Non-linear frequency response of non-isothermal adsorption controlled by micropore diffusion with variable diffusivity

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The concept of higher order frequency response functions (FRFs) is used for the analysis of non-linear adsorption kinetics on a particle scale, for the case of non-isothermal micropore diffusion with variable diffusivity. Six series of FRFs are defined for the general non-isothermal case. A non-linear mathematical model is postulated and the first and second order FRFs derived and simulated. A variable diffusivity influences the shapes of the second order FRFs relating the sorbate concentration in the solid phase and the gas pressure significantly, but they still keep their characteristics which can be used for discrimination of this from other kinetic mechanisms. It is also shown that first and second order particle FRFs offer sufficient information for an easy and fast estimation of all model parameters, including those defining the system non-linearity.

Keywords: non-isothermal adsorption, non-linear frequency response, higher order frequency response functions, micropore diffusion, variable micropore diffusivity, parameter estimation.

INTRODUCTION

Understanding the interaction between a fluid and a solid phase is of fundamental importance to the design of an adsorption process. In the literature, a variety of methods for the investigation of adsorption kinetics are presented. Frequency response (FR), which is in the scope of this paper, is based on the analysis of a quasi-stationary response to a periodic input change for the identification of the kinetic model and the estimation of the constants of the various rate processes involved.

The first paper on the application of frequency response in the investigation of the kinetics of adsorption systems appeared in 1963. Subsequently, a number of research groups were concerned with the theoretical and experimental aspects on this and related topics. Frequency response has usually been investigated in batch systems with forced periodic modulation of the reservoir volume, although FR in semi-batch and continuous flow systems with periodic modulation of the inlet molar flow rate have also been treated.
Almost all investigators assume system linearity, although most adsorption systems are significantly non-linear. As a result, very small amplitudes of input perturbations are required, which results in uncertainty of the measured data and loss of any information about the non-linearity of the system and limits the applications of the obtained results to a range very close to the conditions of the experimental investigation.

This paper is a continuation of investigations of adsorption kinetics by non-linear FR, in which the FR method is extended to the analysis of non-linear adsorption systems.20–24,28 The concept of higher order frequency response functions for analysis of the non-linear FR is used.

Some details about non-linear FR and the concept of higher order FRFs can be found in previous papers.20,23,24,28 Here, only of a few basic facts will be summarized:

– Contrary to the FR of a linear system, which is a periodic function of the same shape and frequency as the input, the FR of a non-linear system in addition to this first, or basic harmonic also contains a DC (non-periodic) component and, theoretically, an infinite number of higher harmonics.

– The concept of higher order frequency response functions29 (FRFs) is based on Volterra series and generalized Fourier transform29 and can be applied for weakly non-linear systems.29 It is applied by substituting the non-linear model of the system by an infinite series of linear frequency response functions of the first, second, third, etc. order. These functions are directly related to the components of the non-linear FR (the first order FRF defines the most significant term of the first harmonic of the FR, the second order FRFs define the most significant terms of the second harmonic and the DC components, etc.) and can be estimated from them, using the procedure given by Lee.30

In our investigations of the FR of adsorption systems, the FRFs representing the models on the adsorber and on the particle scale are distinguished.20,21,28 The adsorber FRFs depend on both the adsorber type and the kinetic mechanism and can be estimated directly from the experimentally measured FR, while the particle FRFs depend only on the kinetic mechanism and have to be calculated from the adsorber ones. As the final aim of FR investigations of adsorption systems is to reveal the kinetic mechanism and to estimate the corresponding kinetic parameters, the particle FRFs are of most interest. It has been shown23,24 that the non-linear FR gives additional information than that obtained from the linear FR and can be used for model discrimination. On the other hand, procedure for calculation of the particle FRFs from the adsorber ones has been established.20,28

In this paper, the higher order FRFs on the particle scale for non-isothermal adsorption governed by micropore diffusion are investigated. This mechanism is common in zeolite type microporous sorbents. The zeolite particles are composed of a large number of microporous microparticles with larger pores between them and with the dominant mass transfer resistance usually arising in the microparticles. A realistic case of variable micropore diffusivity, which is generally a function of both concentration and temperature, is treated. A simple convective heat transfer mechanism (gas film resistance) is considered, which means that the particle temperature is treated as uniform.
This work can be treated as a continuation of the compilation of a library of sets of FRFs corresponding to different kinetic mechanisms,23,24 which is one of the crucial steps in the application of the method of non-linear FR in the identification of the correct kinetic model.28

Earlier, it was shown that second order FRFs give additional information about the kinetic mechanism.23,24 For this reason, together with the fact that the third and higher order FRFs give very complicated mathematical expressions, only the first and second order FRFs will be considered in this paper. Also, the FRFs will be derived only for the case of slab microparticle geometry, for which analytical solutions can be found.

Before the derivation of the FRFs, model equations on the particle scale will be set up. Adsorption of a pure gas will be considered.

MATHEMATICAL MODEL FOR NON-ISOTHERMAL MICROPOROUS DIFFUSION

In order to derive the FRFs on the particle scale, model equations defining adsorption in an adsorbent particle surrounded by a gas of uniform concentration and temperature have to be defined. For the case under consideration, in which the mass transfer is controlled by micropore diffusion, and heat transfer by gas film resistance, the following equations are obtained:

The microparticle material balance

\[
\frac{\partial Q}{\partial t} = \frac{1}{r_\mu^\alpha} \frac{\partial}{\partial r_\mu} \left( D_\mu^\alpha \frac{\partial Q}{\partial r_\mu} \right)
\]  

(1)

The boundary conditions for Eq. (1) are

\[
r_\mu = 0: \frac{\partial Q}{\partial r_\mu} = 0
\]

(2)

which means that the concentration profile in the microparticle is symmetrical and

\[
r_\mu = R_\mu: \quad Q = f(P, T_p)
\]

(3)

which means that local equilibrium is established at the mouth of the micropore, with the adsorption equilibrium relation \( f \), which is generally a non-linear function of the gas pressure and particle temperature.

The mean concentration in the microparticle is

\[
\langle Q \rangle = \frac{\sigma + 1}{R_\mu^\alpha} \int_0^{R_\mu} r_\mu^\alpha Q(r_\mu) dr_\mu
\]

(4)

and the particle heat balance

\[
V_p \rho_p C_{ps} \frac{dT_p}{dt} = (-\Delta H_a) V_p \rho_p \frac{d\langle Q \rangle}{dt} + (ha)(T_g - T_p)
\]

(5)
In Eqs. (1) to (5) \( t \) is time, \( r_\mu \) the microparticle space coordinate, \( R_\mu \) the microparticle half-dimension, \( \sigma \) a shape factor (0 for slab, 1 for cylindrical and 2 for spherical microparticle geometry), \( Q \) the adsorbate concentration in the solid phase, \( T_p \) the particle temperature, \( P \) the gas pressure, \( T_g \) the gas temperature, \( D_\mu \) the micropore diffusivity, which is generally a non-linear function of \( Q \) and \( T_p \)

\[
D_\mu = g(Q, T_p)
\]

\( V_p, \rho_p \) and \( C_{ps} \), the particle volume, density and heat capacity, respectively, \( -\Delta H_a \) the differential heat of adsorption, \( h \) the particle to gas heat transfer coefficient and \( a \) the corresponding surface area.

