Permeability of membranes stacked tightly closed carbon nanotubes

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Abstract. Nanotubes, like fullerenes, can be stacked in potential wells of adjacent tubes, forming a new material with triangular tunnels. This method of cluster formation from nanotubes is called self-laying mode. In this work two methods for calculating permeability of such material by the molecules and atoms of a gas mixture are proposed. In the framework of the first approach, the calculations made it possible to determine the effective radii of the tubes with respect to helium and methane. This method relies on the determination of the sizes of the areas of free passage of molecules, the second on a set of complete statistics on single launches that realize the passage of molecules. The studied ideal carbon structure showed high selectivity with respect to the separation of the methane-helium mixture and was practically impermeable to methane.

1. Introduction

In recent years, many researchers agree that carbon tubes have mechanical and biological compatibility with living tissues, and in this sense are the most durable. A number of experiments are currently being carried out with the introduction of multilayer carbon nanotubes into living nerve tissues, the toxicity of carbon nanotubes and methods for delivering cytotoxic drugs to tumor cells are being discussed [1]. The review of carbon nanotube production methods and approaches to their functionalization for medical applications is given in [2], in particular, the use of carbon tubes as a nanochannel for an ifosfamide antitumor preparation is described in [3].

The article [4] discusses the possibility of using thin films of single-walled carbon nanotubes in optics of the extreme ultraviolet range. Also, membranes based on carbon nanotubes are studied in relation to various components: a membrane of sulfonated carbon nanotubes used to pass protons [5]; the review [6] summarizes the results in understanding the dynamics of excitons in single-walled carbon nanotubes; in [7], it is stated that the flux enhancement and molecular selectivity of carbon nanotubes make them unique conductors of gas components. Particular attention is paid to the adsorption and desorption of molecules on single-walled carbon nanotubes. For example, the adsorption of acetone [8] or benzene by triangular stacking of closed carbon nanotubes [9]. In [10], inert gases are adsorbed in non-defective stackings of carbon nanotubes. Nanotubes as gas sensor materials are discussed in [11]. In article [12], the dynamics of dissipative particles was used to analyze the ability to adsorb sodium dodecyl sulfate inside single-walled nanotubes. In [13], results on low-temperature adsorption of crepton in beams of closed carbon nanotubes are presented.

The permeability of nanoporous structures composed of carbon tubes, graphene plates, and spherical nanoparticles of various radii was studied in [14-20]. The effect of the curvature of a

graphene plate on the passage of gas components through its pairs is considered, the potential fields and drag coefficients of carbon nanoparticles of various shapes are calculated, and the effect of C_{60} rotation on the permeability of the material is considered.

The properties of carbon nanotubes allow us to conclude that they can be used as a material for a separation membrane. The aim of this work is the theoretical construction of a membrane from densely grained closed single-walled carbon nanotubes and the calculation of its permeability with respect to a methane-helium gas mixture.

2. Mathematical model

Permeability is usually understood as the relative magnitude of the mass flux of molecules incident on the membrane to the flux of transmitted molecules. In the problems under consideration, it is appropriate to single out the period of updating the thermodynamic state of the gas $\tau = \lambda / \upsilon$ (λ is the mean free path of molecules, υ is the average thermal velocity of their motion). Within this renewal period, we can talk about the number of falling and passing molecules. Then the definition of permeability will be as follows. Relative permeability is the fraction of transmitted molecules of the number incident on the λ^2-surface, originally located in the λ^3-volume of the gas medium adjacent to the membrane surface.

The study of the process of interaction of a moving molecule with the atoms of the carbon structure under consideration is based on the application of a mathematical model and numerical methods for solving the main problem of molecular dynamics. The interaction between individual atoms or molecules is determined by the classical Lennard-Jones potential. The interaction with the structure is described by the law of independence of actions as the sum of the effects of each atom of the structure on the test molecule under consideration. According to this law, if several forces act on a material point, then they give it an acceleration equal to the geometric sum of those accelerations that they would tell it, acting separately.

