

Investigation of gas transport through porous membranes based on nonlinear frequency response analysis

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Abstract Theoretical development of a new experimental method for investigation of mass transport in porous membranes, based on the principle of the modified Wicke-Kallenbach diffusion cell and the nonlinear frequency response analysis is presented. The method is developed to analyze the transport of a binary gas mixture in a porous membrane. The mixture is assumed to consist of one adsorbable and one inert component. Complex mass transfer mechanism in the membrane, where bulk or transition diffusion in the pore volume and surface diffusion take place in parallel, is assumed. Starting from the basic mathematical model equations and following a rather standardized procedure, the frequency response functions (FRFs) up to the second order are derived. Based on the derived FRFs, correlations between some characteristic features of these functions

on one side, and the whole set of equilibrium and transport parameters of the system, on the other, are established. As the FRFs can be estimated directly from different harmonics of the measured outputs, these correlations give a complete theoretical basis for the proposed experimental method. The method is illustrated by quantifying the transport of helium (inert gas) and C₃H₈ and CO₂ (adsorbable gases) through a porous Vycor glass membrane.

Keywords Porous membranes · Mass transfer mechanisms · Frequency response functions · Transition diffusion · Surface diffusion · Knudsen diffusion

Notation

A	Input amplitude, general and of the dimensionless partial pressure of the adsorbable component in the feed stream
$a_{i,j}$	Dimensionless first derivative of the pore diffusivity
a_s	Dimensionless first derivative of the surface diffusivity
a_Φ	Dimensionless first derivative of the adsorption isotherm
B	Output amplitude, general
b_Φ	Dimensionless second derivative of the adsorption isotherm
D_p , m ² /s	Pore diffusivity
D_s , m ² /s	Surface diffusivity
F_n	n -th order FRF corresponding to the dimensionless partial pressure of the adsorbable component in the closed chamber
G_n	n -th order FRF corresponding to the dimensionless partial pressure of the inert component in the closed chamber

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H_n	n -th order FRF corresponding to the dimensionless total pressure in the closed chamber
J , mol/m ² /s	molar flux
K	Auxiliary parameter (Table 1)
L , m	Membrane thickness
P , Pa	Pressure
p	Dimensionless pressure
Q , mol/m ³	Concentration in the solid phase
q	Dimensionless concentration in the solid phase
R , J/mol/K	Gas constant
T , K	Temperature
V , m ³	Volume
x	Input, general
y	Output, general
z , m	Spatial coordinate

Greek symbols

α	Auxiliary parameter (Table 1)
β	Auxiliary parameter (Table 1)
ε	Porosity
Φ	Adsorption isotherm relation
ϕ	Auxiliary parameter (Table 1)
γ	Auxiliary parameter (Table 1)
φ , rad	Phase shift
τ	Tortuosity factor
ω , rad/s	Frequency

Subscripts

1	Adsorbable component
2	Inert component
I	Open chamber, first harmonic
II	Closed chamber, second harmonic
III	Third harmonic
ads	Adsorbed phase
atm	Atmospheric
g	Gas phase
i	Component i
s	Steady-state
tot	Total

Superscripts

0	Feed
*	Auxiliary FRF

Abbreviations

FR	Frequency response
FRF	Frequency response function

1 Introduction

During the last two decades, remarkable separation effects of microporous and mesoporous membranes have been doc-

umented in the literature (e.g. Janovski and Enke 2002; Baker 2004). Investigation of mass transport in microporous and mesoporous glass membranes has been in the focus of many research groups, including ours (Marković et al. 2010, 2009a, 2009b; Řezníčková Čermaková et al. 2008; Yang et al. 2005; Schlünder et al. 2006; Tuchlenski et al. 1998). Generally, we can say that transport in porous membranes is complex and difficult to predict, with complex mechanisms of gas transport that are still not completely understood. Therefore there is still a need for establishing new and reliable methods which would lead to better understanding of the mass transfer mechanisms and estimating the equilibrium and transport parameters in porous membranes.

Recently, a nonlinear frequency response method for investigation of mass transfer mechanisms in adsorption systems has been developed (Petkovska 2006). It has been shown that it can be useful for identification of the correct kinetic mechanism and for estimation of the equilibrium and kinetic parameters (Petkovska 2006). Some theoretical analysis of nonlinear frequency response of membrane systems have also been performed, for permeation of single gases (Petkovska and Petkovska 2006). This analysis was applied to three different transport mechanisms: solution-diffusion, pore-surface diffusion and viscous flow. It has led to a more general definition and understanding of the membrane permeability, as well as to a methodology for estimation of the equilibrium and kinetic parameters defining the mass transfer (Petkovska and Petkovska 2006).

The aim of this paper is to study the possible applicability of the frequency response method for investigation of permeation of binary gas mixtures, composed of one adsorbable and one non-adsorbable (inert) gas, in porous membranes. The theoretical analysis performed in this work can serve as a basis for developing and applying an experimental technique. The method is illustrated for an experimental system based on modified Wicke-Kallenbach diffusion cell (Novak et al. 1988; Marković et al. 2010; Marković 2009).

2 Some theoretical basics

2.1 Mass transfer mechanisms through porous membranes

Diffusion in porous membranes at normal pressure can be described assuming that the pore space is divided into two separate regions: an internal void filled with a diluted gas, surrounded by the pore walls covered (or not) with a condensed layer of gas molecules (adsorbed phase).

Interactions of the gas molecules in the condensed layer with the pore walls can be described by sorption isotherms which describe the quickly establishing equilibrium between the adsorbed and the local gas concentrations. Gas

diffusion can be described by molecular flow, defined by molecule–molecule and molecule–wall collisions.

One-dimensional mass transfer of a gas specie i through a porous medium can be defined assuming parallel transport occurring in the adsorbed phase and in the void volume, so the total mass flux of component i can be expressed as a sum of the fluxes in the adsorbed and in the gas phase (e.g. Do 1998):

$$J_{tot,i} = J_{ads,i} + J_{g,i} \quad (1)$$

Using the common Fickian definition, the flux in the adsorbed phase in the z direction can be expressed as:

$$J_{ads,i} = -(1 - \varepsilon) D_{s,i} \frac{\partial Q_i}{\partial z} \quad (2)$$

where $D_{s,i}$ is the surface diffusivity of component i , which, in principle, depends on the concentrations of the adsorbed species:

$$D_{s,i} = f(Q_i, Q_j, \dots) \quad (3)$$

In (2) Q_i is the concentration of specie i in the adsorbed phase and ε is the porosity.

On the other hand, the flux in the gas phase in the pore void is defined as:

$$J_{g,i} = -\frac{\varepsilon}{RT\tau} D_{p,i} \frac{\partial P_i}{\partial z} \quad (4)$$

where P_i is the partial pressure of component i in the pores, τ is the so-called tortuosity factor, T is temperature, R the gas constant and $D_{p,i}$ the pore diffusivity of component i . This pore diffusivity quantifies the interactions of the gas molecules in the pore with the pore walls and/or with other gas molecules. Depending on the ratio of the mean free path of the molecule and the pore diameter (the Knudsen number), one or the other interaction can be dominant. For large Knudsen numbers (the Knudsen regime) the interactions of the molecules with the pore walls are determining the mass flux, and the corresponding diffusivity is independent from the gas pressure and composition. On the other hand, at lower Knudsen numbers (transition or bulk regime) the interactions between the gas molecules also influence the mass flux and the pore diffusivity depends on the gas pressure and composition, i.e. on the partial pressures of all components:

$$D_{p,i} = f(P_1, P_2, \dots) \quad (5)$$

For larger pressure differences the contribution of viscous flow should also be taken into account.

In our previous investigations (Marković et al. 2010; Marković 2009) we have used a modified Wicke-Kallenbach cell for investigation of mass transfer in porous glass membranes. The schematic representation of the cell is given in Fig. 1.

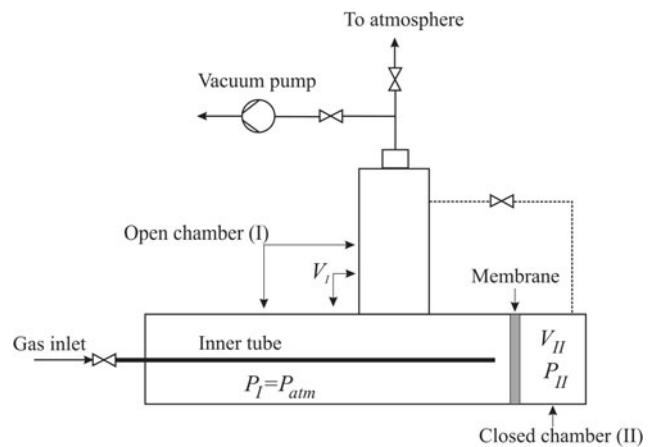


Fig. 1 The modified Wicke-Kallenbach cell—schematic picture

The cell is comprised of two cylindrical chambers divided by the investigated membrane. One, larger chamber is open to the atmosphere, so the pressure in it equals the atmospheric pressure, while the other, smaller chamber is closed and the pressure in it changes owing to the permeation flux. The inner tube in the open chamber is used to introduce the feed gas mixture directly to the membrane surface, so that the gas composition at the surface of the membrane facing to chamber I can be considered equal to the composition of the feed stream. Modulation of this feed composition results with changes of the permeation fluxes of both components through the membrane, and consequently, with changes of the pressure in the closed chamber. In our previous investigations, step modulations were used for investigation of single and binary gas permeation (Marković et al. 2009a, 2009b, 2010; Marković 2009). In this paper, we analyze the possible applicability of sinusoidal modulation of the feed composition, and the potential gain of such operation of the described modified Wicke-Kallenbach cell.

2.2 Nonlinear frequency response

Nonlinear frequency response (FR) is a response of a nonlinear system to a sinusoidal or a co-sinusoidal input perturbation. It has been proven to be a very useful tool for practical investigation of weakly nonlinear systems (Weiner and Spina 1980). A convenient approach used for treatment of frequency response of weakly nonlinear systems is the concept of higher order frequency response functions (FRFs) (Weiner and Spina 1980), which is based on Volterra series and generalized Fourier transform. For some time, this concept has been used for analysis of weakly nonlinear electrical and mechanical systems, as well as in control engineering (Weiner and Spina 1980). In our work, we have been using it for investigation of adsorption kinetics and equilibria (Petkovska and Do 1998, 2000; Petkovska 1999, 2000, 2001, 2005; Petkovska and Petkovska 2003).

