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Міністерство освіти і науки України
Тернопільський національний технічний університетІмені Івана Пулюя

Математичного моделювання і дослідження масопереносу в неоднорідних і нанопористих середовищах

Mathematical modeling and research of mass transfer in heterogeneous and nanoporous media

Pr. Mykhaylo PETRYK
Dr. Igor BOYKO
Pr. N. Lebovka
Pr. J. FRAISSARD

Grants

1. **Project PCH DNIPRO №28282XH «Diffusion compétitive de gaz dans un solide poreux : imagerie RNM et modélisation », 2015-2016** (**Co-Directeurs: Pr. Daniel CANET, Université Henry Poincaré Nancy 1, France; Pr. Mykhaylo PETRYK, Université Nationale Technique Ivan Poulu'y de Ternopil, Ukraine**)

2. **Grants SSHN CampusFrance (2017, 2021)**

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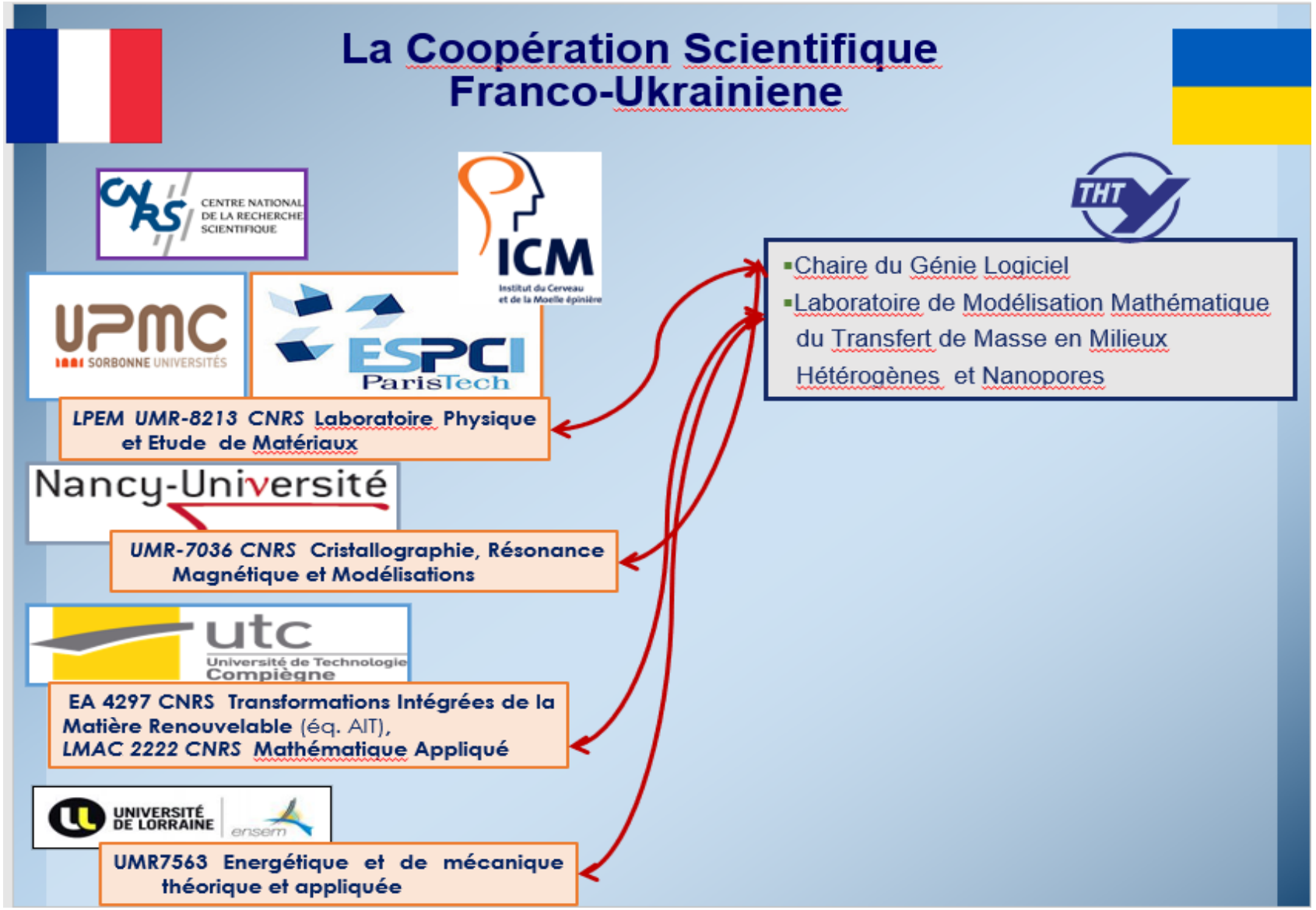
International Cooperation



International Cooperation

Les Projets communs des Recherches

(PCH, CNRS, CampusFrance)

- PCH (Ubert Curien Partnerships) № 28282XH «Diffusion Compétitive de Gaze un Solide Poreux: imagerie NMR et Modélisation» (2013) (Co-Directeurs: **D. Canet**, Université Henry Poincaré Nancy 1, M. Petryk, TNTU,).

- PCH "DNIPRO" «Diffusion Compétitive de Gaze un Solide Poreux: imagerie NMR et Modélisation» (Etape finale 2014). (Co-Directeurs: M. Petryk, D. Canet).

- Projet du CNRS «**DECOL de la SAS PIVERT**. Recherches en Modélisation Mathématique de Solide-Liquide Expression» (l'Uiversité de Technologie de Compiègne, *particip. de M. Petryk,* 2013).

