

# Numerical Investigation of the Water Vapour Diffusivity inside Homogeneous Porous Media

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**Abstract.** This work is devoted to numerical investigation of diffusivity function for water vapour interaction with homogeneous porous media. Molecular dynamics simulation is used to determine the diffusivity function. Various approximations of diffusivity are applied for numerical solution of diffusion equation.

## 1 Statement of the problem

The investigation of the isothermal moisture absorption in unsaturated media is of fundamental interest in areas such as the issue of general safety rules, the physics of the buildings, the reactive transport of fluids through the Earth crust, etc. As a consequence, the study and modeling of the moisture transfer processes in porous materials is of permanent concern.

If the gravity is negligible in comparison with the capillary forces, then the isothermal absorption of the moisture (i.e., water vapour phase) in a macroscopically homogeneous porous material is governed by the one-dimensional diffusion equation [1],

$$\frac{\partial w(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( D(w) \frac{\partial w(x, t)}{\partial x} \right), \quad (1)$$

where  $w(x, t)$  denotes the local volumetric water content ( $\text{m}^3/\text{m}^3$ ) and  $D(w)$  the diffusivity ( $\text{m}^2/\text{s}$ ).

Eq. (1) is solved with the initial and boundary conditions

$$w(t, 0) = w_1, \quad w(t, l_x) = w_2, \quad w(0, x) = \frac{w_2 - w_1}{l_x} \cdot x + w_1. \quad (2)$$

The equations (2) are written under the assumption that the behavior of the water vapour in a homogeneous porous medium is similar to the behavior of the water vapour in an individual through-type pore with suitable hydraulic properties [2–4].

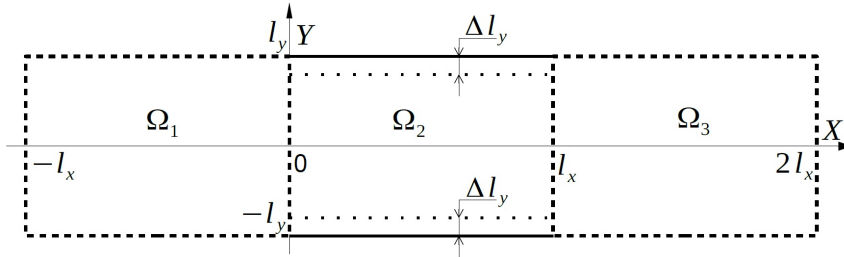
In calculations  $w_1 = 7.92 \text{ ng}/\text{nm}^3$  and  $w_2 = 39.92 \text{ ng}/\text{nm}^3$  – the water vapour densities on the left end of the pore ( $x = 0$ ) and on the right end of the pore ( $x = l_x$ ) – has been used Eq. (2).

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## 2 The molecular dynamics problem

In classical molecular dynamics, the behavior of an individual particle is described by the Newton equations of motion with corresponding interaction potential [5]. The geometrical configuration for the molecular dynamics model of the water vapour diffusion through a pore is shown in Fig. 1.



**Figure 1.** Geometrical configuration of the molecular dynamics model of the through-type pore.

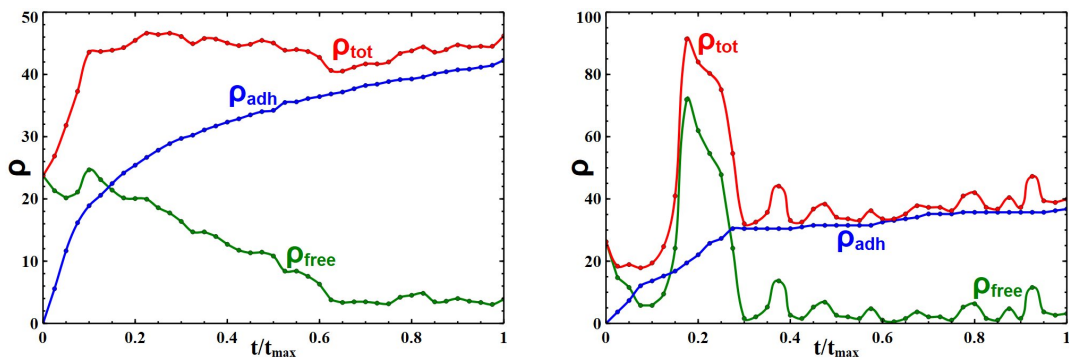
Molecular dynamic simulations have been done under the following boundary conditions for the domains  $\Omega_1$ ,  $\Omega_2$ , and  $\Omega_3$  in Fig. 1. At the boundaries  $\Gamma_{11} = [-l_x \leq x \leq 0; -l_y]$ ,  $\Gamma_{12} = [-l_x; -l_y \leq y \leq l_y]$ , and  $\Gamma_{13} = [-l_x \leq x \leq 0; l_y]$  of the domain  $\Omega_1$  and at the boundaries  $\Gamma_{31} = [l_x \leq x \leq 2l_x; -l_y]$ ,  $\Gamma_{32} = [2l_x; -l_y \leq y \leq l_y]$ , and  $\Gamma_{33} = [l_x \leq x \leq 2l_x; l_y]$  of the domain  $\Omega_3$ , periodic boundary conditions have been assumed. Inbetween  $\Omega_1$ ,  $\Omega_2$ , and  $\Omega_3$ , free flow is assumed to occur. Finally, the boundaries  $\Gamma_{21} = [0 \leq x \leq l_x; -l_y]$  and  $\Gamma_{22} = [0 \leq x \leq l_x; l_y]$  of  $\Omega_2$  are assumed to be isolated walls for the moisture propagation (i.e.,  $w(x, t)$  vanishes identically at these boundaries).

