

Article

Mass Transfer Through Graphene-Based Membranes

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Abstract: The problems related to the transport of gases through nanoporous graphene (NG) and graphene oxide (GO) membranes are considered. The influence of surface processes on the transport of gas molecules through the aforementioned membranes is studied theoretically. The obtained regularities allow finding the dependence of the flux of the gas molecules passing through the membrane on the kinetic parameters which describe the interaction of the gas molecules with the graphene sheets. This allows to take into account the influence of external fields (e.g., resonance radiation), affecting the aforementioned kinetic parameters, on the transport of gas molecules through the membranes. The proposed approach makes it possible to explain some experimental results related to mass transfer in the GO membranes. The possibility of the management of mass transfer through the NG and GO membranes using resonance radiation is discussed.

Keywords: gas transport; adsorption; graphene-based membranes

1. Introduction

The scope of our work is to describe the transport properties with existing models without any additional data. Moreover, the gas separation mechanism for GO membranes is unclear due to inconsistent permeation and separation results reported in the literature.

It is known that graphene-based materials are very efficient in many areas of chemical engineering in particular for the elaboration of new type of batteries for modern electronics [1] and for creation of new types of membranes for the separation of gas mixtures [2]. Graphene is a two-dimensional one-atom-thick sheet of carbon atoms packed in the honeycomb crystal lattices, it is characterized by unique physicochemical properties in particular the high chemical stability, mechanical strength, thermal conductivity and charge mobility [1,2]. It was shown that pristine graphene is impermeable in regard to smallest molecules [2].

A graphene sheet with nano and sub-nano pores, known as nanoporous graphene (NG), is used for the size-selective separation of gas mixtures based on the molecular sieving effect [2]. The permeability and selectivity of NG membranes are higher than the aforementioned values for polymer membranes. Ion bombardment and electron beam exposure are often used to prepare pores in the graphene sheets. As indicated in [3], molecules adsorbed on the graphene sheet and participating in surface diffusion [4] are more likely to find the pores in NG membranes than the gas molecules. Thus, surface diffusion can be one of the main processes affecting the transport of gas molecules through NG membranes [5–7]. It should be noted that the problem related to the management of the transport of gas molecules using the porous graphene is very actual (e.g., for removing carbon dioxide from the gas mixtures) [8]. The core factor affecting permeance of NG membranes is the pore size. However, as indicated in the

aforementioned paper, it is difficult to fabricate defect-free porous membranes in a large scale that have pores matching the kinetic diameters of common gas molecules, ranging from 2.5 to 4.0 Å. The combined use of the ionic liquid and porous graphene for more effective separation of the gas mixtures is considered in [8]. It is demonstrated from classical molecular dynamics simulations that a monolayer of ionic liquid on the NG membrane can be used to control the pore size of porous graphene. However, this method requires modification of the original membrane. In the present paper is discussed the new method to control the gas transport through NG membranes using external fields (e.g., resonance laser radiation) leading to excitation of gas molecules and changing their interaction with the graphene sheet. In this case do not need any modifications of the original membrane. The effect of resonance radiation on the separation of the gas mixtures passing through the dense membranes was considered in [9].

Graphene oxide (GO) can be considered as the oxidized form of graphene [2]. GO membranes contain stacked GO sheets as well as vacancy defects and functional groups distributed in carbon lattice, these membranes can be cheaply produced by oxidation and exfoliation of graphite [2]. The problems related to preparation of GO membranes and mass transfer in them were discussed in particular in [10–12]. In [10] it was shown that self-standing GO membranes demonstrate outstanding performance for hydrogen separations, including mixtures of H₂/CO₂ and H₂/hydrocarbons. An efficient spray-evaporation method was explored in [11] to optimize performance of GO membranes. The very interesting experimental results related to the transport of gases such as CH₄, N₂, CO₂, H₂ and He through GO membranes are given in [12]. These results can be used in a study of the separation of gas mixtures and in a development of new models for mass transfer through GO membranes. The model for the gas transport through GO membranes proposed in the present paper allows explaining some experimental results given in the above-mentioned paper.

Below, we consider the possible influence of the surface processes (including the features of the gas molecule scattering by graphene sheet and surface diffusion of adsorbed molecules) on the transport of gases through the NG and GO membranes. This allows for the dependence to be found of the flux of gas molecules passing through the membranes on the kinetic parameters which describe the interaction of the gas molecules with the graphene sheets. The influence of external fields (e.g., resonance radiation), affecting the aforementioned kinetic parameters, on mass transfer in the graphene-based membranes is discussed. The core idea of this paper consists in the search of new ways to manage mass transfer in the porous graphene and graphene oxide membranes by means of external fields (e.g., resonance radiation) affecting the above-mentioned kinetic parameters.

