

SIMULATION OF GAS DIFFUSION IN POROUS LAYERS OF VARYING STRUCTURE

A. V. Anikeenko,¹ N. N. Medvedev,¹ M. K. Kovalev,²
and M. S. Melgunov²

UDC 544.272,544.723.2

Gas diffusion in porous layers of varying structure was simulated numerically. Mesoporous mesophase material (MMM) and silica gel layers were studied. The former were a set of ordered cylinders; the latter were disordered packings of spheres. The average residence time of a molecule in a layer (return time) and dispersion of this time in relation to the layer depth were calculated. For the same porosity and specific surface of layers, the average return time is independent of the pore structure and increases with the layer depth as a linear function. This is the consequence of the general theoretical result, according to which the duration of molecule wandering in a pore depends only on the ratio of the pore volume to the section area of its windows. Dispersion of the wandering time is sensitive to the pore structure; it is slightly smaller for regular pores than for a complex pore system. The functional dependence of return time dispersion on the layer depth is the same for different layers (the cubic root of dispersion changes with the layer depth as a linear function). This work helps us to understand recent experimental data, which showed that using MMM for gas chromatographic columns increased the efficiency of the latter compared with other columns based on silicon oxide.

Keywords: computer simulation, random wanderings, gas diffusion, mesoporous mesophase materials, porous layers, residence time in a layer, gas chromatography.

INTRODUCTION

Much attention has recently been paid to diffusion of molecules in porous materials [1, 2]. In calculations of diffusion characteristics, the pore structure was generally included phenomenologically, in terms of the diffusion coefficient. Correlating a particular pore structure with diffusion characteristics is a complex problem even for pores of simple form such as cylinder [3, 4]. However, analytical approaches are not applicable to more complex systems. In this case, phenomenological parameters of structure are introduced, for example, the tortuosity coefficient for the complex morphology and connectivity of pores (see, e.g., [5]).

An important characteristic of diffusion is the average time of molecule wandering in a pore. For a porous layer, this is the residence time in a layer from the moment the molecule entered the layer to the moment it quits (return time). Another important characteristic is dispersion of this time. Both parameters affect the delay time and the width of the diffusion of the components of the gas mixture separated on a chromatographic column. Recently, it was shown that using a porous layer

¹Institute of Chemical Kinetics and Combustion, Siberian Division, Russian Academy of Sciences, Novosibirsk; nikmed@kinetics.nsc.ru. ²G. K. Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 50, No. 3, pp. 425-432, May-June, 2009. Original article submitted September 15, 2008.

of a mesoporous mesophase material (MMM) led to higher efficiency of the column compared with the efficiency of the standard columns with an unstructured silica gel layer [6]. We do not yet fully understand the reasons for this. The chemical composition is the same; the only difference lies in the fact that ordinary layers have a complex system of pores, while MMM contains regular mesopores. However, the relationship between structure and diffusion is not evident. The structural features of pores can be annihilated in considering the average characteristics of wandering. Recently, important data were obtained on diffusion in pores. It appeared that the mean residence time in the pore was independent of the pore shape. It depends only on the pore volume V and the total area S of windows through which the gas molecule can enter and quit the pore, namely, $\tau = (4V/S)/\langle v \rangle$, where $\langle v \rangle$ is the mean velocity of the molecule. This was studied [7] by modeling the mean length of the segments of the trajectories of the particles wandering through a circle of a given radius. This tendency was found [8] directly, using numerical simulation of the motion of a gas molecule in voids of four spheres. In [9, 10], the problem was considered in general form. Based on the Chapman–Kolmogorov equation, it was shown that this behavior was independent of the character of diffusion, i.e., that the mean wandering time in a pore depended on the volume and the total area of windows (integrated geometrical characteristics), but not on the particular pore structure.

As to dispersion of the residence time, we do not know of any such universal law for it. Studies of one-dimensional diffusion in a limited space, however, showed that dispersion of the wandering time increased in proportion to the third power of the space length [11]. This gives us hope that dispersion also obeys a certain universal tendency that correlates it with the integrated characteristics of the pore.