For analysis in the frequency domain, it is most convenient to define all dependent variables as non-dimensional deviations from the steady state around which the system oscillates. Their definitions are given in Table I.

| TABLE I. Definitions of the non-dimensional variables and model parameters |
|-----------------|-----------------|-----------------|
| \( p = P - P_s \) | \( q = Q - Q_s \) | \( <q> = Q_s \) |
| \( \xi \) | \( \xi = \frac{-\Delta H_a \rho_p Q_s}{C_{ps} T_s} \) | \( \xi = \frac{h a}{V_p C_{ps}} \) |

The model equations (1) to (5) become

\[
\frac{\partial q}{\partial t} = \frac{1}{r_\mu^2} \frac{\partial}{\partial r_\mu} \left( D_{\mu s} \left( 1 + D_q^{(1)} q + D_T^{(1)} \theta_p \theta_p + D_T^{(2)} \theta_p^2 \theta_p + D_T^{(3)} \theta_p^3 \theta_p + ... \right) \right) \frac{\partial q}{\partial r_\mu}
\]

\[
r_\mu = 0: \frac{\partial q}{\partial r_\mu} = 0
\]

\[
r_\mu = R_\mu: \quad q = a_p p + a_T \theta_p + b_{pp} p^2 + b_{TT} \theta_p^2 + b_{TT} p \theta_p + ...
\]

\[
<q> = \frac{\sigma + 1}{R_\mu} \int_0^{R_\mu} q(r_\mu) dr_\mu
\]

\[
\frac{d\theta_p}{dt} = \xi \frac{d<q>}{dt} + \xi (\theta_g + \theta_p)
\]

In equation (7), the non-linear function \( g \), defined in Eq. (6) is presented in the form of a Taylor series, which is convenient for the application of the concept of higher order FRFs. In this equation \( D_{\mu s} \) is the steady state value of the micropore diffusivity, \( D_q^{(1)} \) is its first order concentration coefficient, \( D_T^{(1)} \) its first order temperature coefficient, \( D_T^{(2)} \) its second order concentration coefficient, \( etc. \) In a similar way, in Eq. (9),
the Taylor series expansion of the adsorption equilibrium function $f$ is used, with $a_p$ representing the first order pressure coefficient, $a_T$ the first order temperature coefficient, $b_{pp}$ the second order pressure coefficient, $b_{TT}$ the second order temperature coefficient and $b_{pT}$ the second order mixed coefficient. The new parameters in Eq. (11) $\xi$ and $\zeta$, which are defined in Table I, represent the modified heat of adsorption and heat transfer coefficients, respectively.

The obtained model relates the changes of the mean sorbate concentration in the particle $\langle Q \rangle$ (or $\langle q \rangle$) and particle temperature $T_p$ (or $\theta_p$) (the output variables) to the changes of the pressure $P$ (or $p$) and temperature of the surrounding gas $T_g$ (or $\theta_g$) (the input variables).

This non-linear model has two sources of non-linearity: one is the non-linear equilibrium relation, which makes the boundary condition at the microparticle surface (Eq. (3) or (9)) non-linear, and the other is the variable diffusivity.

**HIGHER ORDER FREQUENCY RESPONSE FUNCTIONS**

**Definitions**

As described in a previous paper, for the general non-isothermal, non-linear case, six series of frequency response functions are needed to define adsorption on a particle scale, four of them relating each output to each input, and two series of cross-functions relating each output to both inputs. These series are defined in the block diagram presented in Fig. 1. $F$ is used to denote the FRFs corresponding to the output $q$, and $H$ for those corresponding to $\theta_p$. The subscript represents the input variable ($p$ for pressure, and $T$ for the gas temperature). In practice, for the estimation of all six series of particle FRFs, it is necessary to measure the temperature, along with the pressure.

![Fig. 1. A general block diagram of an adsorbent particle.](image)
Also, in the mathematical derivations, the notation $F^*$ is used for the FRFs corresponding to the local concentration in the microparticle $q(r_{\mu})$. The "$F^*$" functions are also functions of $r_{\mu}$.

**Derivation of the first and second order FRFs**

The general procedure for the derivation of the particle FRFs was given in Ref. 28 and illustrated on the example of non-isothermal adsorption governed by micropore diffusion mass transfer with constant diffusivity and convective heat transport. The basic idea of this derivation is to define the inputs as harmonic functions of time, express the outputs in the form of Volterra series, substitute them into the model equations and apply the method of harmonic probing. As a result, a series of sets of linear equations is obtained in which time as an independent variable is replaced by frequency, the output variables are replaced by their corresponding series of FRFs, and the partial differential equations are transformed into ordinary differential equations. The mathematical expressions for the FRFs are obtained by solving these sets of equations.

In order to reduce the number of equations in this paper, only the sets of equations defining the first and second order FRFs corresponding to the model Eqs. (7) to (11), and the resulting mathematical expressions obtained by their solution will be given. Only the case of slab microparticle geometry ($\sigma = 0$), for which analytical solutions can be obtained, is considered. For cylindrical and spherical geometry, the second order FRFs can only be obtained numerically.

**First order FRFs with respect to pressure ($F_{1,p}$ and $H_{1,p}$)**

The easiest way to derive these functions is to define the inputs as $p = A e^{j\omega t}, \theta_{r\mu} = 0$. When the outputs are expressed in the form of Volterra series, substituted into Eqs. (7) and (11) and the terms with $A e^{j\omega t}$ collected, the following set of equations is obtained

$$\frac{d^2 F_{1,p}^*(\omega r_{\mu})}{dr_{\mu}^2} - \frac{j}{D_{\mu\mu}}(\omega r_{\mu}) = 0$$  \hspace{1cm} (12)

$$r_{\mu} = 0; \quad r_{\mu} = R_{\mu}; \quad F_{1,p}^*(\omega, r_{\mu}) = a_p + a q H_{1,p}(\omega)$$  \hspace{1cm} (13)

$$F_{1,p}(\omega) = \frac{1}{R_{\mu}} \int_0^{R_{\mu}} F_{1,p}^*(\omega r_{\mu}) dr_{\mu}$$  \hspace{1cm} (14)

$$H_{1,p}(\omega) = \frac{\xi}{j\omega + \xi} F_{1,p}(\omega)$$  \hspace{1cm} (15)

Equation (12) is a homogeneous ordinary linear differential equation which is easily solved. Its solution, subject to the boundary conditions (13) and (14), is
Integration of this function over the microparticle volume, according to Eq. (15), together with Eq. (16), leads to the following final result

\[
F_{1,p}(\omega, r_{\mu}) = (a_p + a_T H_{1,p}(\omega)) \frac{\exp(\sqrt{\alpha r_{\mu}}) + \exp(-\sqrt{\alpha r_{\mu}})}{\exp(\sqrt{\alpha R_{\mu}}) + \exp(-\sqrt{\alpha R_{\mu}})}
\]  

(17)

where

\[
\Phi(\omega) = \frac{\tanh(R_{\mu} \alpha \sqrt{\omega})}{R_{\mu} \alpha \sqrt{\omega}}; \quad \Lambda(\omega) = \frac{\xi_{j} \omega}{j \omega + \zeta}; \quad \alpha = \frac{f}{\sqrt{D_{\mu} \omega}}
\]  