2. The Theoretical Description of Mass Transfer Through NG Membranes

Firstly, let us consider the transport of molecules of the gas mixture through the NG membrane. The flux density of the gas molecules of component *i* passing through the NG membrane j_{ir} can be presented as [5].

$$j_{ir} = j_{is} + j_{id}, \quad (1)$$

where the value of j_{is} is related to adsorption of the gas molecules of component *i* on the graphene sheet, their diffusion along the graphene sheet to reach the pores and the penetration through the two-dimensional pores to the other membrane side, the value of j_{id} is related to the direct penetration of gas molecules of component *i* through the pores of the NG membrane. We assume, similarly to [3], that the rates of adsorption and desorption of gas molecules are much higher than the diffusion rate of adsorbed molecules along the graphene sheet and the penetration rate of the molecules through the pores to the other side of the NG membrane, as well as that the adsorbed phase on the graphene sheet is in equilibrium with the free gas near the considered side of NG membrane. We suppose also that the number density of adsorbed gas molecules on the graphene sheet is sufficiently small and we can use the Henry law for adsorption of gas molecules, as well as that the size of the pores is greater than the size of the gas molecules and these molecules can penetrate through the two-dimensional pores in the NG membrane.

The value of j_{is} is related to the frequency of encounters of adsorbed molecules of component i with the two-dimensional pores on the unit surface of the graphene sheet Q_{ip} and the probability of transfer (translocation) of the molecules after encounters with the two-dimensional pores onto the other side of the NG membrane (for the sake of simplicity, we assume that the two-dimensional pores are round and have the same diameter). In the case of localized mobile adsorption, for the molecule movement from one site to an adjacent one, the molecule must possess sufficient energy to pass over the energy barrier between the two sites [4]. If this barrier is low compared to the average energy of the molecule, surface diffusion of the adsorbed gas molecules on the graphene sheet can be considered on the basis of the model of the two-dimensional gas [6]. The value of Q_{ip} can be found similarly to the method used in the theory of heterogeneous nucleation [13,14]. In the case of localized mobile adsorption (when surface diffusion is realized by jumping mechanism), the value of Q_{ip} in view of [13] can be written as

$$Q_{ip} = \pi d n_p \frac{1}{4} n_{ia} a_0 v' \exp\left(-\frac{E_{is}}{kT}\right) = \frac{\varepsilon_p}{d} n_{ia} a_0 v' \exp\left(-\frac{E_{is}}{kT}\right). \tag{2}$$

where d is the diameter of the two-dimensional pore, n_p is the number density of the two-dimensional pores on the graphene sheet, n_{ia} is the number density of the adsorbed gas molecules of component i on the graphene sheet, a_0 is the jump distance for the adsorbed molecule (lattice parameter), v' is the vibration frequency of the adsorbed molecule (the values a_0 and v' are assumed usually to be constant), E_{is} is the activation energy for surface diffusion of adsorbed molecules of component i , k is the Boltzmann constant, T is the temperature (we assume further the system to be isothermal), $\varepsilon_p = n_p s_p$ is the porosity of the NG membrane, where $s_p = \pi d^2/4$ is the area occupied by the two-dimensional pore. The flux density of component i passing from one side of the graphene sheet onto its another side j_{ia} can be written as

$$j_{ia} = Q_{ip} \exp\left(-\frac{E_{it}}{kT}\right), \tag{3}$$

where E_{it} is the effective activation energy for the molecule translocation from one side of the graphene sheet onto its another side. The rate constants for different steps in translocation of molecules from one side of the NG membrane onto its another side are considered in [7]).

In the case of the model of the two-dimensional ideal gas for the adsorbed molecules, the value of Q_{ip} in view of [14] is given by

$$Q_{ip} = \pi d n_p \frac{n_{ia}}{\pi} \left(\frac{\pi kT}{2m_i}\right)^{1/2} = \frac{4\varepsilon_p n_{ia}}{d} \left(\frac{kT}{2\pi m_i}\right)^{1/2}, \tag{4}$$

where m_i is the mass of molecules of component i .