In this work, we performed numerical simulation of the wandering of a gas molecule in porous layers of varying structure to determine the return times and their dispersion. MMM layers were modeled by a system of cylinders with varied lengths and wall thicknesses. The silica gel layers were modeled by disordered packings of solid spheres, in which the size of spheres and the porosity and thickness of layers were varied.

SIMULATION PROCEDURE

The motion of gas molecules was modeled in Knudsen’s approximation [3]; that is, collisions of molecules with one another were neglected, and motions between the walls were assumed to be rectilinear and uniform. The reflection from the surface was considered “thermodynamically equilibrium”; i.e., after reaching the wall, the molecule was in the adsorbed state for some time and completely forgot its history. The magnitude and direction of velocity of a molecule that entered a porous layer and rebounds from the walls are set according to the velocity distribution of molecules in a flow well known in gas theory. Recall that the rebound angle of a molecule does not equal the angle of incidence, but is a random value defined as

$$dW_j(\Omega) = \frac{\cos(\theta)}{\pi} d\Omega. \quad (1)$$

In the course of modeling, the velocity of a wandering molecule can be considered constant and equal to the mean velocity \bar{v} for the given temperature. As shown by our calculations, the mean return time and dispersion are the same as for Maxwell’s velocity distribution. The direction of velocity, however, is always chosen in accordance with (1).

The residence time of a molecule adsorbed on the surface is specified by the exponential distribution

$$F(t) = \tau^{-1} \cdot e^{-t/\tau}, \quad (2)$$

where τ is the mean lifetime of the molecule on the surface. For different molecules, this time can be calculated from the Frenkel equation for the adsorption heat $\tau = \tau_0 \cdot \exp(\Delta Q/RT)$, where the τ_0 factor is a of the order of bond vibration time, $\sim 10^{-13}$ s [12].

The MMM layer was modeled as identical cylinders packed into a hexagonal structure (honeycombs). Electron micrographs show exactly this structure of MMM [13] (Fig. 1).

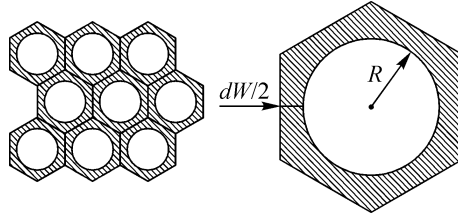


Fig. 1. MMM layer model. The cylindrical pores are ordered into a hexagonal structure (*left*). The unit cell of the packing of cylindrical pores (*right*).

The geometrical parameters of our model are the cylinder radius R , the wall thickness dW , and the cylinder length L set to be the layer depth. The fraction of the section area of cylinders (holes) is recorded as $p = \frac{\pi \cdot R^2}{2\sqrt{3}(R + dW/2)^2}$. This equation also defines the layer porosity because it equals p for the given geometry. Introducing the density of the wall substance ρ , we can record the specific volume $V_{\text{spec}} = \frac{p}{(1-p) \cdot \rho}$ and specific surface of the layer,

$$A_{\text{spec}} = V_{\text{spec}} \cdot \frac{2\pi R}{\pi R^2} = \frac{2p}{(1-p) \cdot R \cdot \rho}.$$

The molecule starts to wander after it falls on the layer. Before that, the molecule was over the layer in the bulk gas. The molecule enters the cylinder with the probability p and falls on the field between cylinders with the probability $(1-p)$. In the former case, its motion in the cylinder is calculated as the motion before it quits; in the latter case, the molecule interacts once with the wall and returns at once to the bulk of the gas. To reduce the calculation time, we need not model the events preceding the appearance of molecules on the fields. In the probability theory, an equation for an arbitrary process with two branches is known,

$$M = pM_1 + (1-p)M_2, D = p\{D_1 + (M_1 - M)^2\} + (1-p)\{D_2 + (M_2 - M)^2\},$$

where M_1, D_1 and M_2, D_2 are the mean values and dispersions of the first and second branches; M and D are the corresponding values for the resulting process. Thus, it suffices to model the wandering of the molecule in the cylindrical pore by evaluating M_1 and D_1 , and for the molecule that hits the fields, one can use M_2 and D_2 calculated once as the means and dispersions of the residence time in the adsorbed state on the wall (2).