In projections on the coordinate axis, the equations of motion of the molecule interacting with the carbon structure are written as follows:

$$m\frac{dU}{dt} = X', m\frac{dV}{dt} = Y', m\frac{dW}{dt} = Z', \text{ where } X' = \sum_{j=1}^{N_p} X'_j, Y' = \sum_{j=1}^{N_p} Y'_j, Z' = \sum_{j=1}^{N_p} Z'_j. \quad (1)$$

Here X', Y', Z' are the projections of the resultant Van der Waals forces from the atoms of the carbon structure, which are defined as simple sums of the force contributions from the nodes of the surface crystal network, N_p is the number of atoms in the carbon material under consideration. Next, we introduce the quantities $X, Y, Z : mX = X', mY = Y', mZ = Z', m$ - rewrite in the form:

$$\frac{dU}{dt} = X, \frac{dV}{dt} = Y, \frac{dW}{dt} = Z, \text{ where } X = \sum_{j=1}^{N_p} a_j \frac{x - x_j^0}{\rho_j}, Y = \sum_{j=1}^{N_p} a_j \frac{y - y_j^0}{\rho_j}, Z = \sum_{j=1}^{N_p} a_j \frac{z - z_j^0}{\rho_j}. \quad (2)$$

Here, the zero index marks the coordinates of the carbon network nodes, and a_j is the acceleration value that the test molecule acquires under the action of the *j*-th atom of the network structure under consideration. This quantity, in terms of the parameters of the Lennard–Jones potential and the distance to the atom of the structure, is expressed as follows:

$$a_j = 24\frac{\varepsilon}{m\rho_j}\left(\frac{\sigma}{\rho_j}\right)^6\left[2\left(\frac{\sigma}{\rho_j}\right)^6 - 1\right]. \quad (3)$$

In equation (3), ρ_j is the distance between the test molecule in question and the *j*-th atom of the carbon structure; ε and σ are the interaction parameters of the pairs of substances included in the *LJ*-potential.

If equations (2) are supplemented with kinematic relations determining the velocity of a point:

$$\frac{dx}{dt} = U, \frac{dy}{dt} = V, \frac{dz}{dt} = W, \quad (4)$$

then we obtain a system of six ordinary differential equations of the first order with respect to six unknowns: x, y, z, U, V, W. To solve this system, we will use the Runge–Kutta method of the standard fourth order of accuracy.

In the case when the system under study consists of heterogeneous molecules (atoms), the Lorentz-Berthelot averaging rules are valid for the parameters ε and σ.

3. Results of calculations

If the short tubes in the vacuum are left to their own devices, they will come closer under the action of the van der Waals forces and, in the end, will fall into the potential holes of the tubes that have already fixed their position. Approximately this method of cluster formation from tubes is called the tube self-laying mode. By providing the appropriate conditions for self-laying, the formation of a supercluster can be achieved. It will be a fragment of the membrane, which in the future we will use to separate the methane-helium mixture.

Self-laying mode can be implemented in a vacuum. For this, it is necessary to have tubes of the same transverse size and approximately the same length. Such tubes themselves must be connected into a stable structure (supercluster of nanotubes).

