

# PERMEABILITY OF ULTRA-THIN AMORPHOUS CARBON FILMS

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**Abstract.** The present paper deals with defining the energy of interaction between an ultra-thin hydrocarbon layer and helium molecules using a modification of the LJ-potential and the continual approach. The suggested approach allows determination of the statistically average motion of a test molecule through material layers under consideration. The obtained results made it possible to localize global sorption zones both inside the layer and at its external borders and to identify the parameters which are responsible for permeability of the layer.

## 1 Introduction

Membrane technologies of gas separation, which are currently under development, require studying permeability of ultra-thin layers. Such structures can be produced by means of vapour deposition or using the method of sputtering or rapid catalyst polymerization. When investigating physical mechanisms of molecular motion through a layer, the same as in the present paper, methods of classical molecular dynamics and wave dynamics are applied [1-8]. In addition, quantum-mechanical description is always of relevance. As for the classical approach, it is realized in the method of global Monte Carlo simulation [9-13] and is further developed in the works which are based on using the continual representation of the interaction energy [14-16].

## 2 Methods

### 2.1 Power centres as sources of interaction energy

The normalized LJ-potential has the following form:

$$\Phi(\rho) = \frac{1}{\rho^{12}} - \frac{1}{\rho^6} \quad (1)$$

where

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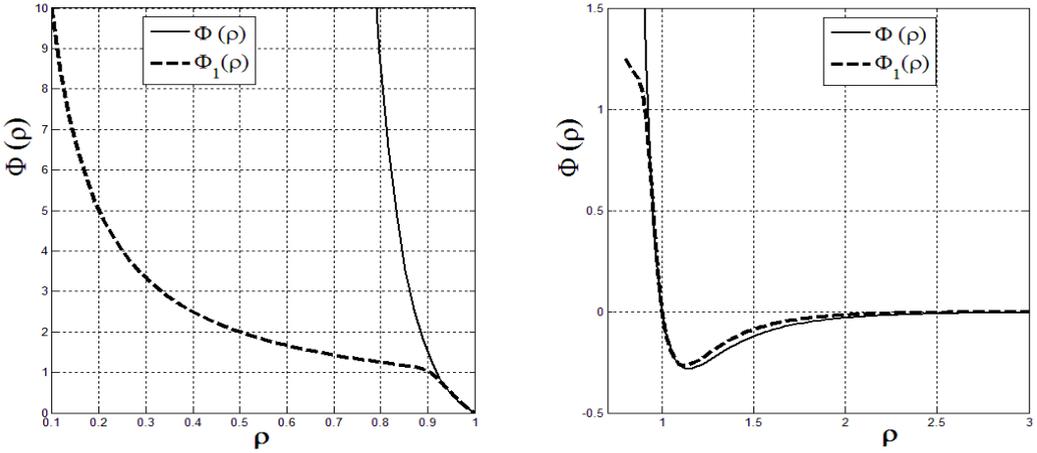
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$$\rho = \sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2} \quad (2)$$

is the distance between the centres of interacting molecules, wherein  $x, y, z, x', y', z'$ , are the Cartesian coordinates of the interacting molecules centres. Equation (1) can be transformed [1]:

$$\Phi_1(\rho) = \frac{1}{\rho} \text{th} \left( \frac{1-\rho^6}{\rho^{11}} \right) \quad (3)$$

Then at  $\rho \rightarrow 0$   $\Phi_1(\rho) \rightarrow \infty$ , in the same way as  $\frac{1}{\rho}$ , i.e. potential (3) in such modification in contrast to (1) becomes intergrable.



**Figure 1.** Comparison of function graphs  $\Phi(\rho)$  and  $\Phi_1(\rho)$ .

This modification of the Lennard-Jones potential is used in the subsequent calculations.

