Molecular dynamic simulation of water vapor interaction with blind pore of dead-end and saccate type [⋆]

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The interaction of water vapor with porous media

The characteristics of water-pore interaction heavily depend on the form and size of the pore.

The pores can be distinguished by the following features: accessibility, shape and size.

The pores according to accessibility can be of these types: closed pores, open pores, blind pores (also called dead-end or saccate pores) and through pores.

The pores can be of these shapes: cylindrical open, cylindrical blind, ink-bottle-shaped, funnel shaped and etc*.

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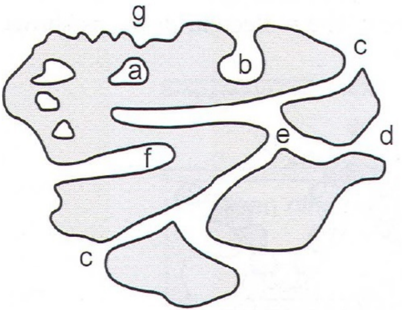
[*] *Rouquerol, J. , D. Avnir, D. , C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger,* Recommendations for the Characterization of Porous Solids (Technical Report). // Pure and Appl. Chem. — 1994,'—vol. 66, — P. 1739-1758.

The interaction of water vapor with porous media



Accessibility:

a: closed pores

b,c,d,e,f: open pores

b, f: blind pores (dead-end or saccate)

e: through pores

Shape:

c: cylindrical open

f: cylindrical blind

b: ink-bottle-shaped

d: funnel shaped

g: roughness

The interaction of water vapor with porous media

In accordance with the IUPAC* classification, pores are characterized by their sizes*:

- Micropores - widths smaller than 2 nm
- Mesopores - widths between 2 and 50 nm
- Macropores - widths larger than 50 nm

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*The International Union of Pure and Applied Chemistry

**McNaught A. D. and Wilkinson A.*, IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). — Blackwell Scientific Publications, Oxford. — 1997.

A complicated problem leads to a non-trivial approach for solving

- It is very complex to describe water-pore interaction therefore we use a special approach - a combination of molecular dynamics and continuous diffusion equation.
- Diffusion coefficient is derived and it can be represented by 4 dimensional function.
- Solving diffusion equation which can be non-stationary parabolic partial differential equation - analytically or numerically.
- In our work, we focus on simpler problem to demonstrate the nature of our approach.

Molecular dynamics model

In classical molecular dynamics the behavior of an individual particle is described by the Newton's equations of motion*, which can be written in the following form

$$m_i \frac{d^2 \vec{r_i}}{dt^2} = \vec{f_i}, \tag{1}$$

where i – a particle number, $(1 \le i \le N)$, N – the total number of particles, m_i – particle mass, $\vec{r_i}$ – coordinates of position, $\vec{f_i}$ – the resultant of all forces acting on the particle. This resultant force has the following representation

$$\vec{f_i} = -\frac{\partial U(\vec{r_1}, \ldots, \vec{r_N})}{\partial \vec{r_i}} + \vec{f_i}^{ex}, \tag{2}$$

where U – the potential of particle interaction, $\vec{f_i}^{ex}$ – a force caused by external fields.

**Gould H., Tobochnik J., Christian W.*, An Introduction to Computer Simulation Methods, Chapter 8. Third edition, 2005, pp. 267-268.

Molecular dynamic model

In our work, we use the Lennard-Jones potential which is the most used to describe the evolution of water in liquid and saturated vapor form

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{3}$$

where r — the distance between the centers of the particles, ε — the depth of the potential well, σ — the distance where the energy of interaction becomes equal to zero. Parameters ε and σ are characteristic for each sort of atom. The minimum of the potential is reached when $r_{min} = \sigma \sqrt[6]{2}$. Values of parameters σ and ε for Lennard-Jones potential are given in Table 1.

H_2O	$\sigma(\text{Å})$	$\varepsilon(eV)$
	3.17	$6.74 \cdot 10^{-3}$

Table 1: Parameter's values for Lennard-Jones potential.

