STUDYING PERMEABILITY OF NANOSTRUCTURES OBTAINED FROM POLYETHYLENE THREADS

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The paper studies process of interaction of a moving molecule with structure atoms. The mathematical description is based on application of Hamiltonian systems model and numerical methods for solving the basic problem of molecular dynamics. The interaction between individual atoms and the simplest molecules is cared out using the classical Lennard-Jones potential. Polyethylene nanostructures are considered as filtering elements for selective separation of natural gas mixtures, in particular, their light components: hydrogen and helium. The influence of geometric dimensions and geometric features of a nanostructure on selectivity of gas mixtures separation is studied.

Key words: *molecular dynamics, nanostructured polyethylene, potential interaction, differential permeability, gas separation*

Introduction

The need for separation of natural gas components is due to the presence of both the final desired product (CH_4) and other impurities (hydrogen sulphide, helium, *etc*.) in natural gas. The presence of a small amount of impurities causes certain difficulties in transportation and application, especially in technological processes of final production. The use of filters obtained from nanomaterials is an innovative method of components separation based on intermolecular interactions [1]. Nanostructures include open carbon nanotubes [2-5], nanochannels [6], nanofibers [7, 8], and ultrathin films [9]. One of the promising methods for separation of natural gas components is using polyethylene nanostructures consisting of curved polyethylene threads lined in the form of an interlacing lattice [10-13]. Polyethylene is a thermoplastic polymer of ethylene. It is an organic compound and has long molecules CH_2–CH_2–CH_2–CH_2, where "–" means covalent bonds between carbon atoms [14]. The distance between carbon atoms and the angles of valence bonds in a polyethylene molecule are shown in fig. 1.

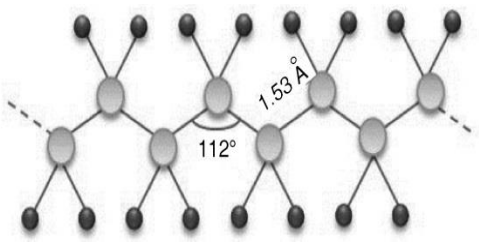

Figure 1. Molecule of polyethylene [15]

If a polyethylene molecule is considered as a separate wire, then the simplest structures

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obtained on the basis of such wires can be effectively described using the *atom-atom* interaction model. However, there is a possibility to further simplify the description. This is possible if we take a linear sequence of ethylene C_2H_4 molecular groups as a wire. Then the process of studying selective separation of gas mixtures will be based on models of particle dynamics in terms of particles interacting with structures composed of six-atom molecular groups. The data presented in fig. 1 can be used to determine the distance between the *beads* (spheres) in the polyethylene molecule model. On the basis of these ideas, we consider the influence which geometric dimensions of cells of a nanoscale structure composed of polyethylene wires have on motion of the gas phase molecules, as well as the effect of system layering on permeability of a nanoporous layer.

The numerical model

Permeability is usually understood as the relative value of mass-flow of molecules incident on the membrane to the flow of penetrating molecules. In the problems under consideration, it is appropriate to single out a renewal period of the thermodynamic state of gas, $\tau = \lambda/\upsilon(\lambda)$ is the mean free path of molecules, υ is the average thermal velocity of motion). Within this renewal period, it is possible to speak of the number of falling and penetrating molecules. In this case, the definition of permeability is: relative permeability is the fraction of penetrating molecules from the total number of molecules incident on the λ^2-surface originally located in the λ^3-volume of the gaseous medium adjacent to the surface of the membrane. Here the Maxwell λ-cube is considered as the minimum volume still providing an equiprobable exit of molecules through its faces.

Investigations of the process of interaction between a moving molecule and atoms of a polyethylene structure are based on application of a mathematical model and numerical methods for solving the fundamental 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 action independence as the sum of effects from each structure atom on the test molecule under consideration. According to this law, if several forces act on a material point, it is imparted acceleration equal to the geometric sum of accelerations which the forces would impart acting separately [16].