Silica gel layer. As a structural model of the silica gel layer, we used a disordered packing of spheres. The initial packing of 10,000 solid spheres of the same radius was created in a cubic box with periodic boundary conditions [14]. To obtain a layer of the specified thickness, we translated the box the required number of times in the vertical direction. The periodic boundary conditions were set in the horizontal directions (Fig. 2).

To accelerate the choice of the nearest spheres for the molecule inside the packing, we used the three-dimensional cell method [15]. Due to this technique, the choice time did not depend on the number of spheres in the layer (instead of the linear dependence in the standard case). This is important in our case because the model contains a large number of spheres.

Calculation of the wandering time in the layer. In the case of MMM, the molecule starts from an arbitrarily chosen place on the upper section of the cylinder. The molecule is assumed to fly uniformly at a given rate in the chosen direction. We calculate the point at which the molecule will hit the wall or the bottom of the cylinder. The flight time to this point is determined as a ratio of the length of the corresponding segment of the trajectory to the current rate of the molecule. The lifetime of the molecule on the wall at the given point is determined as a random value by (2). Then the molecule continues to move at the new rate and random angle determined by (1). We calculate the next point of contact with the wall, and the procedure is continued until the molecule quit the cylinder (reached the upper section). In the case of silica gel, the molecule starts to move from minor height over the basic model box. As in the case of MMM, we calculate the length of the segment of trajectory along the velocity vector to the first point of contact with the sphere (or the bottom of the layer),

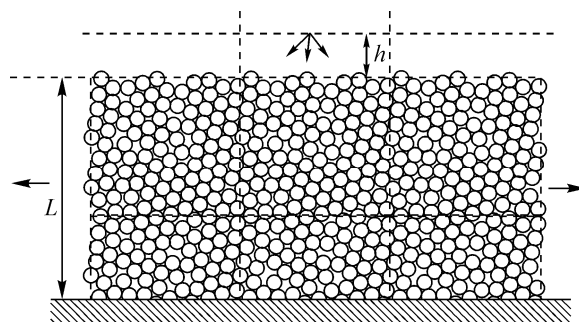


Fig. 2. Silica gel layer model. In the middle of the model is the main box containing a packing of spheres. The box is translated the required number of times in the vertical direction for obtaining the specified depth L . In the horizontal directions, the periodic boundary conditions are used.

TABLE 1. Parameters Used in This Work for Modeling

Radius of the cylinder R , nm	1.09
Wall thickness dW , nm	0.92
Diameter of the sphere, nm	4.0
Edge of the main box, nm	85
Porosity	0.45
Density of material ρ , g/cm ³	2
Specific volume, cm ³ /g	0.41
Specific surface, m ² /g	750
Mean rate of the molecule, m/s	354
Mean adsorption time (at 343 K for isobutane), ns	0.5
No. of trajectories	$5 \cdot 10^5 - 4 \cdot 10^6$

the flight time, the residence time at the contact point, and the direction and rate of the rebound, and the process is continued until the molecule quits the layer.

For each trajectory, we determine the overall residence time in the layer, the trajectory length, and the number of contacts with walls. Many independent launches of the molecule are performed, the statistics on the stated characteristics are collected, and the average value and dispersion are calculated. The number of trajectories in different experiments was varied from five hundred thousand to millions.

For quantitative comparison of the results of diffusion in MMM and silica gel layers, we selected the geometrical parameters of layers such that the layers had approximately the same porosity and specific surface. Table 1 lists the parameters used in this work.