## 2.2 Interaction energy of plane infinite layer

The interaction energy of a molecular aggregate layer can be calculated as follows. Let us use the modified LJ-potential in the dimensional form:

$$\Pi_1(r) = 4\epsilon \left( \frac{\sigma}{r} \right) \text{th} \left[ \left( \frac{\sigma}{r} \right)^{11} - \left( \frac{\sigma}{r} \right)^5 \right], \quad (4)$$

The value  $\rho$  included in this ratio determines the distance between the test molecule and some molecule of the material structure. While changing from Cartesian to cylindrical coordinates  $x = r \cos \varphi$ ,  $y = r \sin \varphi$ ,  $z = z$  in (2), we obtain:

$$\rho = \sqrt{r^2 + r'^2 - 2rr' \cos(\varphi - \varphi') + (z - z')^2}. \quad (5)$$

Let us introduce into consideration the parameter  $q$  as the number density of atoms distribution per unit volume of the material. For the purpose of simplicity, let us assume  $q$  to be constant. Then the impact energy of the layer acting on the test molecule can be determined by the triple integral:

$$U(x, y, z) = q \iiint_V \Pi_1(\rho) dV, \quad (6)$$

where  $V$  is the infinite volume of the layer and  $dV$  is the volume element:

$$dV = H_r H_\varphi H_z dr' d\varphi' dz'. \quad (7)$$

Here  $H_r = 1$ ,  $H_\varphi = r'$ ,  $H_z = 1$ , are Lamé coefficients for cylindrical coordinates.

Introducing (4) and (5) into (6), we obtain:

$$U(r, \varphi, z) = q \int_0^{2\pi} \int_0^\infty \int_{-h}^h \Pi_1 \left( \sqrt{r^2 + r'^2 - 2rr' \cos(\varphi - \varphi') + (z - z')^2} \right) r' dr' dz' d\varphi'. \quad (8)$$

If to perform integration over  $\varphi'$  in (6), one shall deduce an equation which is the same at any  $\varphi$ . Moreover, on integrating over  $r'$  in (6), one shall observe disappearance of the  $r$ -dependence. There will be no dependence on the two coordinates if the test molecule (observer) is placed on the axis  $r = 0$ . Then instead of (6) we find:

$$U(z) = 2\pi q \int_{-h}^h \int_0^\infty \Pi_1 \left( \sqrt{r'^2 + (z - z')^2} \right) r' dr' dz'. \quad (9)$$

### 2.3 Equation of test molecule motion

The proposed continual description of interaction between the layer atoms and the test molecule of the gas component of some mixture allows solving the idealized problem of molecular motion perpendicular to the layer, i.e. recording the one-dimensional formulation for this problem:

$$m \frac{dW}{dt} = - \frac{dU(z)}{dz}, \quad \frac{dz}{dt} = W. \quad (10)$$

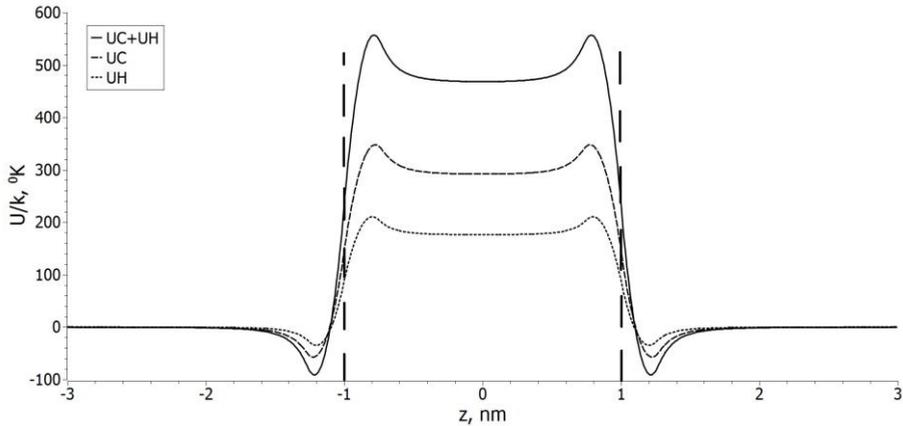
Here  $m$  is the mass of the test molecule,  $z(t)$  and  $W(t)$  are its coordinate and speed,  $U(z)$  is the potential of interaction between the layer and the molecule found using (9).