In the simplest case, the considered carbon structure can be represented as a set of atoms located in given positions. This is the so-called static material model. Such a model is quite acceptable at low and moderate temperatures of gas filtration through nanoporous materials. Let the impact from an individual node of the crystal structure be determined by the classical Lennard-Jones potential:

$$U(\rho_j) = 4\varepsilon\left[\left(\frac{\sigma}{\rho_j}\right)^{12} - \left(\frac{\sigma}{\rho_j}\right)^{6}\right] \tag{1}$$

Then the integral action of all the atoms of the porous material will be a simple sum of their potentials:

$$U_{\Sigma}(x,y,z) = \sum_{j=1}^{N_p} U(\rho_j) \tag{2}$$

Here

$$\rho_j = \sqrt{(x-x_j)^2 + (y-y_j)^2 + (z-z_j)^2}$$

is the distance between the moving gas molecule and the j^{th} structure atom and N_p – the total number of atoms in the structure.

For the interaction potential of a pitchfork eq. (1) the equations of motion of the moving molecule can be written:

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2}=\sum_{j=1}^{N_p}a_j\frac{x-x_j}{\rho_j},\frac{\mathrm{d}^2y}{\mathrm{d}t^2}=\sum_{j=1}^{N_p}a_j\frac{y-y_j}{\rho_j},\frac{\mathrm{d}^2z}{\mathrm{d}t^2}=\sum_{j=1}^{N_p}a_j\frac{z-z_j}{\rho_j} \tag{3}$$

where

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

is the value of acceleration acquired by the moving molecule under the action of the j^{th} structure atom, N_p – the total number of atoms in the structure, m – the mass of the moving molecule, and ε and σ are the parameters of the *LJ*-potential.

The three ODE of the second order are reduced to six first-order equations by a known technique. Further, they can be integrated numerically using the Runge-Kutta technology of the standard fourth-order accuracy. In any case, to obtain a solution to the evolutionary problem on the basis of the equations written out, it is necessary to know the initial conditions that must determine the initial position and initial velocity of the test molecule.

In the case when the system under investigation consists of heterogeneous molecules (atoms), the parameters of ε and σ are based on the Lorentz-Berthelot mixing rule.

Constructing a polyethylene nanostructure

A single-layer polyethylene nanostructure consists of polyethylene threads equally oriented, with respect to the axis, fig. 2.

A net polyethylene nanostructure is obtained as a result of superposition of two single-layer structures on each other, fig. 3.

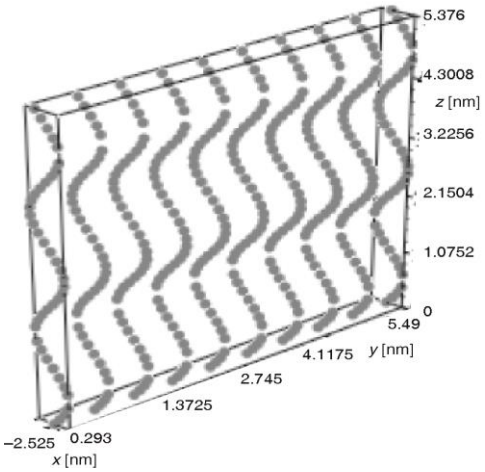

Figure 2. Model of single-layer structure composed of polyethylene threads

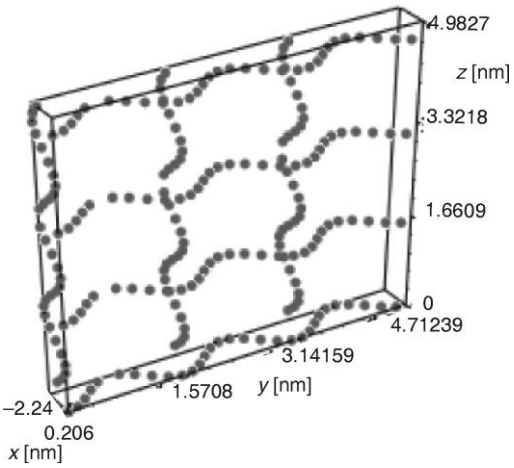

Figure 3. Model of nanonet structure composed of polyethylene threads

Permeability of net nanostructures

If we determine the effective radius of interaction between a polyethylene thread and a specific molecule or atom, considering the size of the permeability windows it is possible to estimate the value of passage degree for one or another component of the gas mixture, at least for a case of a single-layer gas structure. Along with such an assessment, it is necessary to carry out systematic calculations of molecular passage through a spatial network at different speeds and different initial positions of molecules. At the same time, the assessment carried out, according to the law of areas, can be significantly improved by taking into account the influence of the velocity value of molecules on the value of the effective interaction radius of the polyethylene thread.