The most important results of this investigation are that it is possible to discriminate between different kinetic mechanisms using the higher order FRFs (Petkovska and Do 2000; Petkovska and Petkovska 2003; Petkovska 2005) and that both kinetic and equilibrium parameters, including the ones defining the system nonlinearity, can be estimated from the same set of experimental data (Petkovska 1999, 2000, 2006). More details about nonlinear FR and the concept of higher order FRFs can be found in our previous publications, e.g. (Petkovska 2006). Below we give only some basics.

Contrary to the linear FR, which consists only of the basic (first) harmonic, the nonlinear FR also contains a nonperiodic (DC) component and an indefinite number of higher harmonics. Thus, a response of a weakly nonlinear system to a co-sinusoidal change of frequency ω and amplitude A , around its steady state value y_s , can be expressed in the following way:

$$\begin{aligned} y &= y_s + y_{DC} + y_I + y_{II} + y_{III} + \dots \\ &= y_s + y_{DC} + B_I \cos(\omega t + \varphi_I) + B_{II} \cos(2\omega t + \varphi_{II}) \\ &\quad + B_{III} \cos(3\omega t + \varphi_{III}) + \dots \end{aligned} \quad (6)$$

The concept of higher order FRFs assumes replacement of the nonlinear model \mathbf{G} with an indefinite sequence of linear functions (FRFs) of the first, second, third, etc. order: G_1, G_2, G_3 , etc., corresponding to different degrees of nonlinearity (Weiner and Spina 1980). The output of a weakly nonlinear system can be represented in a Volterra series form (Weiner and Spina 1980). For a single harmonic input, the Volterra series becomes:

$$\begin{aligned} y &= y_s + \frac{A}{2} \{ G_1(\omega) e^{j\omega t} + G_1(-\omega) e^{-j\omega t} \} \\ &\quad + \left(\frac{A}{2} \right)^2 \{ G_2(\omega, \omega) e^{2j\omega t} + G_2(-\omega, -\omega) e^{-2j\omega t} \} \\ &\quad + 2G_2(\omega, -\omega) e^0 \} \\ &\quad + \left(\frac{A}{2} \right)^3 \{ G_3(\omega, \omega, \omega) e^{3j\omega t} \\ &\quad + G_3(-\omega, -\omega, -\omega) e^{-3j\omega t} \} \\ &\quad + 3G_3(\omega, \omega, -\omega) e^{j\omega t} \\ &\quad + 3G_3(-\omega, -\omega, \omega) e^{-j\omega t} \} + \dots \end{aligned} \quad (7)$$

By collecting the constant terms in (7), we obtain the DC component:

$$\begin{aligned} y_{DC} &= 2(A/2)^2 G_2(\omega, -\omega) \\ &\quad + 6(A/2)^4 G_4(\omega, \omega, -\omega, -\omega) + \dots \end{aligned} \quad (8)$$

by collecting the periodic terms of frequency ω , the first harmonic:

$$y_I = B_I \cos(\omega t + \varphi_I)$$

$$\begin{aligned} &= \{ (A/2) G_1(\omega) + 3(A/2)^3 G_3(\omega, \omega, -\omega) + \dots \} e^{j\omega t} \\ &\quad + \{ (A/2) G_1(-\omega) \\ &\quad + 3(A/2)^3 G_3(\omega, -\omega, -\omega) + \dots \} e^{-j\omega t} \end{aligned} \quad (9)$$

by collecting the periodic terms of frequency 2ω , the second harmonic:

$$\begin{aligned} y_{II} &= B_{II} \cos(2\omega t + \varphi_{II}) \\ &= \{ (A/2)^2 G_2(\omega, \omega) \\ &\quad + 4(A/2)^4 G_4(\omega, \omega, \omega, -\omega) + \dots \} e^{2j\omega t} \\ &\quad + \{ (A/2)^2 G_2(-\omega, -\omega) \\ &\quad + 4(A/2)^4 G_4(\omega, -\omega, -\omega, -\omega) + \dots \} e^{-2j\omega t} \end{aligned} \quad (10)$$

by collecting the periodic terms of frequency 3ω , the third harmonic:

$$\begin{aligned} y_{III} &= B_{III} \cos(3\omega t + \varphi_{III}) \\ &= \{ (A/2)^3 G_3(\omega, \omega, \omega) \\ &\quad + 5(A/2)^5 G_5(\omega, \omega, \omega, -\omega, -\omega) + \dots \} e^{3j\omega t} \\ &\quad + \{ (A/2)^3 G_3(-\omega, -\omega, -\omega) \\ &\quad + 5(A/2)^5 G_5(\omega, \omega, -\omega, -\omega, -\omega) + \dots \} e^{-3j\omega t}, \end{aligned} \quad (11)$$

etc.

The first order function $G_1(\omega)$ corresponds to the dominant term of the first harmonic, the symmetrical second order function $G_2(\omega, \omega)$ to the dominant term of the second harmonic, the asymmetrical second order function $G_2(\omega, -\omega)$ to the dominant term of the DC component, the third order function $G_3(\omega, \omega, \omega)$ to the dominant term of the third harmonic, etc. There are established procedures for estimation of the FRFs from the amplitudes and phases of different harmonics of the output (Lee 1997), which, on the other hand, are easily obtained by Fourier analysis of the output signal.

In this paper we derive the FRFs up to the second order for permeation of binary gas mixtures (one adsorbable plus one inert component) through porous membranes placed in a modified Wicke-Kallenbach cell and we investigate what information about the mass transfer mechanisms and parameters can be withdrawn from them.

3 Mathematical models

In order to derive the frequency response functions, it is first necessary to postulate the starting model equations. These equations are generally nonlinear.

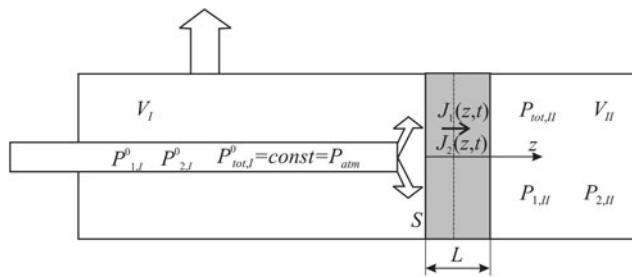


Fig. 2 The modified Wicke-Kallenbach diffusion cell—the main system parameters and variables

3.1 System definition

The nonlinear frequency response method for investigation of mass transport in porous membranes will be developed and illustrated for an experimental system based on the modified Wicke-Kallenbach diffusion cell, which was schematically shown in Fig. 1. In Fig. 2 we show an even more simplified representation in which the main system parameters and variables are defined. The following notation is used in this figure: P_1 , P_2 and P_{tot} are the partial pressures of component 1 and 2 and the total pressure, respectively, J_1 and J_2 are the mass fluxes of components 1 and 2 through the membrane, V is volume, S is the membrane surface area and L is the membrane thickness. The subscripts I and II correspond to the first (open) and second (closed) chamber, respectively, while the superscript 0 corresponds to the feed stream.

The assumptions about the system, used in our further analysis, can be summarized as follows:

- The binary gas mixture is composed of one adsorbable (1) and one nonadsorbable (inert) component (2).
- Initially, the system is in total equilibrium.
- The total pressure in the open chamber is constant.
- The system is isothermal.
- No film resistance to mass transfer at the membrane surfaces exists.
- No back mixing of the flow introduced to the membrane in the open chamber exists, so the composition at the left surface of the membrane is identical to the composition of the inlet flow.
- The gas phase in the closed chamber (II) is ideally mixed.
- The gas in the pores is in local equilibrium with the adsorbed phase.

3.2 Model equations

The model equations consist of the material balance equations for the membrane and the closed cell, for both components. They are listed below:

– The material balance for the adsorbable gas (component 1) in the membrane includes contributions of the gas and adsorbed phase fluxes:

$$\begin{aligned} \frac{\varepsilon}{R} T \frac{\partial P_1(z, t)}{\partial t} + (1 - \varepsilon) \frac{\partial Q_1(z, t)}{\partial t} \\ = - \frac{\partial}{\partial z} \left(\frac{\partial J_{g,i}}{\partial z} \right) - \frac{\partial}{\partial z} \left(\frac{\partial J_{ads,i}}{\partial z} \right) \end{aligned} \quad (12)$$

Using the expression for the adsorbed and gas fluxes defined in (2) and (4) the material balance can be written explicitly:

$$\begin{aligned} \frac{\varepsilon}{R} T \frac{\partial P_1(z, t)}{\partial t} + (1 - \varepsilon) \frac{\partial Q_1(z, t)}{\partial t} \\ = \frac{\varepsilon}{RT\tau} \frac{\partial}{\partial z} \left(D_{p1} \frac{\partial P_1(z, t)}{\partial z} \right) \\ + (1 - \varepsilon) \frac{\partial}{\partial z} \left(D_{s1} \frac{\partial Q_1(z, t)}{\partial z} \right) \end{aligned} \quad (13)$$

According to assumption (viii) (local equilibrium), Q_1 and P_1 are related via an adsorption isotherm relation Φ , which is generally nonlinear:

$$Q_1 = \Phi(P_1) \quad (14)$$

Also, in principle, the pore and surface diffusivities are concentration dependent:

$$D_{p1} = f_1(P_1, P_2) \quad (15)$$

$$D_{s1} = g_1(Q_1) \quad (16)$$

The boundary conditions for (13) are:

– For the left surface of the membrane:

$$z = 0 : P_1(z, t)|_{z=0} = P_{1,I}^0 \quad (17)$$

– For the right surface of the membrane:

$$z = L : \left. \frac{V_{II}}{RT} \frac{\partial P_1(z, t)}{\partial t} \right|_{z=L} = S J_1(z, t)|_{z=L} \quad (18)$$

At the same time, (18) represents the material balance for the closed chamber.

– The material balance for the inert gas (component 2) in the membrane does not include adsorption and surface diffusion effects, but only the contribution of pore diffusion:

$$\frac{\varepsilon}{R} T \frac{\partial P_2(z, t)}{\partial t} = \frac{\varepsilon}{RT\tau} \frac{\partial}{\partial z} \left(D_{p2} \frac{\partial P_2(z, t)}{\partial z} \right) \quad (19)$$

In principle, the diffusivity of this component is also concentration dependent:

$$D_{p2} = f_2(P_1, P_2) \quad (20)$$

The boundary conditions for (19) are:

– For the left surface of the membrane:

$$z=0: \quad P_2(z, t)|_{z=0} = P_{2,I}^0 \quad (21)$$

– For the right surface of the membrane:

$$z=L: \quad \frac{V_H}{RT} \cdot \frac{\partial P_2(z, t)}{\partial t} \Big|_{z=L} = S J_2(z, t)|_{z=L} \quad (22)$$

The contribution of viscous flow was neglected in (12), (13) and (19), owing to small transmembrane pressure differences in the Wicke-Kallenbach cell.