Molecular dynamic model

Verlet Velocity Method

Within the framework of the Verlet Velocity method integrating the equations of motion is performed as follows:

- At the beginning of each step values $r(t)$, $v(t)$, $f(t)$ at the time t are defined or calculated in the previous step.
- First, the coordinates of the particle's new location are calculated at time $t + \Delta t$, then the velocities of particles are calculated at time $t + \frac{\Delta t}{2}$

$$\begin{aligned} r(t+\Delta t) &= r(t) + \Delta t\ v\,(t) + \frac{(\Delta t)^2}{2} a(t), \\ v\left(t + \frac{\Delta t}{2}\right) &= v(t) + \frac{\Delta t}{2}\ \frac{f(t)}{m}. \end{aligned}$$

Molecular dynamic model

- Next, the forces $f(t)$ acting on the particles are recalculated at time $t + \Delta t$.
- Finally, the values of velocities are calculated at time $t + \Delta t$

$$v(t + \Delta t) = v\left(t + \frac{\Delta t}{2}\right) + \frac{\Delta t}{2}\ \frac{f(t + \Delta t)}{m}.$$

Molecular dynamic model

In our work, we use the Berendsen thermostat to account for the effects of heat transfer between a vapor in the pore and the environment. This thermostat uses alternating nonlinear friction in the equations of motion and is realized by the following equations

$$\begin{aligned} \frac{dr_i(t)}{dt} &= v_i(t), \\ \frac{dv_i(t)}{dt} &= \frac{f_i(t)}{m_i} - \chi(t) v_i(t). \end{aligned} \tag{4}$$

Molecular dynamic model

In practice, the velocities of the particles are scaled with a factor

$$\lambda(t) = \left[1 + \frac{\Delta t}{\tau_B}\left(\frac{T_0}{T(t)} - 1\right)\right]^{\frac{1}{2}}. \tag{5}$$

Parameter $\tau_B \in [0.5, 2]$ ps is called the 'rise time' of the thermostat. It describes strength of the coupling of the system to a hypothetical heat bath. For increasing τ_B, the coupling weakens, i.e., it takes longer to achieve given temperature T_0 from current temperature T(t).
The Berendsen algorithm is simple to implement and it is very efficient for reaching the desired temperature from far-from-equilibrium configurations.

A computer simulation of microscopic model

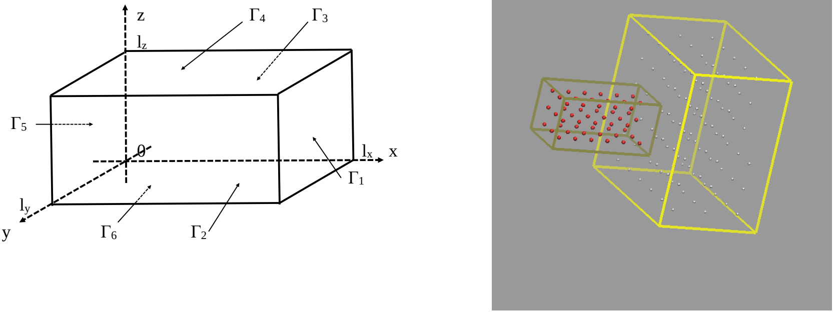


Figure 1: 3D pore and outer space.

A computer simulation of microscopic model

Input data for the drying process

- pore dimensions $l_x = 500$ nm, $l_y = 50$ nm, $l_z = 50$ nm;
- 1000 H_2O molecules in the pore volume $500 \times 50 \times 50$ nm^3 form a saturated water vapor at temperature $T_0 = 25\ ^oC$ and pressure $p_0 = 3.17\ kPa$;
- 1800 molecules in the outer area are 20 % saturated water vapor;
- integration step is $\Delta\ t = 0.016$ ps;
- the calculation was made for the evolution time 65.3 ns;

A computer simulation of microscopic model

The main characteristic of the diffusion process is the diffusion coefficient D.

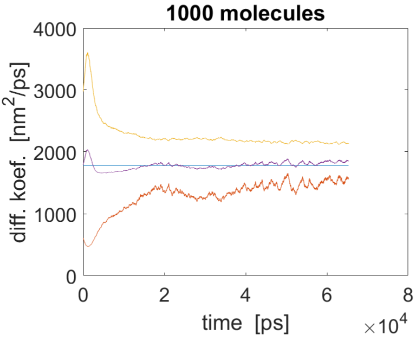


Figure 2: Diffusion coefficients including constant value $D = 1779.1$ [nm^2/ps].

