



## **ANISOTROPIC GAS TRANSFER THROUGH THE COMPOSITE MEMBRANES**

Ivan M. KURCHATOV<sup>1,2)</sup>, Nikolay I. LAGUNTSOV<sup>2)</sup>,  
Alexander Yu. OKUNEV<sup>1)</sup>, Gleb I. PISAREV<sup>1)</sup>,  
Vladimir N. TRONIN<sup>2)</sup>, Valery I. UVAROV<sup>1,3)</sup>

<sup>1)</sup>JSC "Aquaservice", 31, Kashirskoe sh., Moscow, 115409, Russia,  
e-mail: aquaserv@mail.ru

<sup>2)</sup>Moscow Engineering Physics Institute, 31, Kashirskoe sh.,  
Moscow, 115409, Russia

<sup>3)</sup>The Institute of Structural Macrokinetics and Materials Science, Russian  
Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

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### **ABSTRACT**

Using of stochastic dynamics methods, the probability distribution function of molecules by their moving directions in arbitrary porous media, where free molecular flow takes place, was determined. It was shown that, in some cases, the molecules in the channel can generally move athwart the channel, while an average velocity of molecules moving along the channel can significantly decrease. The anisotropic phenomenon and the hysteresis of permeability through composite asymmetric membranes were qualitatively explained.

Keywords: Porous media, Permeability, Stochastic dynamics, Composite membrane, Viscous flow, Free molecular flow

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### **INTRODUCTION**

Gas transfer through a porous membrane is a rather complicated problem, as the structure of media is generally disordered and it cannot be represented by a set of regular objects (cylindrical capillaries, spheres etc.). In the composite membranes – the ones that consist of several layers (substrate, intermediate finely porous, and the functional layers), the flow is getting even more difficult. Permeability can depend on the side of a

\* Corresponding author

membrane to which the flow is fed – to the substrate or to the functional layer. According to a resistance model [1], permeability has to be similar in both cases. A 3-5% difference in flows can be explained by a change in average pressure in viscous flow conditions [2], but when the fluxes fed to different sides of a membrane differ in several times [3] another (new) approach to the description of a membrane permeability has to be used.

### METHODS AND PROCEDURES

When examining membranes that consist of arbitrary structural elements, some generalized parameters are introduced – hydraulic radius, porosity, tortuosity, etc.

We will consider the media with the size of pores, such that the surface flows can be neglected. In these conditions, there can be two independent flow mechanisms through the membrane, i.e. Knudsen (free-molecular)  $J_k$  and viscous flow  $J_{ps}$ , where  $J_{ps}$  consists of viscous Poiseuille flow  $J_p$  and slip flow  $J_s$ . According to Weber's hypothesis, the overall flow is equal to the superposition of these three flows:

$$J = a(\rho/\lambda) J_k + b(\rho/\lambda) J_{ps}, \quad (1)$$

$$J_k = -\frac{2}{3} \frac{\rho V_T}{RT} \frac{dP}{dz}, \quad (2)$$

$$J_{ps} = J_p + J_s = -\frac{\rho^2}{8\eta RT} P \frac{dP}{dz} - \frac{\pi \rho V_T}{32RT} \frac{dP}{dz}, \quad (3)$$

where  $\rho$  - hydraulic radius (determined as doubled pores volume divided by inner surface area),  $\eta$  - viscosity,  $V_T$  – average thermal velocity,  $R$  - absolute gas constant,  $T$  – temperature,  $dP/dz$  – pressure gradient.

Coefficients  $a(\rho/\lambda)$  and  $b(\rho/\lambda)$  can be calculated by formulas:

$$a\left(\frac{\rho}{\lambda}\right) = \left(\frac{\chi\rho}{\lambda}\right) / \left(1 + \frac{\chi\rho}{\lambda}\right) \quad (4)$$

$$b\left(\frac{\rho}{\lambda}\right) = 1 / \left(1 + \frac{\chi\rho}{\lambda}\right), \quad (5)$$

where  $\chi$  depends on the ratio collision number of molecules with a surface and a collision number between molecules. In the case of full accommodation,  $\chi=2$ .