- Projet du CNRS «Modélisation et étude du Transport Molécule en Pressage des Matériaux Celluleux. Génie des Procédés. Pôle Régional de Picardie» (UPRES A CNRS 6067, l'UTC) (*particip. de M. Petryk*, 2001, 2004)

- PICS 2015-2017 № 231937 "Diffusion competitive de gaz en milieu microporeux : Modelisation et imagerie IRM(Co-Directeurs: S. Leclerc, Uiversité Loraine-ENSEM,M. Petryk, TNTU)

- Projet du CNRS «Etudes Experimentales et Modélisatioin Mathématique de la Diffusion Compétitive de Benzene et Hexane dans un Lit Catalytique à Base des Zéolites» (*LPEM UMR-8213 CNRS* ESPCI-UPMCP, Directeur J. Fraissard) (*particip. de M. Petryk*, 2003-2006)

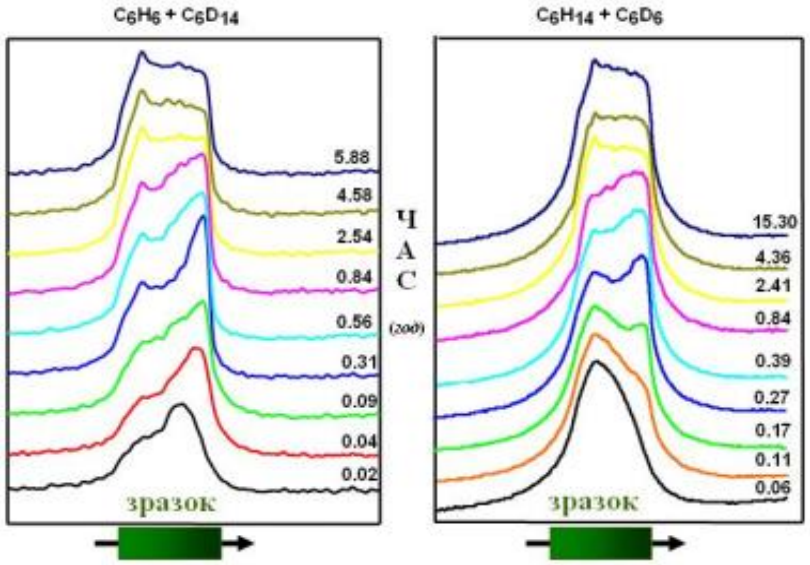
Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

La visite de l'Ambasadeur de la France, M. Jacques FAURE à TNTU (24 Juin 2010)

La rémise des Palmes Académiques

2013- 2022: working visits (l'ESPCI-UPMC, TNTU)

Conference of Professor UPMC Jacques FRAISSARD in TNTU



ESPCI Paris Tech, ICM, TNTU (2017)

2017- 2022: working visit (l'ESPCI-UPMC Paris, TNTU)

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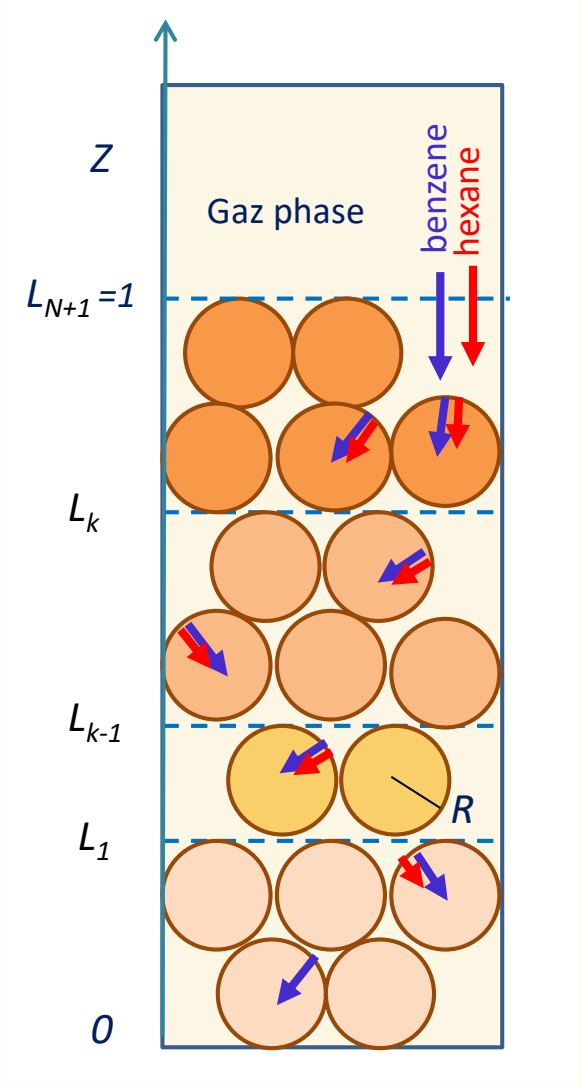
the object under study: heterogeneous nanoporous catalyst



[*Kärger., Ruthven,* **Wiley** (2012),
Petryk et al. **Catalysis Today**, 139(4), 2007]

The principal physical assumptions of model

1. Adsorption is caused by dispersion chemical forces (Jones-Lenard) and the attraction and repulsion electrostatic forces (Van- Der-Waals ).

2. Adsorption takes place in active centers on the adsorbent surface distributed throughout the internal nanopores surface (Langmuir ).

3. The molecular adsorbate layer is formed on the nanopores surface.

4. Adsorbed molecules are retained by active centers during certain time, depending on the temperature [Langmuir I., ***Science*** *(New York, N.Y.),*97, 1950].

5. The nonlinear function of adsorption equilibrium (of Langmuir , Gibbs and Hinshelwood ) between the equilibrium concentration (gas phase) **and the adsorbate concentration** q (solid phase):

$$q\left(c_{eq}\right) = q_{full} b_0 \exp\left(-\frac{\Delta H}{RT}\right)\frac{c_{eq}}{1+bc_{eq}}$$

6. Landau  decomposition of adsorption equilibrium in the point of phase transition.

The mathematical model: system of mass-heat balance

$$\frac{\partial C_s(t,Z)}{\partial t} = \frac{D_{inter_s}}{l^2}\frac{\partial^2 C_s}{\partial Z^2} - e_{\text{inter}}\tilde{K}_s\frac{D_{intra_s}}{R^2}\left(\frac{\partial Q_s}{\partial X}\right)_{X=1} \quad (1)$$

$$-H\frac{\partial T(t,z)}{\partial t} - uh_g\frac{\partial T}{\partial z} - \sum_{s=1}^{m}\Delta\bar{H}_s\frac{\partial \bar{Q}_s}{\partial t} - 2\frac{\alpha_h}{R_{column}}T + \Lambda\frac{\partial^2 T}{\partial z^2} = 0 \quad (2)$$

$$\frac{\partial Q_s(t,X,Z)}{\partial t} = \frac{D_{intra_s}}{R^2}\left(\frac{\partial^2 Q_s}{\partial X^2} + \frac{2}{X}\frac{\partial Q_s}{\partial X}\right) \quad (3)$$

initial conditions: $C_s(t=0,Z)=0;\ Q_s(t=0,X,Z)=0\ ;\ Z\in(0,1),\ X\in(0,1),\ s=\overline{1,m}$, (4)