(20)

First order FRFs with respect to gas temperature \((F_{1,T} \text{ and } H_{1,T})\)

If the inputs are defined as \(p = 0, \theta_g = A e^{j \omega t}\), the model Eqs. (7) to (11) are transformed into

\[
\frac{d^2 F_{1,T}^{*}(\omega, r_{\mu})}{dr_{\mu}^2} - \frac{j}{D_{\mu}} \Omega F_{1,T}^{*}(\omega, r_{\mu}) = 0
\]  

(21)

\[
r_{\mu} = 0: \quad \frac{dF_{1,T}^{*}(\omega, r_{\mu})}{dr_{\mu}} = 0
\]  

(22)

\[
r_{\mu} = R_{\mu}: \quad F_{1,T}^{*}(\omega, r_{\mu}) = a_T H_{1,T}(\omega)
\]  

(23)

\[
F_{1,T}(\omega) = \frac{1}{R_{\mu}} \int_{0}^{R_{\mu}} F_{1,T}^{*}(\omega, r_{\mu}) dr_{\mu}
\]  

(24)

\[
H_{1,T}(\omega) = \frac{\xi_j \omega}{j \omega + \zeta} F_{1,T}(\omega) + \frac{\zeta}{j \omega + \zeta}
\]  

(25)

Again, Eq. (21), with the boundary conditions (22) and (23), is easily solved giving

\[
F_{1,T}^{*}(\omega, r_{\mu}) = a_T H_{1,T}(\omega) \frac{\exp(\sqrt{\alpha r_{\mu}}) + \exp(-\sqrt{\alpha r_{\mu}})}{\exp(\sqrt{\alpha R_{\mu}}) + \exp(-\sqrt{\alpha R_{\mu}})}
\]  

(26)

which, after integration according to Eq. (24), results in the following expressions
\[ F_{1,\tau} (\omega) = \frac{a_{\tau} \Omega (\omega) \Phi (\omega)}{1 - a_{\tau} \Lambda (\omega) \Phi (\omega)} \]  \quad (27)

\[ H_{1,\tau} (\omega) = F_{1,\tau} (\omega) \Lambda (\omega) + \Omega (\omega) = \frac{\Omega (\omega)}{1 - a_{\tau} \Lambda (\omega) \Phi (\omega)} \]  \quad (28)

\( \Phi (\omega) \) and \( \Lambda (\omega) \) are defined as previously in Eq. (20), while

\[ \Omega (\omega) = \frac{\zeta}{j \omega + \zeta} \]  \quad (29)

It should be noticed that the obtained first order FRFs are identical to the expressions corresponding to constant micropore diffusivity. This is to be expected, as the first order FRFs correspond to the linearized model, while the variable diffusivity is one of the sources of the non-linearity of the system.

**Second order FRFs with respect to pressure (\( F_{2,pp} \) and \( H_{2,pp} \))**

The best way to develop these functions is to set the inputs as:

\[ p = A_1 e^{j \omega_1 t} + A_2 e^{j \omega_2 t}, \quad \theta_q = 0. \]

Representing the outputs in the Volterra series form, substituting them into Eqs. (7) to (11) and collecting the terms with \( A_1 A_2 e^{j (\omega_1 + \omega_2) t} \) gives the following set of equations:

\[ \frac{d^2 F^*_{1,pp} (\omega_1, \omega_2, r_{\mu})}{d r_{\mu}^2} - \frac{j}{D_{\mu}} (\omega_1 + \omega_2) F^*_{1,pp} (\omega_1, \omega_2, r_{\mu}) = \]

\[ - \frac{D^{(1)}_q}{2} \frac{d}{d r_{\mu}} \left[ F^*_{1,p} (\omega_1, r_{\mu}) \frac{d F^*_{1,p} (\omega_1, r_{\mu})}{d r_{\mu}} + F^*_{1,p} (\omega_2, r_{\mu}) \frac{d F^*_{1,p} (\omega_2, r_{\mu})}{d r_{\mu}} \right] \]

\[ - \frac{D^{(1)}_T}{2} \frac{d}{d r_{\mu}} \left[ H_{1,p} (\omega) \frac{d F^*_{1,p} (\omega_2, r_{\mu})}{d r_{\mu}} + H_{1,p} (\omega) \frac{d F^*_{1,p} (\omega_1, r_{\mu})}{d r_{\mu}} \right] \]

\[ r_{\mu} = 0: \quad \frac{d F^*_{2,pp} (\omega_1, \omega_2, r_{\mu})}{d r_{\mu}} \]  \quad (30)

\[ r_{\mu} = R_{\mu} : \quad F^*_{2,pp} (\omega_1, \omega_2, r_{\mu}) = a_{\tau} H_{2,pp} (\omega_1, \omega_2) + b_{pp} + \]

\[ + b_{TT} H_{1,p} (\omega_1) H_{1,p} (\omega_2) + b_{pT} H_{1,p} (\omega_1) + H_{1,p} (\omega_2) \]  \quad (31)

\[ F_{2,pp} (\omega_1, \omega_2) = \frac{1}{R_{\mu}} \int_{0}^{R_{\mu}} F^*_{2,pp} (\omega_1, \omega_2, r_{\mu}) d r_{\mu} \]  \quad (32)

\[ H_{2,pp} (\omega_1, \omega_2) = \frac{\zeta (\omega_1 + \omega_2)}{j (\omega_1 + \omega_2) + \zeta} F_{2,pp} (\omega_1, \omega_2) \]  \quad (33)
After substituting the previously derived expressions for $F^*_{1,\mu}$, $F^*_{1,T}$, $H_{1,p}$ and $H_{1,T}$ (Eqs. (17), (26), (19) and (28)), into Eq. (30), the resulting equation, although very complex, can still be solved analytically. The solution process involves some long and tedious algebra, so it will be omitted here. Only the final expressions, which are obtained after integration of function $F^*_{2,pp}$ according to Eq. (33), will be given

$$F_{2,pp}(\omega_1, \omega_2) = \frac{\Phi_1 (\omega_1, \omega_2) \Phi (\omega_1 + \omega_2) + \Phi_2 (\omega_1, \omega_2) \Phi (\omega_1) + \Phi_2 (\omega_2, \omega_2) \Phi (\omega_2)}{1 - \alpha_T \Lambda (\omega_1 + \omega_2) \Phi (\omega_1 + \omega_2)} \tag{35}$$

where

$$\Phi_1 (\omega_1, \omega_2) = b_{pp} + \frac{b_{pT}}{2} \left( H_{1,p}(\omega_1) + H_{1,p}(\omega_2) + b_{TT} H_{1,p}(\omega_1) H_{1,p}(\omega_2) + \frac{D_q^{(1)}}{2} \right)
\times(a_p + a_T H_{1,p}(\omega_1)) \left( a_p + a_T H_{1,p}(\omega_2) \right)
\left[ \frac{\omega_1 + \omega_2}{2 \sqrt{\omega_1 \omega_2}} \tanh(\sqrt{\omega_1 R_{\mu}}) \tanh(\sqrt{\omega_2 R_{\mu}}) \right] +
\frac{D_q^{(1)}}{2} \left[ \frac{\omega_1}{\omega_2} \left( a_p + a_T H_{1,p}(\omega_1) \right) H_{1,p}(\omega_2) + \frac{\omega_2}{\omega_1} \left( a_p + a_T H_{1,p}(\omega_2) \right) H_{1,p}(\omega_1) \right] \tag{35a}$$

$$\Phi_2 (\omega_1, \omega_2) = \frac{a_p + a_T H_{1,p}(\omega_1)}{2} \left[ D_T^{(1)} H_{1,p}(\omega_1) H_{1,p}(\omega_2) - \frac{D_q^{(2)}}{2} \left( a_p + a_T H_{1,p}(\omega_1) \right) \right] \tag{35b}$$