From the Chapman's expression for the viscosity [4], we can write the expression for pressure:

$$P = \pi\eta V_T / 4\lambda$$

Then, using the equations (1) – (5), we get the equation for the molar flow density at arbitrary Knudsen number value:

$$J = J_k + J_p + J_s = -\left(\frac{\pi\rho V_T}{32RT}\right) \frac{dP}{dz} \left\{ \left( f\left(\frac{\rho}{\lambda}\right) + ha \right) \frac{\chi\rho/\lambda}{1 + \chi\rho/\lambda} + g\left(\frac{1}{1 + \chi\rho/\lambda}\right) \right\}, \quad (6)$$

where  $f$ ,  $h$  and  $g$  – correction factors, considering the difference in permeability coefficients in cylindrical capillaries and isotropic porous media. Multiplying the factor  $f$  is found by the formula  $f=2\varepsilon/k$ , where  $k$  – Kozeny-Carman constant,  $\varepsilon$  – porosity.

The parameters  $g$  and  $h$  have to depend on the surface structure. We will examine movements in the porous media in the case of free-molecular movements using stochastic dynamics.

The surface of porous media has irregularities of unknown geometric characteristics, so we can expect the reflection of molecules from the inner surface at the accidental angle.

We will examine the media through which the flow occurs along the  $x$  axis. Let  $\theta$  be the angle between the direction of molecule movement and normal line to axis  $x$ . We will examine the channel in these media, surface of which is determined by the random function  $\zeta(x)$ . To make it simpler, one can assume that all the molecules move with the average thermal velocity  $V_T$ . Then, we can write:

$$\theta_{n+1} = -\theta_n + \zeta(x)$$

where  $n$  – collision number in the channel. In this equation, the first summand is the law of specular reflection, and the second – the influence of the channel irregularity.

In order to pass on to a continuous change of an angle in time, let  $\tau$  be the period of time between two sequential collisions. In isotropic media, for example, formed by spheres, there can be only average time  $\tau$  between two sequential collisions. If all the molecules move with the same average thermal speed  $V_T$ , we can write  $\tau=\rho/V_T$ .

We will rewrite the previous equation in a form:

$$\frac{\theta_{n+1} - \theta_n}{\tau} = -\frac{2\theta_n V_T}{\rho} + \frac{V_T}{\rho} \zeta(x) \quad (7)$$

Replacing the finite difference on the left side (7) by an ordinary derivative:

$$\frac{d\theta}{dt} = -\frac{2\theta V_T}{\rho} + \frac{V_T}{\rho} \zeta(x) \quad (8)$$

We will regard the random function  $\zeta(x)$  as the white noise by the time  $\zeta(t)$ . Then, the function  $\zeta(t)$  will follow the conditions:

$$\begin{aligned}\langle \xi(t) \rangle &= 0, \\ \langle \xi(t)\xi(t') \rangle &= \sigma^2 \delta(t-t'),\end{aligned}$$

where  $\sigma$  – white noise amplitude that describes the surface irregularities.

Particularly, as the first approximation the system of closely packed spheres with irregularities of accidental forms turns to be the system, which can be described by means of white noise. Then, it is valid to replace  $\zeta(x)$  by  $\xi(t)$ , and (8) will be written as:

$$\frac{d\theta}{dt} = -\frac{2\theta V_T}{\rho} + \frac{V_T}{\rho} \xi(t) \quad (9)$$

The stochastic differential equation (9) is the Langevin equation [5]. This equation is similar to Langevin equation in the problem of the Brownian particle motion in relation to its velocity [5]. Then by analogy to the solution of the problem concerning the Brownian particle motion, a mean-square angle  $\langle \theta^2 \rangle$  will be found with the following equation.

$$\langle \theta^2 \rangle = \theta_0^2 \exp\left(-4 \frac{V_T}{\rho} t\right) + \frac{\gamma \rho}{4V_T} \left(1 - \exp\left(-4 \frac{V_T}{\rho} t\right)\right)$$

where  $\gamma$  – certain parameter characterizing the jitter of the pore surface.

From  $\langle \theta^2 \rangle$  we can see that for long periods of time the initial values can be neglected, and mean-square angle approaches the value  $\gamma \rho / (4V_T)$  that is determined by the system itself.

The Langevin equation (9) corresponds with the Fokker-Plank equation [6] concerning the probability distribution function  $f(\theta, t)$ :

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \theta} \left( -\frac{2\theta V_T}{\rho} f \right) + \frac{\sigma^2}{2} \frac{\partial^2}{\partial \theta^2} \left( \frac{V_T^2}{\rho} f \right) \quad (10)$$

The stationary solution (10) of the Fokker-Plank equation looks like:

$$f(\theta) = \frac{\sqrt{\frac{A}{\pi}} \exp(-A\theta^2)}{\operatorname{erf}\left(\frac{\pi}{2} \sqrt{A}\right)} \quad (11)$$

Function  $f(\theta)$  is the even function  $\theta$  and it depends on the parameter  $A=2\rho/(\sigma^2 V_T)$ , the value of which determines the distribution width.