In these equations, the same notations were used as in Sect. 2.1 and in Fig. 2.

For analysis in the frequency domain, it is more convenient to deal with dimensionless input and output variables. The definitions of the new variables are:

$$p_i = \frac{P_i - P_{i,s}}{P_{atm}}, \quad i = 1, 2 \quad (23)$$

$$q_1 = \frac{Q_1 - Q_{1,s}}{Q_{1,s}} \quad (24)$$

In order to apply the concept of higher order FRFs, all non-linear expressions ((14), (15), (16) and (20)) are replaced by their Taylor series expansions around their steady state values:

$$q_1 = a_{\Phi 1} p_1 + b_{\Phi 1} p_1^2 + \dots \quad (25)$$

$$D_{s1} = D_{s1,s} (1 + a_{s1} q_1 + b_{s1} q_1^2 + \dots) \quad (26)$$

$$D_{pi} = D_{pi,s} (1 + a_{i,1} p_1 + a_{i,2} p_2 + b_{i,1} p_1^2 + b_{i,2} p_1 p_2 + b_{i,2} p_2^2 + \dots), \quad i = 1, 2 \quad (27)$$

The coefficients of the Taylor series used in these equations are defined in the following way:

$$a_{\Phi 1} = \frac{P_{atm}}{Q_{1,s}} \frac{\partial Q_1}{\partial P_1} \Big|_s, \quad b_{\Phi 1} = \frac{1}{2} \frac{P_{atm}^2}{Q_{1,s}} \frac{\partial^2 Q_1}{\partial P_1^2} \Big|_s, \quad \dots \quad (28)$$

$$a_{s1} = \frac{Q_{1,s}}{D_{s1,s}} \frac{\partial D_{s1}}{\partial Q_1} \Big|_s, \quad b_{s1} = \frac{1}{2} \frac{Q_{1,s}^2}{D_{s1,s}} \frac{\partial^2 D_{s1}}{\partial Q_1^2} \Big|_s, \quad \dots \quad (29)$$

$$\begin{aligned} a_{i,1} &= \frac{P_{atm}}{D_{pi,s}} \frac{\partial D_{pi}}{\partial P_1} \Big|_s, & a_{i,2} &= \frac{P_{atm}}{D_{pi,s}} \frac{\partial D_{pi}}{\partial P_2} \Big|_s, \\ b_{i,1} &= \frac{1}{2} \frac{P_{atm}^2}{D_{pi,s}} \frac{\partial^2 D_{pi}}{\partial P_1^2} \Big|_s, & b_{i,2} &= \frac{1}{2} \frac{P_{atm}^2}{D_{pi,s}} \frac{\partial^2 D_{pi}}{\partial P_2^2} \Big|_s, \quad (30) \\ b_{i,1} &= \frac{P_{atm}^2}{D_{pi,s}} \frac{\partial^2 D_{pi}}{\partial P_1 \partial P_2} \Big|_s, & \dots, \quad i &= 1, 2 \end{aligned}$$

By introducing these new definitions into the model (13)–(22), the following set of dimensionless equations is obtained:

– The material balance for the adsorbable component in the membrane:

$$\begin{aligned} \frac{\partial^2 p_1}{\partial z^2} &= \alpha_1 \frac{\partial p_1}{\partial t} + \gamma_1 \frac{\partial (p_1^2)}{\partial t} + \beta_1 \frac{\partial^2 (p_1^2)}{\partial z^2} \\ &\quad + 2\phi_1 \frac{\partial}{\partial z} \left(p_2 \frac{\partial p_1}{\partial z} \right) + \dots \end{aligned} \quad (31)$$

with the following boundary conditions:

$$z=0: \quad p_1(0, t) = p_{1,I}^0 \quad (32)$$

$$\begin{aligned} z=L: \quad \frac{\partial p_1}{\partial z} \Big|_{z=L} + \frac{1}{KD_{eff,1}} \frac{\partial p_1}{\partial t} \Big|_{z=L} \\ = \left(\beta_1 \frac{\partial p_1^2}{\partial z} + 2\phi_1 p_2 \frac{\partial p_1}{\partial z} + \dots \right) \Big|_{z=L} \end{aligned} \quad (33)$$

– The material balance for the non-adsorbable component in the membrane:

$$\frac{\partial^2 p_2}{\partial z^2} = \alpha_2 \frac{\partial p_2}{\partial t} + \beta_2 \frac{\partial^2 (p_2^2)}{\partial z^2} + 2\phi_2 \frac{\partial}{\partial z} \left(p_1 \frac{\partial p_2}{\partial z} \right) + \dots \quad (34)$$

with the following boundary conditions:

$$z=0: \quad p_2(0, t) = p_{2,I}^0 = -p_{1,I}^0 \quad (35)$$

$$\begin{aligned} z=L: \quad \frac{\partial p_2}{\partial z} \Big|_{z=L} + \frac{1}{KD_{eff,2}} \frac{\partial p_2}{\partial t} \Big|_{z=L} \\ = \left(\beta_2 \frac{\partial p_2^2}{\partial z} + 2\phi_2 p_1 \frac{\partial p_2}{\partial z} + \dots \right) \Big|_{z=L} \end{aligned} \quad (36)$$

Only the first and second order terms are shown explicitly in these equations. The definitions of the auxiliary parameters introduced in these equations are given in Table 1.

A somewhat simpler model, corresponding to the Knudsen regime of pore diffusion (lower mesopores range), was also considered. In this model, the pore diffusivities were constant, i.e., the coefficients $a_{1,1}, a_{1,2}, a_{2,1}, a_{2,2}$, etc., are all zero. For this case, some auxiliary parameters defined in Table 1 become zero (ϕ_1, ϕ_2 and β_2), and some are simplified:

$$\beta_1 = -\frac{1}{2} \frac{(1-\varepsilon) D_{s1,s} Q_{1,s} (2b_{\Phi 1} + a_{s1} a_{\Phi 1}^2)}{D_{eff,1}}$$

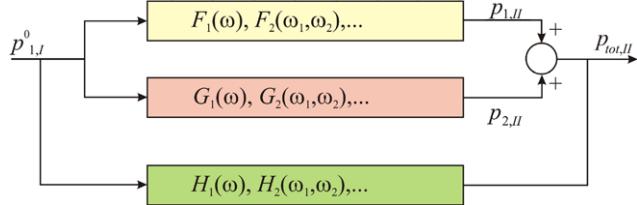
4 Frequency response functions

4.1 Definitions of the inputs, outputs and transfer functions

In the analyzed system, the total pressure of the gas in the open chamber (I) is kept constant, while the gas composition

Table 1 Auxiliary parameters used in (31)–(36)

$K = \frac{SRT}{V_{II} P_{atm}}$	$D_{eff,2} = \frac{\varepsilon}{RT\tau} P_{atm} D_{p2,s}$
$D_{eff,1} = \frac{\varepsilon}{RT\tau} P_{atm} D_{p1,s} + (1 - \varepsilon) D_{s1,s} Q_{1,s} a_{\Phi 1}$	$\alpha_2 = \frac{\tau}{D_{p2,s}}$
$\alpha_1 = \frac{\varepsilon/RT P_{atm} + (1 - \varepsilon) Q_{1,s} a_{\Phi 1}}{D_{eff,1}}$	$\beta_2 = -\frac{1}{2} a_{2,2}$
$\beta_1 = -\frac{1}{2} \frac{\varepsilon/RT P_{atm} D_{p1,s} a_{1,1} + (1 - \varepsilon) D_{s1,s} Q_{1,s} (2b\Phi_1 + a_{s1} a_{\Phi 1}^2)}{D_{eff,1}}$	$\phi_2 = -\frac{1}{2} a_{2,1}$
$\gamma_1 = \frac{(1 - \varepsilon) Q_{1,s} b\Phi_1}{D_{eff,1}}$	
$\phi_1 = -\frac{1}{2} \frac{\varepsilon/RT P_{atm} D_{p1,s} a_{1,2}}{D_{eff,1}}$	

**Fig. 3** Block-diagram representation of the modified Wicke-Kallenbach diffusion cell

(the partial pressures of the components) can change in time. For the binary system considered, this change can be defined as only one input, e.g. the partial pressure of component 1, while the partial pressure of component 2 is changing in the opposite direction:

$$P_{2,I}^0(t) = P_{tot,I}^0 - P_{1,I}^0(t) = P_{atm} - P_{1,I}^0(t) \quad (37)$$

or, in the dimensionless form:

$$p_{2,I}^0(t) = -p_{1,I}^0(t) \quad (38)$$

On the other hand, as a result of this change, the partial pressures of both components, as well as the total pressure in the closed chamber (II) are changing, i.e., they have to be considered as outputs.

Therefore, our system can be represented by the block-diagram shown in Fig. 3.

In Fig. 3 the following notations have been used: (a) $F_1(\omega), F_2(\omega, \omega), \dots$ is the set of FRFs relating the change of the partial pressure of component 1 (adsorbable) in the closed chamber (II) and the modulation of the partial pressure of component 1 in the feed stream, (b) $G_1(\omega), G_2(\omega, \omega), \dots$ is the set of FRFs relating the change of the partial pressure of component 2 (inert) in the closed chamber (II) and the modulation of the partial pressure of component 1 in the feed stream and (c) $H_1(\omega), H_2(\omega, \omega), \dots$ is the set of FRFs relating the change of the total pressure in the closed chamber (II) and the modulation of the partial pressure of component 1 in the feed stream. For a co-sinusoidal modulation of the input:

$$p_{1,I}^0(t) = A \cos(\omega t) = \frac{A}{2} e^{j\omega t} + \frac{A}{2} e^{-j\omega t} \quad (39)$$

the outputs can be expressed as the following indefinite Volterra series:

$$\begin{aligned} p_{1,II}(t) &= \frac{A}{2} (F_1(\omega) e^{j\omega t} + F_1(-\omega) e^{-j\omega t}) \\ &+ \left(\frac{A}{2} \right)^2 (F_2(\omega, \omega) e^{2j\omega t} + 2F_2(\omega, -\omega) e^0 \\ &+ F_2(-\omega, -\omega) e^{-2j\omega t}) + \dots \end{aligned} \quad (40)$$

$$\begin{aligned} p_{2,II}(t) &= \frac{A}{2} (G_1(\omega) e^{j\omega t} + G_1(-\omega) e^{-j\omega t}) \\ &+ \left(\frac{A}{2} \right)^2 (G_2(\omega, \omega) e^{2j\omega t} + 2G_2(\omega, -\omega) e^0 \\ &+ G_2(-\omega, -\omega) e^{-2j\omega t}) + \dots \end{aligned} \quad (41)$$

$$\begin{aligned} p_{tot,II}(t) &= \frac{A}{2} (H_1(\omega) e^{j\omega t} + H_1(-\omega) e^{-j\omega t}) \\ &+ \left(\frac{A}{2} \right)^2 (H_2(\omega, \omega) e^{2j\omega t} + 2H_2(\omega, -\omega) e^0 \\ &+ H_2(-\omega, -\omega) e^{-2j\omega t}) + \dots \end{aligned} \quad (42)$$

4.2 Derivation of the frequency response functions

The derivation of higher order FRFs is standard and can be found in some of our previous publications (e.g. Petkovska 2006). It generally comprises of the following steps:

(1) Defining the input in the form of a co-sinusoidal function (see (39)).