RESULTS OF SIMULATION

Figure 3 compares the probability density functions of the return time calculated for MMM (*left*) and silica gel (*right*) layers with different thicknesses. It can be seen that, irrespective of the structure, the major portion of molecules fly out of the layer after several collisions. This is partly assisted by the fact that the molecule does not spring back by the reflection law from the wall; rather, this is accidental motion that can be directed oppositely to the arrival. Other molecules, however, wander for a long time in the layer. For deeper lying layers, the number of these molecules and the wandering time increase substantially for both MMM and silica gel. In the silica gel layer, these molecules go beyond the basic model box and wander in its periodic images.

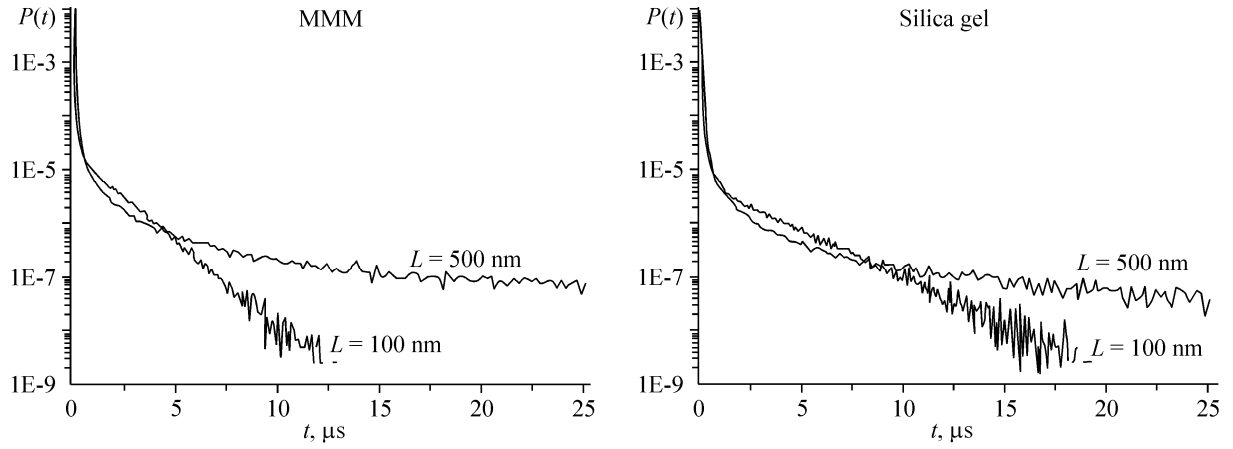


Fig. 3. Probability density functions for the wandering time inside the MMM (*left*) and silica gel (*right*) layers. All functions were normalized to unity.

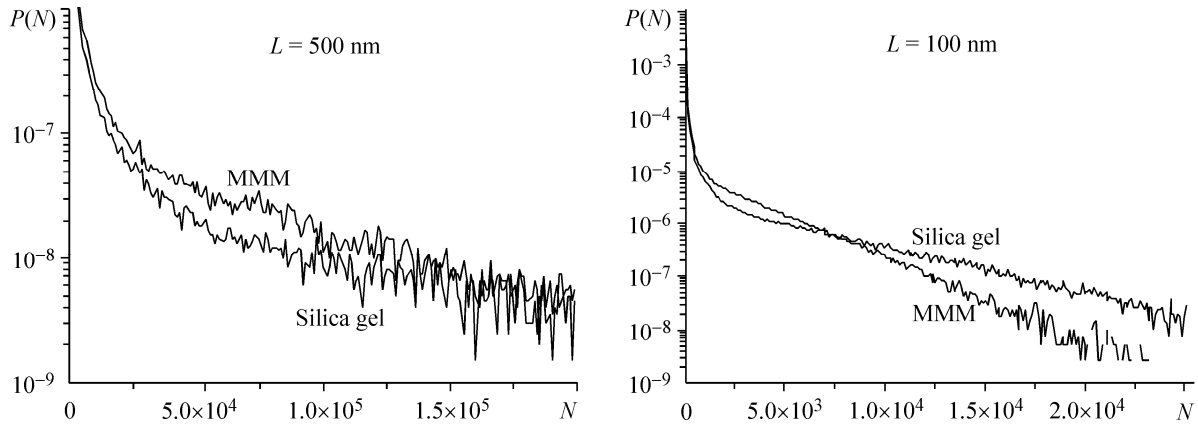


Fig. 4. Probability density functions for the number of collisions of the molecule during its wandering inside the MMM and silica gel layers.

