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Application of Nonlinear Frequency Response to Adsorption Systems with Complex Kinetic Mechanisms

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Abstract. The paper is a contribution to formation of a library of sets of frequency response functions of different orders, for complex kinetic mechanisms typical for adsorption on bidispersed sorbents. The first and second order frequency response functions have been derived starting from a general model, taking into account macro-pore diffusion, micro-pore diffusion, adsorption/desorption kinetics at the micropore mouth and film mass transfer at the particle surface. Simplified models, which neglect one or more mass transfer resistances, were also considered. The frequency response functions were derived for isothermal case, constant diffusion coefficients and planar geometry. The first and second order functions were simulated for the general and for some special cases. Based on these simulation results, some characteristic patterns of the amplitude and phase functions, corresponding to different cases, have been recognized. These patterns can serve as a basis for model and mechanism identification.

Keywords: nonlinear frequency response, adsorption kinetics, complex mechanisms, bidispersed sorbents

Introduction

Nonlinear frequency response (FR) is a quasi-stationary response of a nonlinear system to a periodic sinusoidal or cosinusoidal change of the input. Contrary to linear FR, which consists only of the first (basic) harmonic of the same frequency as the input, nonlinear FR also contains a DC (nonperiodic) term and an indefinite number of higher harmonics. A convenient tool for treating nonlinear FRs is the concept of higher order frequency response functions (FRFs) (Weiner and Spina, 1980), which is based on replacing the nonlinear model **G** with an indefinite sequence of linear FRFs of the first ($G_1(\omega)$), second ($G_2(\omega, \omega)$ and $G_2(\omega, -\omega)$), third ($G_3(\omega, \omega, \omega)$ and $G_3(\omega, \omega, -\omega)$), etc. order, such that $G_1(\omega)$ corresponds to the dominant term of the first harmonic, $G_2(\omega, \omega)$ to the dominant term of the second harmonic, $G_2(\omega, -\omega)$ to the dominant term of the DC component, $G_3(\omega, \omega, \omega)$ to the dominant term of the third harmonic, . . . ,of the system response to a cosinusoidal input of frequency ω (Weiner and Spina, 1980).

Nonlinear frequency response and the concept of higher order FRFs have been proven as useful tools for investigation of weakly nonlinear dynamic systems. Being weakly nonlinear, adsorption systems are good candidates for this method. In our previous work we have applied it to analysis of the most common single isothermal mechanisms of adsorption kinetics (micropore diffusion, macropore-surface diffusion, Langmuir kinetics or film control) (Petkovska and Do, 2000) and to some characteristic cases of more complex mechanisms (nonisothermal micropore diffusion (Petkovska, 2000; Petkovska and Petkovska, 2003) or two simultaneous isothermal micropore diffusion processes (Petkovska and Petkovska, 2003)). These investigations have shown two important results:

1. The second order FRFs corresponding to different mechanisms have different shapes, which can be used for their discrimination (Petkovska and Do, 2000; Petkovska and Petkovska, 2003) and reliable identification of the correct kinetic model.
2. The FRFs can be used for estimation of both kinetic and equilibrium parameters of the identified model (Petkovska, 2000).

One of the crucial steps in application of the nonlinear FR method in investigation of adsorption kinetics is formation of a library of sets of theoretically derived FRFs on the particle scale, corresponding to different kinetics mechanisms (Petkovska, 2001), which can be used for comparison with experimental FRFs (FRFs estimated from experimental FR data). This paper is a contribution to formation of such a library, for complex kinetic mechanisms characteristic for bidispersed adsorbents. In such systems, diffusion on both macro-particle (pellet) and micro-particle scale usually influence the overall adsorption rate. Often, the adsorption/desorption rate at the micropore mouth and/or the film mass transfer at the macro-particle surface also have to be taken into account. In case of significant heat effects, the heat generation and transfer have to be taken into account, as well.

Depending on the kinetic parameters in a particular system, the overall rate of the adsorption process can be defined by a single mechanism, or by combination of two, three or all four mechanisms. A detailed analysis of this problem is given in (Do, 1990).

The theoretical nonlinear FR analysis generally consists of four main steps:

1. Setting up the nonlinear mathematical model;
2. Derivation of the FRFs of different orders corresponding to the defined model;
3. Analysis of the derived FRFs, defining the main features of the FRFs corresponding to the investigated mechanism, in order to facilitate its reliable discrimination from other mechanisms;
4. Development of procedures for estimation of the equilibrium and kinetic parameters from the FRFs.