In practice, the response to a single harmonic input is usually considered in that case, only the second order FRFs corresponding to $\omega_1 = \omega_2 = \omega$ and $\omega_1 = -\omega_2 = \omega$ are of interest. The first one corresponds to the most significant term of the second harmonic, while the second one corresponds to the most significant term of the DC component. It can easily be shown that

$$F_{2,pp}(\omega, \omega) = \frac{\Phi_1 (\omega, \omega) \Phi (2\omega) + 2 \Phi_2 (\omega, \omega) \Phi (\omega)}{1 - \alpha_T \Lambda (2\omega) \Phi (2\omega)} \tag{37}$$

$$H_{2,pp}(\omega, \omega) = F_{2,pp}(\omega, \omega) \Lambda (2\omega) \tag{38}$$

with:

$$\Phi_1 (\omega, \omega) = b_{pp} + b_{pT} H_{1,p}(\omega) + b_{TT} H_{1,p}^2 (\omega) + \frac{D_q^{(1)}}{2}
\times(a_p + a_T H_{1,p}(\omega))^2 \tanh^2 (\sqrt{\omega R_{\mu}}) + D_T^{(1)} \left( a_p + a_T H_{1,p}(\omega) \right) H_{1,p}(\omega) \tag{37a}$$

$$\Phi_2 (\omega, \omega) = \frac{a_p + a_T H_{1,p}(\omega)}{2} \left[ D_T^{(1)} H_{1,p}(\omega) - \frac{D_q^{(2)}}{2} \left( a_p + a_T H_{1,p}(\omega) \right) \right] \tag{37b}$$
and
\[ F_{2,pp}(\omega, -\omega) = \varphi_1(\omega, -\omega) + 2 \text{Re}(\varphi_2(\omega, -\omega) \Phi(\omega)) \] (39)
\[ H_{2,pp}(\omega, -\omega) = 0 \] (40)

with:
\[ \varphi_1(\omega, -\omega) = b_{pp} + b_{pT} \text{Re}(H_1, p(\omega)) + b_{TT}|H_1, p(\omega)|^2 \] (39a)
\[ + \frac{D^{(1)}_q}{2} [(a + a_T H_1, p(\omega))]^2 - D^{(1)}_T \text{Re}[(a_p + a_T H_1, p(\omega)) H_{1, p}(-\omega)] \]
\[ \varphi_2(\omega, -\omega) = -\frac{1}{2} \left[ \frac{D^{(1)}_T H_{1, p}(-\omega) + D^{(2)}_q}{a_p + a_T H_{1, p}(-\omega)} \right] \] (39b)

Second order FRFs with respect to gas temperature \((F_{2,TT} and H_{2,TT})\)

Similar to the previous case, if the inputs are defined as: \(p = 0\), \(\theta_g = A_1 e^{j\omega t} + A_2 e^{j\omega t}\), the set of Eqs. (7) to (11) is transformed into
\[
\frac{d^2 F_{2,TT}(\omega_1, \omega_2, r_\mu)}{dr_\mu^2} - \frac{j}{D^{(1)}_T} (\omega_1 + \omega_2) F_{2,TT}^*(\omega_1, \omega_2, r_\mu) = \noindent
\frac{D^{(1)}_q}{2} \frac{d}{dr_\mu} \left[ F_{2,TT}^*(\omega_1, r_\mu) \frac{dF_{1,TT}^*(\omega_2, r_\mu)}{dr_\mu} + F_{2,TT}^*(\omega_2, r_\mu) \frac{dF_{1,TT}^*(\omega_1, r_\mu)}{dr_\mu} \right] + \frac{D^{(1)}_T}{2} \frac{d}{dr_\mu} \left[ H_{1,TT}(\omega) \frac{dF_{1,TT}^*(\omega_2, r_\mu)}{dr_\mu} + H_{1,TT}(\omega_2) \frac{dF_{1,TT}^*(\omega_1, r_\mu)}{dr_\mu} \right] \]
(41)
\[ r_\mu = 0: \quad \frac{dF_{2,TT}^*(\omega_1, \omega_2, r_\mu)}{dr_\mu} = 0 \] (42)
\[ r_\mu = R_\mu: \quad F_{2,TT}^*(\omega_1, \omega_2, r_\mu) = a_T H_{2,TT}(\omega_1, \omega_2) + b_{pp} + b_{TT} H_{1,TT}(\omega_1) H_{1,TT}(\omega_2) \] (43)
\[ F_{2,TT}(\omega_1, \omega_2) = \frac{1}{R_\mu} \int_{0}^{R_\mu} F_{2,TT}^*(\omega_1, \omega_2, r_\mu) dr_\mu \] (44)
\[ H_{2,TT}(\omega_1, \omega_2) = \frac{\zeta(\omega_1 + \omega_2)}{j(\omega_1 + \omega_2) + \zeta} F_{2,TT}(\omega_1, \omega_2) \] (45)

Again, the tedious solution procedure will be omitted and only the final expressions given:
\[
F_{2,TT}(\omega_1, \omega_2) = \frac{\Psi_1(\omega_1, \omega_2) \Phi(\omega_1 + \omega_2) + \Psi_2(\omega_1, \omega_2) \Phi(\omega_1) \Phi(\omega_2) + \Psi_2(\omega_2, \omega_1) \Phi(\omega_2)}{1 - a_T \Lambda(\omega_1 + \omega_2)} \tag{46}\]

\[
H_{2,TT}(\omega_1, \omega_2) = F_{2,TT}(\omega_1, \omega_2) \Lambda(\omega_1 + \omega_2) \tag{47}\]

where

\[
\Psi_1(\omega_1, \omega_2) = H_{1,TT}(\omega_1) H_{1,TT}(\omega_2) \times \left[ b_{TT} + \frac{D_q^{(1)} a_T^2}{2} \left( \frac{\omega_1 + \omega_2}{2} \tanh(\alpha \sqrt{\omega_1 R_{\mu}}) \tanh(\alpha \sqrt{\omega_2 R_{\mu}}) \right) \right] \tag{46a}\]

\[
\Psi_2(\omega_1, \omega_2) = H_{1,TT}(\omega_1) H_{1,TT}(\omega_2) \left[ \frac{D_T^{(1)} a_T}{2} \frac{\omega_1}{\omega_2} - \frac{D_T^{(2)} a_T^2}{4} \right] \tag{46b}\]