TABLE 2. Average Characteristics for the Distributions of Figs. 3 and 4

Sample	$\langle t \rangle$, ns	D , ns ²	$\langle N \rangle$	Sample	$\langle t \rangle$, ns	D , ns ²	$\langle N \rangle$
MMM, $L = 100$ nm	42.3	$0.955 \cdot 10^5$	83.5	MMM, $L = 500$ nm	207.2	$1.120 \cdot 10^7$	409.3
Silica gel, $L = 100$ nm	42.0	$1.709 \cdot 10^5$	83.0	Silica gel, $L = 500$ nm	213.1	$2.247 \cdot 10^7$	421.0

The number of collisions with the wall is exactly proportional to the wandering time in the layer. This is understandable because the residence time on the wall has a definite mean value, and the average length of the trajectory (the flight time) is also, on average, proportional to the number of collisions. Therefore, the probability density functions for the number of collisions with walls are similar to the functions for the return time (Fig. 4). However, now we compare layers with different structures, but the same thickness. It can be seen that silica gel has larger numbers of long-wandering molecules than MMM. This can be explained by the fact that the pores among spheres are more complex than cylinder, and molecules can well be lost among spheres. At intermediate times, the probability of an outlet from the layer is higher for silica gel but lower for MMM (Fig. 4). The reason is not clear as yet.

However, despite the considerable difference in the pore structure, the average characteristics of wandering differ but slightly between MMM and silica gel layers. Table 2 lists the mean values $\langle t \rangle$ and dispersions D of the return time, and

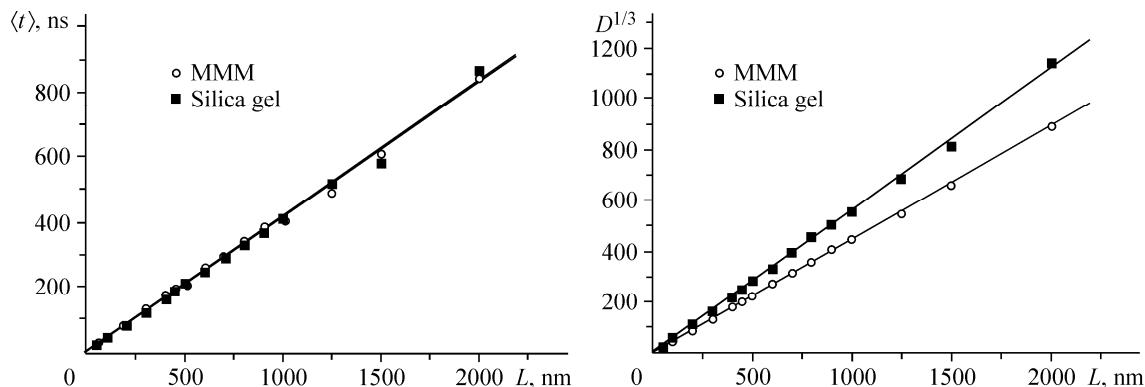


Fig. 5. Dependence of the mean return time (*left*) and the cubic root of the dispersion of this time (*right*) on the thickness of the MMM and silica gel layers.

also the mean numbers of collisions $\langle N \rangle$ for the distributions shown in Figs. 3 and 4. For the same layer depth, these values are almost the same for MMM and silica gel. The only difference is observed for dispersion, which is two times higher for silica gel than for MMM with the same layer thickness.

