Permeability of nanonet structures constructed on the basis of carbon tubes

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Abstract. An approximate integration of a potential of paired molecular interactions over the circumferential coordinate is used to find the potential of the interaction between a molecule and an infinite carbon nanotube (CNT). Based on the obtained energy of interaction between the tube and the molecules, local effective radii of the investigated carbon structures with respect to the molecules of the separated gas mixture are found. This makes it possible to calculate permeability of a single-layer, along with a two-layer CNT packing. The conducted research allowed calculating permeability of a nanonet structure as permeability of a two-layer packing of carbon nanotubes for the first time.

1. Introduction
An effective membrane should be both of high-performance and selectivity. Experience shows that productivity of a membrane increases with a decrease in its thickness. Extremely thin membranes of porous graphenes have a thickness of only one atom. From the standpoint of membrane construction on the basis of straight-line carbon wires, a one-layer packing is extremely thin. At the same time, an extremely thin network structure is a two-layer packing of the same rectilinear CNTs. A possibility of theoretical studies on permeability of layers composed of various nanoparticles is provided by the experience which the authors of the present paper have gained in their research in the sphere of nanomechanics. Mechanical resistance of nanoparticles, their centrifugal and gravitational sedimentation, as well as thermophoresis of particles of various shapes, in particular, graphene flakes, was considered in [1-4]. In [5] permeability of porous graphenes was studied from the standpoint of Schrödinger wave dynamics. The mathematical model of undulating graphenes is presented in [6]. The same approach, based on the continual representation of the interaction energy on the basis of the modified LJ-potential, was used in [7] to study sorption properties of bodies. In [8], on the basis of the wave permeability model, the authors investigated passage of matter through composite membranes. Moving forward in the direction of theoretical developments, with respect to separation of mixtures, an energy barrier determined by a system of two nanoparticles was found in [9]. Paper [10] is devoted to porous graphenes. Work [11] considers passage of molecules through an open carbon nanotube (CNT). Article [12] presents a mathematical model for a tunnel constructed of spherical carbon nanoparticles. Modes of low-energy interaction of molecules with an open CNT are discussed in [13].
In [14] the subject of research is wave permeability of a layer of compacted spherical particles. Separation of methane-helium mixtures by means of a layer of a porous graphene was considered in [15].

2. The «molecule - infinite CNT» interaction potential

There is an exact analytic solution to the problem of the interaction between a molecule and an infinite tube expressed in terms of hypergeometric functions [16, 17]. In this paper, having carried out an approximate integration with respect to the circumferential coordinate, a compact expression is obtained in the class of functions of the basic potential which provides, like the $LJ$-potential itself, simplicity of computations in a set of statistical data. At the same time, we get a brilliant agreement with the exact solution [16, 17]. There is a basic work on the interaction of surface carbon nanoparticles [18], however, the interaction potential «molecule - fullerene particle» was obtained by V.Y. Rudyak earlier [19]. The latest works by this author relate to physics of the condensed state [20, 21]. Returning to the problems of gas components passage, we will briefly describe the scheme for constructing an approximate solution in the case of an infinite nanotube.

The interaction of a test molecule with structure atoms constituting the rectilinear carbon nanotube (CNT) will be considered on the basis of the Lennard-Jones intermolecular interaction potential:

$$\Phi_\delta(r) = \sum_{m=12,6} \frac{C_m}{S_1} \int_0^z \left( \int_{-\infty}^\infty \rho^2 (\rho^2 + \rho^2) \frac{m}{2} d\rho \right) d\phi.$$  \hspace{1cm} (2)

Here $\rho^2 = \rho^2 + \rho^2 - 2\rho \cos \phi; \rho \phi d\rho$ is the area element; $S_1$ is the area per one molecule (atom) of the structure. The sum consists of two terms, the second term being taken with the minus sign. The integral in parentheses (2) can be taken using the differentiation technology in terms of a parameter or with the help of a package that provides symbolic calculations, for example, «Maple». As a result, we get

$$\int_{-\infty}^\infty \left( \rho^2 + \rho^2 \right)^{m/2} d\rho = b_m \rho^{m+1}, \quad (m = 12, 6),$$  \hspace{1cm} (3)

where $b_{12} = \frac{63}{256} \pi, \quad b_6 = \frac{3}{8} \pi$.