It is seen from Equations (2) and (4) that, at the constant ε_p , the value of Q_{ip} increases with a decrease in the pore diameter d . The flux density of molecules of the component i related to the direct flux of molecules passing from the gas phase near one side of the NG membrane into the gas phase near another membrane side (the gas phase pathway) j_{id} according to [7] can be presented as

$$j_{id} = \varepsilon_p \left(\frac{p_i}{(2\pi m_i kT)^{1/2}}\right) G_{i,gas}, \tag{5}$$

where p_i is the partial pressure of component i of the gas mixture, the value of $G_{i,gas}$ describes the correction to the Knudsen equation for the gas flux of molecules of component i passing through the sub-nanometer two-dimensional pore (this correction is related to the sufficiently small value of d/d_m , where d_m is the kinetic diameter of gas molecules). The value of $G_{i,gas}$ according to [7] can be written as

$$G_{i,gas} = \exp\left(-\frac{\Delta E_{i,gas}}{kT}\right), \tag{6}$$

where $\Delta E_{i,\text{gas}}$ is the energy barrier height relative to the gas phase in the transport of gas molecules of component i through the two-dimensional pore. It is seen from Equations (5) and (6) that the value of j_{id} decreases with an increase in $\Delta E_{i,\text{gas}}$.

A decrease in the flux density of gas molecules j_{id} passing through the NG membrane on the basis of the steric consideration is discussed in [5]. The reduction in the value of $G_{i,\text{gas}}$ in Equation (5) and accordingly in the value of j_{id} is related in this case to the fraction of molecule trajectories that intersect the NG membrane within the pore diameter but cannot permeate the pore. It should be noted that $G_{i,\text{gas}} \rightarrow 1$ with an increase in d/d_m . The resulting flux density of gas molecules passing through NG membrane j_{ir} for the case of localized mobile adsorption in view of Equations (2), (3), and (5) is given by

$$j_{ir} = \varepsilon_p \left[\frac{1}{d} a_0 v' (n_{iaf} - n_{iap}) \exp\left(-\frac{E_{is} + E_{it}}{kT}\right) + \left(\frac{p_{if}}{(2\pi m_i kT)^{1/2}} - \frac{p_{ip}}{(2\pi m_i kT)^{1/2}} \right) G_{i,\text{gas}} \right], \quad (7)$$

where p_{if} and p_{ip} are the partial pressures of component i at the feed and permeate sides of the NG membrane, n_{iaf} is the number density of adsorbed molecules of component i on the feed side of the membrane, n_{iap} is the number density of adsorbed molecules of component i on the permeate side of the NG membrane.

The number density of adsorbed molecules of component i n_{ia} on the graphene sheet at the aforementioned assumptions can be written as [4]

$$n_{ia} = \frac{\alpha_i \tau_i p_i}{(2\pi m_i kT)^{1/2}} = \frac{\alpha_i \tau_i n_i v_i}{4}. \quad (8)$$

where α_i is the sticking coefficient of molecules of component i , τ_i is the adsorption time for the molecules of the component i ($\tau_i = \tau_0 \exp(E_{ia}/(kT))$, where the value of the pre-exponential factor τ_0 is assumed usually to be constant, E_{ia} is the adsorption energy), $v_i = (8kT/(\pi m_i))^{1/2}$ is the mean thermal velocity of gas molecules of component i , and n_i is the number density of molecules of component i in the gas phase.

In the case when the adsorbed phase on the graphene sheet can be modeled by the ideal two-dimensional gas the resulting flux density of gas molecules passing through the NG membrane j_{ir} in view of Equations (3)–(5) can be written as:

$$j_{ir} = \varepsilon_p \left[\frac{4}{d} (n_{iaf} - n_{iap}) \left(\frac{kT}{2\pi m_i} \right)^{1/2} \exp\left(-\frac{E_{it}}{kT}\right) + \left(\frac{p_{if}}{(2\pi m_i kT)^{1/2}} - \frac{p_{ip}}{(2\pi m_i kT)^{1/2}} \right) G_{i,\text{gas}} \right]. \quad (9)$$

Equations (7)–(9) show that the influence of resonance (e.g., laser) radiation on the porous graphene membrane allows the transport of gas molecules through the membrane and separation of gas mixtures to be managed due to a change in the radiation field of the values of α_i and τ_i (these values can be different for excited by radiation and unexcited molecules [9]). A decrease in the values of α_i and τ_i for molecules of foreign gases under the effect of resonance radiation can lead to the purification of the graphene sheets from the adsorbed molecules of foreign gases and to a decrease in their transport through NG membranes.

It is seen from Equations (7) and (9) that heating of the gas-membrane system by radiation leading to an increase in the system temperature also affects the transport of gas molecules through the NG membrane and accordingly the separation of gas mixtures passing through the membrane.