## 3 Calculation Results

The continual description of the interaction energy in the material of a layer allows calculating molecular motion both at the approach to the layer and inside. The calculation results for molecular motion through the material are shown in Figure 3-5. However, at first, we will consider the nature of the interaction energy distribution for the case of a 2 nm thick layer interacting with test helium molecules nearby. Within the scopes of this paper, we have considered a polyethylene film which can be produced by means of catalyst polymerization. As the basis of the theory we used the nuclear concept of defining the interaction energy of the layer. Since the number of hydrogen atoms in polyethylene is about twice greater than that of carbon, while the total carbon impact appears to be stronger, we took into account the contributions from both hydrocarbon components.

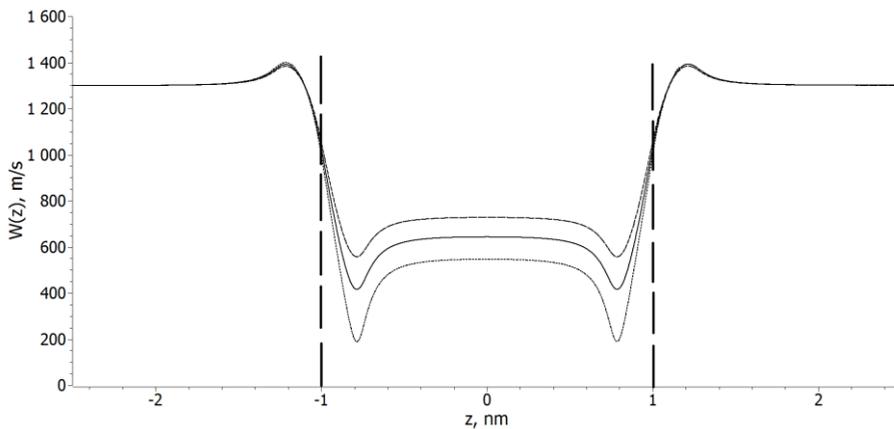
Figure 2 (bottom - to top) shows interaction energies of all hydrogen atoms (within the layer) and of all carbon atoms separately, as well as the total interaction energy of the total mass of atoms (solid curve). The derivative of the total energy is given in the right-hand part of the fundamental equation of a single molecule dynamics. Presenting this equation as a system of two ordinary differential equations (10) we integrate it numerically using the Runge-Kutta scheme of the fourth-order accuracy.

For the purpose of realizing the idea of translation to fractional positions on the space, we used the linear interpolation of the gradient of the interaction energy. All integrals determining the interaction energy of the layer's material components are found using the trapezoid rule.



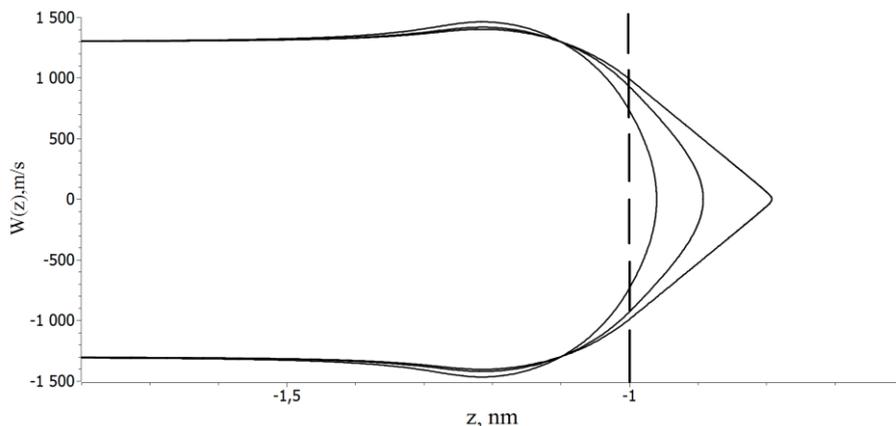
**Figure 2.** Interaction energy of layer atoms.