Owing to the limited volume of this manuscript and to the great complexity of Step 4, the analysis in this paper will be limited to the first 3 steps. As our previous investigations have shown that the second order functions give enough information for model discrimination (Petkovska and Do, 2000), only the first and second order FRFs will be derived and analyzed. The analysis will also be limited to isothermal conditions (negligible heat effects).

Definition of the Model Equations

The general isothermal model, in which the kinetics of diffusion on both macro- and micro-particle scale, as well as the adsorption/desorption kinetics and the film mass transfer resistance are taken into account, is postulated, using the following assumptions: Fickian diffusion both on the micro- and macro-particle scale; Langmuiran adsorption kinetics at the micropore mouth and linear driving force in the stagnant film at the particle surface. The mathematical model on the particle scale can be defined by the following equations:

- The material balance for the micro-particle:

$$\frac{\partial Q_\mu}{\partial t} = \frac{1}{r_\mu}\frac{\partial}{\partial r_\mu}\left(r_\mu^{\sigma_\mu} D_\mu \frac{\partial Q_\mu}{\partial r_\mu}\right) \tag{1}$$

with the boundary conditions:

$$r_\mu = 0 : \frac{\partial Q_\mu}{\partial r_\mu} = 0 \tag{2}$$

$$r_\mu = R_\mu : D_\mu \frac{\partial Q_\mu}{\partial r_\mu} = K_a C_i (Q_{\mu 0} - Q_\mu) - K_d Q_\mu \tag{3}$$

- The material balance for the macro-particle:

$$(1-\varepsilon)\frac{\partial Q_i}{\partial t} + \varepsilon\frac{\partial C_i}{\partial t} = \varepsilon\frac{1}{r^\sigma}\frac{\partial}{\partial r}\left(D_p r^\sigma \frac{\partial C_i}{\partial r}\right) \tag{4}$$

with

$$Q_i = \frac{\sigma_\mu + 1}{R_\mu^{\sigma+1}}\int_0^{R_\mu} r_\mu^\sigma Q_\mu(r_\mu)\, dr_\mu \tag{5}$$

The boundary conditions for Eq. (4) are:

$$r = 0 : \frac{\partial Q_i}{\partial r} = \frac{\partial C_i}{\partial r} = 0 \tag{6}$$

$$r = R : D_p \frac{\partial C_i}{\partial r} = k_m (C_b - C_i) \tag{7}$$

- The mean value of the concentration in the particle:

$$\begin{aligned}\langle Q\rangle &= \frac{\sigma+1}{R^{\sigma+1}}\int_0^R r^\sigma Q(r)\, dr \\ &= \frac{\sigma+1}{R^{\sigma+1}}\int_0^R r^\sigma((1-\varepsilon)Q_i(r) + \varepsilon C_i(r))\, dr\end{aligned} \tag{8}$$

The following notaions were used in Eqs. (1)–(7): *independent variables*: t is time, r the spatial coordinate of the macro-particle and r_μ the spatial coordinate of the micro-particle; *concentrations*: C_b—

adsorbate concentration in the bulk fluid around the particle, Q– total adsorbate concentration (in the pores plus adsorbed) in the particle at position r, C_i—adsorbate concentration in the fluid phase within the particle pores, at position r, Q_i—adsorbate concentration in the solid phase at position r, equal to the mean concentration in the micro-particles at that position, Q_μ— adsorbate concentration in the micro-particle at position r_μ, $Q_{\mu 0}$—concentration in the micropores corresponding to maximal coverage, $\langle Q \rangle$—mean concentration in the macro-particle; *rate parameters*: D_p—pore diffusion coefficient, D_μ—micropore diffusion coefficient, K_a—adsorption rate constant, K_d—desorption rate constant, k_m—film mass transfer coefficient; *other parameters*: R—macro-particle half-dimension, R_μ—micro-particle half-dimension, ε particle (macro)porosity, σ—the macro-particle shape factor, σ_μ—the micro-particle shape factor (the shape factor is 0 for planar, 1 for cylindical and 2 for spherical geometry).

In case of fast adsorption/desorption kinetics, when equilibrium is practically established at the micropore mouth, the boundary condition (3) is transformed in the following way:

$$r_\mu = R_\mu : Q_\mu = \Phi(C_i) = \left.\frac{\partial \Phi}{\partial C_i}\right|_s (C_i - C_s) + \frac{1}{2}\left.\frac{\partial^2 \Phi}{\partial C_i^2}\right|_s (C_i - C_s)^2 + \cdots \qquad (9)$$

where Φ is the adsorption isotherm relation (generally nonlinear), which has been represented in a Taylor series form, for convenience.