Figure 5 shows the dependence of the mean return time $\langle t \rangle$ and its dispersion D on the layer depth L . The linear dependence of the mean time on the depth for MMM is fully consistent with the above-mentioned theoretical conclusion that the mean wandering time within a limited space depends only on the ratio of the space volume to the windows area [7-10]. Indeed, $V/S \sim L$ for the cylinder because the volume of the cylinder is $V = S \cdot L$, where S is the area of the base that plays the role of a window to the cylinder. For the silica gel layer, we have no simple interpretation of the linear dependence. It remains to note that for individual voids and complex pore systems, the mean wandering time is determined by the integrated geometrical parameters. The dependences shown in Fig. 5 (*left*) coincide completely; i.e., for the same layer thickness, the mean return time was the same for silica gel and MMM layers with the same porosity and specific surface.

For dispersion, Fig 5 (*right*) also shows the dependence on the layer depth. However, here the linear dependence on L is observed for the cubic root of dispersion. This functional dependence was discussed in [11], in which the authors studied the wandering of a point on a one-dimensional segment of length L . A theoretical study of three-dimensional wandering of molecules in layers with different structures deserves special attention. We think the given dependence also reflects the general properties of stochastic wandering. In contrast to the mean value, dispersions differ between layers. For the MMM layer, the dispersion of the return time is always smaller than for silica gel for the same layer depth.

EVALUATION OF THE CONTRIBUTION TO COLUMN EFFICIENCY

In the theory of chromatography, the height equivalent to a theoretical plate (HETP) is used for evaluating the column efficiency and determined empirically by

$$H = X / N, \quad (3)$$

where X is the length of the column; N is the “number of plates” equal to T^2/σ^2 , where T is the measurable time of exit of the peak maximum from the column; σ^2 is dispersion of the peak. On the other hand, this characteristic satisfies the Van Deemter equation

$$H = A + B/u + Cu,$$

where u is the rate of gas motion along the capillary; A , B , and C are definite coefficients [16].

Our aim was to evaluate the contribution of our calculated parameters (mean return time $\langle t \rangle$ and its dispersion D) to HETP. The contribution to the total peak dispersion due to the residence of molecules in the layer can be recorded as $\delta\sigma^2 = nD$. Here n is the mean number of occurrences of the molecule in the layer during the gas motion through the column.

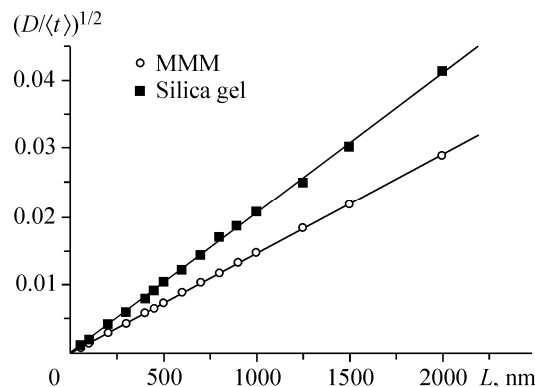


Fig. 6. Dependence of $(D/\langle t \rangle)^{1/2}$ on the thickness of the MMM and silica gel layers with the same porosity and specific surface.

It is evaluated as $n = t_c/\langle t \rangle$, where t_c is the overall residence time in a stationary layer for the residence time in the column; $\langle t \rangle$ is the duration of one entrance. Substituting these equations in (3), we obtain the contribution to the column efficiency of residence in the layer,

$$\delta H = u \cdot k \cdot \frac{D}{\langle t \rangle}.$$

Here $u = X/T$ is the rate of gas motion in the column; $k = t_c/T$ is a dimensionless factor related to the known Henri coefficient. Note that δH is linearly related to the gas rate u . This means that the contribution to the column efficiency relates to the third term of the Van Deemter equation. In other words, the coefficient determined via our calculated parameters contributes to the C coefficient of this equation. In chromatography, it is considered that the smaller the H , the higher the column efficiency. This means that the lower the $D/\langle t \rangle$ for a porous layer, the higher the column efficiency.