Figure 3 shows the rate of a helium molecule passage through a hydrocarbon layer, the density of carbon atoms (bottom – to top) being  $q_c = 38, 34, 30 \text{ nm}^{-3}$ . In addition, the density of hydrogen atoms in respective variations is twice as high. Each rate curve given in Figure 3 qualitatively reproduces the behaviour of the inverted curve of the interaction energy. Regular polyethylene possesses the number density of carbon atoms  $q_c = 47 \text{ nm}^{-3}$  and is impassable for helium atoms at a rate corresponding to the reference temperature.

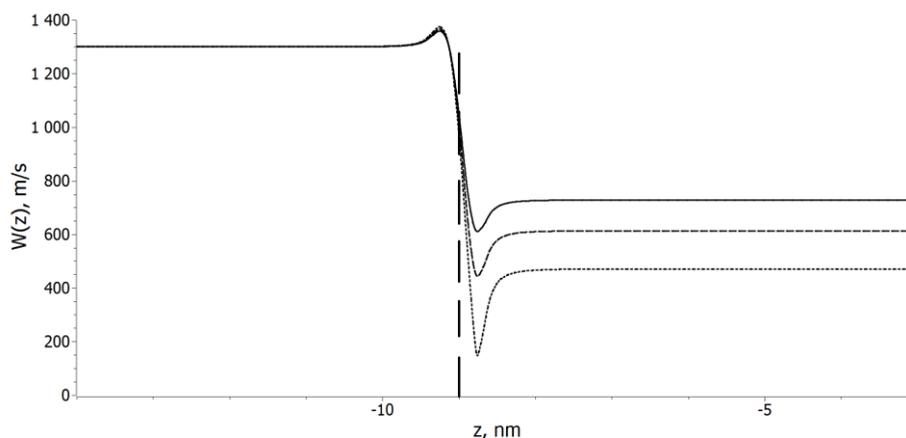


**Figure 3.** Rate of test molecules in permeable layer.

Figure 4 presents the cases of an impermeable film. Here curve 1 is  $q_c = 50$ , curve 2 - 43, and curve 3 -  $40 \text{ nm}^{-3}$ . It is seen that even an impermeable film is penetrated by an average molecule to a particular depth, the molecule being then pushed back by the layer. Figure 5 presents the calculation results for an 18 nm thick layer with the same values of  $q_c$  as in Figure 3, i.e. permeable values of the number density of carbon atoms. Increasing the thickness of the layer almost by an order does not change the permeability properties of the layer. For the test molecule it is important to overcome the energy barrier at the left boundary of the layer (which is the same in two cases considered), while inside the layer the molecule moves at a constant rate.



**Figure 4.** Reflection of molecules from impermeable layer.



**Figure 5.** Molecular rate depending on molecule's location in front of or inside layer calculated at  $q_c = 30, 34, 38$  nm<sup>-3</sup> (top – to bottom).

## 4 Conclusion

In the paper we have considered the problem of permeability for an ultra-thin infinite homogeneous hydrocarbon layer of uniform thickness. We suggested an approach according to which the interaction energy of individual material structure atoms of the layer is replaced by the interaction potential continual distribution. This idealization allows reducing the layer permeability problem to a one-dimensional problem of molecular motion perpendicular to the layer. The problem is solved with application of the Runge-Kutta method. The calculation results showed that a polyethylene film, even ultra-thin, is impermeable for helium at an average rate corresponding to the ambient temperature. However, reducing the number density of material structure atoms of the layer by 20% makes it permeable. Moreover, the layer thickness is not a critical parameter with regard to permeability. The essential indicators here are the material grade (parameters  $\sigma$  and  $\varepsilon$  in the LJ-potential) and the number density of molecules and atoms of the layer.

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