About a permeability of graphene pores

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Abstract. The present paper theoretically studies helium and helion passage through pores in a graphene sheet using classical molecular dynamics. It was found that, within the frame of the suggested model, for considerably large pores with the diameter of 0.75 nm, helium permeates much better than helion, which is quite an unexpected result in itself.

1. Introduction
In [1, 2] practical aspects of $^4$He, $^3$He and H$_2$ molecules’ penetration through graphene pores are considered. In this paper, using numerical methods, we solve the problem of defining the permeability gap for CH$_4$, $^4$He and $^3$He within a graphene structure containing a hole in the crystal lattice. [3] reports and describes in detail the simulation model of energetically stable vacancies in graphene plates, as well as presents the results of modelling the process of separation for mixtures CO$_2$-CH$_4$, CO$_2$-N$_2$ with the help of these structures. Regarding the separation properties, a comparison with carbon nanotubes having similar diameters or the S/V ratio is made. The results obtained can be used in applications connected with adsorption of CO$_2$. [4] studies permeability of graphene sheets containing nanopores with the diameter of 0.32 nm - 0.64 nm. Components of a methane-butane mixture were separated. Unexpected results were obtained: in the case of large pores, butane penetrates much better than methane.

2. Molecular-kinetic description
In our theory, interaction between individual molecules is determined by the classical Lennard-Jones potential. Interaction with the structure, in turn, is described by the law of action independence as the sum of each structure molecule’s impact onto a given test molecule. According to this law, if a material point is influenced by several forces, it acquires acceleration equal to the geometric sum of accelerations that it would acquire in case of those forces acting separately [5].

The total potential of interaction between the structure molecules and the test molecule can be written as the sum of individual potentials:

$$\Phi = 4\varepsilon \sum_{j=1}^{N_s} \left[ \frac{\sigma}{\rho_j} \right]^{12} - \left[ \frac{\sigma}{\rho_j} \right]^{6},$$

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where \( \rho_j \) is the distance between the considered molecules and the \( j \)-th molecule of the structure; \( \sigma \) and \( \varepsilon \) are the parameters of the interaction between the pairs of substances; \( \sigma \) is the repulsion radius for the molecular pairs; \( \varepsilon \) is the depth of the potential well for the corresponding pairs of identical molecules.

The values of the constants \( \varepsilon \) and \( \sigma \), included in the Lennard-Jones potential, for homogeneous pairs of substances, are given in the table 1.

| Interacting molecules | Relative depth of the potential well \( \varepsilon/k \) (K) | Influence radius of the interaction potential \( \sigma \) (nm) |
|-----------------------|----------------------------------------------------------|---------------------------------------------------------|
| \(^3\text{He} - ^3\text{He}\) | \( \varepsilon/k = 10.2 \) [K] | \( \sigma = 0.256 \) [nm] |
| \(\text{He} - \text{He}\) | \( \varepsilon/k = 10.2 \) [K] | \( \sigma = 0.228 \) [nm] |
| \(\text{CH}_4 - \text{CH}_4\) | \( \varepsilon/k = 148 \) [K] | \( \sigma = 0.38 \) [nm] |

If the system under study consists of heterogeneous molecules (atoms), for the parameters \( \varepsilon \) and \( \sigma \) the following averaging rules (the Lorentz-Berthelot mixing rules) are observed:

\[
\sigma_{CH} = \frac{\sigma_{CC} + \sigma_{HH}}{2}, \quad \varepsilon_{CH} = \left(\varepsilon_{CC} \cdot \varepsilon_{HH}\right)^{1/2}
\]

(2)

It is known that the Lennard-Jones potential is attractive at long distances, has a minimum at the point \( r = \sqrt{2}\sigma \) and is strongly repulsive at short distances [6]. The view of the potential is shown in figure 1.

\[\text{Figure 1. View of the Lennard-Jones potential.}\]

In order to define the permeability gap for each of the gases, we take the average value of the parameter \( \sigma \) as the minimum.

Peculiarities of applying the method of classical molecular dynamics with nanofiltration objectives are introduced in [7-11].

Figures 2-4 show permeability gaps for methane, helium, and helion with 12 remote nodes.
In order to verify these results a series of molecular-ballistic tests was conducted. At first, shots were made from the point of the remote interior node of the graphene plate, which is included neither in the permeability gap of helium, nor in that of helion: $x_0=1.5$, $y_0=0.4$. It was determined that molecules of both gases pass through the defect. Then shots were made from the position displaced from this node to the left by a quarter of the distance between carbon molecules in the graphene crystal structure (0.036 nm). For this position, helium test results appeared to be positive and those of helion - negative (see figures 5 and 6).

As it can be seen from figure 6 the helion molecule, reaching the graphene plate, was repulsed and passed along. Despite the fact that helion possesses a greater heat rate and a smaller mass than helium, a graphene plate does not show greater permeability for it.
3. Summary
We analyzed pores having zero areas of permeability gaps for all neutral molecules under study, including the helium isotope in question. Despite the simplicity of the mathematical model, which does not take account of carbon-carbon bonds within a graphene plate, as well as changing force fields on the edge of the pore, the calculations give correct relations between permeabilities of individual components. The calculations show that perforated graphene sheets can not be used for separation of a helion-helium mixture.

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