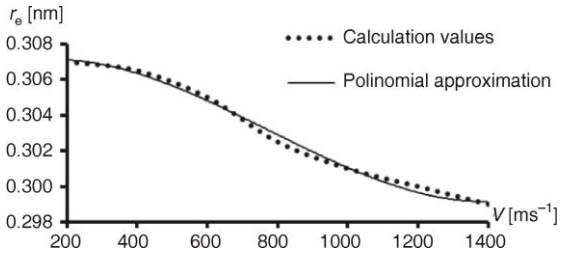

Figure 4. Effective radius of polyethylene thread in single-layer structure, with respect to helium

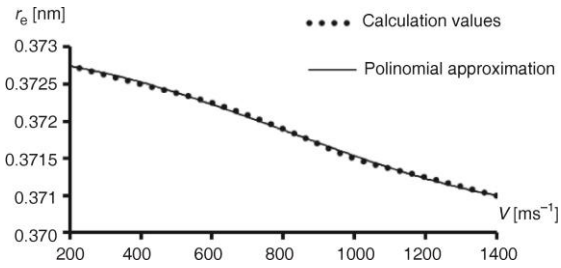

Figure 5. Effective radius of polyethylene thread in single-layer structure, with respect to CH_4

Figures 4 and 5 show calculation results for effective radius distribution of nanowires $r_e = r_e(V)$ depending on speed, with respect to helium and CH_4.

The effective radius, $r_e\ (V)$, of the thread is calculated by the method of approaching two linear polyethylene crystals as half the limiting distance of passage of molecules/atoms between them. This distance decreases with an increase in molecular velocity, so it is possible to suggest the following analytical polynomial approximations:

$$r_e\ (V,\ \mathrm{He}) = 3V^3 10^{-12} - V^2 10^{-8} + 2V10^{-6} + 0.244 \tag{4}$$

$$r_e\ (V,\ \mathrm{CH_4}) = -8V^3 10^{-14} - 2V^2 10^{-9} + 5V10^{-7} + 0.3145 \tag{5}$$

Also, approximations allow setting the minimum sizes of permeability windows for moving test particles and obtain an estimate of relative permeability of a flat polyethylene network:

$$D(h) = \int_0^\infty \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \exp\left(-\frac{m}{2kT}V^2\right) V^2 \left\{\frac{S_{\mathrm{pr}}}{h^2}\right\} \mathrm{d}V \tag{6}$$

where k is the Boltzmann constant, T – the absolute temperature, m – the mass of the molecule (atom), h – the cell dimension, and V – the velocity of the molecule (atom).

Expression (6) is based on the Maxwell distribution, with respect to the velocity modulus. The expression in curly braces is the relative value of the free passage area for molecules (atoms) penetrating through the cell of the polyethylene network:

$$S_{\mathrm{pr}}(V) = \begin{cases} 0, & h - 2r_e(V) \le 0 \\ h - 2r_e(V), & h - 2r_e(V) > 0 \end{cases} \tag{7}$$

In case of absolutely free passage of particles through the cell, the expression in the curly braces is equal to one. The result of integration, in this case, is also equal to unity. This case corresponds to complete passage of all components through an absolutely transparent surface which, in reality, should be a screen filter.

Figure 6 shows the results of calculating the relative fraction of penetrating molecules from the number of those falling on the cell of the polyethylene network.

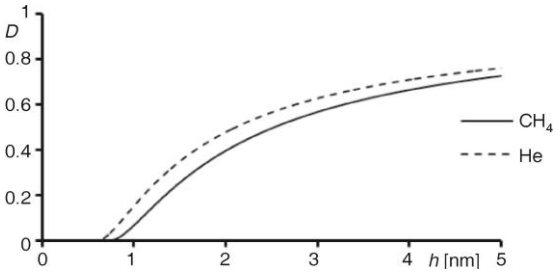

Figure 6. Permeability of networked nanostructure for CH_4 and helium

It is seen that as the size of the cell increases, the fraction of penetrating molecules/atoms rapidly grows, while separation selectivity of the CH_4-helium mixture $\chi = D_{He} / D_{CH_4}$ decreases. As can be seen from fig. 7, high selectivity is shown by the cell with a size slightly less than one nanometre.