On the other hand, if the mass transfer resistance of the film at the particle surface is negligible, the boundary condition (7) becomes:

$$r = R : C_i = C_b \qquad (10)$$

Also, depending on the time constants corresponding to diffusion on the micro- and on the macro-particle scale, one or the other mechanism can determine the overall rate of the adsorption process.

Frequency Response Functions

The general procedure for derivation of frequency response functions of different orders have been described in detail in Petkovska (2001). Following this procedure, the first and second order FRFs were derived for the general model given by Eqs. (1)–(8). For convenience, the model equations were first transformed in such a way that all concentrations were defined as nondimensional (relative) deviations from their steady-state values. The derived FRFs are defined on the particle level, i.e. they correspond to the response of the nondimensional deviation of the mean concentration in the particle $\langle q \rangle = (\langle Q \rangle - \langle Q_s \rangle / \langle Q \rangle_s$ to cosinusoidal change of the nondimensional concentration of the adsorbate in the bulk fluid around the particle $c_b = (C_b - C_s)/C_s$.

Owing to the limited space here, the derivation procedure will be omitted. The derived expressions for the first- and second-order FRFs are listed below. These expressions were obtained for constant diffusion coefficients ($D_\mu = \text{const}$, $D_p = \text{const}$) and for planar micro- and macro-particle geometry ($\sigma_\mu = 0, \sigma = 0$).

First order FRF

This function corresponds to the dominant term of the first harmonic of $\langle q \rangle$.

$$G_1(\omega) = \frac{\varepsilon C_s + (1-\varepsilon) K_a C_s (Q_{\mu 0} - Q_{\mu s})/(K_d + K_a C_s)}{\varepsilon C_s + (1-\varepsilon) Q_{\mu s}} \gamma(\omega) \Phi(\alpha(\omega)\sqrt{\omega} R) \qquad (11)$$

Second Order FRFs

Two second order FRFs can be defined: one corresponding to the dominant term of the second harmonic of $\langle q \rangle$:

$$G_2(\omega, \omega) = \Lambda(\omega)\left(\xi(\omega) G_1(2\omega) - \frac{\alpha^2(\omega)}{2\alpha^2(\omega) - \alpha^2(2\omega)} \Phi(\alpha(\omega)\sqrt{\omega} R) - \frac{1-j}{2}\frac{1}{\cosh^2(\alpha(\omega)\sqrt{\omega} R)}\right) \qquad (12)$$

and the other corresponding to the dominant term of the DC component:

$$G_2(\omega, -\omega) = -\frac{(1-\varepsilon)(Q_{\mu 0} - Q_{\mu s})}{\varepsilon C_s + (1-\varepsilon) Q_{\mu s}} \left(\frac{K_a C_s}{K_d + K_a C_s}\right)^2 Re(\varphi(\omega)) |\gamma(\omega)|^2 \times \frac{\alpha^2(\omega)\Phi(\alpha(\omega)\sqrt{\omega}R) + \alpha^2(-\omega)\Phi(j\alpha(-\omega)\sqrt{\omega}R)}{\alpha^2(\omega) + \alpha^2(-\omega)} \tag{13}$$

In Eqs. (11)–(13) the following groups have been defined:

$$\beta = \sqrt{\frac{j}{D_\mu}} \tag{14}$$

$$\Phi(X) = \frac{\tanh(X)}{X} \tag{15}$$

$$\varphi(\omega) = \left(\frac{R_\mu}{K_d + K_a C_s}\Phi(\beta\sqrt{\omega}R_\mu)\omega j + 1\right)^{-1} \tag{16}$$

$$\alpha(\omega) = \sqrt{\frac{j}{\varepsilon D_p}\left(\varepsilon + (1-\varepsilon)\frac{K_a(Q_{\mu 0} - Q_{\mu s})}{K_d + K_a C_s}\varphi(\omega)\Phi(\beta\sqrt{\omega}R_\mu)\right)} \tag{17}$$

