Weierstraß–Institut
für Angewandte Analysis und Stochastik

im Forschungsverbund Berlin e.V.

Preprint ISSN 0946 – 8633

Coupling of adsorption and diffusion in porous and granular materials. A 1-D example of the boundary value problem

Bettina Albers

submitted: 21st May 1999

Weierstrass Institute
for Applied Analysis
and Stochastics
Mohrenstraße 39
D – 10117 Berlin
Germany
E-Mail: albers@wias-berlin.de

Preprint No. 492
Berlin 1999

1991 Mathematics Subject Classification. 76S05, 73Q05, 73S10.

Key words and phrases. Adsorption, flows in porous and granular materials.

Edited by
Weierstraß–Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
D — 10117 Berlin
Germany

Fax: + 49 30 2044975
E-Mail (X.400): c=de;a=d400-gw;p=WIAS-BERLIN;s=preprint
E-Mail (Internet): preprint@wias-berlin.de
World Wide Web: http://www.wias-berlin.de/

Abstract

In the paper we present a macroscopic continuum model of adsorption in porous materials consisting of three components. We consider the flow of a fluid component through channels of the skeleton. It serves as carrier for an adsorbate whose mass balance equation contains a source term. The source consists of two parts: a Langmuir contribution connected with bare sides on internal surfaces which becomes in equilibrium the Langmuir isotherm, and changes of the internal surface driven by the source of porosity. The model for the latter contribution is new. Parameters of this model are analyzed by means of an example of solution of a boundary value problem for the full set of field equations which describes the transport of pollutants in soils.

1 Introduction

Adsorption processes where particles from a liquid solvent attach to the surface of a solid material appear quite often in nature. Examples are the pollution transport with rainwater in soil (organic materials like pesticides in agriculture, heavy metals in the subsoil of filling stations), tips through which salts of industry and of households are transported, the storage of atomic waste in salt layers or the penetration of moisture in plaster and concrete.

A look into history shows that the good capability for adsorption of porous materials was known very early. Already in 1777 FONTANA examined adsorption processes of gases on coal (see: [1]). One of the first attempts to use one single formula to describe such processes was undertaken by H. FREUNDLICH in 1909. He found empirically an expression which is a relation between the amount of gas adsorbed on a flat surface to the partial pressure in the adsorbate. Since 1914 I. LANGMUIR studied the foundations of adsorption and developed his own theory which he gradually improved by experiments. Incidentally for this work he was awarded in 1932 with the Nobel Prize for chemistry. This theory is based on the assumption that the transfer of particles from the fluid/ gaseous phase to the surface of the solid depends on the number of *bare sides* on this surface. From this assumption he derived the well-known Langmuir-isotherm for the fraction of occupied sides in phase equilibrium. It is used in the adsorption model which will be presented in Chapter 2 of this paper (see also: [2], [3]).

It is common to describe adsorption processes by means of scalar equations which follow by a closure of partial mass balance equations. This leads to so-called reaction-diffusion equations. There exists an extensive literature of such a model concerning particularly its mathematical properties. Much less extensive are discussed physical flaws of the scalar model which, for instance, neglects entirely processes in skeleton. This is the main reason for the construction of the present continuous model based on the concepts of the modern theory of porous media. Under special assumptions this model can be reduced to the reaction-diffusion-equation as we show in Section 2.3.

In this work the model will be illustrated by a one-dimensional example. In Chapter 3 the problem is formulated, Chapter 4 contains the presentation of balance equations and constitutive relations. In Chapter 5 the initial and boundary conditions are specified. They are, as usual for porous materials, of third type. In Chapter 6 the problem is solved by application of a regular perturbation method and a Laplace transform. The last chapter illustrates the results of this example.