3. Developing of the Model for Mass Transfer Through GO Membranes

Graphene oxide is used for the production of highly effective membranes for the purification of water and separation of gas mixtures [2]. The GO membrane can be considered as a composite, comprised of pristine and oxidized parts of the system consisting of graphene sheets. The GO

membranes have two types of pores: the slit-like pores between the GO sheets and the small holes in the sheets related to defects in the GO sheets [2]. The empty space between the non-oxidized regions of GO monolayered sheets can be assumed lying in the range 0.4–0.9 nm. Distance between the point-like defects in the graphene sheets can be estimated as 10.0–13.3 nm [11]. The proposed in the present paper model for the description of mass transfer in GO membranes is related to following main points (which can serve as a kind of the scheme to describe the theoretical model and its novelty): the transport of gas molecules in GO membranes is realized mainly through the slit-like pores formed by graphene sheets. Mass transfer in these pores can be affected by the processes such as adsorption and desorption of gas molecules, surface diffusion of adsorbed molecules on the pore walls, and the gas molecule scattering by the pore walls. The external fields (e.g., resonance laser radiation) can affect the parameters characterizing the aforementioned processes that allows to develop new methods controlling mass transfer in GO membranes without modification of the membranes. The proposed model gives also the ability to explain some experimental results given in [12].

The effective diffusion coefficient for the activated Knudsen diffusion (or in other words translational diffusion) of component *i* of a gas mixture in the nanoscale slit-like pore of the GO membrane with the flat parallel pore walls D_{ie} according to [15] can be written as

$$D_{ie} = \frac{1}{3} H_{ie} v_i \exp\left(-\frac{E_{id}}{kT}\right), \quad (10)$$

where $H_{ie} = H - d_{im}$ is the effective accessible distance between the pore walls in relation to molecules of component *i* (the accessible pore width [15]), d_{im} is the kinetic diameter of molecule of component *i*, *H* is the real width of the slit-like pore, E_{id} is the energy barrier for the activated Knudsen diffusion, which depends on the pore width. It is worth noting that the pre-exponential factor in Equation (10) in the case of the cylindrical pore is equal to $d_{ie} v_i / 3$, where d_{ie} is the effective diameter of the cylindrical pore in relation to molecules of the component *i* ($d_{ie} = d_c - d_{im}$, where d_c is the real diameter of the cylindrical pore [16]). It follows from the aforementioned that the greater the molecule size (the kinetic diameter d_{im}) the smaller the effective pore diameter and respectively the diffusion coefficient. The value of E_{id} in Equation (10) decreases with a decrease in the value of d_{im}/H . As indicated in [12], the activation energy for the diffusion of gas molecules in the cylindrical pore is small (close to zero) at $d_{im}/d_c < 0.6$ (in the case of the slit-like pore we should to use the value of d_{im}/H instead of d_{im}/d_c). It is worth to note that Equation (10) corresponds to the case of diffuse molecule scattering by the pore walls. For the sake of simplicity, further we assume that the value of E_{id} in Equation (10) is small (close to zero) and $H_{ie} = H$. Under these assumptions and Equation (10), we can estimate the diffusion coefficient of the classic Knudsen diffusion for the slit-like pore as

$$D_{i,Kn} = \frac{1}{3} H v. \quad (11)$$

The experimentally observed excess of the measured value of the flux of light gas molecules passing through the carbon nanotubes in relation to the value of the flux of gas molecules according to the classic Knudsen diffusion was discussed in [17]. As indicated in [17], this effect can be related to specular reflections of gas molecules from the pore walls. The Maxwell diffuse-specular model of gas molecule scattering leads to the factor $\psi_i = (2 - f_i)/f_i$ in the value of the diffusion coefficient in the classic Knudsen diffusion [18]. Here f_i is the coefficient characterizing the probability of diffuse scattering of gas molecules of component *i*. The value $1 - f_i = f_{i,sp}$ describes the probability of specular reflection of gas molecules of component *i*. The probability of specular reflections of molecules from the pore walls depends in particular on the surface roughness, the relationship between the masses and sizes of molecule (atom) of the gas phase and the dense phase (pore walls) and on the adsorption energy of gas molecules.

Let us consider the dependence of the value of $f_{i,sp}$ on the mass of molecules of a gas phase in the simplest case of a smooth and clean (without adsorbed molecules) surface. The probability of elastic

(which is assumed to be specular) reflection $f_{i,sp}$ of the gas molecule of component i according to [19] can be presented as

$$f_{i,sp} = \exp\left(-\frac{E_{ic}}{kT}\right). \tag{12}$$

where E_{ic} is the specific energy of the interaction of the gas molecules of component i with the pore walls, which depends on the adsorption energy E_{ia} and can be estimated for light gas particles as

$$E_{ic} \approx 4 \frac{m_i}{m_w} E_{ia}, \tag{13}$$

where m_w is the mass of molecules (atoms) of the dense phase (material of the pore walls).