boundary conditions for coordinate X of the crystallit and Langmuir's equilibrium :

$$\frac{\partial}{\partial X}Q_s(t,X=0,Z)=0\ ,\ Q_s(t,X=1,Z)=\frac{K_s(T)C_s(t,Z)}{1+\sum_{s_1=1}^{m}K_{s_1}(T)C_{s_1}(t,Z)},\ s=\overline{1,m}\ , \quad (5)$$

boundary conditions for coordinate Z:

$$C_s(t,1)=1,\ \frac{\partial C_s}{\partial Z}(t,Z=0)=0,\qquad t>0 \quad (6)$$

$$T(t,\mathrm{Z})|_{Z=1}=T_{initial}\ ,\frac{\partial}{\partial \mathrm{z}}T(t,\mathrm{Z})|_{Z=0}=0 \quad (7)$$

where $K_s(T)=k_{0s}\exp\left(-\frac{\Delta H_s}{R_g T}\right)$.

[*Kärger., Ruthven,* **Wiley** (2012),
*Petryk et a*l. **Catalysis Today**, 139(4), 2007]

The mathematical model: isothermal system of mass

$$\frac{\partial C_j(t,Z)}{\partial t} = \frac{D_{inter_j}}{l^2}\frac{\partial^2 C_j}{\partial Z^2} - e_{inter_j}\frac{D_{intra_j}}{R^2}\left(\frac{\partial Q_j}{\partial X}\right)_{X=1}, \quad (1)$$

$$\frac{\partial Q_j(t,X,Z)}{\partial t} = \frac{D_{intra_j}}{R^2}\left(\frac{\partial^2 Q_j}{\partial X^2} + \frac{2}{X}\frac{\partial Q_j}{\partial X}\right) \quad (2)$$

initial conditions:

$$C_j(t,Z)_{|t=0} = 0, \qquad Q_j(t,X,Z)_{|t=0} = 0;\ X \in (0,1),\ j = \overline{1,3}, \quad (3)$$

boundary conditions for coordinate X of the crystallite (particle):

$$\frac{\partial}{\partial X} Q_j(t,X,Z)_{|X=0} = 0, \quad (4)$$

$$Q_j(t,X=1,Z)_{|X=1} = \frac{K_j C_j(t,Z)}{1+K_1 C_1(t,Z)+K_2 C_2(t,Z)+K_3 C_3(t,Z)}, \text{ **Langmuir** co-**adsorption** equilibrium} \quad (5)$$

boundary conditions for coordinate Z:

$$C_j(t,Z)_{|Z=1} = C_j^{in}, \qquad \frac{\partial}{\partial Z} C_j(t,Z)_{|Z=0} = 0. \quad (6)$$

The non-homogeneous boundary problem A_m solution

The transition to originals

$$C_{j_m}(t,X,Z) = -\Gamma_j \int_0^1 L^{-1}\left[\mathcal{H}_j^*(p,Z,\xi) - \mathcal{K}_j^*(p,Z,\xi)\right] * F_{j_m}(t,\xi)\,d\xi, \qquad (39)$$

$$C_{j_m}(t,X,Z) = -\frac{3}{e_{\text{inter}_j}} \frac{l^2}{R^2} \frac{D_{\text{intra}\,j}}{D_{\text{inter}_j}} \int_0^t \left(\begin{array}{l} \int_Z^1 \left(\mathcal{H}_j^-(t-\tau,Z,\xi) - \mathcal{K}_j^-(t-\tau,Z,\xi)\right) F_{j_m}(\tau,\xi)\,d\xi + \\ + \int_0^Z \left(\mathcal{H}_j^+(t-\tau,Z,\xi) - \mathcal{K}_j^+(t-\tau,Z,\xi)\right) F_{j_m}(\tau,\xi)\,d\xi \end{array} \right) d\tau, \qquad (40)$$

Calculation of originals of components of function of influence

Components $\mathcal{H}_j(t,Z,\xi)$ **(**Applying the Heaviside)

$$L^{-1}\left[\frac{f_j^h(p)}{\gamma_j(p)\,sh\left[\gamma_j(p)\right]ch\left[\gamma_j(p)\right]}\right] = \sum_{s=1}^{\infty}\sum_{k=1}^{\infty} \frac{f_j^h\left(\beta_{ks}^j\right) e^{\frac{D_{\text{intra}\,j}}{R^2}\left(\beta_{ks}^j\right)^2 t}}{\omega_j^1\left(\beta_{ks}^j\right)} + \sum_{s_1=1}^{\infty} \frac{f_j^h\left(\mu_{s_1}^j\right) e^{\frac{D_{\text{intra}\,j}}{R^2}\left(\mu_{s_1}^j\right)^2 t}}{\nu_j^2\left(\mu_{s_1}^j\right)} + \sum_{k_1=1}^{\infty} \frac{f_j^h\left(\eta_{k_1}^j\right) e^{\frac{D_{\text{intra}\,j}}{R^2}\left(\eta_{k_1}^j\right)^2 t}}{\omega_j^2\left(\eta_{k_1}^j\right)}$$

f_j^h, $h = \overline{1,4}$ - the numerators of the 2 components $\mathcal{H}_j^-(t-\tau,Z,\xi)$, $\mathcal{H}_j^+(t-\tau,Z,\xi)$ - the functions of influence (38),

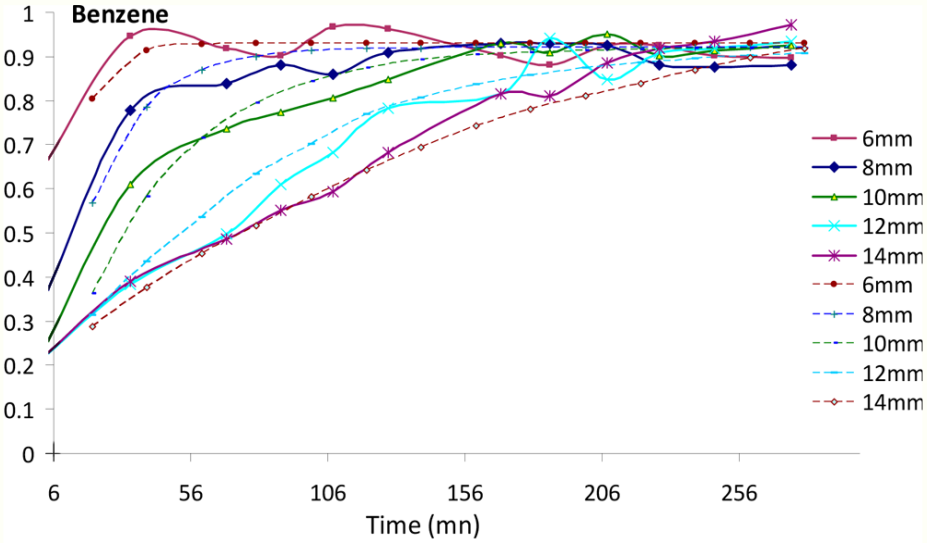
The non-homogeneous boundary problem A_m solution