$$\gamma(\omega) = \left(\left(\varepsilon\frac{C_s}{Q_{\mu s}} + (1-\varepsilon)\frac{K_a C_s}{K_d + K_a C_s}\frac{Q_{\mu 0} - Q_{\mu s}}{Q_{\mu s}}\varphi(\omega)\Phi(\beta\sqrt{\omega}R_\mu)\right)\frac{R}{k_m}\frac{Q_{\mu s}}{C_s}\Phi(\alpha(\omega)\sqrt{\omega}R)\omega j + 1\right)^{-1} \tag{18}$$

$$\Lambda(\omega) = -\frac{(1-\varepsilon)(Q_{\mu 0} - Q_{\mu s})}{\varepsilon C_s + (1-\varepsilon)Q_{\mu s}}\left(\frac{K_a C_s}{K_d + K_a C_s}\right)^2 \varphi(\omega)\Phi\left(\alpha(\omega)\sqrt{\omega}R\right)\varphi(2\omega)\Phi\left(\alpha(2\omega)\sqrt{2\omega}R\right)\gamma^2(\omega) \tag{19}$$

$$\xi(\omega) = \frac{Q_{\mu s}}{\varepsilon D_p C_s}\left\{\left(\frac{j}{2\alpha^2(\omega) - \alpha^2(2\omega)} - \frac{1}{\alpha^2(2\omega)}\right)\frac{1}{\cosh^2(\alpha(\omega)\sqrt{\omega}R)} + \frac{\gamma(\omega) - 2}{\gamma(\omega)}\frac{j}{2\alpha^2(\omega) - \alpha^2(2\omega)}\right\} \tag{20}$$

For special cases, i.e. for simpler models, these expressions simplify, in the following way:

- For negligible film mass transfer resistance $\gamma(\omega) \to 1$;
- For fast adsorption-desorption and equilibrium at the micropore mouth $\varphi(\omega) \to 1$;
- For fast diffusion on the micro-particle level (high $D_\mu/R_\mu^2)\Phi(\beta\sqrt{\omega}R_\mu) \to 1$;
- For fast diffusion on the macro-particle level (high $D_p/R^2)\Phi(\alpha\sqrt{\omega}\mathrm{R}) \to 1$.

Simulation and Analysis

A number of models of different complexity can be derived from the general model defined by Eqs. (1)–(8) (Do, 1990). We will limit our analysis to four models, with two, three or four mass transfer mechanisms influencing the overall adsorption rate, all of them based on the existence of two major mass transfer resistances in the adsorption particle, on the micro- and on the macro-particle level:

- MODEL 1—the micropore-macropore model. This model is obtained from the general one for negligible mass transfer resistance in the stagnant film and at the micropore mouth.
- MODEL 2—the micropore-macropore-adsorption model. This model takes into consideration the finite adsorption/desorption rate at the micropore mouth, but neglects the film mass transfer resistance.
- MODEL 3—the micropore-macropore-film model. This model takes into account the film mass transfer resistance, but assumes equilibrium at the micropore mouth.
- MODEL 4—the micropore-macropore-adsorption-film model. This is the general model taking into account all four mechanisms of mass transfer. Equations (1)–(8) and (11)–(20) correspond to this case.

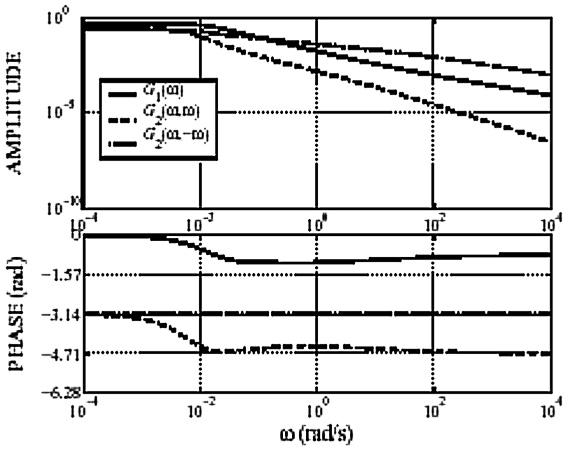

Figure 1. The first and second order FRFs for MODEL 1 (micropore-macropore mechanism).

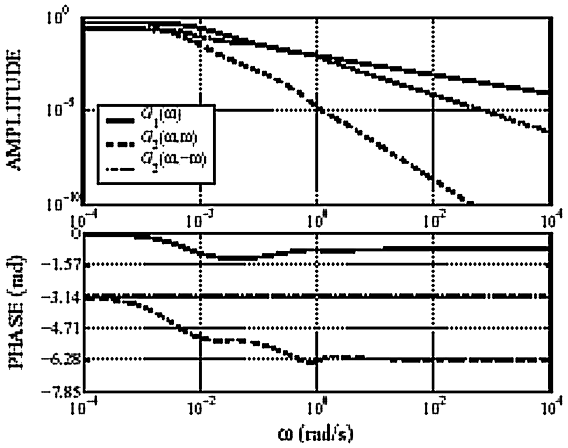

Figure 2. The first and second order FRFs for MODEL 2 (micropore-macropore-adsorption mechanism).