For \(\omega_1 = \omega_2\), this solution becomes

\[
F_{2,TT}(\omega, \omega) = \frac{\Psi_1(\omega, \omega) \Phi(2\omega) + 2 \Psi_2(\omega, \omega) \Phi(\omega)}{1 - a_T \Lambda(2\omega) \Phi(2\omega)} \tag{48}\]

\[
H_{2,TT}(\omega, \omega) = F_{2,TT}(\omega, \omega) \Lambda(2\omega) \tag{49}\]

with

\[
\Psi_1(\omega, \omega) = H_{1,TT}^2(\omega) \left[ b_{TT} + \frac{D_q^{(1)} a_T^2}{2} (1 + \tanh^2(\alpha \sqrt{\omega R_{\mu}})) - D_T^{(1)} a_T \right] \tag{48a}\]

\[
\Psi_2(\omega, \omega) = H_{1,TT}^2(\omega) \left[ \frac{D_T^{(1)} a_T}{2} - \frac{D_T^{(2)} a_T^2}{4} \right] \tag{48b}\]

and for \(\omega_1 = -\omega_2\)

\[
F_{2,TT}(\omega_1, -\omega_2) = \Psi_1(\omega, -\omega) + 2 \text{Re}(\Psi_2(\omega, -\omega) \Phi(\omega)) \tag{50}\]

\[
H_{2,TT}(\omega, -\omega) = 0 \tag{51}\]

with

\[
\Psi_1(\omega, -\omega) = H_{1,TT}^2(\omega) \left[ b_{TT} + \frac{D_q^{(1)} a_T^2}{2} + D_T^{(1)} a_T \right] \tag{50a}\]

\[
\Psi_2(\omega, -\omega) = H_{1,TT}^2(\omega) \left[ \frac{D_T^{(1)} a_T}{2} + \frac{D_T^{(2)} a_T^2}{4} \right] \tag{50b}\]
Second order FRFs with respect to pressure and temperature ($F_{2,pT}$ and $H_{2,pT}$)

Defining the inputs as $p = A_1 e^{jw_1 t}$, $q = A_2 e^{jw_2 t}$, transforms Eqs. (7) to (11) into the following set of equations:

$$
\frac{d^2 F_{2,pT}^* (\omega_1, \omega_2, \gamma_{\mu})}{dr_{\mu}^2} - \frac{j}{D_{\mu}} (\omega_1 + \omega_2) F_{2,pT}^* (\omega_1, \omega_2, \gamma_{\mu}) = -D_q^{(1)} \frac{d}{dr_{\mu}} \left[ F_{1,1}^* (\omega_1, \gamma_{\mu}) \frac{dF_{1,1}^* (\omega_2, \gamma_{\mu})}{dr_{\mu}} + F_{1,2}^* (\omega_2, \gamma_{\mu}) \frac{dF_{1,2}^* (\omega_1, \gamma_{\mu})}{dr_{\mu}} \right]
$$

$$
-D_T^{(1)} \frac{d}{dr_{\mu}} \left[ F_{1,1}^* (\omega_1) \frac{dF_{1,1}^* (\omega_2, \gamma_{\mu})}{dr_{\mu}} + F_{1,2}^* (\omega_2) \frac{dF_{1,2}^* (\omega_1, \gamma_{\mu})}{dr_{\mu}} \right]
$$

$$
r_{\mu} = 0: \quad \frac{dF_{2,pT}^* (\omega_1, \omega_2, \gamma_{\mu})}{dr_{\mu}} = 0
$$

$$
r_{\mu} = R_{\mu}: \quad F_{2,pT}^* (\omega_1, \omega_2, \gamma_{\mu}) = a_T H_{2,pT} (\omega_1, \omega_2) + b_{TT} H_{1,T} (\omega_2) + a_T H_{1,pT} (\omega_1) H_{1,T} (\omega_2)
$$

$$
F_{2,pT}^* (\omega_1, \omega_2) = \frac{1}{R_{\mu}} \int_0^{R_{\mu}} \left[ F_{2,pT}^* (\omega_1, \omega_2, \gamma_{\mu}) \right] \, d\gamma_{\mu}
$$

$$
H_{2,pT} (\omega_1, \omega_2) = \frac{-\xi (\omega_1 + \omega_2)}{j (\omega_1 + \omega_2) + \xi} F_{2,pT}^* (\omega_1, \omega_2)
$$

The final solution of the set of Eqs. (52) to (56) is:

$$
F_{2,pT} (\omega_1, \omega_2) = \frac{\eta_1 (\omega_1, \omega_2) \Phi (\omega_1 + \omega_2) + \eta_2 (\omega_1, \omega_2) \Phi (\omega_1) + \eta_3 (\omega_1, \omega_2) \Phi (\omega_2)}{1 - a_T \Delta (\omega_1 + \omega_2) \Phi (\omega_1 + \omega_2)}
$$

$$
H_{2,pT} (\omega_1, \omega_2) = F_{2,pT} (\omega_1, \omega_2) \Lambda (\omega_1 + \omega_2)
$$

where

$$
\eta_1 (\omega_1, \omega_2) = b_T H_{1,T} (\omega_2) + b_{TT} H_{1,pT} (\omega_1) H_{1,T} (\omega_2) + D_q^{(1)} a_T (a_T + a_T H_{1,pT} (\omega_1)) H_{1,T} (\omega_2)
$$

$$
\times \left( 1 + \frac{\omega_1 + \omega_2}{2 \sqrt{\omega_1 \omega_2}} \tanh (\alpha \sqrt{\omega_1 R_{\mu}}) \tanh (\alpha \sqrt{\omega_2 R_{\mu}}) \right)
$$

$$
+ D_T^{(1)} H_{1,T} (\omega_2) \left( a_T + a_T H_{1,pT} (\omega_1) \right) \frac{\omega_1}{\omega_2} + a_T \frac{\omega_2}{\omega_1}
$$

(57a)
\[ \eta_2 (\omega_1, \omega_2) = \left( \frac{D_T^{(1)} \omega_1 + D_q^{(1)} a_T}{\omega_2} \right) \left( a_p + a_T H_{1,p} (\omega_1) \right) H_{1,T} (\omega_2) \] (57b)

\[ \eta_3 (\omega_1, \omega_2) = \left( \frac{D_T^{(1)} \omega_1 + D_q^{(1)} a_T}{\omega_2} \right) \left( a_p + a_T H_{1,p} (\omega_0) \right) H_{1,T} (\omega_2) \] (57c)