A computer simulation of microscopic model

Input data for the wetting process

- pore dimensions $l_x = 500$ nm, $l_y = 50$ nm, $l_z = 50$ nm;
- 200 H_2O molecules in the pore volume $500 \times 50 \times 50$ nm^3 are 20 % saturated water vapor;
- 9000 molecules in the outer area form a saturated water vapor at temperature $T_0 = 25\ ^oC$ and pressure $p_0 = 3.17\ kPa$;
- integration step is $\Delta\ t = 0.016$ ps;
- the calculation was made for evolution time 65.3 ns;

A computer simulation of microscopic model

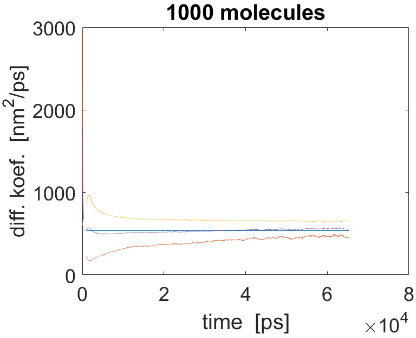


Figure 3: Diffusion coefficients including constant value $D = 536.33$ [nm^2/ps].

Macroscopic diffusion model

Let us denote the water vapor concentration as $w_v(x, y, z, t)$ $[ng/(nm)^3]$ where x, y, z are space independent variables and t is time independent variable. Then, we consider the following macroscopic diffusion model

$$\frac{\partial w_v}{\partial t} = D\Big(\frac{\partial^2 w_v}{\partial x^2} + \frac{\partial^2 w_v}{\partial y^2} + \frac{\partial^2 w_v}{\partial z^2}\Big) \tag{6}$$

$$0 < x < l_x, \quad 0 < y < l_y, \quad 0 < z < l_z, \quad t > 0$$

$$w_v(x, y, z, 0) = w_{v,0} \qquad 0 \leq x \leq l_x, \quad 0 \leq y \leq l_y, \quad 0 \leq z \leq l_z \tag{7}$$

$$\frac{\partial w_v}{\partial n}(t)\Big|_{(x,y,z)\in\Gamma_2\cup\Gamma_3\cup\Gamma_4\cup\Gamma_5\cup\Gamma_6} = 0 \qquad t > 0 \tag{8}$$

$$-D\frac{\partial w_v}{\partial x}(t)\Big|_{(l_x,y,z)\in\Gamma_1} = \beta[w_v(l_x, y, z, t) - w_{v,out}(t)] \tag{9}$$

$$0 \leq y \leq l_y, \quad 0 \leq z \leq l_z, \quad t > 0.$$

Macroscopic diffusion model

Where

- D is the diffusion coefficient $[(nm)^2/ps]$;
- l_x, l_y, l_z are 3D pore dimensions $[nm]$;
- $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5, \Gamma_6$ are boundaries of 3D pore (Γ_1 is free boundary while the rest boundaries are isolated);
- $w_{v,0}$ is the initial concentration of water vapor $w_{v,0} = 2.304 \cdot 10^{-17}$ for the drying process and $w_{v,0} = 0.4608 \cdot 10^{-17}$ for the wetting process $[ng/(nm)^3]$;
- $w_{v,out}(t)$ is the water vapor concentration in outer space $[ng/(nm)^3]$;
- β is the coefficient of water vapor transfer from pore space to outer space, $\beta = 50000$ $[nm/ps]$.

Macroscopic diffusion model

We suppose that the outer space water vapor concentration is expressed as

$$w_{v,out}(t) = \varphi_0 \cdot w_{sv}(T_0),$$

where φ_0 is the relative humidity of outer space ($0 \leq \varphi_0 \leq 1$) and $w_{sv}(T_0)$ is saturated water vapor concentration at outer temperature T_0.
The linear problem (6)–(9) can be solved exactly using the variables separation method and the result of the solution is

$$w_v(x,y,z,t) = w_{sv}(T_0) \cdot \varphi_0 + \left[w_{v,0} - w_{sv}(T_0) \cdot \varphi_0 \right] \cdot \qquad (10)$$

$$\cdot \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} e^{D\lambda_{mnp} t} c_{mnp} \cos(\alpha_{xm} x) \cos(\alpha_{yn} y) \cos(\alpha_{zp} z)$$

$$0 \leq x \leq l_x \qquad 0 \leq y \leq l_y \qquad 0 \leq z \leq l_z \qquad t > 0.$$