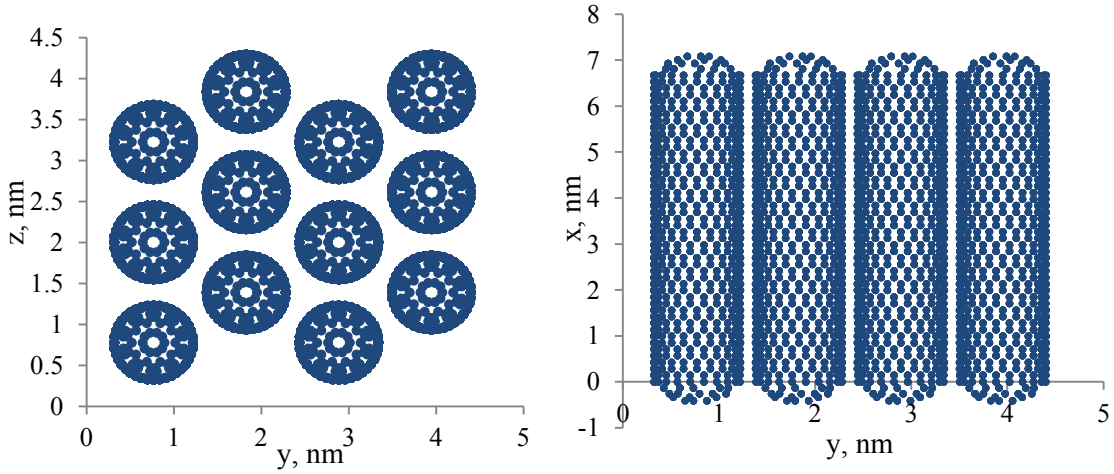

Figure 1. Dense packing of closed nanotubes with a radius of 0.452 nm.

In figure 1 shows a system of single-layer closed nanotubes folded in a self-stacking mode, when each of the tubes enters the potential wells of adjacent tubes. The minimum distance between them is 0.32 nm. If the tubes of approximately the same size and Van der Waals forces hold them in equilibrium, making them parallel to each other, then we get a more or less uniform layer with a thickness equal to the length of the tube. This stacking is a tunnel structure because it contains laterally impenetrable triangular tunnels where free molecules can move axially with respect to the tubes.

In the case of closed nanotubes, only the annulus is free for the passage of helium atoms, hydrogen molecules, and some other simple substances. Methane molecules no longer pass through the resulting tunnels. This fact can be established by simply shelling the system under consideration, or by finding the permeability cells of triangular tunnels for helium and methane. Hereinafter, we used for calculations the authors programs written in Fortran 90 in the Visual Studio programming environment.

The borders of these cells, i.e. curvilinear frames are determined by the effective radii of the tubes with respect to the components under consideration. The mentioned radii were determined as half of the limiting distances between the axes of the tubes, ensuring that molecules and atoms do not pass into the gap between the surfaces of the tubes. It turned out that the effective radii also depend on the velocities of the moving particles. In a representative velocity range, this is 5.5% of the radius.

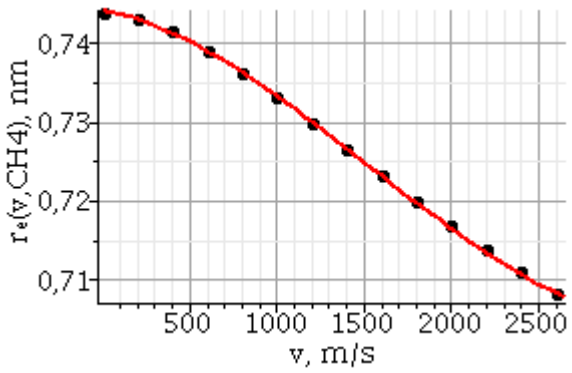

Figure 2. Effective radius of a closed nanotube with respect to a methane molecule.

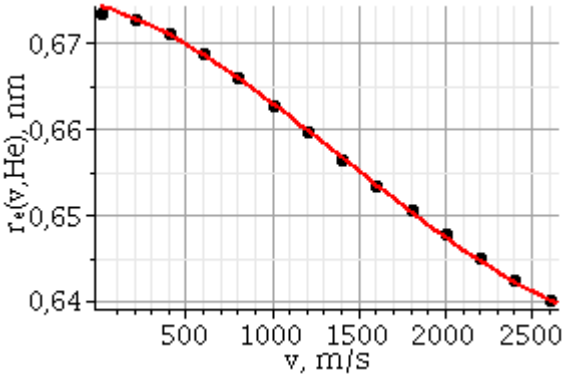

Figure 3. Effective radius of a closed nanotube with respect to the helium atom.