Then, instead of (12), we can write

$$\Phi_\delta(r) = \sum_{m=12,6} \frac{b_m}{S_1} C_m \int_{-\infty}^\infty \rho^{m+1} d\phi.$$  \hspace{1cm} (4)

Now in the parentheses is the integral over $\phi$ from 0 to $2\pi$. This integral contains an embedded cosine function, because $\rho$ depends on $\cos \phi$. We note here that further application of symbolic calculations leads to an immense analytical result which will be inconvenient in future practical work.

We will take an integral with respect to the angular coordinate approximately by dividing the period $\cos \phi$ into four segments and using the trapezoid method formula to calculate the integral with respect to $\phi$ from the power function of the distance $\rho$ which includes the above-mentioned $\cos \phi$. This formula contains the values of $\rho$ at five points, but due the symmetry of distribution of $\cos \phi$ with respect to the line $\phi = \pi$, only three remain.

As a result, we get
\[ \int_{0}^{2\pi} \rho^{m+1} d\phi = \frac{\pi}{2} \left[ \rho(0)^{m+1} + 2\rho\left(\frac{\pi}{2}\right)^{m+1} + \rho(\pi)^{m+1} \right]. \]  

We note that for the distance from the centre of the test molecule to the material point on the surface of the cylinder the following relations are valid:

\[ \rho(0) = r - a; \quad \rho\left(\frac{\pi}{2}\right) = \left(r^2 + a^2\right)^{\frac{1}{2}}; \quad \rho(\pi) = r + a. \]  

Introducing (5) and (6) into (4) we find:

\[ \Phi_s(r) = K_{11} \left[ (r-a)^{-11} + 2\left(r^2 + a^2\right)^{\frac{11}{2}} + (r+a)^{-11} \right] - K_{12} \left[ (r-a)^{-5} + 2\left(r^2 + a^2\right)^{\frac{5}{2}} + (r+a)^{-5} \right]. \]

Here \( r \) is the distance from the centre of the test molecule to the axis of the tube; \( a \) is the radius of the nanotube: \( K_{11} = \frac{b_1^2 C_{12} a \pi}{S_1}; \quad K_{12} = \frac{b_2^2 C_1 a \pi}{S_1}; \quad b_1 = \frac{63}{256} \pi; \quad b_2 = \frac{3}{8} \pi; \quad C_{12} = 4\varepsilon\sigma^2; \quad C_s = 4\varepsilon\sigma^4; \quad S_1 \) is the area per one molecule (atom) of the tube’s wall material; \( \varepsilon, \sigma \) are the parameters of the LJ-potential.

3. Permeability of a single-layer packing of CNTs

We will consider the process of free molecules passage through a gap between two parallel nanowires. Let us introduce the concept of the width of the local permeability zone:

\[ h_w(v) = h - 2r_e(v), \]  

where \( h \) is the distance between the axes of the wires; \( r_e(v) \) is the effective radius of the wire calculated as half the limiting distance of molecular passage between the axes with a certain velocity \( v \). Then for molecular systems that obey the Maxwell distribution the relative number of molecules passing between the wires is

\[ D(h) = \frac{4}{\sqrt{\pi}} \int_{0}^{\infty} \alpha^2 e^{-\omega^2} \left[ \frac{h_w(v)}{h} \right] dv. \]  

Here \( \alpha = \frac{m}{2kT} \); \( k \) is the Boltzmann constant; \( T \) is the absolute temperature; \( m \) is the mass of the free molecule.

If the expression in square brackets is set equal to one, the integral in (8) is the Maxwell distribution function with respect to the velocity \( v \).