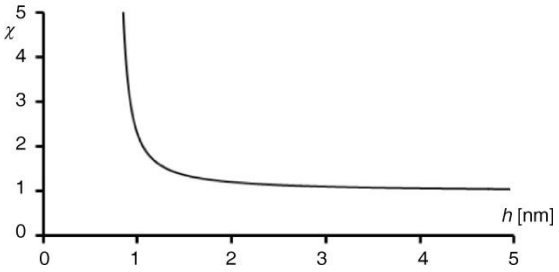

Figure 7. Separation degree of CH_4-helium mixture

High selectivity is the main property of the separation layer of the membrane. Even at low membrane productivity, high selectivity values allow obtaining high quality of mixture separation.

It was also noted that spatial net polyethylene structures, in contrast to flat carbine networks, exhibit geometric features leading to an effect of particle sorption at the limiting values of the cell sizes close to the sizes of the permeability windows. In addition, a helium atom passes through the barrier and returns back to get involved in the cyclic movement, figs. 8-10. Accumulation of sorption molecules (atoms) near the membrane is a very harmful trend which leads to a sharp decline in productivity.

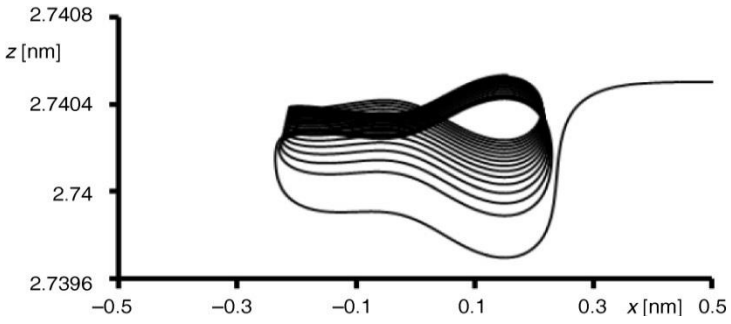

Figure 8. Projection of helium atom trajectory on *xz* plane

Thus, even ideal nanocellular polyethylene structures designed on the basis of separated polymer wires have a pronounced ability to capture penetrating particles. If the ideal location of polymeric wires is violated, their twisting and random interweaving will only enhance the determined sorption effect. Therefore, polymeric matrices which are used in membrane technologies do not provide the desired result in terms of selectivity.

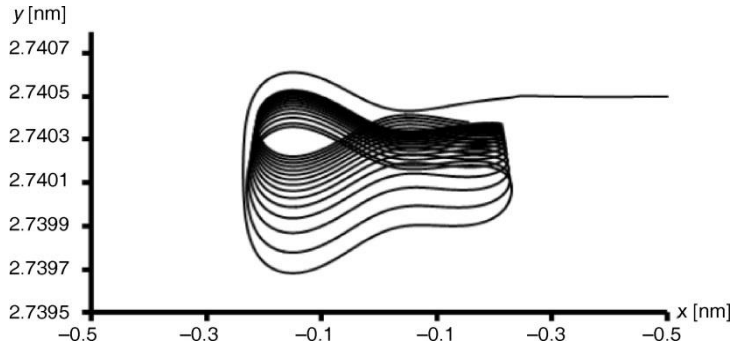

Figure 9. Projection of helium atom trajectory on *xy* plane

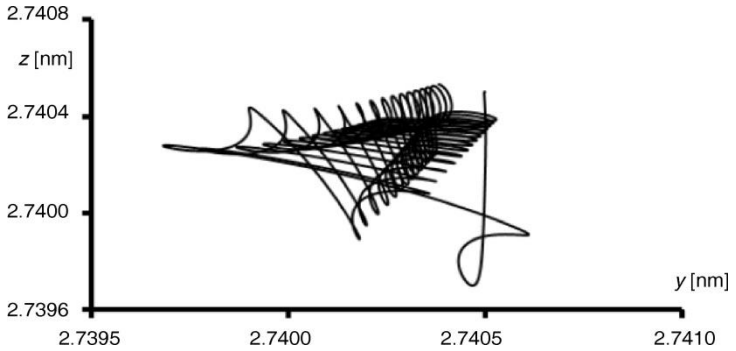

Figure 10. Projection helium atom trajectory on *yz* plane

Conclusion

Permeability of polyethylene nanoscale structures, with respect to CH_4 molecules and helium atoms, was investigated. The research was based on laws of molecular dynamics. The obtained results allow estimating permeability of polyethylene structures, as well as their use as selective nanofilters for natural gas. For each moving particle under consideration we defined the effective radii of polyethylene threads for a wide range of particle velocities and found the corresponding cell sizes in the net structure.

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