It is seen from Equations (12) and (13) that the smaller the values of m_i and E_{ia} at the constant value of m_w , the greater the probability of elastic reflections of gas molecules. In particular, this fact can lead to a sufficiently large probability of specular reflections of light gas particles such as H_2 and He from the walls of the carbon nanotubes. The similar regularities may apparently take place in the transport of gases through the slit-like pores of GO membranes.

In the backscattering scheme, it is supposed that a fraction f_i of molecules of component i is scattered according to the cosine law (diffuse scattering) and a fraction $1 - f_i$ is scattered in the direction opposite to the velocity of incident molecules and the value of $\psi_i = f_i/(2 - f_i)$ [20]. The backscattering may occur in the case of the roughness of the pore walls and adsorption of molecules of a foreign gas on the pore walls. It was shown in [21] that adsorption of one component of a gas mixture on the pore walls can influence the scattering of the second component of a gas mixture that affects the flux of the gas molecules of the second component passing through the channel (pore). The problems related to the effect of adsorption, surface diffusion, specular reflection, and backscattering of the gas molecules on the gas flux passing through a long cylindrical channel (pore) in the free molecular regime of gas flow are considered in [20–23].

It is worth noting that surface diffusion of molecules adsorbed on the walls of the slit-like pores of the GO membrane can also increase the flux of molecules passing through the pores. Let us estimate the influence of surface diffusion of molecules adsorbed on the walls of the slit-like pore of the GO membrane on the total flux of molecules passing through the pore. For the sake of simplicity, we assume that the total flux of molecules of component i passing through the slit-like pore can be presented as a sum of the flux of the gas molecules and the surface flux of adsorbed gas molecule on both walls of the pore (the additive approximation). Taking into account Equation (8) and the aforementioned assumptions, the total flux of molecules passing through some effective cross-section of the slit-like pore $\sigma_e = Hl$, where l is the length of the line on the flat pore wall which is directed perpendicularly to the direction of mass transfer, can be written as

$$J_{it} = -Hl\psi_i D_{i,Kn} \frac{dn_i}{dx} - 2lD_{is} \frac{dn_{ia}}{dx} = -HlD_{i,Kn} \left(\psi_i + \frac{1}{2H} \frac{D_{is}v_i\tau_i\alpha_i}{D_{i,Kn}} \right) \frac{dn_i}{dx}, \tag{14}$$

where x is the longitudinal coordinate directed along the slit-like pore in the direction of mass transfer and D_{is} is the coefficient of surface diffusion which, for the model of localized surface diffusion on the graphene sheets, is given by [4]:

$$D_{is} = D_{i0} \exp\left(-\frac{E_{is}}{kT}\right), \tag{15}$$

where the value of D_{i0} is usually assumed to be constant.

Let us introduce the dimensionless value $J_{i0} = J_{it}/J_{i,Kn}$, where $J_{i,Kn}$ is the flux of molecules passing through the effective cross-section of the slit-like pore σ_e by the classic Knudsen diffusion

$$J_{i,Kn} = -HlD_{i,Kn} \frac{dn_i}{dx}. \tag{16}$$

Taking account Equations (14) and (16), we can write the following equation for J_{i0}

$$J_{i0} = \psi_i + \gamma_i, \quad (17)$$

where $\gamma_i = D_{is}v_i\tau_i\alpha_i/(2HD_{i,KN})$. We assume that parameters related to the interaction of gas molecules with the slit-like pore walls (in particular ψ_i , α_i , τ_i and D_{is}) are the surface-average values in relation to graphitic areas and oxidized regions of the GO sheets. Equation (17) gives the possibility of analyzing the influence of different factors, related to the interaction of gas molecules with the walls of the slit-like pore, on mass transfer through the pore.

Let us consider the joint influence of surface diffusion and the Maxwell diffuse-specular scheme of the molecule scattering (when $\psi_i = (2 - f_i)/f_i$) or the backscattering scheme for molecules (when $\psi_i = f_i/(2 - f_i)$) on mass transfer in the slit-like pore with the flat parallel walls. Figure 1 shows the dependence of the value of J_{i0} on f_i for the different values of parameter γ_i in Equation (17) for the Maxwell diffuse-specular scheme of the gas molecule scattering and the backscattering scheme.