The width of the local permeability zone is determined using the following conditions:

\[ h_w(v) = \begin{cases} 0, \text{если } h - 2r_e(v) \leq 0, \\ h - 2r_e(v), \text{если } h - 2r_e(v) > 0. \end{cases} \]  

after which the permeability coefficient \( D \) is calculated by formula (8).

The distribution \( D(h) \) is found in the interval from 0.95 to 5.95 nm (in the case of wires of a radius equal to 0.475 nm) with a digitization every 0.75 nm. It is more convenient to plot \( \lg \chi \) on the vertical axis of separation, since very high values of the degree of mixture separation (more than two orders) are recorded in the range from 1.552 to 1.603 nm.

Figures 1-3 present the summarized data of systematic calculations on the determination of the local (corresponding to the given level of velocities) effective radii of the interaction between a standard CNT \((r_p = 0.475 \text{ nm})\) and methane molecules and helium atoms.
Figure 1. Effective radius of CNT with respect to methane.

Figure 2. Effective radius of CNT with respect to helium.

Figure 3. Effective radii of CNTs in relation to methane and helium.

Figures 4 and 5 show calculation results of permeability and the degree of separation of a methane-helium mixture for a single-layer packing of parallel tubes. The generalizing data on the characteristics of the membrane are presented in Table 1.

Figure 4. Coefficients of helium and methane passage depending on distance between axes of standard CNTs. Single-layer packing of CNTs.
Figure 5. Degree of separation of methane-helium mixture. Single-layer packing of CNTs.

Table 1. Performance of membrane of parallel CNTs (single-layer packing).

| Distance between axes of wires, nm | Performance of membrane | Degree of mixture separation |
|-----------------------------------|-------------------------|-----------------------------|
| [1.419; 1.552]                    | Low                     | Very high                   |
| [1.552; 1.603]                    | Good                    | Above 100 units             |
| [1.603; 1.755]                    | High                    | From 100 to 2 units         |

The local effective radii of these carbon structures calculated by the method of convergence of two parallel wires have the following analytical approximations (the result is expressed in nm):

\[
r_v(CH) = a_0 v^3 - a_1 v^2 - a_2 v + a_3,
\]

\[
r_v(He) = b_0 v^3 - b_1 v^2 - b_2 v + b_3,
\]

where \( a_0 = 1.93154 \times 10^{-12}, a_1 = 9.09157 \times 10^{-9}, a_2 = 2.09756 \times 10^{-6}, a_3 = 0.8076 \)

\( b_0 = 1.71516 \times 10^{-12}, b_1 = 7.73388 \times 10^{-9}, b_2 = 2.55181 \times 10^{-6}, b_3 = 0.73721 \).

The limiting distance of approach can be determined from the distribution of the energy of interaction between two identical parallel tubes. Such a distribution was obtained in [20].

Calculations of permeability show that for \( h \) varying from 1.419 to 1.552 nm (wider than the limiting zone for carbon) there is a "dead zone" which is characterized by the fact that neither methane molecules nor helium atoms pass between the wires. When analyzing permeability of CNT packings, it should be taken into account that the limiting distance of approach for these carbon structures is 0.32 nm.

4. Permeability of a two-layer packing of tubes

Let us denote by \( D_1 \) the value of the fraction of molecules passing through the first stage, and by \( D_2 \) the fraction of those passing through the second stage of the separation system composed of two layers of tubes. From the previous we can write:

\[
D_j = D.
\]

where \( D \) is calculated by formula (8).

Now we will consider the second step. Passage through the second layer can be considered as a complex event the probability of which is determined by the product of the transmission probabilities of each of the layers. In addition, multiple reflections of molecules trapped between the two layers should be taken into account, as well. As a result, eventually, they are equally likely to come out in one direction or in the other moving along the normal to the layers of the packing.
Since the probability of passage through each of the following for the first layer is equal to \( D \), the second layer will be passed by the following part of molecules incident on the surface of the first layer:

\[
D_2 = D \cdot D' + \frac{D'}{2}.
\]  

(13)

The first term determines the contribution due to the direct passage through the double layer, the second - the contribution of the re-reflections. The value of \( D' \) in the last relation takes into account the increased intensity of molecular motion in the space between the packings which is determined by the following circumstance. Molecules moving through the permeability zone between the two wires pass through the potential well where they acquire additional velocity due to the action of the van der Waals forces from the second row of the packing. Therefore, when free particles (molecules) enter the mode of re-reflections between the two layers of the packing, they move with a velocity higher than that which they had when approaching the carbon structure. Because of this, passage through the second layer is not equivalent to passage through the first layer. The average value of the increase in velocity is determined by the average value of the depth of the potential well.