(2) Expressing the partial pressures of both components in the Volterra series form:

$$\begin{aligned} p_1(z, t) &= \frac{A}{2} (F_1^*(z, \omega) e^{j\omega t} + F_1^*(z, -\omega) e^{-j\omega t}) \\ &+ \left(\frac{A}{2} \right)^2 (F_2^*(z, \omega, \omega) e^{2j\omega t} + 2F_2^*(z, \omega, -\omega) e^0 \\ &+ F_2^*(z, -\omega, -\omega) e^{-2j\omega t}) + \dots \end{aligned} \quad (43)$$

$$\begin{aligned}
p_2(z, t) = & \frac{A}{2} (G_1^*(z, \omega) e^{j\omega t} + G_1^*(z, -\omega) e^{-j\omega t}) \\
& + \left(\frac{A}{2} \right)^2 (G_2^*(z, \omega, \omega) e^{2j\omega t} + 2G_2^*(z, \omega, -\omega) e^0 \\
& + G_2^*(z, -\omega, -\omega) e^{-2j\omega t}) + \dots
\end{aligned} \quad (44)$$

In these equations we have introduced two series of auxiliary FRFs, $F_1^*(z, \omega)$, $F_2^*(z, \omega, \omega)$, ... and $G_1^*(z, \omega)$, $G_2^*(z, \omega, \omega)$, ... , which are functions of frequency and the position in the membrane z . For $z = L$ these functions become identical to the corresponding F - and G -functions defined in (40) and (41), i.e., $F_1^*(L, \omega) = F_1(\omega)$, $F_2^*(L, \omega, \omega) = F_2(\omega, \omega)$, ... and $G_1^*(L, \omega) = G_1(\omega)$, and $G_2^*(L, \omega, \omega) = G_2(\omega, \omega)$.

(3) Substituting the expressions defined in steps 1 and 2 into the corresponding model equations and boundary conditions.

(4) Applying the method of harmonic probing to the equations obtained in Step 3 (collecting the terms with the same power of the input amplitude and same frequency and equating them to zero). In this step, the set of PDEs with p_1 and p_2 as dependent variables of z and t , is transformed into a larger set of ODEs, with F_1^* , F_2^* , ... and G_1^* , G_2^* , ... as dependent variables of z and frequency ω .

(5) Integration of the equations obtained in Step 4. As a result, the overall FRFs $F_1(\omega)$, $F_2(\omega, \omega)$, ... and $G_1(\omega)$, $G_2(\omega, \omega)$, ... are obtained. The H -functions are obtained by summing the corresponding F - and G -functions:

$$H_1(\omega) = F_1(\omega) + G_1(\omega) \quad (45)$$

$$H_2(\omega, \omega) = F_2(\omega, \omega) + G_2(\omega, \omega) \quad (46)$$

$$H_2(\omega, -\omega) = F_2(\omega, -\omega) + G_2(\omega, -\omega) \quad (47)$$

and so on.

The derivation procedure is recurrent, i.e., the first order FRFs have to be derived first, than the second, and so on.

The ODEs corresponding to the first and second order FRFs, obtained in Step 4 are given in [Appendix](#). These ODEs were integrated using the Matlab Symbolic Math Toolbox and the first and second order FRFs were derived. The resulting expressions are very cumbersome and therefore they are omitted from this manuscript. But, the derived functions were used for simulation and analysis.

4.3 Simulation and analysis of the frequency response functions

In order to graphically illustrate the shapes of the derived FRFs, they were simulated for a Vycor glass membrane and two different gas mixtures: propane/helium and carbon-dioxide/helium. For the Vycor glass membrane He acts as an inert (non-adsorbable component 2), while C_3H_8 and CO_2 are acting as adsorbable components (component 1)

Table 2 Numerical data used for simulations of the FRFs: the system parameters

Volume of the closed chamber	$V_H = 5 \text{ cm}^3$
Membrane surface area	$S = 1.766 \text{ cm}^2$
Pressure in the open chamber	$P_{atm} = 101.325 \text{ kPa}$
Steady-state partial pressure of component 1	$P_{1,s} = 5 \text{ kPa}$

Table 3 Numerical data used for simulations of the FRFs: the membrane properties

Membrane thickness	$L = 0.6 \text{ mm}$
Pore diameter	$d_p = 4.2 \text{ nm}$
Porosity	$\varepsilon = 0.249$
Tortuosity	$\tau = 10$

Table 4 Numerical data used for simulations of the FRFs: component parameters

Parameter	C_3H_8/He mixture	CO_2/He mixture
$a_{\Phi 1}$	19.0	19.4
$b_{\Phi 1}$	-23.3	-16.7
$D_{s1,s} \times 10^9 [\text{m}^2/\text{s}]$	1.352	3.01
a_{s1}	0.0643	0.0442
$D_{p1,s} \times 10^8 [\text{m}^2/\text{s}]$	1.467	1.504
$D_{p2,s} \times 10^8 [\text{m}^2/\text{s}]$	4.863	4.983
$a_{1,1} \times 10^4$	-4.02	-2.73
$a_{1,2} \times 10^4$	-4.02	-2.73
$a_{2,1} \times 10^4$	-13.3	-9.06
$a_{2,2} \times 10^4$	-13.3	-9.06

(Marković 2009). The numerical data used in these simulations are given in Table 2 (the system parameters), Table 3 (the membrane parameters) and Table 4 (the parameters corresponding to the adsorbable and non-adsorbable components).

The parameters listed in Table 4 were estimated based on our previous work (Marković 2009). It should be noticed that the derivative parameters, $a_{11} = a_{12}$ and $a_{21} = a_{22}$ are symmetrical. This is the consequence of using the Fuller-Schettler-Giddings correlation (Poling et al. 2000) for the pressure dependence of the diffusion parameters, which is symmetrical towards both partial pressures.

The simulated first and second order F -, G - and H -functions are shown in Fig. 4 (for the C_3H_8/He mixture) and Fig. 5 (for the CO_2/He mixture). Standard Bodé-plot representation is used (the amplitudes are represented in log-log and the phases in semi-log diagrams).

The following features of the FRFs can be observed from Figs. 4 and 5:

1. The first order function $F_1(\omega)$ tends to 1 (amplitude 1 and phase 0) when $\omega \rightarrow 0$, while $G_1(\omega)$ tends to -1 (amplitude -1 and phase 180°).

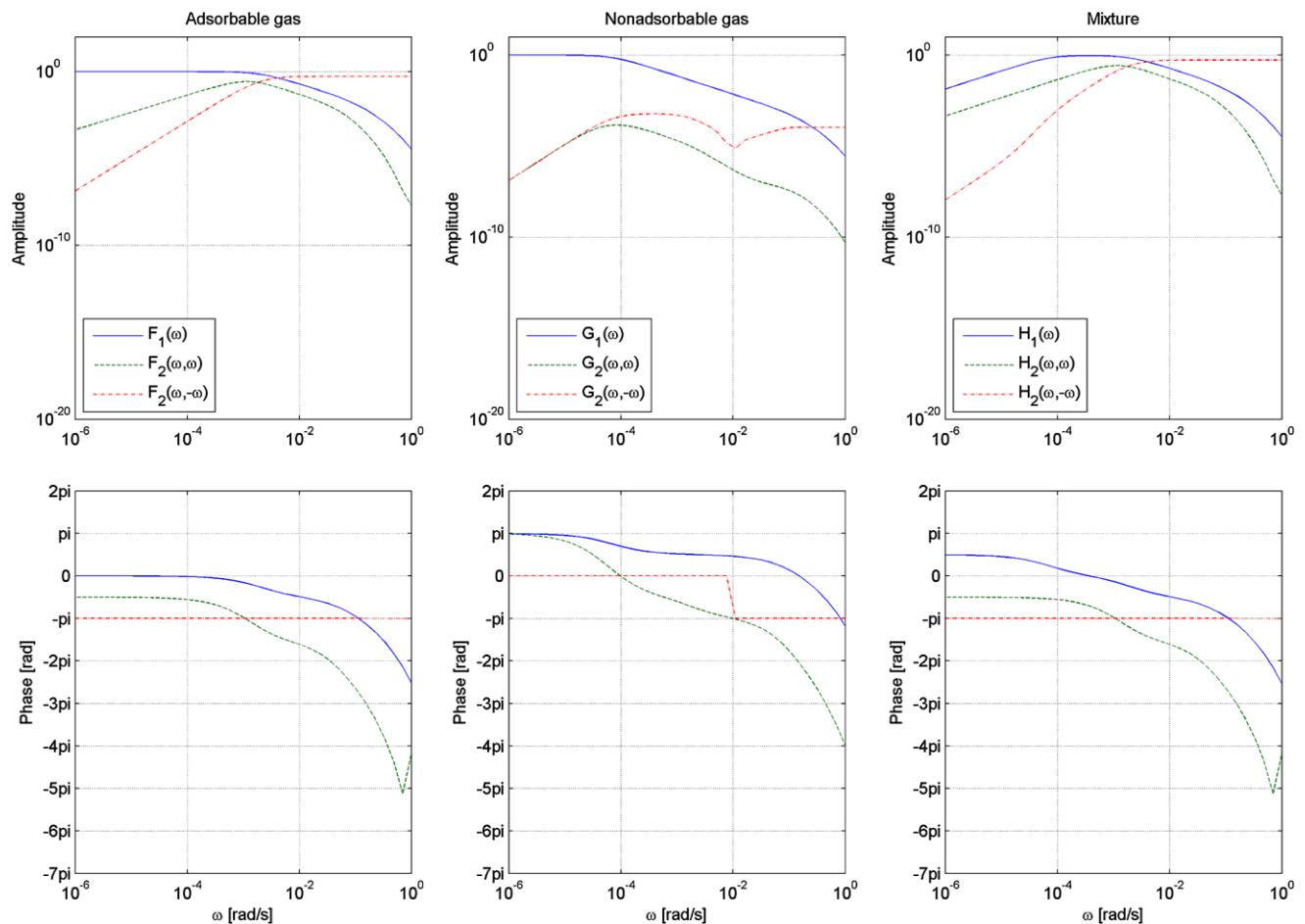


Fig. 4 The simulated first and second order F -, G - and H -functions, for the $\text{C}_3\text{H}_8/\text{He}$ mixture

tude 1 and phase π). At the same time the $H_1(\omega)$ function tend to 0 (amplitude 0 and phase $\pi/2$), with the slope of the low-frequency asymptote +1. This is in accordance with the physical behavior of the system, where for slow changes (low frequencies) of the input the components 1 and 2 interchange in the closed chamber, while the total pressure stays unchanged.

