Abstract: The present paper focuses on analysing selective properties of a membrane made of graphene sheets in terms of separation of methane-helium mixtures. The regular allocation of pores allows considering a representative fragment of space near the investigated membrane. Sampling of molecules with respect to velocity values is performed on the basis of the Maxwell distribution which is valid at a distance from the membrane. The frequency of molecular strikes against the surface of the membrane is determined by the gas state parameters and the size of the representative fragment. The particles are started from the input face of the representative fragment with a frequency which is characteristic for methane molecules and their accumulation inside and near the membrane is investigated. The mobile particles which are present in the carbon structure increase the potential barrier of graphene sheets. This new barrier is used in the wave model of helium atoms passing through porous graphene sheets.

Keywords: MOLECULAR DYNAMICS; METHANE-HELIUM MIXTURES; POROUS GRAPHENES; COMPOSITE MEMBRANES, SORPTION MOLECULES, POTENTIAL BARRIERS, WAVE MASS TRANSFER MECHANISM; PERMEABILITY; SELECTIVITY.

1. Introduction

Membranes with pores of nanometre scales are used in technology and biomedical research. Functionally analysed graphene membranes aimed for separation of binary gas mixtures [1–6] have great prospects from the standpoint of industrial application. The mechanism of gas penetration through porous ultra-fine membranes is of a great interest in relation to separation of gas mixtures, in particular, for solving such tasks as obtaining helium from natural gas. At normal pressures, the lengths of free paths of molecules in most gases are significantly greater than the diameter of selective pores. Therefore, while describing movements of molecular components in the vicinity of ultra-thin membranes, it is acceptable to use the model of the Knudsen particle stream. However, a lot of membranes are capable of adsorbing filtered gases, and in this case, interactions of free molecules are inevitable.

At a distance from the membrane the flow of molecules is supposed to be Maxwellian. This means that most molecules never reach the membrane at all. Such molecules are considered to be "odd" in terms of theoretical determination of membrane permeability and selectivity. In addition, the considered membranes themselves are characterized by strong dispersion generating a large number of "odd" molecules.

When studying selectivity of membranes, the method of directed concentrated molecular flows proves to be effective. Such flows are directed straight towards the free surface of a pore. If defects in a graphene sheet are created regularly, it becomes possible to select a periodic element of space in the form of a tunnel with specularly reflecting lateral surfaces. The reflections of molecules from the side surfaces of the tunnel imitate side transitions in the layer adjacent to the membrane. Such tunnels allow studying scattering and transmission, including obliquely directed flows of molecules.

In the present work particle dynamics in membrane tunnels is studied on the basis of the model of atom-molecular interactions. In addition, the authors conduct an assessment of composite nanoporous carbon membranes with respect to separation of methane-helium mixtures.

2. The mathematical model of methane molecules movement

A mathematical model for a set of moving particles, including oscillating atoms of the carbon structure, does not allow for a reliable estimate of the permeability value for an individual component of a gas mixture. Therefore, within the scopes of the present work, the barrier theory of molecules passing through a porous layer is applied to achieve this goal. According to this theory, a 1D-distribution of the interaction energy produced by the membrane with respect to a moving molecule or atom is constructed. This distribution must necessarily be finite. Consequently, the energy of the barrier is determined on the basis of integrable versions of interaction potentials. After that, a test molecule is selected and the minimum velocity of passing the barrier by this molecule is found. All particles having a velocity above the minimum velocity limit also pass this barrier. Therefore, the integral of the Maxwell distribution within the range from the limiting velocity value to infinity determines the percentage of passing molecules of the considered category. It is always possible to achieve consistency of the results obtained by this method with calculation data corresponding to the flow model.

3. The mathematical model of helium atoms movement

We use a porous graphene with a pore diameter of the order of one nanometre as a molecular sieve, in the case when methane molecules hit it, and as a sieve for quantum sieving, in the case of helium atoms. The de Broglie wavelength for helium atoms at temperatures of the order of 300 K is a value which exceeds the diameter of the atom. This gives grounds for using the wave theory when describing the process of these particles passing through ultra-thin membranes composed of graphene layers. Considering the particle dynamics model, it is convenient to find the number of methane molecules “lingering” in front of the graphene sheets. Then, it is possible to “freeze” their state by including the interaction energy from these molecules into the average interaction energy from the graphene sheet and solve the problem of wave passage through the barrier of a given shape.

To determine the number of helium atoms which pass through the barrier constructed in this way we will proceed from the stationary Schrödinger equation:

\[ \frac{d^2 \Psi}{dx^2} + \frac{2m}{\hbar^2} (E - U(x)) \Psi = 0. \]

Here \( \Psi \) is the wave function; \( E \) is the kinetic energy of the helium atom; \( U(x) \) is the barrier energy distribution; \( m \) is the mass of the helium atom; \( \hbar = D \sqrt{m \epsilon} \); \( D \) is the diameter of the carbon atom; \( \epsilon \) is the depth of the potential well in the pair interaction between the helium atom and the carbon atom.