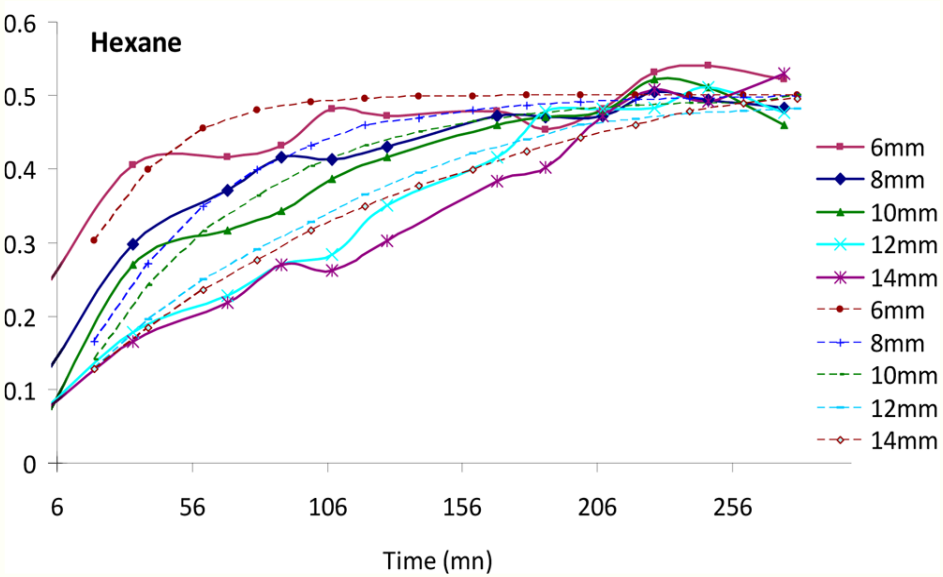
Calculation $N_{j_m}(t,X,Z)$.

$$L^{-1}\left[N^*_{j_m}(p,X,Z)\right] = L^{-1}\left[K_j C^*_{j_m}(p,Z) - F^*_{j_m}(p,Z)\right] * L^{-1}\left[\frac{sh\left(R\sqrt{\frac{p}{D_{intra_j}}}X\right)}{sh\left(R\sqrt{\frac{p}{D_{intra_j}}}\right)}\right] \tag{41}$$

$$Q_{j_m}(t,X,Z) = \int_0^t \left(K_j C_{j_m}(t-\tau,Z) - \sum_{s=0}^{m-1}\sum_{k=1}^{3} \frac{K_j K_k}{K_1^2} C_{j_s}(t-\tau,Z) C_{k_{m-1-s}}(t-\tau,Z) \right) \cdot$$
$$\cdot \left(2\frac{D_{intra_j}}{R^2} \sum_{k_2=0}^{\infty} \frac{\pi k_2 \cdot sin(k_2 \pi X)()}{(-1)^{k_2+1} X} exp\left(-\frac{D_{intra_j}}{R^2} {k_2}^2 \pi^2 t) \right) \right) d\tau, \quad j = \overline{1,3} \tag{42}$$

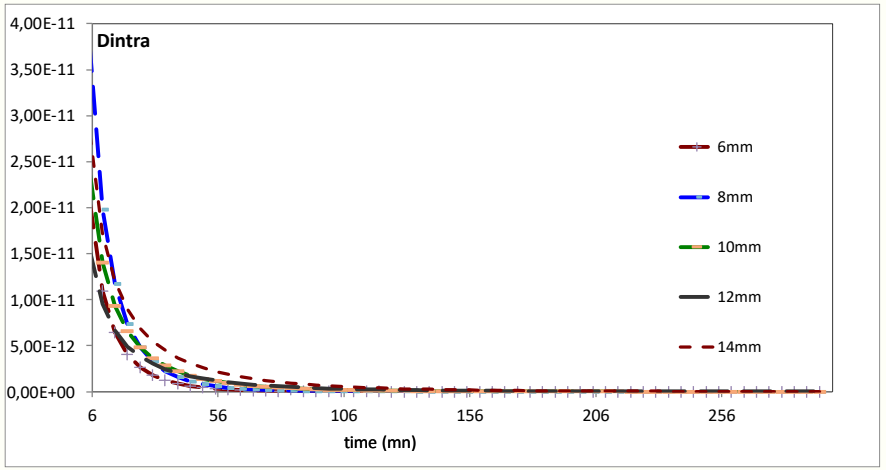
Experimental Results: Gasous benzene and hexane adsorption curves