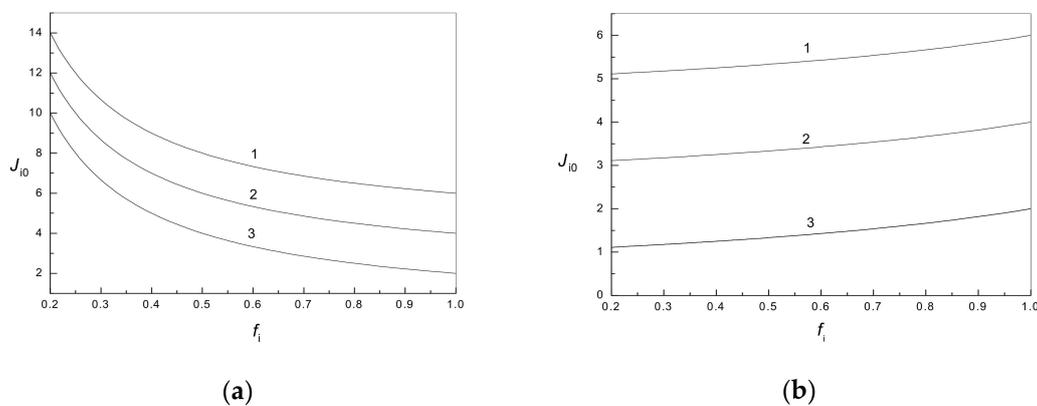


Figure 1. Dependence of J_{i0} on f_i for different values of parameter γ_i : 1: $\gamma_i = 5$, 2: $\gamma_i = 3$, 3: $\gamma_i = 1$; (a) A diffusion-specular scheme of gas molecule scattering; (b) A backscattering scheme for gas molecules.

It is seen from Figure 1 that in the case of a diffuse-specular scheme of molecule scattering the value of J_{i0} increases with an increase in γ_i and decreases with an increase in f_i and in the case of a backscattering scheme J_{i0} increases with an increase in both γ_i and f_i .

4. Validation of Model; Discussing and Comparing the Model With Experimental Data

The very interesting experimental results related to gas transport through GO membrane are given in [12]. These results can be used in the study and optimization of processes such as the separation of gas mixtures and purification of gas phase on the impurity component by means of GO membranes. The authors of the aforementioned paper note that for gas permeation, different transport models were proposed, and these models negate each other and cannot be used to explain the results of the aforementioned paper. The explanation of these experimental results is necessary for understanding the mechanism of mass transfer in GO membranes. Let us consider some results presented in the above-mentioned paper. Figure 1 in this paper shows that the permeance for the three larger molecules CH_4 , N_2 and CO_2 corresponds to the data that follow from the classic theory of the Knudsen diffusion. The permeance for the two smaller molecules He and H_2 are relatively far above these data. To explain these results authors of the above-mentioned paper, propose a two-pathway transport model for GO membranes: the inter-sheet pathway A and the inner-sheet pathway B. The inter-graphene sheet pathway (pathway A) is composed primarily of inter-galleries between stacked GO sheets which can be modeled by slit-like pores. The inner-sheet pathway (pathway B) represents the structural defects of the GO sheets and it is modeled in this paper by a straight channel. It is also assumed that the tortuosity factor for the pathway A is much greater than for the pathway B (the tortuosity factor for

pathway B is assumed to be unity). The obtained experimental results are explained by a difference in the permeance for the larger molecules (CH₄, N₂ and CO₂) and for the smaller molecules (H₂ and He) for the pathways A and B. The greater permeance for smaller molecules in GO membrane is explained by their greater permeance by the pathway B. The transport of gas molecules through GO membranes is considered on the basis of the solution-diffusion model. The total permeance for the GO membrane in relation to gas molecules is written in the above-mentioned paper as a sum of the permeances by the pathway A and the pathway B. It should be noted that in a great quantity of graphene sheets of GO membranes, defects of individual sheets can be overlapped by adjacent graphene sheets [24,25] that leads to an increase in the tortuosity factor in diffusion of gas molecules through the membrane by the pathway B and accordingly to a significant decrease in the permeance by the pathway B. As indicated in [25], the average area percentage of holes within a GO sheet is only approximately 2%, which is too small to make a significant impact on the permeability of GO membranes and only the interlayer galleries are assumed to be the major mass-transport pathways. It is worth to note that the model proposed in [12] does not include the parameters characterizing the features of the gas molecule scattering by the walls of pores in GO membranes and surface diffusion of molecules adsorbed on the walls of slit-like pores.