Figure 6 shows the square roots of $D/\langle t \rangle$ for MMM and silica gel layers as functions of the layer depth L . Importantly, $D/\langle t \rangle$ is smaller for MMM than for silica gel, which indicates that MMM is preferable to silica gel for gas chromatography. However, it should be minded that here we model layers with the same porosity and specific surface. Varying these parameters and the layer depth, we can arbitrarily change the layer efficiency. For example, a thin MMM layer will be less effective than a thick silica gel layer, other conditions being equal. Therefore, interpretation of reasons for the difference in the efficiency of real chromatographic columns with MMM and silica gel requires correct consideration of all these factors.

CONCLUSIONS

We performed numerical simulation of gas diffusion in porous layers with different structures (ordered cylinders that serve as the models of the MMM layer with calibrated pores and disordered packings of spheres that serve as models of a porous silica gel layer). The trajectories of wandering inside the layer were calculated in the Knudsen approximation. The mean return time and its dispersion were determined in relation to the geometrical parameters of the structure. The universal (for MMM and silica gel) linear dependence of the mean wandering time on the layer depth was found. This is consistent with theoretical predictions that the mean wandering time in a pore depends only on the integrated geometrical parameters (the pore volume and the area of windows, through which gas molecules and enter and quit). Another universal dependence was found for the dispersion of the wandering time. The cubic root of dispersion increased with the layer depth as a linear function. This nontrivial relationship deserves a special theoretical study.

An equation was obtained for the contribution of the mean value and dispersion of the return time to the term that is linear with respect to the flow rate in the Van Deemter equation. Based on the results of modeling it follows that for layers

that are similar in porosity and specific surface, the MMM layer gives higher column efficiency (smaller contribution to HETP) than the silica gel layer.

This work was supported by the Russian Foundation for Basic Research (grant No. 06-03-08102-ofi).

REFERENCES

1. A. P. Karnaukhov, *Adsorption. Texture of Disperse and Porous Materials* [in Russian], Nauka, Novosibirsk (1999).
2. V. B. Felonov, *Introduction to the Physical Chemistry of the Formation of Supramolecular Structures, Adsorbents, and Catalysts* [in Russian], Siberian Division, Russian Academy of Sciences, Novosibirsk (2002).
3. M. Knudsen, *Ann. Phys.*, **28**, 75-130 (1909).
4. W. G. Pollard and R. D. Present, *Rhys. Rev.*, **73**, No. 7, 762-774 (1948).
5. J. M. Zalc, S. C. Reyes, and E. Iglesia, *Chem. Eng. Sci.*, **59**, 2947-2960 (2004).
6. Yu. V. Patrushev, V. N. Sidelnikov, M. K. Kovalev, and M. S. Melgunov, *Zh. Fiz. Khim.*, **82**, No. 7, 1-4 (2008).
7. S. Blanco and R. Fournier, *Europhys. Lett.*, **61**, No. 2, 168-173 (2003).
8. A. V. Anikeenko, "Modeling the diffusion of gas molecules in media with a complex pore system," Dissertation, Novosibirsk State University (2003).
9. A. Mazzolo, *Ann. Nucl. Energy*, **32**, 549-557 (2005).
10. O. Benichou, M. Coppey, M. Moreau, et al., *Europhys. Lett.*, **70**, No. 1, 42-48 (2005).
11. S. Redner, *A Guide to First-Passage Processes*, Cambridge University Press, New York (2001).
12. A. V. Kiselev and Y. I. Yashin, *Gas Adsorption Chromatography*, Plenum Press, New York (1969).
13. M. E. Davis, *Nature*, **417**, 813-821 (2002).
14. K. Lochmann, A. V. Anikeenko, A. Elsner, et al., *Eur. Phys. J. B*, **53**, 67-76 (2006).
15. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford (1987).
16. K. I. Sakodynskii, V. V. Brazhnikov, S. A. Volkov, et al., *Analytical Chromatography* [in Russian], Khimiya, Moscow (1993).