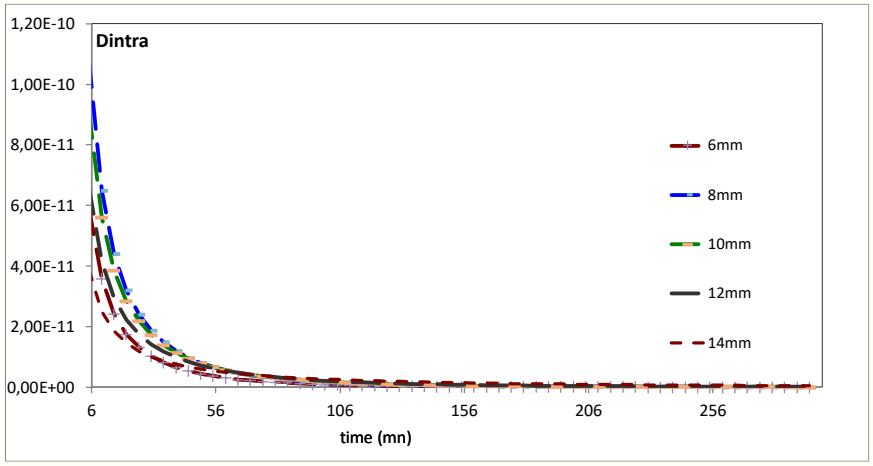


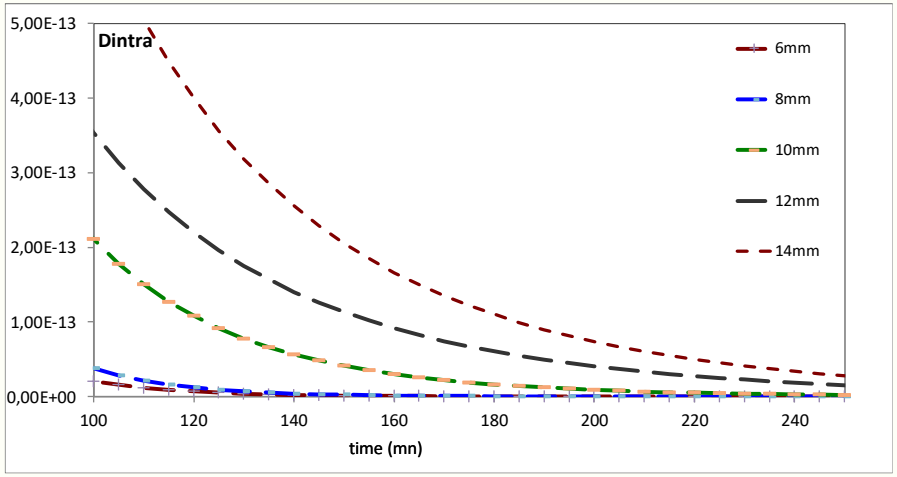


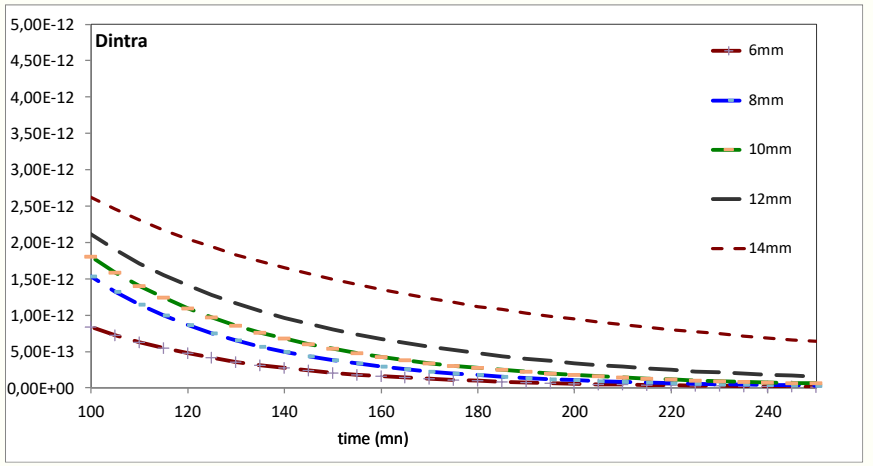
Evolution *versus* time of the benzene and hexane concentrations (arbitrary units) at different levels of the sample (*continuous* - experimental curves; *dotted* – their approximations used for simulation)

intraparticle space: co-diffusion coefficients identification



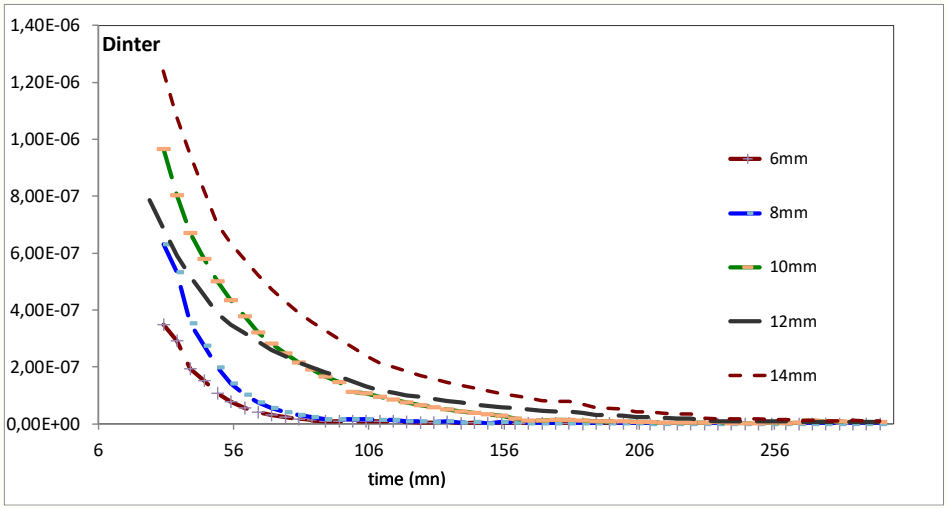


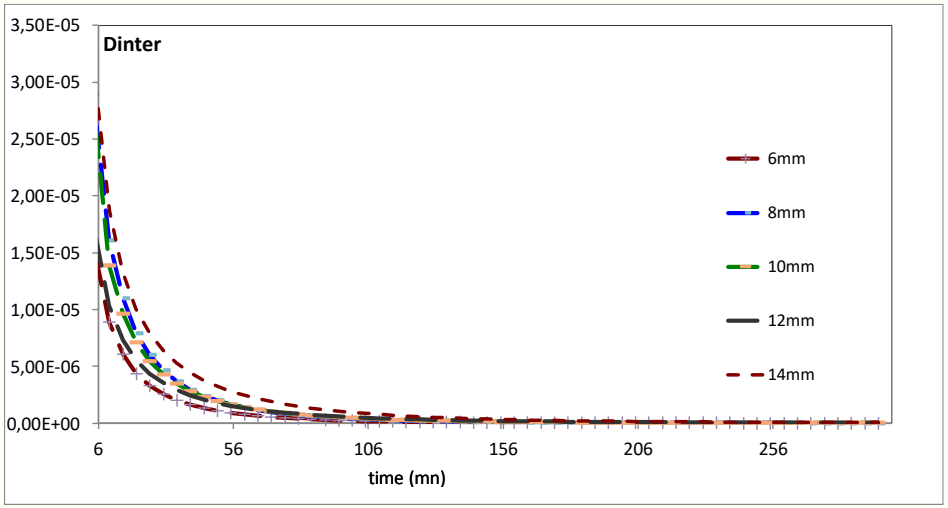




Variation of intracrystallite diffusion coefficients (arbitrary units) for benzene $D_{intra,1}$ (left) and hexane $D_{intra,2}$ (right) against time, at different positions in the bed. (top) time range 6-240 mn, (bottom) time range 100-240 mn.