2. The symmetrical second order FRFs, $F_2(\omega, \omega)$, $G_2(\omega, \omega)$ and $H_2(\omega, \omega)$ all tend to 0 both at low and at high frequencies and go through wide maximums in the middle-frequency range. It should be noticed that the amplitudes of $F_2(\omega, \omega)$ are several orders of magnitude higher than the amplitudes of $G_2(\omega, \omega)$, which is a result of much stronger nonlinearity associated with component 1, originating from the nonlinearity of adsorption isotherm and variable surface and pore diffusivities, while the nonlinearity associated with component 2 is much weaker as it originates only from the variable pore diffusivity. The $H_2(\omega, \omega)$ function, which is the sum of $F_2(\omega, \omega)$ and $G_2(\omega, \omega)$, is therefore practically identical to $F_2(\omega, \omega)$. The slopes of the low-frequency asymptotes in the am-

plitude diagrams for $F_2(\omega, \omega)$, $G_2(\omega, \omega)$ and $H_2(\omega, \omega)$ are +1, +2 and +1, respectively.

3. The asymmetrical second order functions $F_2(\omega, -\omega)$, $G_2(\omega, -\omega)$ and $H_2(\omega, -\omega)$ tend to 0 for $\omega \rightarrow 0$ (the slopes in the amplitude graphs are for all three functions +2) and have horizontal asymptotes for $\omega \rightarrow \infty$. The behavior of the $G_2(\omega, -\omega)$ is especially interesting, with a sharp minimum corresponding to a change of sign (the phase changes from 0 to $-\pi$, which means that the function changes from positive to negative). In the low frequency range, $F_2(\omega, -\omega)$ and $G_2(\omega, -\omega)$ are of the same order of magnitude, so they both influence the $H_2(\omega, -\omega)$ function. For the CO_2/He system (Fig. 5) this even results with change of sign. In the high-frequency range the $F_2(\omega, -\omega)$ function becomes again predominant.

The simulation results obtained for the simplified model, considering only Knudsen diffusion in the pore diffusivity term, are shown in Figs. 6 and 7. For this case the G_2 -functions become nonexistent, as diffusion of the non-adsorbable component 2 with constant diffusivity is es-

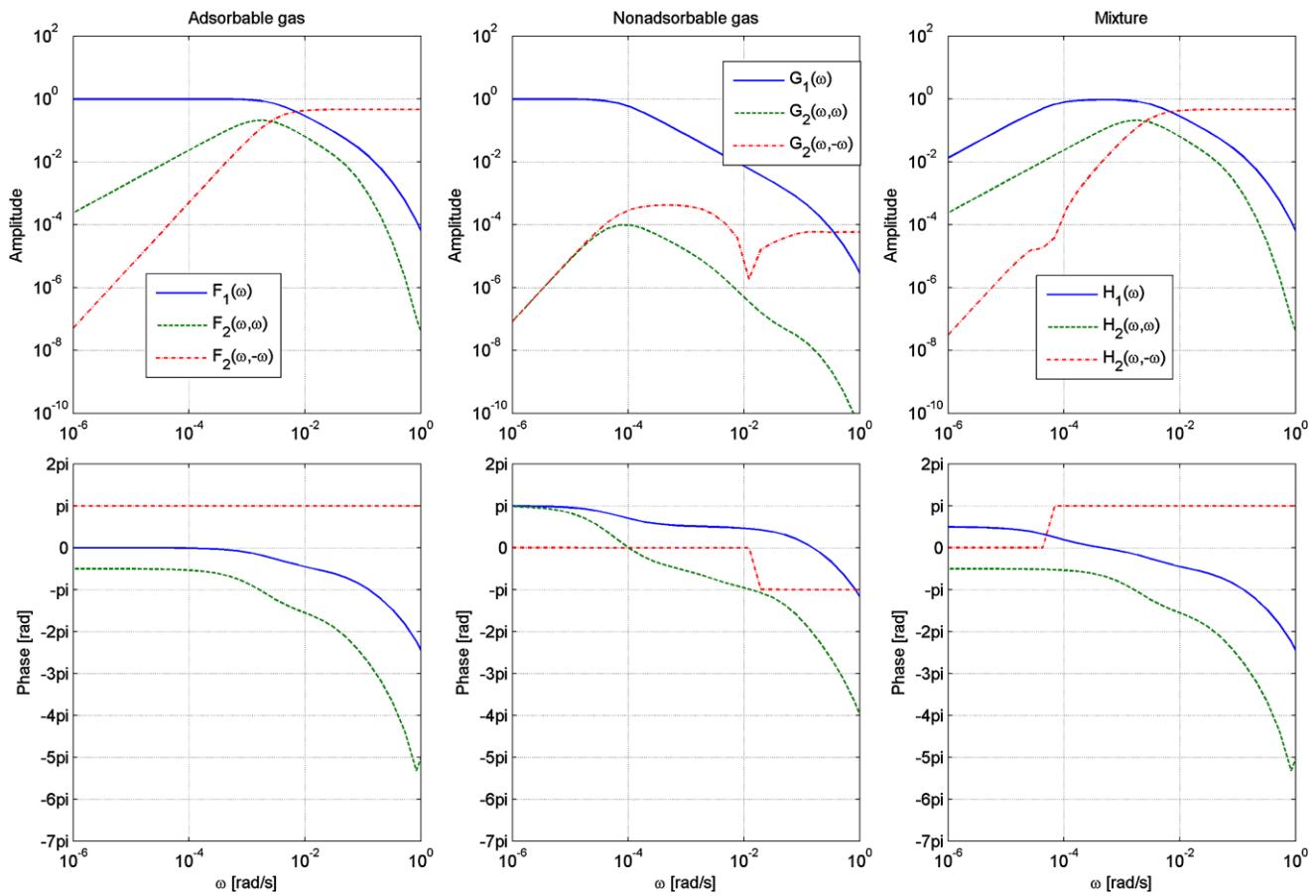


Fig. 5 The simulated first and second order F -, G - and H -functions, for the CO_2/He mixture

entially a linear process. As a consequence, $H_2(\omega, \omega) = F_2(\omega, \omega)$ and $H_2(\omega, -\omega) = F_2(\omega, -\omega)$.

One of the advantages of the nonlinear FR method over the linear methods which was observed in our investigation of adsorption systems is that it enables model discrimination based on the differences of shapes of the second order FRFs corresponding to different kinetic mechanisms (Petkovska and Do 2000; Petkovska and Petkovska 2003; Petkovska 2005). Therefore, it would be valuable if discrimination between the models corresponding to the bulk or transient regime and the Knudsen regime would be possible based on the shapes of the functions shown in Figs. 4 and 5 on one, and 6 and 7 on the other side. The most interesting in this sense are the H -functions which correspond to the change of the total pressure in the closed chamber, which can be easily measured.

The comparison of Figs. 6 and 4 and Figs. 7 and 5 shows that the only visible difference in shapes is in the amplitude diagram of the $H_2(\omega, -\omega)$ function in the lower frequency range. Figure 8 shows comparison of the amplitudes of the $H_2(\omega, -\omega)$ functions for the two models. The differences in the shapes of the corresponding functions are obvious for both systems. These differences become even more obvious

if the $H_2(\omega, -\omega)$ function is multiplied with the square of frequency (ω^2) and plotted versus frequency. Nevertheless, it should be noticed that the amplitudes of the $H_2(\omega, -\omega)$ functions have very low values in the low-frequency range, which can have a negative impact on the accuracy of their estimated values from experimental data.

Additionally, comparing the features of the functions obtained for adsorbable and nonadsorbable gases shows that it would be possible to distinguish whether a component is adsorbable or not, based on the shapes of the second order FRFs, even without any previous examination of gas adsorption affinity.

5 Estimation of the model parameters from the first and second order FRFs

The FRFs can, in principle, be estimated from frequency response experiments, by using (8)–(11), which relate these functions to the harmonics of the output. This procedure is well known and its details can be found in the literature e.g. (Petkovska 2006; Lee 1997). The final aim is to use these experimental FRFs for estimation of the main system parameters.