Macroscopic diffusion model

Here, c_{mnp} are coefficients of unity expansion

$$c_{mnp} = \begin{cases} \frac{4\sin(\alpha_{xm} l_x)}{2 l_x \alpha_{xm} + \sin(2\alpha_{xm} l_x)} & \text{if } n = 0;\ p = 0;\ m = 1, 2, 3, \ldots \\ 0 & \text{if } m, n, p = 1, 2, 3, \ldots \end{cases}$$

and λ_{mnp} are eigenvalues where

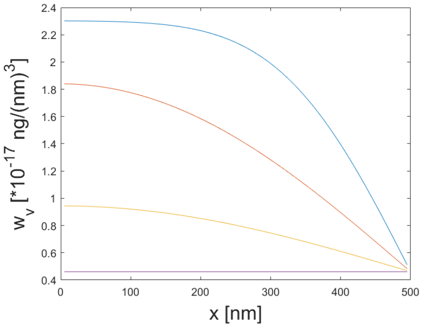
$$\lambda_{mnp} = -\alpha_{xm}^2 - \alpha_{yn}^2 - \alpha_{zp}^2,$$

$$\alpha_{yn} = \frac{n\pi}{l_y}, \qquad n = 0, 1, 2, \ldots \qquad \alpha_{zp} = \frac{p\pi}{l_z}, \qquad p = 0, 1, 2, \ldots$$

and α_{xm} are solutions of the equation

$$\alpha_{xm} \cdot \tan(\alpha_{xm} l_x) = \beta / D, \qquad m = 1, 2, 3, \ldots.$$

Macroscopic diffusion model



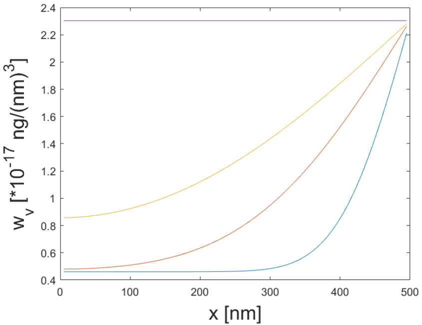


Figure 4: The dynamics of water vapor concentration at different time moments $t = 6,\ 30,\ 90,\ 65300$ ps (cross section at $y = l_y/2$ and $z = l_z/2$). The drying process is on left side from top to bottom. The wetting process is on right side from bottom to top.

Comparing microscopic and macroscopic diffusion models

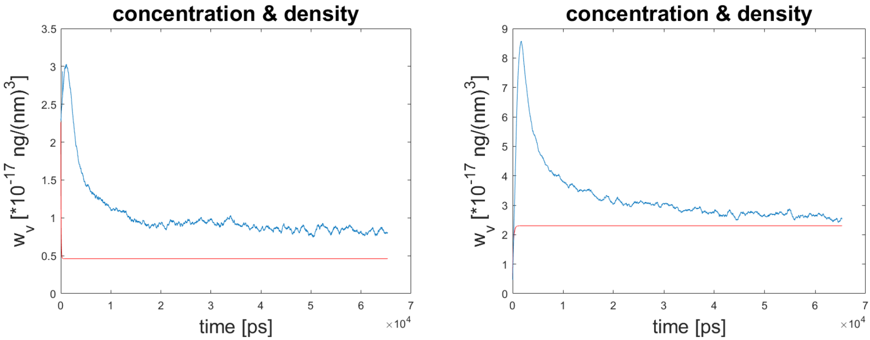


Figure 5: The dynamics of water vapor concentration (red curve) versus density (blue curve).The drying process (left) and the wetting process (right).

Combination of molecular dynamics and diffusion equation

Now we are ready to formulate our complex approach for the computer simulation of water-pore interaction. If the diffusion coefficient is not a constant, but depends on the coordinate and/or concentration of diffusing quantity, it is necessary to have a full picture of space distribution for the diffusion coefficient at every time step of diffusion process.

Therefore our approach consists of two stages.

1. To get distribution of the diffusion coefficient $D(\mathbf{r}, t)$.
2. To solve the diffusion equation in the most general case in accordance with Fick's Second Law

$$\frac{\partial\varphi(\mathbf{r}, t)}{\partial t} = \nabla \cdot (D(\mathbf{r}, t)\nabla\varphi(\mathbf{r}, t))$$

The φ is a density of diffusing physical quantity, which may be the number of particles, mass, energy, electric charge, or any other scalar extensive quantity.

Thank you for your attention!