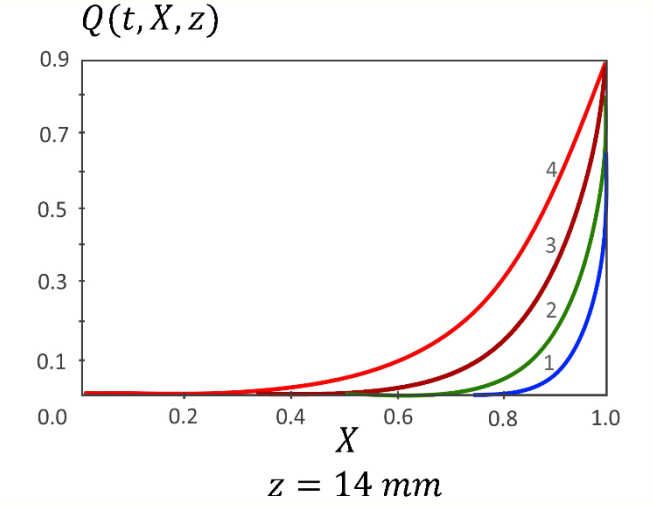
interparticle space: co-diffusion coefficients identification

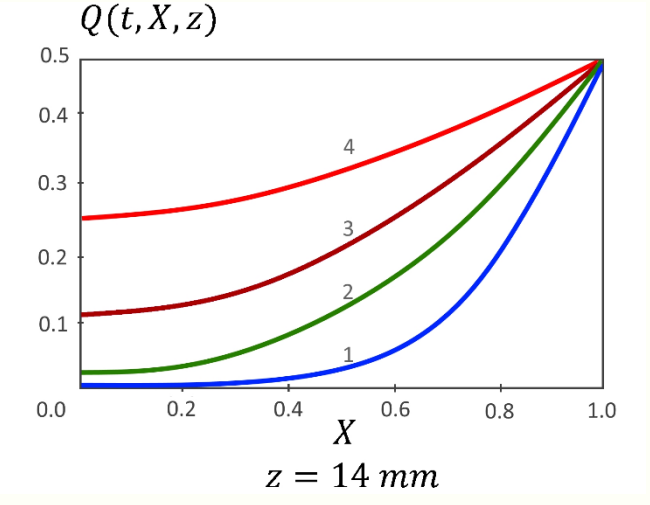


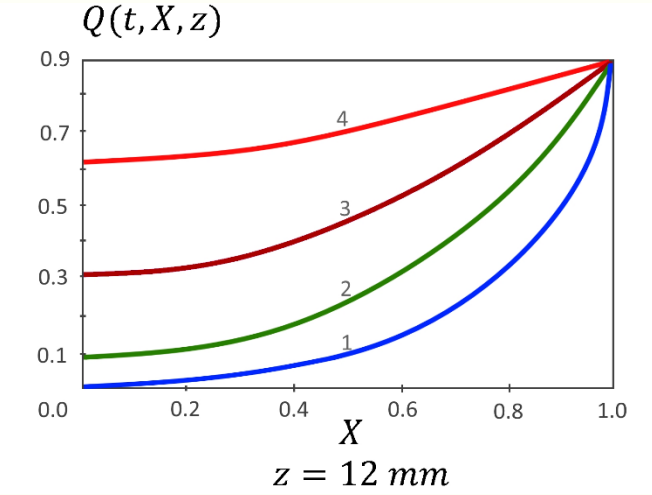


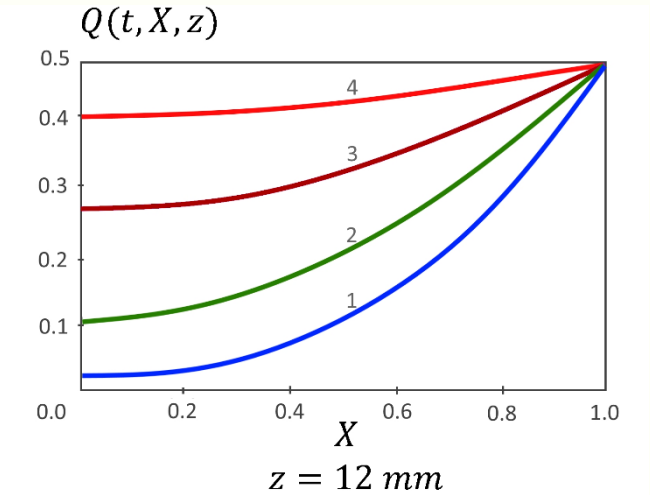
Variation of intercrystallite diffusion coefficients (a.u.) for benzene (left), and hexane (right) against time at different positions of the bed

Computer Simulation: **adsorbates concentrations in the intracrystallites nanopores**