The number of molecules going through an arbitrary cross-section in the  $x$  direction is determined from:

$$N = 2 \int_0^{\pi/2} n f(\theta) V_h \sin(\theta) d\theta \quad (12)$$

In the case of equiprobability of distribution of molecular directions by angles, the number of molecules going through the arbitrary cross-section in the  $x$  direction in a unit of time is written as:

$$N_{eq} = \int_0^{\pi/2} \frac{1}{2} n V_h \sin\theta \cos\theta d\theta = \frac{1}{4} n V_h \quad (13)$$

By comparing Eq. (12) and (13) and considering (11) we are enabled to draw a conclusion that in the case of defined pressure drop on the border of the porous media the value of free-molecular flow considering tangling of trajectory of molecule's move noticeably decreases. This result comes directly from the analysis of the function  $f(\theta)$  (11), since with the increase of velocity vector deviation from the normal line to the surface, the value  $f(\theta)$  rapidly decreases.

The parameter  $g$  in the equation (6) can be defined from the comparison of the equations of Knudsen flows in the case of distribution equiprobability by angles and in the case of distribution (11). The dependence of the  $h$  parameter on the characteristics of the channel surface irregularity can be determined by the comparison of slip velocities on the surface. It is essential to emphasize the fact that the white noise characteristics come to the general equation of the flow (6) only in terms of the  $g$  and  $h$  parameters. In other words, the form of equation (6) remains the same.

The parameter  $\chi$  from equation (6) in the case of the anisotropic distribution function (11) can be calculated using (12).

## RESULTS AND DISCUSSIONS

The results obtained enabled us to explain qualitatively an experimental dependence of composite polymer membrane permeability on the pressure drop on it.

The experiments were carried out using the apparatus that enables measuring permeability under both integral and differential conditions. Flow rate measuring was carried out using the constant pressure method. For fastening the experiment a special cell, that enabled measuring the permeability in the wide range of change in pressure and pressure drop was used.

The asymmetric PVTMS (polyvinyltrimethylsilane) membrane was the object of research. It has three clearly defined layers: diffusive (homogeneous) of 0.1-0.2  $\mu$  width, finely porous of 10-15  $\mu$  width and pore size up to 0.3  $\mu$ , and the layer with large (up to 4  $\mu$ ) transport pores. An overall membrane width was about 150  $\mu$ . The influence of transport pores on the permeability of the membrane was considered to be small.

In figure 1 we can see the dependence of helium permeability on the pressure drop. High pressure at the cell input changed in the range from 1 to

3 bars; low pressure at the cell output was kept about 1 bar. On the graph we can see that permeability depends on the side to which the flow is fed. If the flow is fed to the non-porous selective layer, permeability slightly changes in dependence on the pressure. But when the flow is fed to the porous substrate layer, its value noticeably increases with the increase of average pressure. In the case of low pressure the difference between permeability increases twice in values. Moreover, permeability in the case of gas fed to the substrate layer is noticeably lower. A decreasing of influence of permeability value anisotropy with an increase in pressure is connected with the increasing fraction of viscous flow which is determined only by the channel form not depending on the surface characteristics.

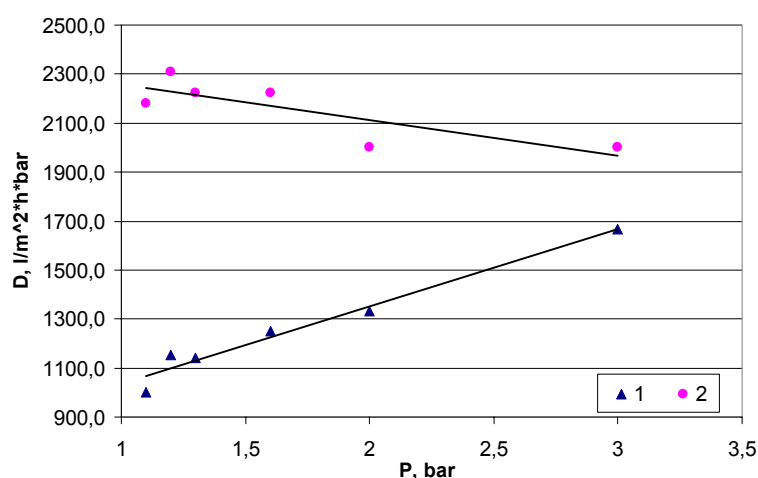


Fig. 1. Dependence of PVTMS membrane's helium permeability on the high pressure: 1 – gas fed to porous substrate, 2 – gas fed to selective layer.

