Permeability of a triangular packing of open nanotubes

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Abstract. We consider a layer of open nanotubes identically oriented in space. We investigate permeability of a nanoporous carbon system for a regular triangular packing of tubes. Curves defining layer permeability depending on the degree of spatial proximity of tubes are constructed.

1 Introduction

Problems of nanoporous structures permeability are of a great importance in solving tasks of gas separation, water treatment, as well as for the study of life support conditions in biological systems. Graphenes, fullerenes and nanotubes are ideal surface carbon systems. If to use a regular spatial packing for these atomic systems, the resulting structures will also be ideal and convenient to study using mathematical methods. The resulting spatial structures containing molecule-impenetrable clusters of carbon atoms and nanoscale pores are interesting in terms of gas passage through the constructed layers. Despite the obvious idealization of matrix structures of carbon atoms with respect to the actually existing nanoporous systems, conclusions on permeability of ideal objects are significant for development of practical gas separation technologies.

If the Lennard-Jones potential is modified in a certain way, performing integration over the surface of a 2D-material (nanotubes, graphenes) it is possible to find the interaction energy of long nanotubes or relatively large graphene plates. This could allow defining an equivalent homogeneous layer and determining its permeability. Previously, the integral impact of volume nanoparticles using the method of defining particularities was found in the papers [1-7]. Continuous integration on the basis of a modified LJ-potential was tested in [8-14]. This approach can provide significant advances in theoretical studies on membrane transport of neutral particles, as well as in solving numerous problems of surface phenomena physics [15-21].

According to the data in [22], the average longitudinal dimension of tubes is of the order of 10^3 nm. Such tubes contain about 10^5 carbon atoms. Therefore, studying interactions between these structures and molecules and atoms of gas components should be conducted using continual models of energy distribution over the tube surface.

The classical Lennard-Jones potential has a too strong singularity at zero and can not be integrated neither over the surface nor the volume. Without changing the nature of the Van der Waals forces action in the determining area of intermolecular distances, we reduced the value of singularity to $1/r$. Therefore, the resulting modified potential, in this respect,

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became equivalent to the potentials of Newton or Coulomb which, as known, are integrable both over the surface and the volume.
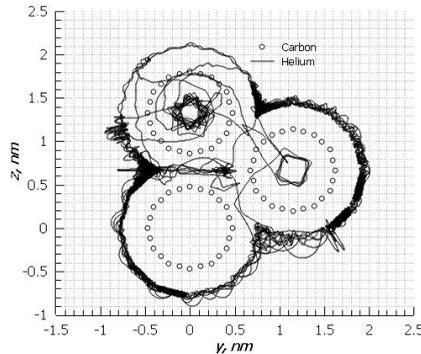
Fig. 1 Trajectory of low-energy helium atoms **O** – carbon atoms; **- -** helium trajectory.

However, if to take a short piece of a tube, such as of 12 rows containing carbon atoms located in the axial direction for which it appears that its length is equal to 1.136nm, it is quite acceptable to study permeability on the basis of the model of discrete-positioning of carbon atoms. At the same time, we have to remember that the problem of a single molecule moving through the structure is six-parameter (three parameters of position and three components of velocity) and requires too many launches of molecules for the purpose of determining the permeability coefficient of the nanoporous structure. Fast molecules either pass through the structure, or get reflected from it having an uninformative trajectory. Low-energy molecules move around the structure until they are knocked out of it by faster molecules. Within a limit, such spatial orbital motion is infinite and it clearly shows the presence of permeability zones in the structure. With the help of the discrete model it is quite appropriate to consider a packing of a small number of tubes.

Fig. 1 illustrates several trajectories of low-energy molecules having an initial velocity of the range [50, 100] m/s. The molecules were launched through a packing along the nanotubes axes, however, they did not leave the layer composed of the tubes but got involved in the sorption motion. Therefore, we further took into account their presence in the barrier of the packing. The contribution of existing sorption molecules into the value of the energy barrier was approximately 15% (compared with the contribution made by the energy carbon structure atoms). Calculations show that permeability of the tube with the length of 1.136 nm is the same as that of the tube of 10^3nm.

Let us consider a carbon nanotube of an arbitrary length and find its interaction energy by integration. Thus, in case of continuous integration over a 2D-material surface, we should have a convergent value of the integral action. The above mentioned modification has the form:

$$dU(\rho) = 4q\varepsilon\left(\frac{\sigma}{\rho}\right)\text{th}\left[\left(\frac{\sigma}{\rho}\right)^{11} - \left(\frac{\sigma}{\rho}\right)^5\right]ds \quad , \tag{1}$$

where dU is the energy of the selected fragment; ε, σ are the LJ- potential parameters; ρ is the distance between the centre of the test molecule and the centre of the elementary area on the surface of the 2D-material; q is the distribution density of energy sources on the surface; ds is the elementary area on the tube surface. For a flat or a cylindrical graphene structure it is easy to find that $q \approx 28$ nm^{-2}; and for a spherical - q$\approx$20nm^{-2}. Naturally, introducing cylindrical coordinates and integrating (1) over the side surface of the open nanotube we obtain

$$U(r,z) = 4\varepsilon aq \int\limits_{0}^{2\pi}\int\limits_{0}^{1}\left(\frac{\sigma}{\rho}\right)\text{th}\left[\left(\frac{\sigma}{\rho}\right)^{11} - \left(\frac{\sigma}{\rho}\right)^{5}\right]d\varphi'dz' \tag{2}$$

Moreover, $\rho = \sqrt{r^2 + a^2 - 2ar\cos\varphi' + (z - z')^2}$; a is the radius of the nanotube; l is its

length; r,z are the cylindrical coordinates; φ', z' are the integration variables. The double integration in (2) can be performed numerically, using the trapezoidal rule consistently for each of the integrals.