The calculated values of the radii with respect to the components under consideration are shown in figures 2 and 3. It can be seen that the values of the radii with a change in velocity in the representative range differ by 10%, but with dense tube stacking this difference is critical with respect to the passage of methane molecules. The system of tightly packed closed single-walled nanotubes turned out to be impassable for methane molecules.

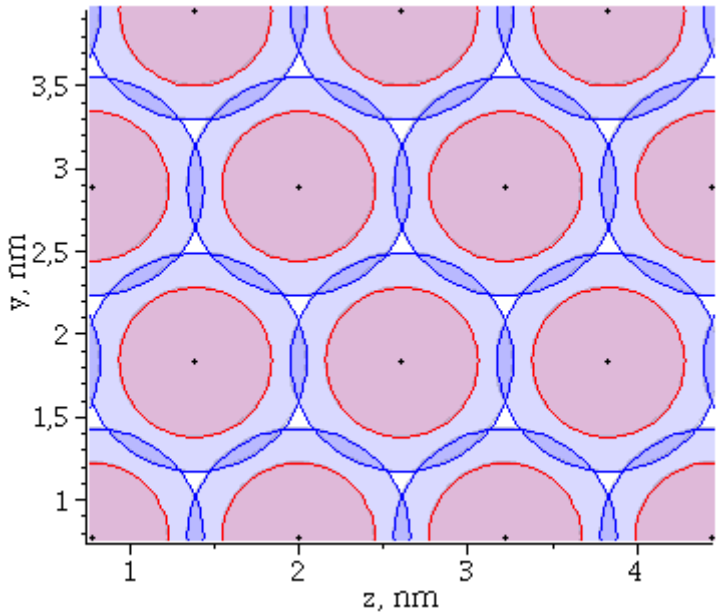

Figure 4. General view of the permeability cells of the dense packing of closed nanotubes relative to helium atoms with an initial velocity of U_0 = 1360 m/s.

In figure 4 shows the permeability cells of the system under consideration with respect to helium atoms. It can be seen that the triangular permeability cells are quite small. This suggests that the membrane performance of identically oriented closed nanotubes will be small if the area law is used to evaluate productivity. In relation to the case under consideration, the law of areas can be formulated as follows. The number of molecules passed per unit time through the specific surface should be proportional to the ratio of the area of the permeability cell to the size of the surface of the membrane membrane (the area of the triangle with the vertices on the axes of the tubes). The ratio of these areas is only 3%. However, the relative productivity of such a membrane can, in principle, be higher due to the fact that the molecules can be drawn into a triangular tunnel, expanding the area of the molecules entering the free motion region.

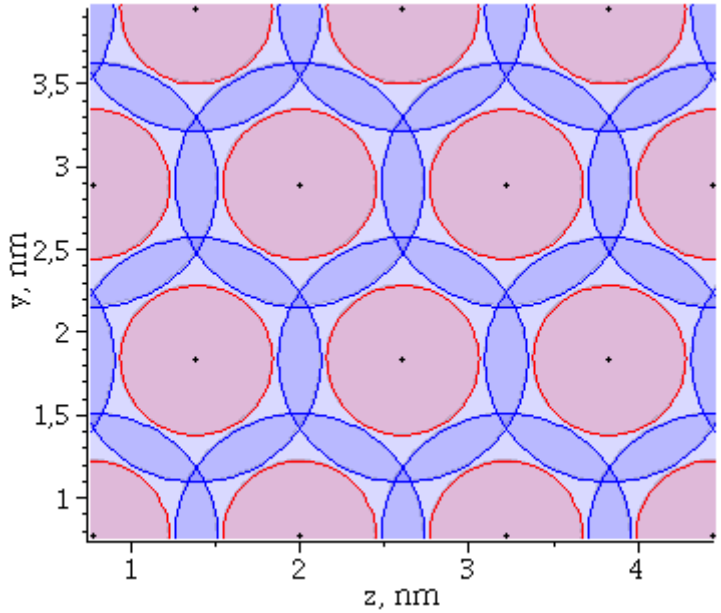

Figure 5. General view of the pseudo-permeability cells of the tight packing of closed nanotubes relative to methane molecules with an initial velocity of U_0 = 680 m/s.