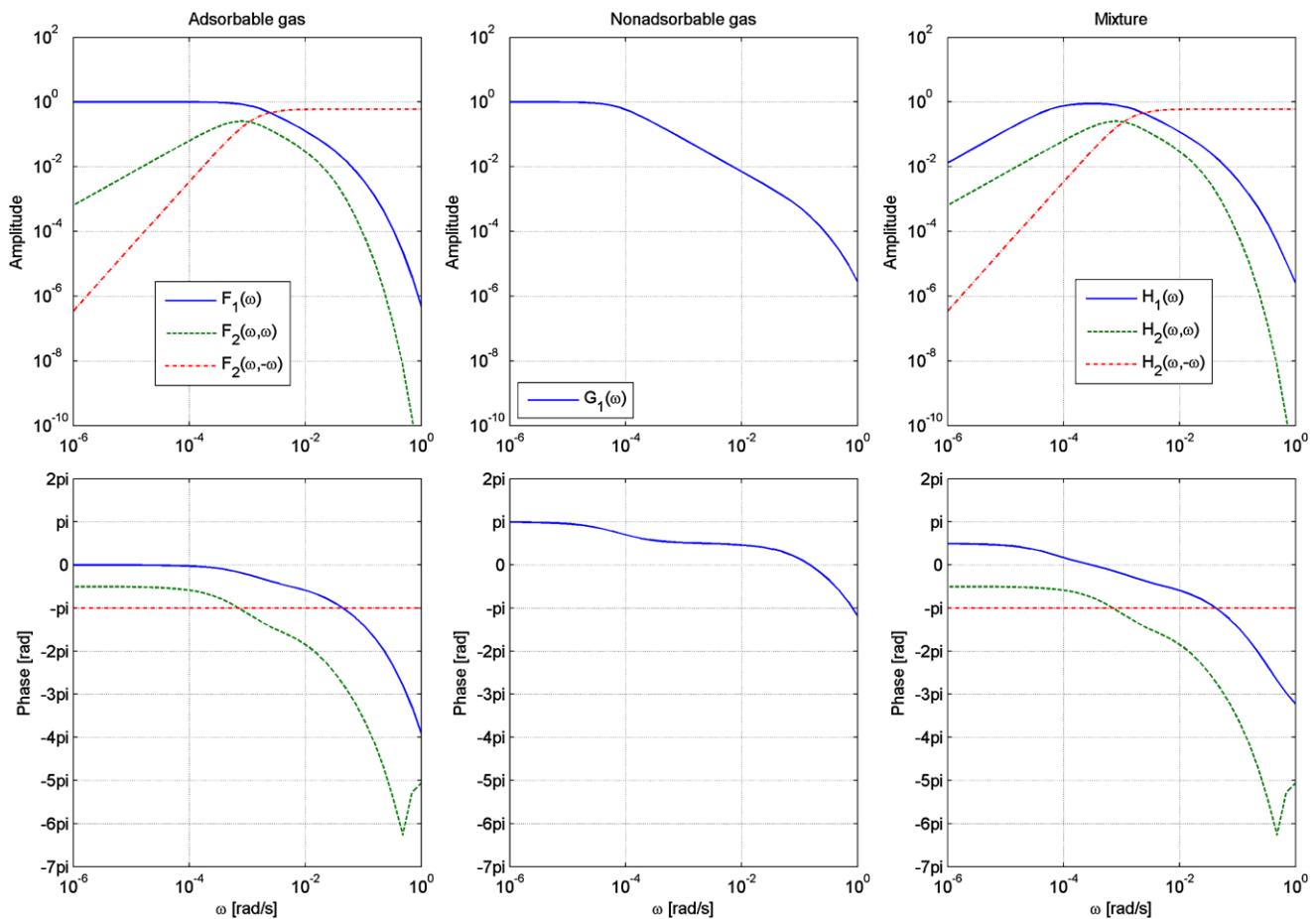


Fig. 6 The simulated first and second order F -, G - and H -functions, for the $\text{C}_3\text{H}_8/\text{He}$ mixture, for the simplified model corresponding to Knudsen regime in the gas phase (plus surface diffusion for the adsorbable gas)

In our previous analysis of the nonlinear frequency response of membrane systems with single permeating gases (Petkovska and Petkovska 2006) we have shown that the FRFs have some characteristic features which can be used for direct estimation of the system parameters. In this Section we will explore the possibilities for estimation of the main system parameters for the case of permeation of binary mixtures composed of one adsorbable and one inert component.

5.1 Estimation of the model parameters from the first and second order F - and G -functions

It has been shown that an important source of information, both in investigation of adsorption (Petkovska 2006) and membrane transport of pure gasses by frequency response method (Petkovska and Petkovska 2006), is the imaginary part of the first order FRF, i.e., its extremum. In Fig. 9, we show the imaginary parts of the first order F -, G - and H -functions, obtained for the $\text{C}_3\text{H}_8/\text{He}$ system (a similar picture is obtained for the CO_2/He system). It can be shown

that, in general, the $F_1(\omega)$ function has a minimum for a characteristic frequency:

$$\omega_1^* = D_{\text{eff},1} K \quad (48)$$

while the $G_1(\omega)$ function has a maximum, and the corresponding characteristic frequency is:

$$\omega_2^* = D_{\text{eff},2} K \quad (49)$$

As can be seen from Fig. 9, when these two characteristic frequencies differ substantially (which will be the case whenever there is substantial contribution of surface diffusion to the transport of the adsorbable component through the membrane), the $H_1(\omega)$ function, which is the sum of $F_1(\omega)$ and $G_1(\omega)$, has a minimum and a maximum at the same positions. The characteristic frequencies which can be obtained from the positions of these extrema are directly related to the effective diffusivities for the adsorbable and inert component, and can therefore be used for estimation of these transport coefficients.

It was also shown in our previous publication (Petkovska and Petkovska 2006) that the low- and high-frequency as-

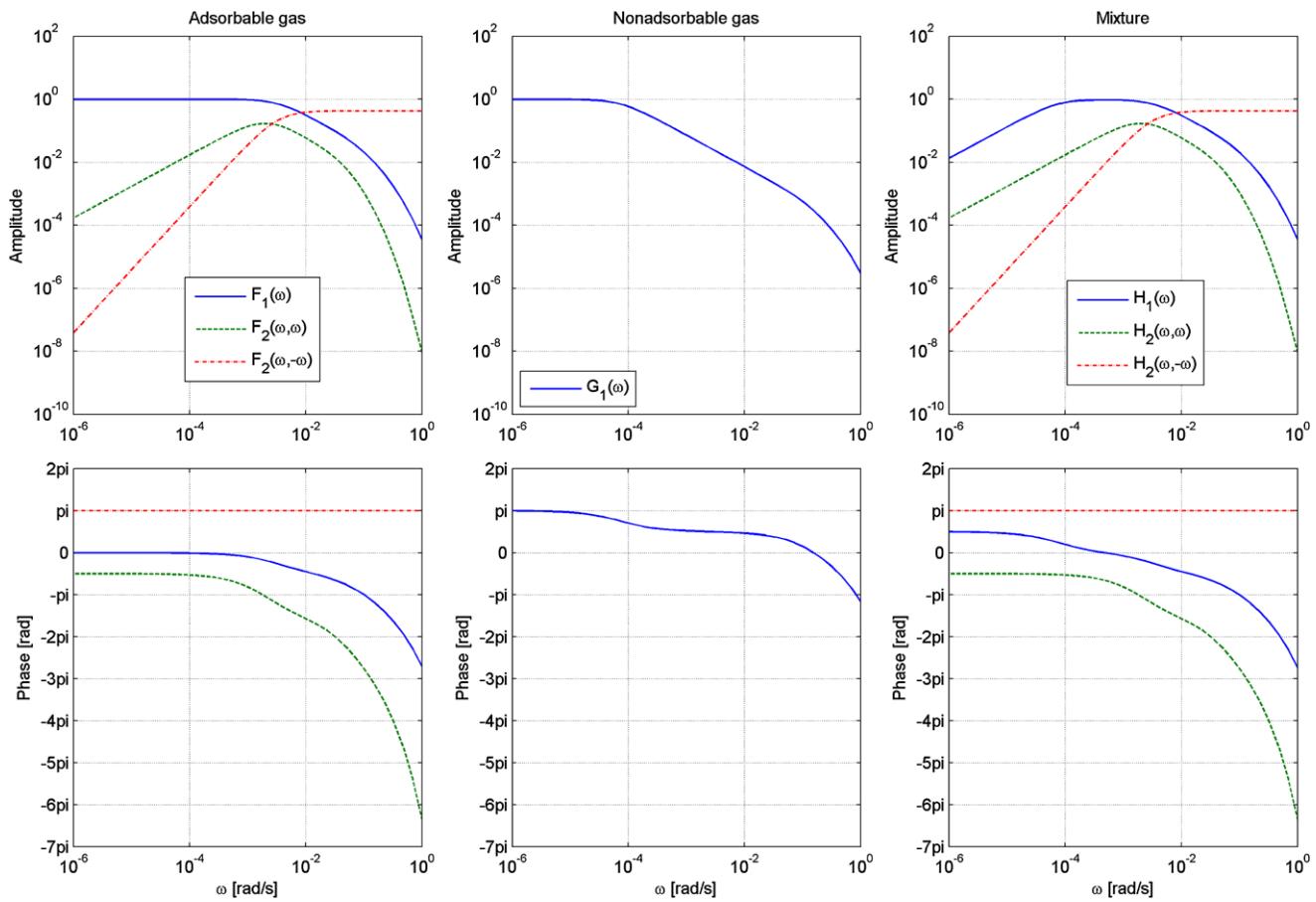


Fig. 7 The simulated first and second order F -, G - and H -functions, for the CO₂/He mixture for the simplified model corresponding to Knudsen regime in the gas phase (plus surface diffusion for the adsorbable gas)

ymptotes of some of the FRFs can be related to the system parameters. The following asymptotic functions were derived:

$$\lim_{\omega \rightarrow 0} \frac{dF_1(\omega)}{d\omega} = -j \left(\frac{1}{KD_{eff,1}} + \frac{1}{2}\alpha_1 \right) \quad (50)$$

$$\lim_{\omega \rightarrow 0} \frac{dG_1(\omega)}{d\omega} = j \left(\frac{1}{KD_{eff,2}} + \frac{1}{2}\alpha_2 \right) \quad (51)$$

$$\lim_{\omega \rightarrow 0} \frac{F_2(\omega, \omega)}{\omega} = -j \left(\alpha_1(\beta_1 - \phi_1) + 2\frac{\beta_1 - \phi_1}{KD_{eff,1}} + \gamma_1 \right) \quad (52)$$

$$\lim_{\omega \rightarrow 0} \frac{G_2(\omega, \omega)}{\omega} = -j \left(\alpha_2(\beta_2 - \phi_2) + 2\frac{\beta_2 - \phi_2}{KD_{eff,2}} \right) \quad (53)$$

$$\lim_{\omega \rightarrow \infty} F_2(\omega, -\omega) = -\beta_1 + \frac{2\alpha_1\phi_1}{\alpha_1 + \alpha_2} \quad (54)$$

$$\lim_{\omega \rightarrow \infty} G_2(\omega, -\omega) = -\beta_2 + \frac{2\alpha_2\phi_2}{\alpha_1 + \alpha_2} \quad (55)$$

$$\lim_{\omega \rightarrow 0} \frac{F_2(\omega, -\omega)}{\omega^2} = -\frac{1}{12}\alpha_1^2(2\beta_1 - 5\phi_1) - \frac{1}{4}\alpha_1\alpha_2\phi_1$$

$$\begin{aligned} & - \frac{\alpha_1(2\beta_1 - 5\phi_1) + 2\alpha_2\phi_1}{3KD_{eff,1}} \\ & - \frac{\alpha_1\phi_1}{3KD_{eff,2}} - \frac{\phi_1}{K^2D_{eff,1}D_{eff,2}} \\ & - \frac{\beta_1 - 2\phi_1}{K^2D_{eff,1}^2} \end{aligned} \quad (56)$$

$$\begin{aligned} \lim_{\omega \rightarrow 0} \frac{G_2(\omega, -\omega)}{\omega^2} & = -\frac{1}{12}\alpha_2^2(2\beta_2 - 5\phi_2) - \frac{1}{4}\alpha_2\alpha_1\phi_2 \\ & - \frac{\alpha_2(2\beta_2 - 5\phi_2) + 2\alpha_1\phi_2}{3KD_{eff,2}} \\ & - \frac{\alpha_2\phi_2}{3KD_{eff,1}} - \frac{\phi_2}{K^2D_{eff,2}D_{eff,1}} \\ & - \frac{\beta_2 - 2\phi_2}{K^2D_{eff,2}^2} \end{aligned} \quad (57)$$