2 Adsorption/Diffusion Model

2.1 Microscopic level of description

We investigate a flow of a fluid-adsorbate mixture through channels of a porous medium. Particles of adsorbate settle down on the surface of the skeleton so that their kinematics changes from that of the fluid to that of the skeleton. The extent of adsorption depends on various factors but the surface area of the solid is most important of them if particles of adsorbate stick to the skeleton due to weak van der Waals forces. In such a mechanism we neglect the influence of capillary effects and chemical reactions. Certainly this limits the applicability of the model. There exist numerous methods for quantitative evaluation of this area, e.g. through measurements of adsorption itself (on the modelling of adsorption see the forthcoming paper [2]). For the purpose of the present work, where the skeleton is considered to be a soil, we lean on a value of the internal surface mentioned by J. BEAR in [4].

Another quantity which influences the adsorbed amount is the number of *bare* and *occupied sides* on the surface of the solid, which I. LANGMUIR introduced in his classical works on adsorption (e.g. [5], [6], [7]) .

2.2 Macroscopic level of description

On the macroscopic level of description we denote by ξ the normalized fraction of occupied sides per unit volume, i.e. the fraction of bare sides is $1-\xi$. This field is interpreted as a number of occupied sides in a representative elementary volume (*REV*). *REV* is small in comparison with the volume of the whole flow regime but big against volumes of single pores of the skeleton. If we denote the internal surface area of the pores in the *REV* by f_{int} and the mass of adsorbate per unit area of this surface by m_A then the rate of transfer of mass from the liquid to the solid phase per unit time determining the mass source is given by the relation

$$\hat{\rho}^A = -\frac{m^A}{V}\frac{d\left(\xi\, f_{int}\right)}{dt} = -\frac{m^A}{V}\left(f_{int}\frac{d\xi}{dt} + \xi\frac{d\, f_{int}}{dt}\right), \tag{2.2.1}$$

where V is the REV-volume.

The first contribution on the right-hand side describes the change of the fraction of occupied sides and is specified by the Langmuir evolution equation

$$\frac{d\xi}{dt} = a\left(1-\xi\right)p^A - b\xi e^{-\frac{E_b}{kT}}, \tag{2.2.2}$$

where p^A is the partial pressure of the adsorbate in the fluid phase and a and b are material parameters. The energy barrier E_b for particles adsorbed on the skeleton is assumed to be constant. Furthermore k denotes the Boltzmann constant and T is the absolute temperature.

In full phase equilibrium the adsorption rate (first term of the right hand side of (2.2.2)) is equal to the desorption rate (second term) so that the time change of occupied sides is equal to zero. Then we get from (2.2.2) the well-known Langmuir isotherm of occupied sides

$$\xi_L = \frac{\frac{p^A}{p_0}}{1+\frac{p^A}{p_0}}, \qquad \text{with} \qquad p_0 := \frac{b}{a}e^{-\frac{E_b}{kT}}. \tag{2.2.3}$$

The other part of (2.2.1) is the change of the internal surface. We assume that this change is coupled with relaxation of the porosity n, which is described by the balance equation of porosity (For detailed information about the new model for porous bodies with the balance equation of porosity see: WILMANSKI [9], [10]).

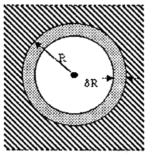
This means that there are two mechanisms due to which the mass source is unequal to zero: An isothermal equilibrium change of ξ can be produced by a change of partial pressure p^A. This yields a new phase equilibrium, i.e. another point on the Langmuir isotherm. Secondly, changes of the internal surface are driven by the source of porosity $\hat{n}$.