For \( \omega_1 = \omega_2 \), Eqs. (57) to (58) become

\[ F_{2,pT} (\omega, \omega) = \frac{\eta_1 (\omega \omega) + (\eta_2 (\omega \omega) + \eta_3 (\omega \omega)) \Phi (\omega)}{1 - a_T \Lambda (2\omega) \Phi (2\omega)} \] (59)

with:

\[ \eta_1 (\omega, \omega) = b_{pT} H_{1,T} (\omega) + b_{pT} H_{1,p} (\omega) H_{1,T} (\omega) + D_q^{(1)} a_T (a_p + a_T H_{1,p} (\omega)) \]
\[ \times H_{1,T} (\omega) \left( 1 + \tanh^2 (\alpha_\omega \omega R_0) \right) - D_T^{(1)} (a_p + a_T + a_T H_{1,p} (\omega)) H_{1,T} (\omega) \] (59a)

\[ \eta_2 (\omega, \omega) + \eta_3 (\omega, \omega) = - D_q^{(1)} a_T (a_p + a_T H_{1,p} (\omega)) H_{1,T} (\omega) \]
\[ - D_T^{(1)} (a_p + a_T + a_T H_{1,p} (\omega)) H_{1,T} (\omega) \] (59bc)

and for \( \omega_1 = -\omega_2 = \omega \)

\[ F_{2,pT} (\omega, -\omega) = \eta_1 (\omega, -\omega) + \eta_2 (\omega, -\omega) \Phi (\omega) + \eta_3 (\omega, -\omega) \Phi (-\omega) \] (61)

\[ H_{2,pT} (\omega, -\omega_2) = 0 \] (62)

with

\[ \eta_1 (\omega, -\omega) = b_{pT} H_{1,T} (-\omega) + b_{pT} H_{1,p} (\omega) H_{1,T} (-\omega) + D_q^{(1)} a_T (a_p + a_T H_{1,p} (\omega)) \]
\[ - D_T^{(1)} (a_p + a_T + a_T H_{1,p} (\omega)) H_{1,T} (-\omega) \] (61a)

\[ \eta_2 (\omega, -\omega) = - (D_T^{(1)} + D_q^{(1)} a_T / 2) (a_p + a_T H_{1,p} (\omega)) H_{1,T} (-\omega) \] (61b)

\[ \eta_3 (\omega_1, -\omega_2) = - (D_T^{(1)} + D_q^{(1)} a_T (\omega_1) / 2) a_T H_{1,T} (-\omega) \] (61c)

It should be noticed that, contrary to the second order FRFs \( F_{2,pp} \) and \( F_{2,TT} \), which are symmetrical \( (F_{2,pp} (\omega_1, \omega_2) = F_{2,pp} (\omega_2, \omega_1)) \) and \( (F_{2,TT} (\omega_1, \omega_2) = F_{2,TT} (\omega_2, \omega_1)) \), the crossfunction \( F_{2,pp} (\omega_1, \omega_2) \) is asymmetrical \( (F_{2,pp} (\omega_1, \omega_2) \neq F_{2,pp} (\omega_2, \omega_1)) \).

**Illustration - adsorption of CO\textsubscript{2} on silicalite-1**

As an illustration, some simulation results of the first and second order FRFs, using the expressions derived in the previous section, will be given. The simulation parameters are given in Table II. They correspond to literature data on the adsorption of CO\textsubscript{2} on silicalite-1,\textsuperscript{12} to steady state pressure and temperature \( P_s = 10 \, \text{kPa} \) and \( T_s = 298 \, \text{K} \), and to moderate heat transfer resistances. The isotherm pressure and temperature coefficients \( (a_p, a_T, b_{pp}, b_{TT} \text{ and } b_{pT}) \) were obtained by expanding the Langmuir equilibrium relation.
into a Taylor series. The diffusivity concentration and temperature coefficients $D_q(1)$ and $D_T(1)$ were obtained from a Taylor series expansion of a function based on the well known Darken equation for the concentration dependence and the Arrhenius type relation for the temperature dependence of the micropore diffusivity

$$D_{q} = D_{0} \frac{d(\ln P)}{d(\ln Q)}; \quad D_{T} = D_{0}^* \exp \left( \frac{E}{R_{S} T_{P}} \right)$$

TABLE II. Data for simulation (adsorption of CO$_2$ on silicalite-1, $P_s = 10$ kPa, $T_s = 298$ K)$^{12}$

<table>
<thead>
<tr>
<th>Microparticle data</th>
<th>$\sigma = 0$ (slab shape); $R_{m} = 15$ $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium parameters</td>
<td>$a_{p} = 0.911, \quad a_{T} = -7.1069$</td>
</tr>
<tr>
<td>$b_{pp} = -0.0811, \quad b_{TT} = 29.8932, \quad b_{pT} = -5.8415$</td>
<td></td>
</tr>
<tr>
<td>Physical and transport parameters</td>
<td>$D_{qs} = 2.7443 \times 10^{-9}$ m$^2$/s, $D_{q}^{(1)} = -0.0977, \quad D_{T}^{(1)} = 0.0037$</td>
</tr>
<tr>
<td>$\zeta = 3.01 \times 10^{-2}, \quad \zeta = 0.5$ s$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

The simulation results are presented in Figs. 2a to 2d. The FRFs are complex functions of frequency. They are represented in the form of amplitude and phase characteristics, using the classical Bode plot representation (the amplitudes in log-log and the phases in semi-log diagrams). The functions $H_{2,pp}(\omega, -\omega)$ and $H_{2,TT}(\omega, -\omega)$, which are identically equal to zero, are not shown.

In Fig. 2a, the FRFs corresponding to the isothermal case (the parameter $\zeta$ very large) are given. Notice that for this case the “$F_{p}$” FRFs describe the system completely.
ANALYSIS AND DISCUSSION

Characteristic features of the frequency response functions

First, the characteristic features of the second order FRFs corresponding to micropore diffusion with a variable diffusion coefficient will be considered. For comparison, the complete set of FRFs for micropore diffusion with a constant diffusivity \( D_q^{(1)} = D_f^{(1)} = 0 \) are given in Fig. 3. All the other simulation parameters are from Table II (the same as in Fig. 2). Again, the FRFs obtained for the isothermal case are added in Fig. 3a.

Fig. 2. The simulated first and second order FRFs for adsorption of CO\(_2\) on silicalite-1\(^{12}\) at 10 kPa and 298 K: (a) “\(F_p\)” (\(q\) vs.\(p\)) functions + “\(F_p\)” functions for the isothermal case; (b) “\(H_p\)” (\(\theta_p\) vs. \(p\)) functions; (c) “\(F_T\)” (\(q\) vs. \(\theta_g\)) and “\(F_{pT}\)” (\(q\) vs. \(p\) and \(\theta_g\)) functions; (d) “\(H_T\)” \(\theta_p\) vs. \(\theta_g\) and “\(H_{pT}\)” \(\theta_p\) vs. \(p\) and \(\theta_g\) functions.

NON-ISOTHERMAL ADSORPTION
Inspection of Figs. 2 and 3 shows that the only recognizable difference in the shapes of the FRFs corresponding to variable and to constant diffusivities can be found in the second “FP” functions, both for the isothermal and for the non-isothermal case. The function $F_2,pp(w, -w)$ seems especially useful in this sense: it has horizontal asymptotes both for low and for high frequencies, which are equal for the case of constant diffusivity and unequal for the case of variable diffusivity. It is also important to notice that the functions $F_2,pp(\omega, -\omega)$ and $F_2,pp(\omega, \omega)$ still have shapes which enable the distinction of the micropore diffusion mechanism from other kinetic mechanisms (e.g., for

Fig. 3. The simulated first and second order FRFs for the case of constant diffusivity $D_q^{(1)} = D_f^{(1)} = 0$, the other simulation parameters the same as given in Fig. 2): (a) “$F_p,q$” ($q$ vs. $p$) functions + “$F_p,p$” functions for the isothermal case; (b) “$H_p,p$” ($\theta_p$ vs. $\theta_p$) functions; (c) “$F_T$” ($q$ vs. $\theta_q$) and “$F_{p,T}$” ($q$ vs. $p$ and $\theta_q$) functions; (d) “$H_T$” ($\theta_p$ vs. $\theta_q$) and “$H_{p,T}$” ($\theta_p$ vs. $p$ and $\theta_q$) functions.
the macropore diffusion mechanism, the amplitude of $F_{2,pp}^{\omega}(\omega, \omega)$ changes the slope several times, while the amplitude of $F_{2,pp}^{\omega}(\omega, -\omega)$ is a descending function of $\omega^{23,24}$.