In order to explain figure 1 we will examine the two-layer composite membrane that consists of a non-porous selective layer and finely porous substrate layer, where the free-molecular conditions are fulfilled and molecular trajectory tangling phenomenon is possible. In figure 2, the scheme of the flows moving in the two-layer composite porous membrane is presented. We will consider that anisotropic stochastic moving of molecules takes place in the first layer (a layer with relatively large pores). The area of pores of the first layer labeled as  $S_1$ , the second layer -  $S_2 = \zeta S_1$ . The concentration of molecules outside the membrane before the first layer is  $N_1$ , and after the second layer it is  $N_2$ . Inside the first layer the concentration changes from  $n_1$  to  $n_1^*$ , and in the second layer from  $n_2^*$  to  $n_2$ .

If the gas is fed to the first layer side, molecules go through the layer with relatively large pores, then in the boundary region of the two layers, only a part of molecules penetrates through it and goes through the second layer; the rest of the molecules interacts with the boundary region in the

same way as with the channel border. This interaction leads to replacing one distribution function to another. Before the interaction the advantage directions were athwart the channel, after – along the channel.

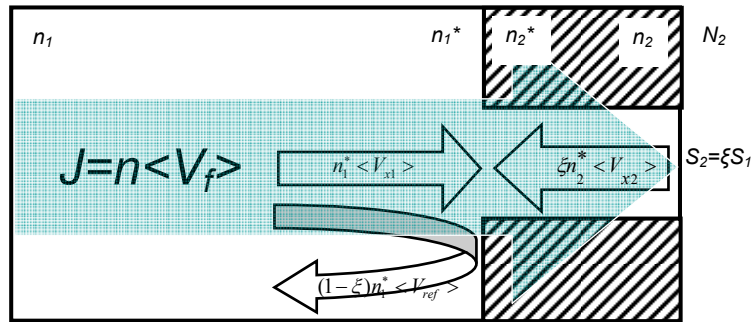


Fig.2. Scheme of the flows moving in the two-layer composite membrane.

It means that, after the interaction with the boundary region, molecules have considerably large average projection of velocity along the channel  $\langle V_{ref} \rangle$ , then before the interaction  $\langle V_{x1} \rangle$ . Moreover, after the interaction, molecules are directed from the boundary region to the first layer.

Balance equations at the environment/first layer boundary, at the boundary region of the two layers, and at the second layer/environment can be written as:

$$\begin{aligned}
 J &= \frac{1}{4} N_1 V_T - n_1 \langle V_{x1} \rangle \\
 J &= n^*_1 \langle V_{x1} \rangle - \xi n^*_2 \langle V_{x2} \rangle - (1-\xi)n^*_1 \langle V_{ref} \rangle \\
 J &= \xi (n_2 \langle V_{x2} \rangle - \frac{1}{4} N_2 V_T)
 \end{aligned}
 \tag{14}$$

Simultaneously, with diffusion equations (such as equation (6)) for the both layers, balance equations (14) describe the permeability of the two layer membrane. According to this model the necessary condition for permeability anisotropy is the anisotropic distribution of molecules by their moving directions. If the condition  $\langle V_{x1} \rangle < \langle V_{ref} \rangle$  is fulfilled, then the flow from the first layer (with anisotropic stochastic moving of molecules) to the second one can be lower several times than the reverse flow.

It is significant that in the case of full accommodation balance, equations analysis gives no anisotropic effect.

### EXPERIMENTAL PART

In figure 1 the dependences of the membrane permeability versus the pressure an the membrane cell input in the case of gas fed to the substrate (curve 1) and to the selective layer (curve 2) is presented. We can see that curve 2 is situated above curve 1 as the result of permeability anisotropy. It is interesting that the curve 1 is a rapidly increasing function because of

increase in viscous flow part. The character of curve 2 is mainly determined by properties of the selective layer and the permeability change weakly depends on pressure.

In figures 3 and 4 the dependences of the membrane permeability on the pressure at the membrane cell input (in the case of gas fed to the substrate (fig.3) and to the selective layer (fig.4)) are presented.