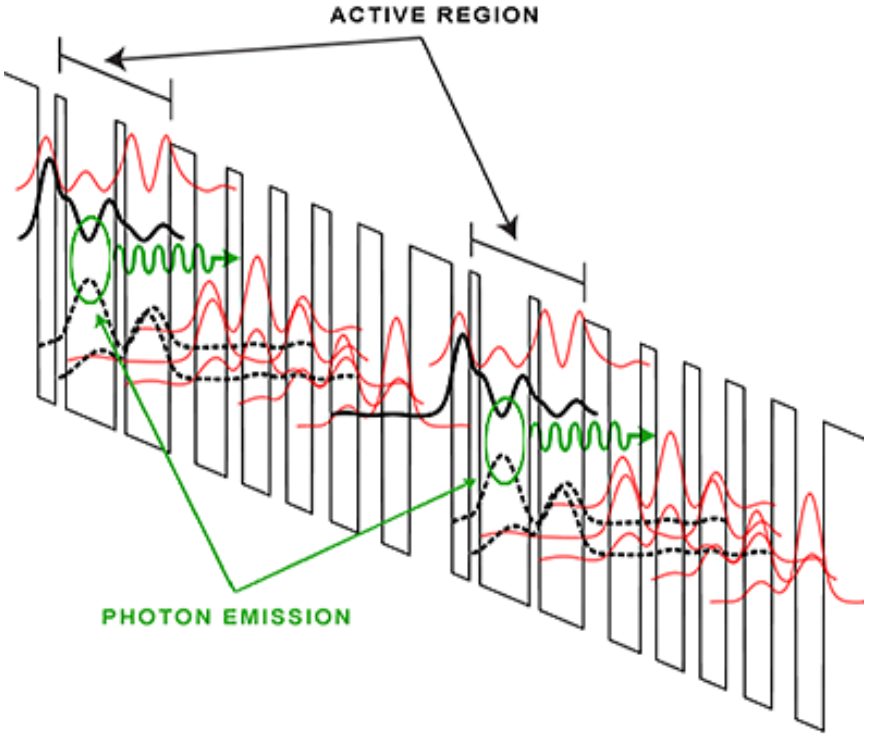


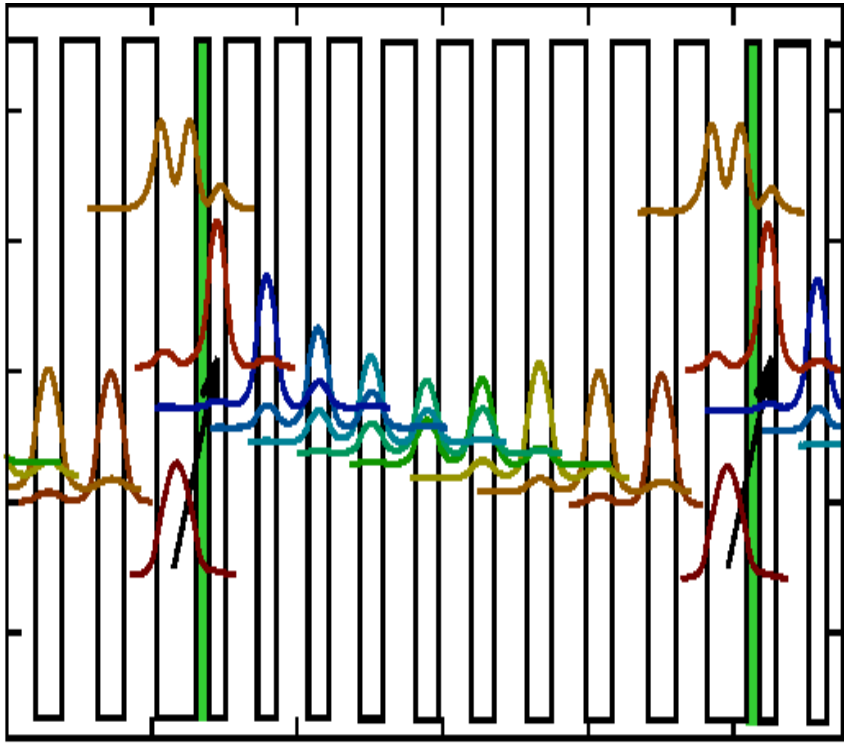


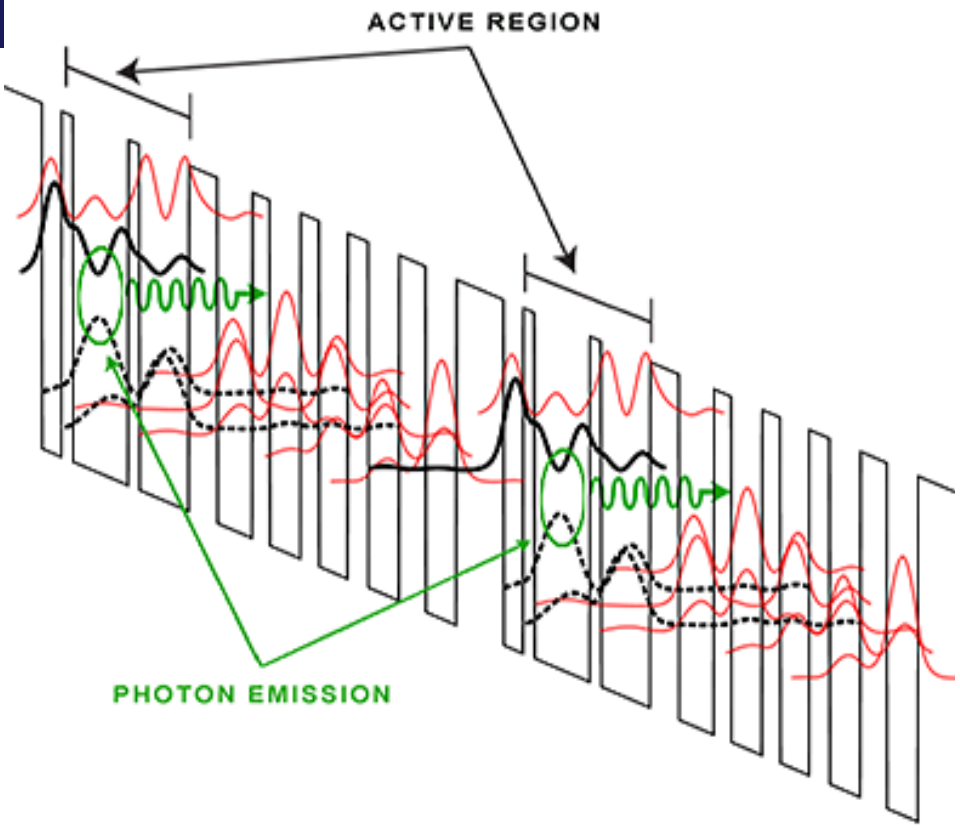


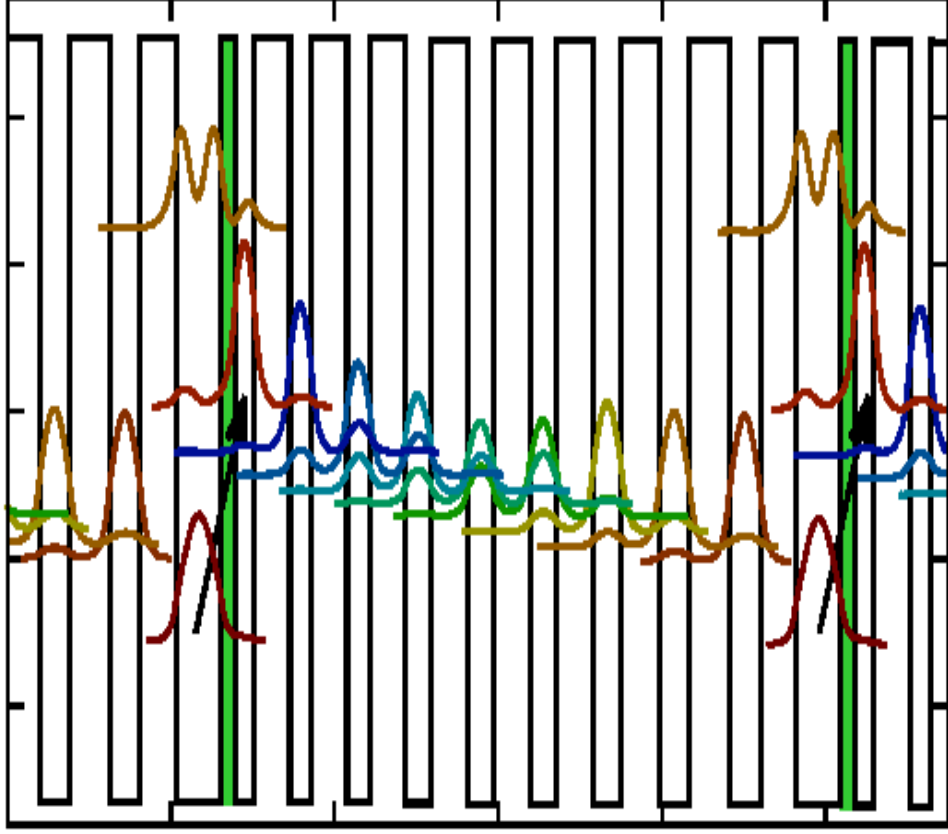
Distribution of the benzene (left) and hexane (right) concentrations in the intracrystallite space from the surface (abscissa 1) to the center (abscissa 0) of the crystallites, at different times *1- dark blue: t = 25 min.; 2 -green: t 50 min; 3 - brown: t =100 min.; 4 - red: t =200 min*

2. Modeling multilayer resonant-tunneling nanostructures based on semiconductor double and triple compounds of gallium arsenide (GaAs, AlAs, AlGaAs) and nitrides of the III group (GaN, AlN, AlGaN) и (GaN, AlN, AlGaN)









- Каскади та їх частини мають бути узгодженими між собою
- Електронні стани у наносистемі є квазістаціонарними
- Модель закритої наносистеми недостатня

Conclusion

The main result of this part of the project is the possibility, from a single experiment, of simultaneously distributing several co-diffusing gases in a porous solid and of using the high performance methods of mathematical modeling to analyze for each of them the distribution of their concentrations in the intra and inter-crystallite spaces.

Using experimental NMR data and proposed co-adsorption models, the identification procedures for calculating the co-diffusion coefficients for two or more components in intra- and inter-crystallite spaces are developed. These procedures use the gradient identification methods and rapid analytic methods based. The co-diffusion coefficients were obtained as a function of time for different positions along the catalyst bed. In particular, those in the intracrystallite space were computed by the analytical method which allowed a calculation with a relatively high degree of discretization over time and to reduce practically twice the volume of iterative calculations.

Main References

1. *Lebovka N., Petyk M., Tatochenko M. and Vygornitskii N.* Two-stage random sequential adsorption of discorectangles and disks on a two-dimensional surface. **Physical Review E**. Vol.**108**, 024109 (2023) DOI:https://doi.org/10.1103/PhysRevE.108.024109 (**Quartile 1**, impact factor **2.707**)

2. *Petryk M., Boyko I., Fessard J.,Lebovka N.* Modelling of non-isothermal adsorption of gases in nanoporous adsorbent based on Langmuir equilibrium. **Adsorption**. Springer (Publised : 8 Juine 2023) doi.org/10.1007/s10450-023-00389-9 (**Quartile 2,** impact factor 2.95)