The investigation of the influence of variable diffusivity on the functions $F_{2,pp}^{\omega}(\omega, \omega)$ and $F_{2,pp}^{\omega}(\omega, -\omega)$ showed that it was mostly related to the concentration coefficient $D_q^{(1)}$. The amplitudes of $F_{2,pp}^{\omega}(\omega, \omega)$ and $F_{2,pp}^{\omega}(\omega, -\omega)$ obtained with four different values of $D_q^{(1)}$: 0, $-0.0977$, $-0.1954$ and $-0.4885$ are shown in Fig. 4. The first value corresponds to constant diffusivity (the same as in Fig. 3), the second is equal to the value in Table II (the same as in Fig. 2), and the third and fourth value are multiples, by two and by five, of the value in Table II. The influence of $D_q^{(1)}$ on the high frequency asymptotes is obvious, especially for the function $F_{2,pp}^{\omega}(\omega, -\omega)$.

The other FRFs will not be discussed, as they show the same patterns as for the case of non-isothermal micropore diffusion with constant diffusivity.$^{28}$

Estimation of model parameters

One of the advantages of the non-linear over the linear FR is that the second order FRFs give valuable information for the identification of the correct mathematical model, i.e., the most probable kinetic mechanism. Another advantage is that it enables estimation of the model parameters, including the ones defining the system non-linearity. A fast and easy way of estimating all the parameters of the defined model (non-isothermal micropore diffusion with variable diffusivity and convective heat transfer mechanism) will be shown here.

Estimation of the equilibrium parameters

The equilibrium parameters $a_p$, $a_T$, $b_{pp}$, $b_{TT}$ and $b_{pT}$ can all be estimated from the low frequency asymptotes of some of the FRFs. It is easily shown that

$$a_p = \lim_{\omega \to 0} F_{1,p}^{\omega}(\omega) \quad (65)$$

$$a_T = \lim_{\omega \to 0} F_{1,T}^{\omega}(\omega) \quad (66)$$
It is not surprising that the “linear” equilibrium parameters $a_p$ and $a_T$ are obtained from the first order (linear) FRFs, while the “non-linear” parameters $b_{pp}$, $b_{TT}$, and $b_{pT}$ can be estimated only from the second order FRFs. These five parameters actually represent the first and second derivatives of the adsorption equilibrium relation in non-dimensional form in the steady state point, so they give information about the form of this relation.

**Estimation of the diffusion parameters**

The problem of the estimation of the micropore diffusivity for the isothermal case and constant diffusivity has been solved long ago.\textsuperscript{3} It can be calculated from the position of the maximum of the so called out-of-phase characteristic function,\textsuperscript{3} which is actually another name for the absolute value of the imaginary part of the function $F_{1,p}$.\textsuperscript{18} For micropore diffusion and slab microparticle geometry, it is proportional to the function $F(p)$, defined in Eq. (20) (notice that for the isothermal case, Eq. (18) reduces to $F_{1,p}(p) = a_pF(p)$). The frequency at which this maximum is obtained satisfies the following condition

\[
\frac{R_i^2}{D_p} \omega_{\text{max}} = 2.656
\]  

For the known microparticle size, the micropore diffusivity can be easily calculated from Eq. (70). Nevertheless, for non-isothermal cases, the determination of the diffusion coefficient becomes much more complex, as the out-of-phase function has two maxima.\textsuperscript{7,9} The out-of-phase functions for the non-isothermal and for the isothermal case presented in Fig. 2 are shown in Fig. 5.
This problem can be solved if the whole set of FRF needed to describe the non-isothermal micropore diffusion is available. If a new function is defined as the ratio of \( \frac{F_{1,T}(\omega)}{H_{1,T}(\omega)} = \Phi(\omega) \) it has the same form as \( F_{1,p} \) for the isothermal case (its imaginary part is also presented in Fig. 5). Using this result, the micropore diffusivity at steady state \( D_{\text{ms}} \) can be determined from the location of the maximum of \( \text{Im}(G) \).

The diffusivity concentration and temperature coefficients \( D_q^{(1)} \) and \( D_T^{(1)} \) have to be determined from the second order FRFs. The first one can be easily obtained from the high frequency asymptote of the function \( F_{2,pp}(\omega, -\omega) \) (see Fig. 4b)

\[
\lim_{\omega \to 0} F_{2,pp}(\omega - \omega) = b_{pp} + \frac{D_q^{(1)} a_p^2}{2}
\]

The temperature coefficient \( D_T^{(1)} \) cannot be estimated directly. However, a new function can be defined

\[
W(\omega) = \frac{F_{2,TT}(\omega - \omega)}{[H_{1,T}(\omega)]^2} = b_{TT} + \left( \frac{D_q^{(1)} a_T^2}{2} + D_T^{(1)} a_T \right) [1 - \text{Re}(F(\omega))]
\]

which has a horizontal high frequency asymptote from which \( D_T^{(1)} \) can be calculated

\[
\lim_{\omega \to \infty} W(\omega) = b_{TT} + \frac{D_q^{(1)} a_T^2}{2} + D_T^{(1)} a_T
\]

**Estimation of \( \xi \) and \( \zeta \)**

These parameters cannot be estimated directly from any of the particle FRFs. However, if one defines

\[
Z(\omega) = \frac{H_{1,p}(\omega)}{F_{1,p}(\omega)} = \Lambda(\omega) = \frac{\xi j\omega}{\zeta + j\omega}
\]

it is possible to estimate the parameter \( \xi \) from the high frequency asymptote

\[
\lim_{\omega \to \infty} Z(\omega) = \xi
\]

On the other hand, the definition of another function

\[
X(\omega) = \frac{H_{1,p}(\omega)}{F_{1,T}(\omega)} = \frac{a_p \Lambda(\omega)}{a_T} = \frac{a_p \xi}{a_T \zeta}
\]

enables the estimation of the parameter \( \zeta \), from the slope of the imaginary part of \( X \).
\[ \text{Im}(X(\omega)) = \frac{a_p}{a_T} \frac{\zeta}{\omega} = K \omega \Rightarrow \frac{1}{a_T} \frac{\zeta}{\omega} = \frac{a_p}{a_T} \frac{\zeta}{K} \] (78)

It should be recalled that the parameter \( \zeta \) carries information on the heat of adsorption, and \( \zeta \) on the heat transfer coefficient (see Table I).

CONCLUSIONS

The investigated case: non-isothermal non-linear adsorption governed by micropore diffusion with variable diffusivity is a highly realistic problem in a number of commercial microporous adsorbers. The proposed method, analysis of non-linear FR using the concept of higher order frequency response functions, although rather complex, can successfully treat such problems. The definition of the FRFs on the particle scale enables the analysis to be focused on the kinetic mechanism in the particle, which is the final aim of the investigation. One of the important steps in the application of the method is the generation of a certain library of sets of FRFs corresponding to different mechanisms and analyzing their patterns which can be used for the discrimination between different mechanisms. This work is part of the effort of compiling such a library.

