemical synthesis is solved. The critical size of a spherical nucleus $R_{crit}$ is found from the condition of maximum $d(\Delta G)/dR=0$ of the Gibbs free energy, defined in [6] as the sum of its bulk and surface components $\Delta G=-(4/3)\pi R^3 \Delta \mu/Va+4\pi R^2 \sigma(R)$. Here $R_{crit}$
\[ l_o[1-2\delta/l_o+(2\delta/l_o+1)/2] \text{ and } R_{cr}=2\sigma(\infty)Va/\Delta\mu \] are given, respectively, with and without regard to the dependence of the surface tension on the particle size at small radii, \( \sigma(R) \approx \sigma(\infty)/(1+2\delta/R) \), \( l_o=\sigma(\infty)Va/\Delta\mu \), \( \delta \) is the “Tolman length”.

2. Conclusion

In conclusion, it should be noted that the presented results indicate a close relationship between the fractal self-organization of structural-phase inhomogeneity in nanostructured materials and the processes of heat and mass transfer in them. This makes it possible to purposefully influence their characteristics when creating new materials with desired properties.

3. References

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