3. *Lebovka N., Petyk M., Vorobiev E.* Monte Carlo simulation of dead-end diafiltration of bidispersed particle suspensions. **Physical Review E**. Vol.**106**. 064610 (2022) DOI 10.1103/PhysRevE.106.064610 (**Quartile 1**, impact factor **2.707**)

4. *Petryk M.,Canet D., Sergienko I., Deineka V.,Fraissard J*. Competitive Diffusion of Gases in a Zeolite Bed: NMR and Slice Selection Procedure, Modelling and Parameter Identification. **Journal of Physical Chemistry C**. ACS. (2015). Vol. 119, Issue 47, 26519–26525. (**Quartile 1**, impact factor 4.772)

5. *Petryk M., Khimitch A., Petryk M.M., Fraissard J*. Experimental and computer simulation studies of dehydration on microporous adsorbent of natural gas used as motor fuel. **Fuel**. Vol. 239, 1324–1330 (2019). (**Quartile 1**, impact factor **8.035**)

$\Omega_{k_t} = (0, t^{total}) \times \Omega_k$, $\left(\Omega_k = (L_{k-1}, L_k), k = \overline{1, N+1}, L_0 = 0 < L_1 < ... < L_{N+1} = 1\right)$

Main References

6. *Boyko I., Petryk M., Fraissard J*. Spectrum and normalized modes of acoustic phonons in multilayer nitride-based nanostructure. **Europien Physical Journal B**. Vol. 93, Article number : 57 (2020) (**Quartile 2,** , impact factor **1.398**)

7. *Leclerc S., Petryk M., Canet D., Fraissard J*. Competitive diffusion of gases in a zeolite using proton NMR and a slice selection procedure. **Catalysis Today**, Vol. 187, Issue 1, 104-107 (2012). (**Quartile 1**, impact factor **5.3**)

8. *Petryk M., Leclerc S., Canet D., Fraissard J*. Modeling of gas transport in a microporous solid using a sclice selection procedure: Application to the diffusion of benzene in ZSM5. **Catalysis Today**, Vol. 139, Issue 3, 234-240 (2008). (**Quartile 1** , impact factor **5.3**)

9. *Petryk M., Vorobiev E*. Numerical and Analytical Modelling of Solid-Liquid Expression from Soft Plant Materials. **AIChE J. Wiley** (2013) Vol. 59, Issue 12, 4762–4771. (**Quartile 1**, impact factor **4.17**)

10. *Petryk M., Vorobiev E.* Liquid Flowing from Porous particles During the Pressing of Biological Materials. **Computer and Chem. Engineering**. Vol. 31, Issue 10, 1336-1345. (2007) (**Quartile 1** , impact factor **3.845**)

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Математичного моделювання і дослідження масопереносу в неоднорідних і нанопористих середовищах
Mathematical modeling and research of mass transfer in heterogeneous and nanoporous media

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