The analysis of the FRFs for the investigated mechanism demonstrated three major things:

1. The FRFs corresponding to micropore diffusion with variable diffusivity maintain the main characteristics which distinguish the micropore diffusion mechanism from other mechanisms.

2. The second order FRF \( F_{2,pp}(\omega, -\omega) \), relating the sorbate concentration in the solid phase and the gas pressure, gives enough information to make a decision on whether in a particular case the micropore diffusivity in the system is variable or can be treated as constant.

3. The first and second order FRFs offer enough information for the fast and easy estimation of all the parameters defined in the model. Estimation of the parameters related to the non-linearity of the system is especially significant.

Considering all this, this work can be used as another proof of the superiority of the non-linear FR method over the classical linear FR one.

NOTATION

- \( a \) – particle to gas heat transfer surface area, m\(^2\)
- \( a_p \) – first order pressure coefficient of the adsorption equilibrium function
- \( a_T \) – first order temperature coefficient of the adsorption equilibrium function
- \( b \) – Langmuir isotherm parameter, Pa\(^{-1}\) (Equation 63)
- \( b_0 \) – pre-exponential factor of the Langmuir isotherm parameter \( b \), Pa\(^{-1}\) (Equation (63))
- \( b_{pp} \) – second order pressure coefficient of the adsorption equilibrium function
- \( b_{TT} \) – second order temperature coefficient of the adsorption equilibrium function
- \( b_{pT} \) – mixed second order pressure and temperature coefficient of the adsorption equilibrium function
\( C_{ps} \) – particle heat capacity, \( \text{j/g/K} \)
\( D_m \) – micropore diffusivity, \( \text{cm}^2/\text{s} \)
\( D_{ms} \) – micropore diffusivity at steady state, \( \text{cm}^2/\text{s} \)
\( D_0 \) – the corrected diffusivity, \( \text{cm}^2/\text{s} \) (Equation (64))
\( D_0^* \) – pre-exponential factor of the corrected diffusivity, \( \text{cm}^2/\text{s} \) (Equation (64))
\( D_{1(1)} \) – first order concentration coefficient of the micropore diffusivity
\( D_{2(1)} \) – first order temperature coefficient of the micropore diffusivity
\( E \) – activation energy for micropore diffusion, \( \text{J/mol} \) (Equation (64))
\( F_{p,p,\ldots,p} (\omega_1, \ldots, \omega_n) \) – \( n \)-th order \( <q> \) vs. \( p \) FRF
\( F_{n,p,\ldots,p} (\omega_1, \ldots, \omega_n, r_\mu) \) – \( n \)-th order \( q(r_\mu) \) vs. \( p \) FRF
\( F_{n,T,\ldots,T} (\omega_1, \ldots, \omega_n, r_\mu) \) – \( n \)-th order \( <q> \) vs. \( \theta_g \) FRF
\( F_{n,p,T,\ldots,T} (\omega_1, \ldots, \omega_n, r_\mu) \) – \( n \)-th order \( q(r_\mu) \) vs. \( \theta_g \) FRF
\( F_{n,p,\ldots,p,T,\ldots,T} (\omega_1, \ldots, \omega_n, r_\mu) \) – \( n \)-th order \( q(r_\mu) \) vs. \( p \) and \( \theta_g \) FRF
\( h \) – particle to gas heat transfer coefficient, \( \text{J/m}^2\text{K/s} \)
\( H_{p,p,\ldots,p} (\omega_1, \ldots, \omega_n) \) – \( n \)-th order \( \theta_p \) vs. \( p \) FRF
\( H_{n,T,\ldots,T} (\omega_1, \ldots, \omega_n) \) – \( n \)-th order \( \theta_p \) vs. \( \theta_g \) FRF
\( H_{n,p,T,\ldots,T} (\omega_1, \ldots, \omega_n) \) – \( n \)-th order \( \theta_p \) vs. \( p \) and \( \theta_g \) FRF
\( j \) – imaginary unit (\( \sqrt{-1} \))
\( k \) – temperature coefficient of the Langmuir isotherm parameter, \( \text{K}^{-1} \) (Equation (63))
\( P \) – pressure, \( \text{kPa} \)
\( p \) – non-dimensional pressure
\( Q \) – concentration in the adsorbent particle, \( \text{mol/cm}^3 \)
\( q \) – non-dimensional concentration in the adsorbent particle
\( Q_0 \) – concentration in the adsorbent particle at maximal coverage, \( \text{mol/cm}^3 \) (Equation 63)
\( R \) – gas constant, \( \text{J/mol/K} \)
\( R_m \) – microparticle half-dimension, \( \text{cm} \)
\( r_\mu \) – microparticle spatial coordinate, \( \text{cm} \)
\( t \) – time, \( \text{s} \)
\( T_g \) – gas temperature, \( \text{K} \)
\( T_p \) – particle temperature, \( \text{K} \)
\( V_p \) – particle volume, \( \text{cm}^3 \)

\textbf{Greek letters}

\( \theta_g \) – non-dimensional gas temperature
\( \theta_p \) – non-dimensional particle temperature
\( \rho_p \) – particle density, \( \text{g/cm}^3 \)
\( \sigma \) – shape factor
\( \xi \) – modified heat of adsorption coefficient (Table I)
\( \zeta \) – modified particle to gas heat transfer coefficient, \( \text{s}^{-1} \) (Table I)
\( \omega \) – frequency, \( \text{rad/s} \)
ИЗВОД

НЕЛИНЕАРНИ ФРЕКВЕНТНИ ОДЗИВ НЕИЗОТЕРМНог АДСОРПЦИОНОГ СИСТЕМА ЧИЈА ЈЕ КИНЕТИКА КОНТРОЛИСАНА ДИФУЗИЈОМ КРОЗ МИКРОПОРЕ СА ПРОМЕНЉИВОМ ДИФУЗИВНОШЋУ

МЕНКА ПЕТКОВСКА

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Коришћењем концепта фреквентних преносних функција вишег реда, извршена је анализа кинетике нелинеарне адсорпције на нивоу честице сорбента, за случај неизотермне дифузије кроз микропоре са променљивом дифузионшћу, као ограничавајућег механизма. Дефинисано је шест серија фреквентних преносних функција које су потребне да опишу систем за општи неизотермни случај. Поштавши од математичког модела на нивоу честице, изведени су израzi за фреквентне преносне функције првог и другог реда. Извршена је симулација ових функција са параметрима одређеним из литературних података који одговарају адсорпцији CO2 на силикалиту-1. Нађено је да променљива дифузионшћа значајно удостоји облик фреквентних преносних функција другог реда које повезују промену концентрације у чврстој фази и промену притиска. Међутим, ове функције и даље задржавају своје карактеристике на основу којих се адсорпција директована дифузијом кроз микропоре може разликовати од других кинетичких механизама. Такође је показано да се из фреквентних преносних функција првог и другог реда добија довољно информација на основу којих се број и једноставно могу одредити сви параметри модела, укључујући и они који дефинишу нелинеарност система.

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REFERENCES

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