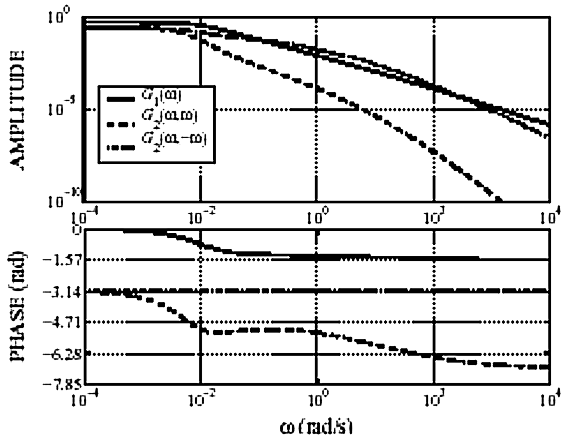

Figure 3. The first and second order FRFs for MODEL 3 (micropore-macropore-film mechanism).

Table 1. Summary of the high-frequency behavior of the first and second order FRFs for the four models analyzed.

	Slope of the amplitude for $\omega \to \infty$			Phase for $\omega \to \infty$	
Model	$G_1(\omega)$	$G_2(\omega,\omega)$	$G_2(\omega,-\omega)$	$G_1(\omega)$	$G_2(\omega,\omega)$
1	-0.5	-1.0	-0.5	$-\pi/4$	$-3\pi/2$
2	-0.5	-2.0	-1.0	$-\pi/4$	-2π
3	-1.0	-2.5	-1.5	$-\pi/2$	$-9\pi/4$
4	-1.0	-3.5	-2.0	$-\pi/2$	$-11\pi/4$

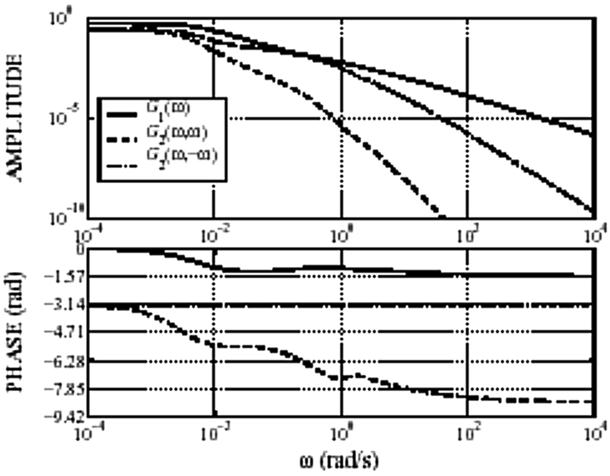

Figure 4. The first and second order FRFs for MODEL 4 (micropore-macropore-adsorption-film mechanism).

The first and second order FRFs were simulated for these four cases. A choice of the simulation results, corresponding to MODELS 1, 2, 3 and 4 is given in Figs. 1–4, respectively. Standard Bodé plot representation is used in these figures (amplitudes in log-log and phases in semi-log diagrams).

The results presented in these figures correspond to equal time constants for all mass transfer mechanisms taken into consideration (100 s).

Some of the characteristic features of these functions can be observed in the high frequency range: the slopes of the amplitudes and the asymptotic values of the phases, for $\omega \to \infty$. These features are summarized in Table 1, for the four models analyzed.

Conclusions

The analysis of the high frequency asymptotes of the first and second order FRFs for four complex mechanisms (micropore-macropore, micropore-macropore-adsorption, micropore-macropore-film and micropore-macropore-adsorption-film) shows that the slopes of the high-frequency asymptotes of the amplitudes of $G_2(\omega, \omega)$ and $G_2(\omega, -\omega)$ as well as the high-frequency asymptotes of the phases of $G_2(\omega, \omega)$ have different values for all four models. Using this fact, one could identify the correct model for adsorption on a bidispersed sorbent (i.e. the mechanisms playing role in it), supposing that nonlinear frequency response experimental data, which could be used for estimation of the first and second order FRFs, were available.

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