In principle, these eight equations can be used for estimation of the auxiliary parameters $\alpha_1, \alpha_2, \beta_1, \beta_2, \phi_1, \phi_2$ and γ_1 , once the effective diffusivities $D_{eff,1}$ and $D_{eff,2}$ have

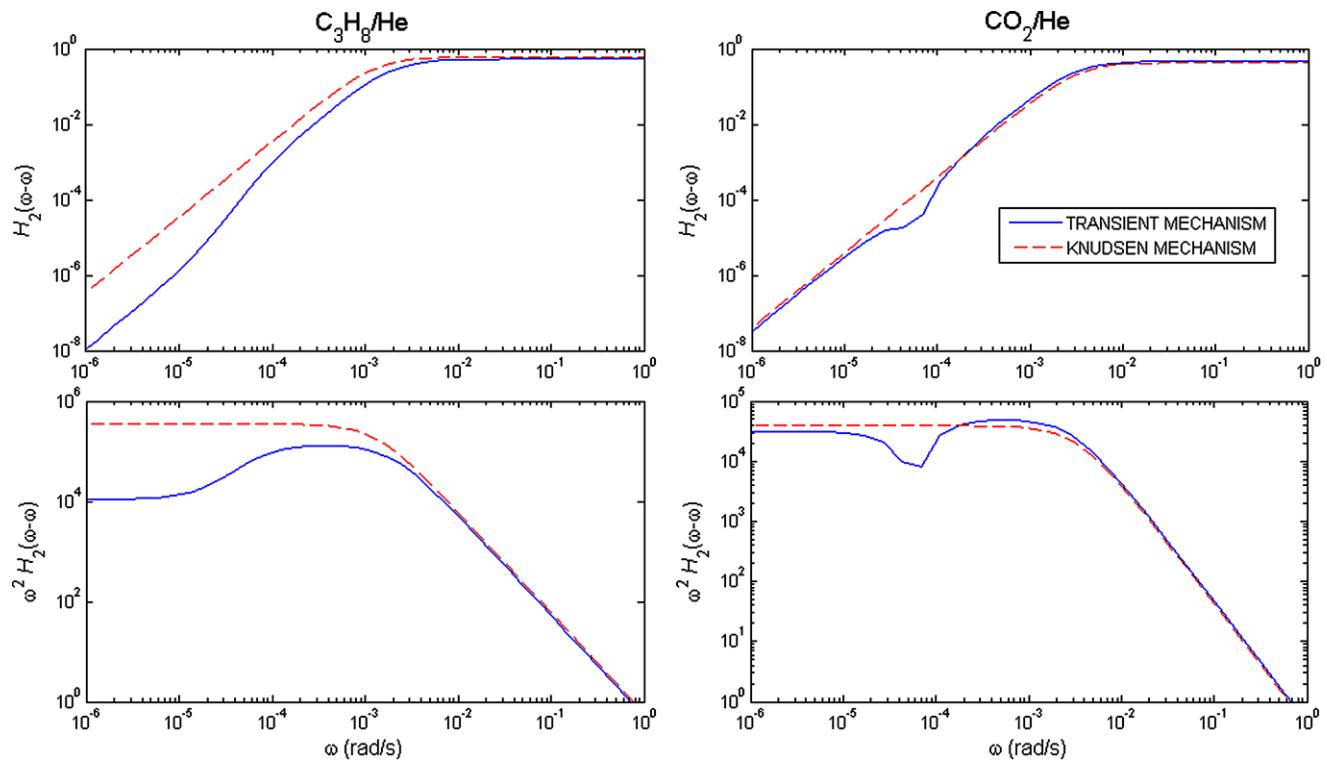


Fig. 8 Comparison of the $H_2(\omega, -\omega)$ (top row) and $\omega^2 H_2(\omega, -\omega)$ functions (bottom row) for transient and Knudsen mechanisms in the gas phase (plus surface diffusion in the adsorbed phase) for the C_3H_8/He mixture (left) and the CO_2/He mixture (right)

been estimated from the extrema of the first order FRFs imaginary parts, as shown in Fig. 9.

These auxiliary parameters are related to the physical parameters of the system, as defined in Table 1. The following model parameters are not known in advance and would be a subject to estimation from the first and second order FRFs: the diffusivities corresponding to the steady-state $D_{p1,s}$, $D_{p2,s}$ and $D_{s1,s}$, their first derivatives $\frac{\partial D_{p1}}{\partial P_1}$, $\frac{\partial D_{p2}}{\partial P_2}$ ($\frac{\partial D_{p1}}{\partial P_2} = \frac{\partial D_{p1}}{\partial P_1}$, $\frac{\partial D_{p2}}{\partial P_1} = \frac{\partial D_{p2}}{\partial P_2}$) and $\frac{\partial D_{s1}}{\partial Q_1}$, and the first and second derivative of the adsorption isotherm $\frac{\partial Q_1}{\partial P_1}$ and $\frac{\partial^2 Q_1}{\partial P_1^2}$. In principle, it should be possible to calculate all these values from the estimated values of the auxiliary parameters. Nevertheless, a more detailed inspection of the definitions of the auxiliary parameters shows that some of them contain the same piece of information (e.g. both $D_{eff,2}$ and α_2 depend only on $D_{p2,s}$, while $\beta_2 = \phi_2 = a_{2,2}$). Also, it is not possible to calculate the pore and surface diffusivities of the adsorbable component $D_{p1,s}$ and $D_{s1,s}$ separately, but only the effective diffusivity $D_{eff,1}$. Our analysis shows that the parameters that can be calculated separately from the features of the first and second order FRFs are: $D_{eff,1}$, $D_{p2,s}$, $\frac{\partial D_{p1}}{\partial P_1}$, $\frac{\partial D_{p2}}{\partial P_2}$, $\frac{\partial D_{s1}}{\partial Q_1}$, $\frac{\partial Q_1}{\partial P_1}$ and $\frac{\partial^2 Q_1}{\partial P_1^2}$.

One should be aware that the F - and G -functions can be estimated from experimental FR data only if continuous measurement of the partial pressures of both compo-

nents in the closed chamber $P_{1,II}$ and $P_{2,II}$ is possible. This would demand simultaneous measurement of the total pressure and the composition in the closed chamber. Typically, in the modified Wicke-Kallenbach cell only the pressure difference between the closed and the open chamber is measured (Marković 2009).

5.2 Estimation of the model parameters from the first and second order H -functions

The H -functions correspond to the change of the total pressure in the closed chamber and consequently they can be estimated from those measurements. The theoretical H -functions are obtained as a simple sum of the corresponding F - and G -functions (see (45)–(47)). The same is valid for their limiting values. Nevertheless, the number of equations obtained from the limiting values and the extrema of the H -functions is smaller than the number of unknown parameters that need to be estimated.

If we now consider the simpler case for which solely Knudsen mechanism applies for the gas diffusion in the pore volume, the FRFs become simpler and the number of unknown parameters decreases. The characteristic limiting values obtained from the H -functions become:

$$\lim_{\omega \rightarrow 0} \frac{H_1(\omega)}{d\omega} = j \left(\frac{1}{KD_{eff,2}} + \frac{1}{2}\alpha_2 - \frac{1}{KD_{eff,1}} - \frac{1}{2}\alpha_1 \right) \quad (58)$$

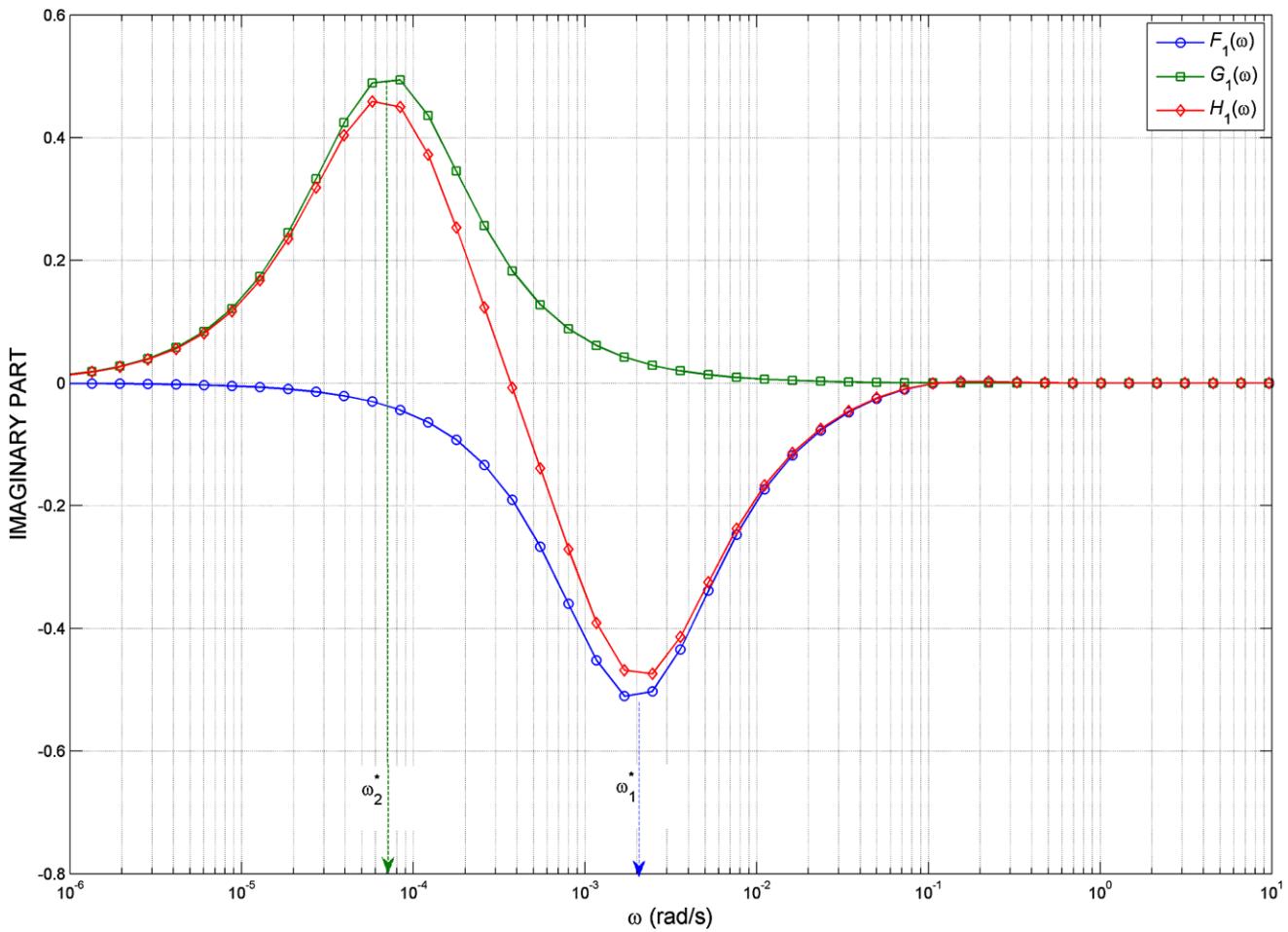


Fig. 9 The imaginary parts of the first order functions

$$\lim_{\omega \rightarrow 0} \frac{H_2(\omega, \omega)}{\omega} = -j \left(\alpha_1 \beta_1 + 2 \frac{\beta_1}{KD_{eff,1}} + \gamma_1 \right) \quad (59)$$

$$\lim_{\omega \rightarrow \infty} H_2(\omega, -\omega) = -\beta_1 \quad (60)$$

$$\lim_{\omega \rightarrow 0} \frac{H_2(\omega, -\omega)}{\omega^2} = -\frac{1}{12} 2\beta_1 \alpha_1^2 - \frac{2\beta_1 \alpha_1}{3KD_{eff,1}} - \frac{\beta_1}{K^2 D_{eff,1}^2} \quad (61)$$