The model involving the parameters describing features of scattering of gas molecules by the walls of the slit-like pores in GO membranes allows explaining some experimental results which are given in [12] without using the concept of two pathways for the transport of gas molecules in GO membranes. It is worth to note that presented in aforementioned paper experimental data show that the presence of molecules of CO₂ in the system can lead to a decrease in the permeance of H₂ molecules in the GO membrane in comparison with diffusion only H₂ molecules (without the presence of CO₂ molecules). This effect can be explained by the influence of strongly adsorbed CO₂ molecules on the scattering of weakly adsorbed H₂ molecules. The fraction of diffusely scattered H₂ molecules f_H can be estimated as $f_H = f_1(1 - \theta_C) + f_2\theta_C = \theta_C(f_2 - f_1) + f_1$ [20], where f_1 is the fraction of diffusely scattered H₂ molecules on a part of the surface not occupied by adsorbed CO₂ molecules, f_2 is the fraction of diffusely scattered H₂ molecules on a part of the surface occupied by adsorbed molecules of CO₂, θ_C is the surface coverage by molecules of CO₂ of the pore walls.

Let us consider for simplicity the case when the parameter γ_i in Equation (17) is much less than the value of ψ_i and the effect of surface diffusion on mass transfer through the slit-like pore can be neglected (in particular this can take place for molecules H₂ due to small values of the adsorption energy and sticking coefficient for these molecules). In this case, the value of $W_H = J_H/J_{H,Kn}$, where J_H is the flux of molecules H₂ passing through the slit-like pore, $J_{H,Kn}$ is the flux of H₂ molecules passing through the pore in accordance with the classic Knudsen equation, is given by

$$W_H = \psi_H = \frac{2 - f_H}{f_H} = \frac{2 - [\theta_C(f_2 - f_1) + f_1]}{\theta_C(f_2 - f_1) + f_1}. \tag{18}$$

Figure 2 shows the dependence of W_H on θ_C at $f_1 = 0.2$ for different values of f_2 .

It is seen from Figure 2 that the value of J_H decreases with an increase in f_2 and θ_C . Figure 3 shows the dependence of W_H on f_1 for different values of θ_C at $f_2 = 1$.

It is seen from Figure 3 that the value of W_H increases with a decrease in f_1 . Taking into account [20,26] and aforementioned assumptions, we can write the following equation for the permeance F_H for H₂ molecules passing through the GO membrane by aforementioned pathway A in the presence of adsorbed molecules of CO₂ on the walls of the slit-like pores:

$$F_H = \left(\frac{1}{L}\right) \left\{ \frac{H'v_H\varepsilon[2 - \theta_C(f_2 - f_1) - f_1]}{3RT\xi[\theta_C(f_2 - f_1) + f_1]} \right\}, \tag{19}$$

where L is the GO membrane thickness, H' is the mean value of H for slit-like pores, v_H is the mean thermal velocity of molecules of H_2 , R is the gas constant, while ε and ξ are the porosity and tortuosity for the aforementioned pathway A in the GO membrane.

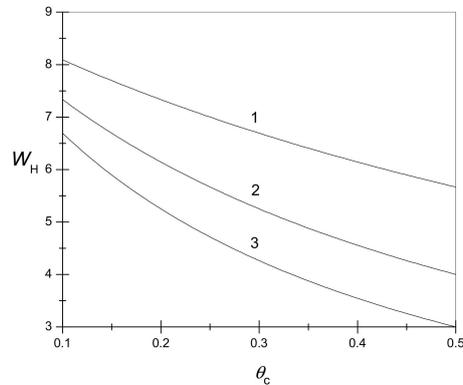


Figure 2. Dependence of W_H on θ_C at $f_1 = 0.2$; 1: $f_2 = 0.4$, 2: $f_2 = 0.6$, 3: $f_2 = 0.8$.

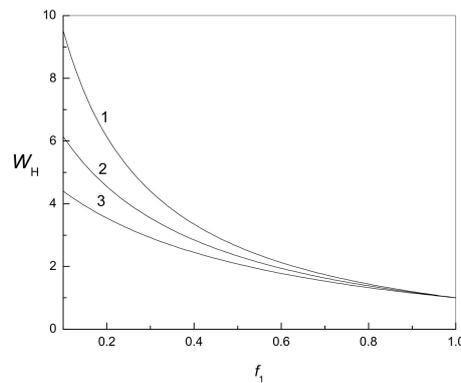


Figure 3. Dependence of W_H on f_1 for different values of θ_C at $f_2 = 1$; 1: $\theta_C = 0.1$, 2: $\theta_C = 0.2$, 3: $\theta_C = 0.3$.