Being located between the layers, molecules receive an increase in speed of the following order:

\[
\Delta v = \frac{2 \Delta U}{m(v + v')}.
\]  

(14)

Here \( \Delta U \) is the average depth of the potential well; \( v \) is the velocity of the molecule as it approaches the first layer; \( v' \) is the rate of re-reflections.

Remembering that

\[
v' = v + \Delta v
\]  

(15)

from (14) we find:

\[
\Delta v = \sqrt{v^2 + \frac{2}{m} \Delta U} - v.
\]  

(16)

The last relation shows that, in the general case, molecules located between the layers no longer obey the Maxwell distribution. However, if the depth of the well is large, the value of the increase in velocity is no longer dependent on the velocity itself:

\[
\Delta v \approx \sqrt{\frac{2}{m} \Delta U}.
\]  

(17)

It should be noted that at distances of the order of the nanotubes limiting approach (this distance lies between 0.3 nm for fullerenes and 0.34 nm for graphene sheets in graphite) we deal with exactly this kind of situation. In this case, the nature of the Maxwell distribution does not change, but the shift along the velocity axis equal to \( \Delta v \) is fixed to the right. Therefore, \( D' \), which is included in formula (13), is defined as follows:

\[
D'(h) = \frac{4}{\sqrt{\pi}} \int_0^\infty \alpha^{3/2} e^{-\alpha v^2} v^\frac{3}{2} \frac{h_{av}(v)}{h} dv,
\]  

(18)

where the lower limit of integration \( \Delta v \) is determined from (17) and \( \Delta U \) is found from calculations of the energy distribution of the interaction between the molecule and all the surrounding tubes.

Thus, those molecules which accelerated in the potential well and got engaged in the process of re-reflection, pass through the second layer better compared with the molecules which are in front of the first layer of the CNT packing.

Calculations were carried out for the case \( D' = D \). It was found that the range of the packing step which provides a high degree of separation is somewhat wider than in the single-layer system, and the degree of separation is higher (Table 2).

**Table 2.** Performance of membrane of parallel CNTs (two-layer packing).
| Distance between axes of wires, nm | Performance of membrane | Degree of mixture separation |
|-----------------------------------|-------------------------|-----------------------------|
| [1,419; 1,552]                   | Low                     | Very high                   |
| [1,552; 1,604]                   | Good                    | Above 100 units             |
| [1,604; 1,802]                   | High                    | From 100 to 2 units         |

In figures 6 and 7 are the distributions of the components relative permeability and the degree of separation of a methane-helium mixture by a two-layer packing of nanotubes.

![Figure 6. Coefficients of passage of molecules through two-layer packing of CNTs.](image)

![Figure 7. Degree of separation of He/CH₄. Two-layer packing of CNTs.](image)

5. Conclusion

When analyzing mass transfer through a packing of CNTs, the method of local molecular transmission zones proves to be effective. The method consists in finding the effective radii of CNTs corresponding to each particular velocity of a molecule approaching a wire. On the basis of these data, it is possible to determine the relative width of the local molecular transmission zone \( \frac{h_{\nu}}{h} \). Further, this distribution is used in conjunction with the Maxwellian velocity distribution to find the total number of molecules passing through a single-layer packing. The probability of passing through a two-layer packing of tubes is made up of the probability of direct passage through two successive barriers and a fraction of molecules passing through the entire separation system as a result of re-reflections within this system. The found permeability of a double layer of a straight tubes packing simulating a network structure is used to determine the degree of separation of a binary gas mixture.

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