When the integration in (2) is completed, we can find the radius-averaged value of the potential. In this case, the integrated potential will depend only on the coordinate z. Let us denote it as $W_1(z)$. To assess permeability of the rectangular packing of nanotubes we will use the method of molecular penetration through an equivalent homogeneous layer. With regard to the case of packing shown in Fig. 2, the energy of this layer is determined as follows. Potential (2) is averaged by the radius equal to the side of the shaded fragment, with the help of which the whole area under consideration is parqueted. The obtained average value of the potential $W_1(z)$ is determined by the influence of only one tube. Since in the considered case the nearest neighbours of the selected elementary fragment are three tubes, due to the symmetry of the influences, the average value of the potential in the shaded area will be $W(z) = 3W_1(z)$. The influence of other tubes is neglected because their contributions are really small. On defining the average potential, we can launch a test molecule perpendicular to the shaded area, i.e. along the axes of the tubes. Passing through the uniform layer, such molecule will not experience any effects diverting it from the straight path. Therefore, the equation of motion for such molecule is one-dimensional:

$$m\frac{dw}{dt} = -gradW(z)\cdot \tag{3}$$

Here m is the mass of the molecule penetrating through the layer; w is the velocity component with respect to the nanoporous layer.

This equation, when applied to the passage through the averaged barrier, encompasses all the statistics related to the location of the molecule's starting point with respect to the tubes which make up the parqueting element. We will try to take into account the statistics on the velocity values using the Maxwell distribution, which is as follows:

$$f(v) = \frac{dN}{Ndv} = \frac{4v^2}{\sqrt{\pi}}\lambda^{3/2}e^{-\lambda v^2}\cdot \tag{4}$$

Here f is the distribution function; v is the velocity module of the molecule; $\lambda = \dfrac{m}{2kT}$, k

is the Boltzmann constant; T is the absolute temperature; N is the number of molecules per unit volume; dN is the fraction of molecules whose velocities are in the range of $[v, v + dv]$.
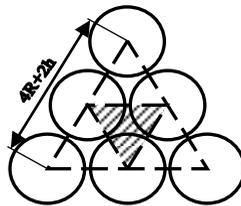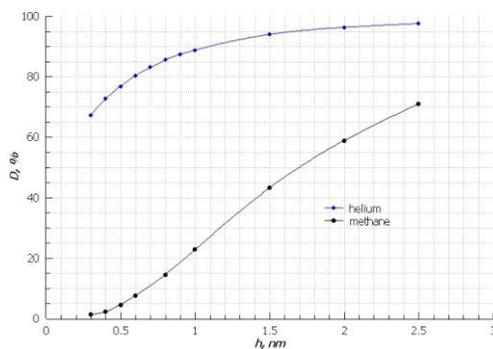

Fig. 2 Triangular packing of nanotubes.

Practical calculations show that, if at a certain velocity a molecule passes through the packing of nanotubes, it can pass through it at a greater value of velocity as well. So, finding the minimum speed of passage and further integrating the Maxwell distribution from this value to infinity, we can define the fraction of molecules which pass through the packing. The minimum velocity values for helium atoms and methane molecules for the considered triangular packing of tubes are shown in Fig. 3. The next figure represents the distribution of the permeability coefficients for helium and methane as well. Fig. 4 shows that at $0.3 \leq h \leq 1.0$ nm the structure provides good separation basing on the permeability coefficient, i.e. it functions as a separator.

To integrate equation (4) it is quite useful to apply the standard version of the Runge-Kutta scheme of the fourth-order accuracy.
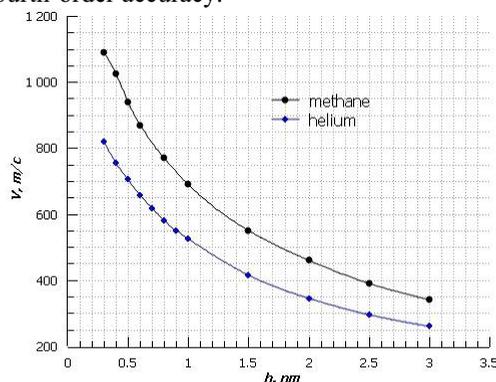
Fig. 3 Limit permeability rate for triangular packing. Black – methane; blue – helium.

Fig. 4 Permeability curve for triangular packing of nanotubes in respect of helium atoms (blue) and methane molecules (black).

2 Summary

The calculations made it possible to easily find the minimum limit velocity of passage through the homogeneous layer for a given type of molecules and to assess by its value the degree of molecular passage through this layer. Comparing the obtained permeability values for various components of the initial gas mixture, we can draw conclusions about selective properties of a layer of parallel nanotubes or other structures created on the basis of 2D carbon materials. In the present study we found that, at least for a triangular packing of identically oriented tubes, the layer functions as a separator at the tubes convergence values *h* equal to 0.3 to 1 nm.

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