Let us rewrite equation (1) in a form which is convenient for further transformations:

\[ \frac{d^2 \Psi}{dx^2} + (K^2 - V(x)) \Psi = 0, \]

where \( K^2 = \frac{2m}{\hbar^2} E, \ V(x) = \frac{2m}{\hbar^2} U(x) \).
At a distance from the membrane (about 10 nm and more), both to the right and to the left of it, \( V(x) = 0 \), therefore, in these zones equation (2) takes the form:

\[
\frac{d^2\Psi}{dx^2} + K^2\Psi = 0 .
\]

Particular solutions of the last equation are exponents with imaginary indices: \( e^{iKx}, e^{-iKx} \). The first exponent determines the wave incident on the membrane; the second determines the reflected wave. A linear combination of these functions also satisfies equation (3). Then, taking into account that the reflected wave is summed with the incident wave, while behind the membrane there is only the transmitted wave (as a certain fraction of the incident wave), we will write the following as the mathematical boundary conditions for the function \( \Psi(x) \):

\[
\Psi(x) = e^{iKx} + be^{-iKx}, \quad \Psi(x) = ae^{iKx} .
\]

The first function is an asymptotic boundary condition to the left of the barrier; the second - to the right. The constants \( a, b \) in relations (4) have the meaning of the transmission and reflection coefficients in terms of the energy profile distributed along the \( x \)-axis.

The stationary Schrödinger equation (2) has a second order with respect to the spatial coordinate and contains the non-zero barrier energy. It has two fundamental solutions \( \Psi_1(x) \) and \( \Psi_2(x) \) which can be obtained as a result of solving two successive Cauchy problems with the following initial conditions:

\[
\Psi_1(0) = 0, \quad \Psi_2(0) = 1, \quad \frac{d\Psi_1(x)}{dx} \bigg|_{x=0} = 1, \quad \frac{d\Psi_2(x)}{dx} \bigg|_{x=0} = 0 .
\]

Then the solution for the problem of a wave passing through a barrier of a given shape can be written as a superposition of fundamental solutions:

\[
\Psi(x) = C_1\Psi_1(x) + C_2\Psi_2(x) .
\]

Here \( C_1 \) and \( C_2 \) are the integration constants. These constants, as well as the transmission and reflection coefficients \( a \) and \( b \), are found from the “matching” conditions of the constructed solution given in (5) with asymptotic values (4).

Let the left boundary of the computational domain be defined by the coordinate \( x = 0 \) and the right - by the coordinate \( x = x_q \). Both boundaries must be at such a distance from the barrier that the Van der Waals forces can be neglected. Then the above mentioned “matching” conditions are as follows:

\[
\begin{align*}
1 + b &= C_2, \\
iK - biK &= C_1, \\
ae^{iKx} &= C_1\Psi_1(x) + C_2\Psi_2(x), \\
aKe^{-iKx} &= C_1\Psi_1'(x) + C_2\Psi_2'(x).
\end{align*}
\]

The system of algebraic relations (7)-(10) allows finding the coefficients \( a, b, C_1, C_2 \).

4. Results and discussion

Figure 1 shows calculation results for the trajectories of methane molecules interacting with the two-layer structure of a porous graphene which were obtained from the corpuscular theory. Each graphene sheet has regular pores in the form of two carbon cycles (twelve carbon atoms). The distance between the sheets is 0.9 nm. This distance can be ensured by placing a small amount of \( C_{20} \) fullerenes between the sheets.

![Fig. 1. Trajectories of methane molecules launched from positions close to pore centre](image)

Molecules started from different positions of the entrance section of a tunnel containing only one pore behave differently. All particles pass through the centre of the pore through a relatively small permeability window. They are included in sorption movements, i.e. they “linger” between or near the plates for some time. The sorption capture time can be estimated from calculations. Selectivity determined for a single-layer system by the method of directed concentrated flows appears to be equal to four units. In a two-layer system, by changing the distance between the plates, a significantly higher selectivity can be achieved.

Figure 2 shows distribution of the coefficient correlating to helium particles passing through a two-layer carbon-carbon membrane. The horizontal axis represents the number of steps in terms of the depth of the computational domain.

![Fig. 2. Distribution of coefficient corresponding to helium atoms passage over thickness of two-layer membrane](image)

5. Conclusion

The calculations show that the region between two graphene sheets is a region of accumulation of helium atoms in which they interact with each other and with atoms of the carbon structure, i.e. in a bound state. Additionally, there are such distances between graphene sheets which provide a sharp increase in the coefficient of passage of the inert component atoms determined by the conditions of “matching” given in (7)-(10). This effect can be explained by the occurrence of the wave resonance which accompanies passage of a particular component. In this case, the other component is found outside the resonance conditions and has a low level of the transmission coefficient.

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6. Literature