In figure 5 shows a flat section of a dense stacking of closed nanotubes with repulsion radii found with respect to methane molecules having a velocity. It is seen that the effective radii of the tubes completely overlap the triangular tunnels, providing free movement of methane molecules. Thus, according to the theory of permeability cells, the dense packing of nanotubes is impassable for methane.

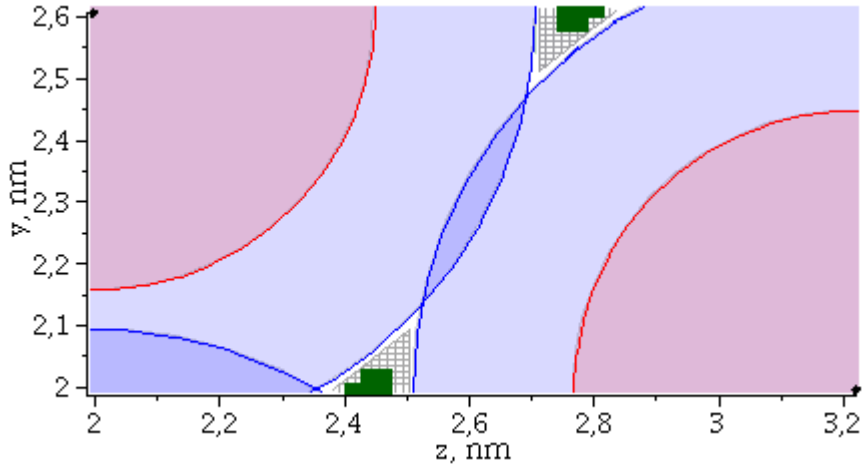

Figure 6. The tightness permeability cell of closed nanotubes relative to helium atoms and their initial positions in the permeability cell.

In figure 6 shows a rectangular cell of triangular tube laying. Such rectangles, as well as triangles with vertices on the axes of the tubes, parquet the entire surface of the membrane. Rectangular cells are significantly more convenient. With their help, it is easier to construct a grid of the initial positions of the beam of molecules incident on the membrane surface and it is easier to construct an incoming tunnel that spans the entire space to find a complete set of statistics. However, if the incident CH_4 molecule moves along the geometric axis of the triangular tunnel (perpendicular to the surface of the membrane), and its velocity is not lower than 1940 m/s, then it passes through the tunnel safely. The

probability of such an event being realized is extremely small, since the simpler components of this event are unlikely, but the very fact that a complex spatial barrier can be overcome by a high-velocity methane molecule is confirmed by calculations of the motion of a high-velocity molecule along the tunnel axis. Nevertheless, the method of permeability cells and the law of areas, as expressing the average statistical characteristics, give zero methane permeability, hence an infinite degree of mixture separation. In connection with the foregoing, it would be more correct to speak of an almost impenetrable membrane with respect to methane and a very high degree of separation of the methane-helium mixture.

4. Conclusion

The molecular dynamics calculations performed made it possible to find the effective radii of the tubes of standard transverse size with respect to helium and methane. This, in turn, made it possible to use the method of permeability cells and the area law to calculate the permeability of self-stacking nanotubes. According to the method found, the studied carbon structure was impermeable to methane. Helium atoms move inside triangular tunnels with a velocity of 1.5 times higher than the velocity of entry into the tunnel and therefore quickly leave it. Because of this, the material seems to be self-cleaning from particles inside.

Acknowledgments

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