Let us consider the correlation between the experimental results for permeance of H_2 in the GO membrane from reference [12] and the results obtained on the basis of the proposed model. It is worth to note that the aforementioned correlation can be made only qualitatively. This is related to the fact that in the description of experimental results in the above-mentioned paper do not participate parameters characterizing the interaction of gas molecules with the pore walls but in the approach used in the present paper the aforementioned parameters play an essential (in some cases the main) role. It is seen from Figure 2 in the above-mentioned paper that the permeance of weakly adsorbed molecules of pure H_2 can be relatively far above the data which correspond to the classic Knudsen diffusion. The similar dependence for the permeance of pure H_2 (when $\theta_C = 0$) follows from Equation (19) of the present paper in $f_1 < 1$. Figure 3 in the aforementioned paper shows the experimental results for the transport of H_2 in the presence in the system of strongly adsorbed CO_2 molecules. It is seen from this figure that the permeance of H_2 in the presence of CO_2 is smaller than the permeance of pure H_2 . This result follows also from Equation (19) in the case $\theta_C > 0$ and $f_2 > f_1$.

It is worth to note that the influence of resonance radiation on the sticking coefficient and the adsorption time of the molecules of CO_2 due to excitation of these molecules can lead to a decrease in the values of above-mentioned parameters for molecules of CO_2 and accordingly to a decrease in the value of θ_C . This in turn leads to an increase in the permeance of H_2 . The aforementioned effect can be used in particular in the separation of H_2/CO_2 mixtures. Heating of the membrane by radiation also leads to a decrease in θ_C on the walls of slit-like pores of the GO membrane and accordingly to

an increase in the permeance of H₂. The aforementioned effects can be used to manage processes such as the membrane separation of gas mixtures and cleaning of gases from impurity molecules. We hope to perform in the near future experiments associated with the verification of the presented theoretical results.

Note that the shape of gas molecules can also affect the transport of gases through GO and NG membranes [10,27]. The influence of the molecule shape on the kinetic diameter of molecules, and accordingly on the transport of gas through GO membrane is discussed in [10]. In [27] it was shown by means of molecular dynamics simulations how the size, shape, and functionalization of pores in NG membranes affect the permeance of CO₂, H₂S, and CH₄ molecules.

5. Conclusions

The transport of gas molecules through NG and GO membranes, taking into account the influence of the surface processes on graphene sheets, was studied theoretically. The combined effect of the features of molecule scattering by graphene sheets and surface diffusion of adsorbed molecules on these sheets on the transport of gas molecules through GO membranes was analyzed. It was shown that some experimental results given in [12] can be explained on the basis of the one-pathway model for mass transfer in GO membranes (diffusion of gas through the slit-like pores of the membranes). In particular, it was shown that the presence in the system of CO₂ molecules can decrease the permeance of H₂ molecules that corresponds to the experimental results given in the aforementioned paper. It was shown that resonance radiation affecting parameters such as the sticking coefficient and adsorption time of gas molecules can be used for the management of mass transfer through NG and GO membranes. The presented results can be used in the intensification and optimization of processes such as the separation of gas mixtures and natural gas purification using graphene-based membranes. Of course, much more future measurements where we can consider these and possibly other models need to be performed, but that is out of the scope of the present manuscript.

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Nomenclature

D_{Kn}	diffusion coefficient in classic theory of Knudsen diffusion
D_s	coefficient of surface diffusion
E_a	adsorption energy
E_s	activation energy of surface diffusion
E_t	activation energy of molecule translocation
E_d	energy barrier of activated Knudsen diffusion
d	diameter of two dimensional pores of porous graphene membrane
d_c	diameter of cylindrical pore
d_m	kinetic diameter of molecule
F_H	permeance for H ₂
f	probability of diffuse scattering of gas molecules
f_{sp}	probability of elastic (which is assumed to be specular) reflection
H	width of slit-like pore
J	flux density of molecules passing through slit-like channel (pore)
j	flux density of molecules passing through porous graphene

k	Boltzmann constant
L	thickness of graphene oxide membrane
m	mass of gas molecule
m_w	mass of molecules (atoms) of dense phase (material of pore walls).
n	number density of gas molecules
n_a	number density of adsorbed molecules
n_p	number density of the two-dimensional pores on the graphene sheet
p	gas pressure
x	coordinate directed along slit-like pore in direction of mass transfer
Q_p	frequency of encounters of adsorbed molecules with the two-dimensional pores
v	mean thermal velocity of gas molecules
T	temperature
Greek symbols	
α	sticking coefficient of molecules
ε_p	porosity of porous graphene membrane
θ_C	surface coverage by molecules of CO ₂ of pore walls in graphene oxide membrane
σ_e	effective cross-section
τ	adsorption time of molecules
Subscripts	
a	adsorption
C	CO ₂
d	direct
e	effective
f	feed
HH ₂	
i	component i
m	molecule
p	permeate
s	surface
sp	specular

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