From these values and the extrema of the $\text{Imag}(H_1(\omega))$ (Fig. 9) one can determine the following parameters: $D_{eff,1}$, $D_{p2,s}$, $\frac{\partial D_{s1}}{\partial Q_1}$, $\frac{\partial Q_1}{\partial P_1}$ and $\frac{\partial^2 Q_1}{\partial P_1^2}$.

6 Conclusions

The main idea of this paper was to check the theoretical potential of the nonlinear frequency response analysis for investigation of permeation of binary gas mixtures of one adsorbable and one inert component through porous membranes. The analysis was performed for a known and

previously used experimental setup, the modified Wicke-Kallenbach diffusion cell. The FRFs up to the second order were derived for the case of nonlinear adsorption isotherm and variable surface diffusivity for the adsorbable component, and variable pore diffusivities of both components. A simpler case with constant pore diffusivities (corresponding to Knudsen regime) was also considered. The analysis has shown the following:

1. The shape of the $H_2(\omega, -\omega)$ function, which can be estimated from the DC-component, offers theoretical pre-conditions to distinguish between the bulk/transient and the Knudsen regime of diffusion in the pore volume.
2. Some characteristic features of the system FRFs (the extrema of the first order FRFs and the limiting values of the FRFs for the low and high frequencies) were identified, which contain information about the system parameters, and can, therefore be used for estimation of the model parameters from experimental FR results.
3. Theoretically, a large number of the system parameters: the effective diffusivity of the adsorbable component, the pore diffusivity of the inert component, the pressure and

concentration coefficients of the pore and surface diffusivities and the first and second derivatives of the adsorption isotherm, can be estimated from the characteristic features of the first and second order FRFs corresponding to the partial pressures of the adsorbable (the F -functions) and the inert component (the G -functions) in the closed chamber of the Wicke-Kallenbach diffusion cell. In order to estimate these functions, on-line measurements of the pressure and composition in the closed cell would be necessary.

4. For the case of Knudsen regime in the gas phase, all system parameters (the effective diffusivity of the adsorbable component, the pore diffusivity of the inert component, the first derivative of the surface diffusivity and the first and second derivatives of the adsorption isotherm) can be estimated from the characteristic features of the FRFs corresponding to the total pressure in the closed chamber (the H -functions). In order to estimate these functions it is enough to measure only the change of the total pressure in the closed chamber of the modified Wicke-Kallenbach diffusion cell.

5. It is not possible to estimate the pore and surface diffusivities of the adsorbable component separately, but only the effective diffusivity. Distinctions between the pore and surface diffusivities can be determined from measurements at higher temperatures, for which surface diffusion would be negligible.

To summarize, our theoretical analysis has shown good theoretical potential of the nonlinear FR analysis for investigation of mass transfer in porous membranes and the modified Wicke-Kallenbach diffusion cell appears to be a good experimental setup for its application. Therefore, the nonlinear frequency response method seems worth of experimental application.

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Appendix: The ODEs obtained in Step 3 of the derivation procedure

The equations defining the first order FRFs are obtained by collecting the terms with $\frac{A}{2}e^{j\omega t}$.

From (31) one obtains:

$$\frac{d^2F_1^*(z, \omega)}{dz^2} - \alpha_1 j\omega F_1^*(z, \omega) = 0 \quad (62)$$

with boundary conditions:

$$z=0: \quad F_1^*(z, \omega)|_{z=0} = 1 \quad (63)$$

$$z=L: \quad \frac{dF_1^*(z, \omega)}{dz}\Big|_{z=L} + \frac{j\omega}{KD_{eff,1}} F_1^*(z, \omega)\Big|_{z=L} = 0 \quad (64)$$

and from (34):

$$\frac{d^2G_1^*(z, \omega)}{dz^2} - \alpha_1 j\omega G_1^*(z, \omega) = 0 \quad (65)$$

with boundary conditions:

$$z=0: \quad G_1^*(z, \omega)|_{z=0} = -1 \quad (66)$$

$$z=L: \quad \frac{dG_1^*(z, \omega)}{dz}\Big|_{z=L} + \frac{j\omega}{KD_{eff,1}} G_1^*(z, \omega)\Big|_{z=L} = 0 \quad (67)$$

The equations defining the symmetric second order FRFs are obtained by collecting the terms with $(\frac{A}{2})^2 e^{j2\omega t}$.

From (31), the following ODE is obtained:

$$\begin{aligned} & \frac{d^2F_2^*(z, \omega, \omega)}{dz^2} - 2\alpha_1 j\omega F_2^*(z, \omega, \omega) \\ &= 2\gamma_1 j\omega F_1^{*2}(z, \omega) + \beta_1 \frac{d^2F_1^{*2}(z, \omega)}{dz^2} \\ &+ 2\phi_1 \frac{d}{dz} \left(G_1^*(z, \omega) \frac{dF_1^*(z, \omega)}{dz} \right) \end{aligned} \quad (68)$$

with boundary conditions:

$$z=0: \quad F_2^*(z, \omega, \omega)|_{z=0} = 0 \quad (69)$$

$$\begin{aligned} z=L: \quad & \frac{dF_2^*(z, \omega, \omega)}{dz}\Big|_{z=L} + \frac{2j\omega}{KD_{eff,1}} F_2^*(z, \omega, \omega)\Big|_{z=L} \\ &= \beta_1 \frac{dF_1^{*2}(z, \omega)}{dz}\Big|_{z=L} \\ &+ 2\phi_1 \left(G_1^*(z, \omega) \frac{dF_1^*(z, \omega)}{dz} \right)_{z=L} \end{aligned} \quad (70)$$

while from (34), one obtains:

$$\begin{aligned} & \frac{d^2G_2^*(z, \omega, \omega)}{dz^2} - 2\alpha_1 j\omega G_2^*(z, \omega, \omega) \\ &= +\beta_1 \frac{d^2G_1^{*2}(z, \omega)}{dz^2} + 2\phi_1 \frac{d}{dz} \left(F_1^*(z, \omega) \frac{dG_1^*(z, \omega)}{dz} \right) \end{aligned} \quad (71)$$

with boundary conditions:

$$z=0: \quad G_2^*(z, \omega, \omega)|_{z=0} = 0 \quad (72)$$

$$\begin{aligned}
z = L: \quad & \frac{dG_2^*(z, \omega, \omega)}{dz} \Big|_{z=L} + \frac{2j\omega}{KD_{eff,1}} G_2^*(z, \omega, \omega) \Big|_{z=L} \\
& = \beta_1 \frac{dG_1^{*2}(z, \omega)}{dz} \Big|_{z=L} \\
& + 2\phi_1 \left(F_1^*(z, \omega) \frac{dG_1^*(z, \omega)}{dz} \right)_{z=L} \quad (73)
\end{aligned}$$

Finally, the equations defining the asymmetric second order FRFs are obtained by collecting the terms with $(\frac{A}{2})^2 e^0$.

From (31), the following ODE is obtained:

$$\begin{aligned}
& \frac{d^2 F_2^*(z, \omega, -\omega)}{dz^2} \\
& = +\beta_1 \frac{d^2 (F_1^*(z, \omega) F_1^*(z, -\omega))}{dz^2} \\
& + \phi_1 \frac{d}{dz} \left(G_1^*(z, \omega) \frac{dF_1^*(z, -\omega)}{dz} \right. \\
& \left. + G_1^*(z, -\omega) \frac{dF_1^*(z, \omega)}{dz} \right) \quad (74)
\end{aligned}$$

with boundary conditions:

$$z = 0: \quad F_2^*(z, \omega, -\omega)|_{z=0} = 0 \quad (75)$$

$$\begin{aligned}
z = L: \quad & \frac{dF_2^*(z, \omega, -\omega)}{dz} \Big|_{z=L} \\
& = \beta_1 \frac{d(F_1^*(z, \omega) F_1^*(z, -\omega))}{dz} \Big|_{z=L} \\
& + \phi_1 \left(G_1^*(z, \omega) \frac{dF_1^*(z, -\omega)}{dz} \right. \\
& \left. + G_1^*(z, -\omega) \frac{dF_1^*(z, \omega)}{dz} \right)_{z=L} \quad (76)
\end{aligned}$$

and from (34):

$$\begin{aligned}
& \frac{d^2 G_2^*(z, \omega, -\omega)}{dz^2} \\
& = +\beta_1 \frac{d^2 (G_1^*(z, \omega) G_1^*(z, -\omega))}{dz^2} \\
& + \phi_1 \frac{d}{dz} \left(F_1^*(z, \omega) \frac{dG_1^*(z, -\omega)}{dz} \right. \\
& \left. + F_1^*(z, -\omega) \frac{dG_1^*(z, \omega)}{dz} \right) \quad (77)
\end{aligned}$$

with boundary conditions:

$$z = 0: \quad G_2^*(z, \omega, -\omega)|_{z=0} = 0 \quad (78)$$

$$\begin{aligned}
z = L: \quad & \frac{dG_2^*(z, \omega, -\omega)}{dz} \Big|_{z=L} \\
& = \beta_1 \frac{d(G_1^*(z, \omega) G_1^*(z, -\omega))}{dz} \Big|_{z=L} \\
& + \phi_1 \left(F_1^*(z, \omega) \frac{dG_1^*(z, -\omega)}{dz} \right. \\
& \left. + F_1^*(z, -\omega) \frac{dG_1^*(z, \omega)}{dz} \right)_{z=L} \quad (79)
\end{aligned}$$

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