This source $\hat{n}$ describes the intensity of the dissipative changes of porosity per unit time and volume of the porous material. Motivated by elementary considerations about changes of the internal surface and of the porosity in a porous medium yielding film adsorption[1] we assume

---

[1] As an example let us consider a porous body with spherical holes connected with each other by negligibly small channels (one of the holes is shown in the picture). A film adsorption process takes place if the adsorbate settles down on the internal surface in an almost homogeneous manner. This yields small changes of the radius R of the pores, say δR. If N is the number of holes in REV then the total volume of holes V^F and the internal surface f_{int} in REV are satisfying the relations

$$V^F = N\cdot\tfrac{4}{3}\pi R^3, \quad \delta V^F = N\cdot 4\pi R^2\delta R \;\Rightarrow\; \tfrac{\delta n}{n} = 3\tfrac{\delta R}{R}$$
$$f_{int} = N\cdot 4\pi R^2, \quad \delta f_{int} = N\cdot 8\pi R\delta R \;\Rightarrow\; \tfrac{\delta f_{int}}{f_{int}} = 2\tfrac{\delta R}{R}$$
$$\Rightarrow \tfrac{\delta n}{n} \propto \tfrac{\delta f_{int}}{f_{int}}.$$



$$\frac{1}{f_{int}} \frac{d f_{int}}{dt} \propto \frac{\hat{n}}{n}. \tag{2.2.4}$$

In the following we proceed to formulate the continuum model of adsorption.

2.3 Three-dimensional continuum model

In the flow process under consideration the fluid and the adsorbate flow with a common velocity $\mathbf{v}^F$ through the skeleton which has the velocity $\mathbf{v}^S$. Fluid, adsorbate and skeleton have the current mass densities ρ^F, ρ^A and ρ^S, respectively. Then the mass balance equations have the form

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\hat{\rho}^A, \\ \frac{\partial \rho^F}{\partial t} + \operatorname{div}\left(\rho^F \mathbf{v}^F\right) &= 0, \\ \frac{\partial \rho^A}{\partial t} + \operatorname{div}\left(\rho^A \mathbf{v}^F\right) &= \hat{\rho}^A, \end{aligned} \tag{2.3.1}$$

where $\hat{\rho}^A$ denotes the intensity of the mass source.

Using the definitions

$$\rho^L := \rho^F + \rho^A, \qquad c := \frac{\rho^A}{\rho^F + \rho^A}, \qquad \hat{c} := \frac{\hat{\rho}^A}{\rho^F + \rho^A}. \tag{2.3.2}$$

we transform the balances (2.3.1) into the following ones

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\rho^L \hat{c}, \\ \frac{\partial \rho^L}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F\right) &= \rho^L \hat{c}, \\ \frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c &= (1-c)\,\hat{c}. \end{aligned} \tag{2.3.3}$$

The momentum balance equations have the form

$$\begin{aligned} \frac{\partial \rho^S \mathbf{v}^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S\right) &= \hat{\mathbf{p}}^S, \\ \frac{\partial \rho^L \mathbf{v}^F}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F \otimes \mathbf{v}^F + p^L \mathbf{1}\right) &= \hat{\mathbf{p}}^F, \end{aligned} \tag{2.3.4}$$

where the partial stress tensors of fluid components are spherical. The partial pressure in the liquid phase (i.e. in the fluid and adsorbate phases together) is the sum of the partial pressures in the fluid p^F, and in the adsorbate p^A. We expect according to Dalton's law that $p^A \cong cp^L$ and the concentration of the adsorbate in the fluid is assumed to be small. Furthermore $\mathbf{T}^S$ denotes the partial Cauchy stress tensor in the skeleton, $\hat{\mathbf{p}}^F = -\pi\left(\mathbf{v}^F - \mathbf{v}^S\right) + \rho^L \hat{c} \mathbf{v}^F$ is the momentum source in the liquid and $\hat{\mathbf{p}}^S = \pi\left(\mathbf{v}^F - \mathbf{v}^S\right) - \rho^L \hat{c} \mathbf{v}^S$ is the momentum source in the skeleton where π denotes the permeability coefficient.