The standard Lennard-Jones potential  $U_{LJ}(r)$  [6] with  $\sigma = 3.17\text{\AA}$  and  $\varepsilon = 6.74 \cdot 10^{-3}$  eV is assumed for the simulation of the particle interaction inside  $\Omega_1$ ,  $\Omega_2$  and  $\Omega_3$  domains except for a thin layer of width  $\Delta l_y$  near the boundaries  $\Gamma_{21}$  and  $\Gamma_{22}$ . Here  $r$  is the distance between the centers of the particles.

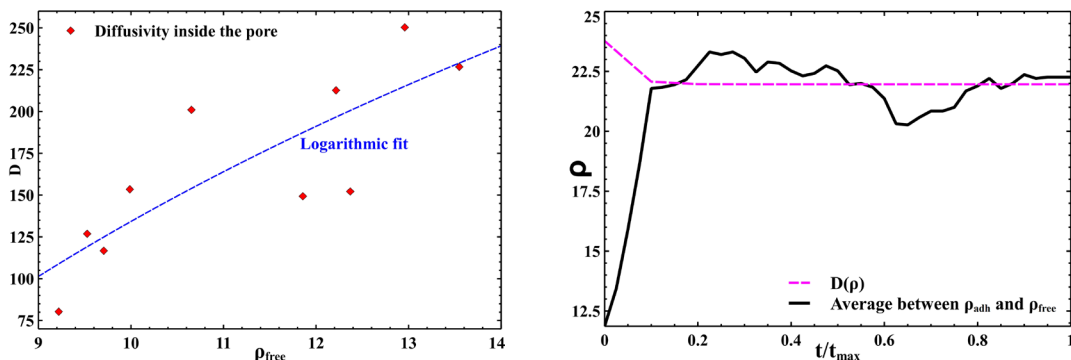
Because of the adhesion of the molecules to the pore walls it is necessary to take into account their interaction. It can be described by the Lennard-Jones 9-3 wall potential  $U_{9-3}(\xi)$  [7]. Here  $\xi$  is the distance between the water molecule and the pore wall surface along the perpendicular to the wall. For the two-dimensional model of the through-type pore  $\xi$  equals  $\Delta y$ , the distance from the water molecule to the pore wall along the  $y$  coordinate (Fig. 1).

The Newton equations of motion were integrated by the well known Velocity Verlet method [8]. A Berendsen thermostat [9] is used for the temperature calibration and the control inside the three domains  $\Omega_1$ ,  $\Omega_2$ , and  $\Omega_3$ . The Andersen thermostat [10] is used for the simulation of the interaction of the water molecules with the walls of the pore to account for the sticking effect of vapour particles to the pore walls. This thermostat acts on particles entering into the thin layer of width  $\Delta l_y$  near the pore walls and leads to corresponding modification of the Velocity Verlet method. The pressure in the pore was controlled using a formula based on the virial equation [11]. The diffusivity function was calculated from the known Einstein relation for the two-dimensional case  $\partial \langle r^2(t) \rangle / \partial t = D$ , where  $r^2(t)$  is the mean-squared distance over which the labeled particles have moved at the time  $t$  [11].

At the initial time, the particles are evenly distributed across all three domains  $\Omega_1$ ,  $\Omega_2$  and  $\Omega_3$  in accordance with the initial and boundary conditions (2). Initial velocities are randomly selected from  $[-1, 1]$  with the normal distribution, then they are set such as the total velocity (momentum) vanishes, and then they are changed to achieve the desired initial temperature  $T_0 = 35^\circ\text{C}$ . For the calculation of the distribution of the diffusion coefficient and the water vapour concentration along the  $x$ -axis, inner space of the pore was divided into 10 equal layers along it.



**Figure 2.** Time dependence of the densities averaged over the pore volume (left) and densities averaged over two central layers of the inner space of the pore (right).  $\rho$  is the density of the water vapour in  $[\text{ng}/\text{nm}^3 \times 10^{-18}]$ ,  $t_{\text{max}} = 16663.2$  ps.



**Figure 3.** Approximation of the diffusivity as a function of  $\rho$  by the logarithmic function (left). Comparison of the averaged density-curves calculated by the diffusion equation with the logarithmic approximation of the diffusivity and MD-curves (right).  $\rho$  is the density of the water vapour in  $[\text{ng}/\text{nm}^3 \times 10^{-18}]$ ,  $t_{\text{max}} = 16663.2$  ps.

### 3 Computer simulations

Figure 2 presents the calculated time evolution for the density of adhered water molecules  $\rho_{\text{adh}}$ , the density of moving water molecules  $\rho_{\text{free}}$  and the total density of the water molecules in the pore  $\rho_{\text{tot}}$  averaged over the pore (left picture) and at the center of the pore (right picture).

Figure 3 left presents the logarithmic approximation of the diffusivity function. This approximation is used for the numerical solution of the diffusion equation (1) by an implicit finite difference scheme [12]. Results of the diffusion equation solution (1) are presented in Figure 3 right.

As can be seen from Figure 3 right, the logarithmic approximation of the diffusivity function in concentration  $\rho$  make it possible to better describe the time evolution of the concentration of the water vapour averaged over the molecules moving in, respectively adhering to the pore.

## 4 Conclusions

Our simulations show that the water vapour interaction with a porous media the diffusivity presents a very complicated dependence on the density. Molecular dynamics simulations produce a sufficiently realistic picture of the water vapour interaction with a pore if the computer model takes into account the interaction of the water molecules with the pore walls. The solution of the diffusion equation strongly depends on the average between the density of stuck liquid water molecules and the density of moving liquid water molecules but not on the total density of water vapour as a function of time and coordinates.

## Acknowledgments

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