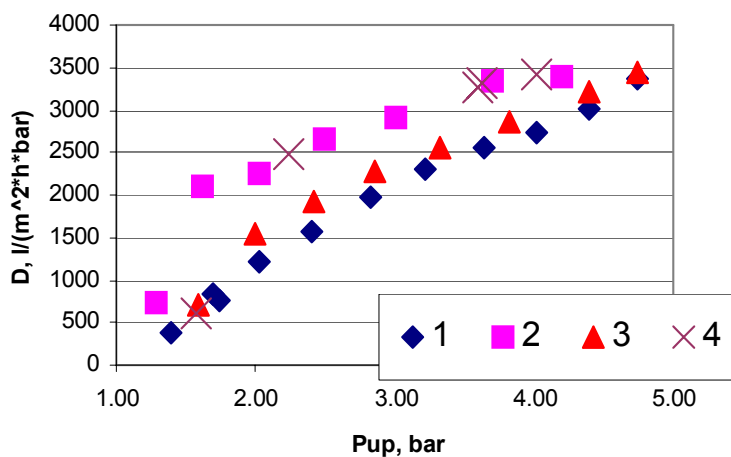


Fig.3. Dependence of PVTMS membrane's nitrogen permeability on the high pressure when the flow is fed to the substrate layer side: 1 – cycle 1, increasing pressure; 2 – cycle 1, decreasing pressure; 3 – cycle 2, increasing pressure; 4 – cycle 2, decreasing pressure.

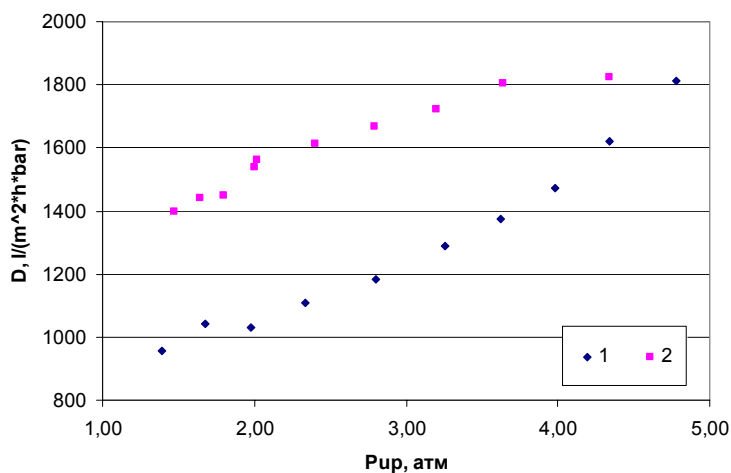


Fig.4. Dependence of PVTMS membrane's nitrogen permeability on the high pressure when the flow is fed to the selective layer side: 1 – increasing pressure, 2 – decreasing pressure.



In figure 3, the dependence is derived in a certain succession: at the beginning of experiment, pressure increased from 1 to 5 atmospheres (curve 1), and after that decreased from 5 to 1 atmosphere (curve 2). It turned out that the curves in figure 3 do not coincide at all. A relationship by its appearance looks like hysteresis, moreover curve 2 goes higher than curve 1. It is interesting to point out the fact that in the second cycle of pressure increase (curve 3) the dependence of permeability is close to the first cycle of curve 1.

In figure 4 we see the same type of dependence – when pressure decreases the permeability curve goes up.

The curves on figures 3 and 4 (hysteresis phenomenon) can be interpreted on the basis of anisotropic distribution function of molecules by their moving directions. Let us examine one layer porous membrane where anisotropic distribution function of molecules by their moving directions takes place. Flow through the layer depends on its concentration. Flow equations (12) and (13) we can see, that process of decreasing concentration in the porous membrane is slower than an increase in concentration. It means that if we increase feed pressure, the concentration of molecules in the membrane increases, and consequently the flow increases too, what we can see on the curve 1. As pressure decreases, the concentration of molecules in the membrane decreases not immediately, because the majority of molecules there move across the channel and only a small portion of molecules leave the finely porous layer (12). It leads to the situation that in the case of decreasing feed pressure flow through the membrane is found to be higher than at the same feed pressure but under different conditions of its change (increasing or decreasing).

### CONCLUSION

The probability distribution function of molecules along the movement direction in the porous media was calculated. It was shown that the molecules in the channel in some cases can move generally athwart the channel, while the average velocity of molecules' moving along the channel can appreciably decrease. These effects are determined by specific interactions between the molecules and the internal pores surface.

The anisotropy phenomenon of the flow value, when it is fed to the substrate and to the selective layer was qualitatively explained. The hysteresis phenomenon for the flow going through the composite asymmetric membranes in sequential cycles of increasing and decreasing pressure was revealed and qualitatively explained.

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