The above balance equations reduce to the reaction-diffusion-equation under simplifying assumptions which we are due to present. This equation is often used by mathematicians to describe processes in porous and granular materials (see: [8]). First of all the motion of the skeleton is neglected which bears the consequence that the equations for the skeleton are not required. Furthermore the form of the Cauchy stress tensor for the fluid is restricted to the case that $T^F = -p^F 1$. Admittedly we use this form also in our continuum model but there it is not the only possibility. Neglecting the acceleration terms in the momentum balance for the liquid we obtain

$$\frac{\partial p^F}{\partial x} = -\pi v^F,$$

which is the Darcy law. We insert this into the mass balance $(2.3.1)_2$ and arrive at

$$\frac{\partial \rho^F}{\partial t} - \operatorname{div}\left(\rho^F \frac{1}{\pi} \operatorname{grad} p^F\right) = 0.$$

With the additional limitation that the entire mass density ρ is nearly constant and that $\rho^F = c^F \rho$ we are able to write the equation for the concentration

$$\frac{\partial c^F}{\partial t} = \operatorname{div}\left[D\left(c^F\right) \operatorname{grad} c^F\right] \quad \text{with} \quad D = c^F \frac{1}{\pi} \frac{\partial p^F}{\partial c^F}.$$

This is the required equation. Obviously, it is possible to describe solely highly limited cases. Several characteristics of porous media cannot be described by this equation even if it will be generalized by means of an additional scalar equation which is supposed to account for capillary effects. The above procedure does not account for mass exchange. However it is also possible to use mass balance $(2.3.1)_3$ which contains a mass source instead of $(2.3.1_2)$ to get such an equation which also describes adsorption processes.

Let us return to the continuum model for adsorption. For the scalar field of porosity we have an additional balance equation as introduced in [9], [10]. For small deformations of the skeleton it has the form

$$\frac{\partial n}{\partial t} + \mathbf{v}^S \cdot \mathrm{grad} n + n_E \mathrm{div}\left(\mathbf{v}^F - \mathbf{v}^S\right) = \hat{n} = -\frac{\Delta}{\tau}. \tag{2.3.5}$$

Here n_E denotes the equilibrium value of porosity, $\Delta = n - n_E$ is the deviation of the porosity from this value and τ is the *relaxation time of porosity.* This form of the source of porosity $\hat{n}$ is based on assumptions on small deviations from thermodynamic equilibrium.

For foundations of the model of adsorption see: [2], for the three dimensional model in application to homogeneous adsorption in porous materials: [3]. In the following we show a one-dimensional version of the model with mass exchange and diffusion.

3 One-dimensional example

We consider the above model of a porous body for a simple system in which the fluid carries an adsorbate and flows through channels in average in x-direction due to a difference of the external pressure, with p_l at $x = 0$ being larger than p_r at $x = l$.

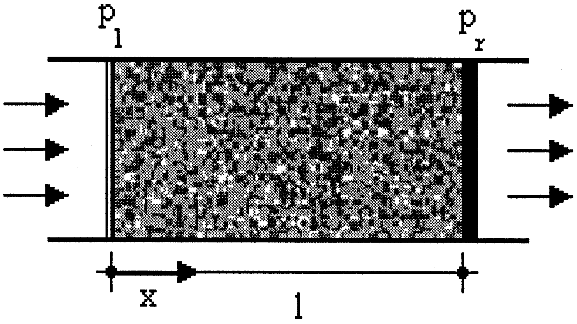


Fig. 3.1: A 1-D flow of a fluid with adsorbate through porous body.

The isothermal process is described by the fields

$$\left\{\rho^S, \rho^L, c, v^F, v^S, e^S, \Delta, f_{int}, \xi\right\}. \tag{3.1}$$

where v^F and v^S are x-components of $\mathbf{v}^F$ and $\mathbf{v}^S$, respectively and e^S denotes the stretch in x-direction.

The first six quantities of this set are the customary fields for a one-dimensional flow process in a threecomponent porous medium. However the last three arise due to mass exchange processes which, in turn, are caused by changes of the internal surface and changes of the partial pressure according to the Langmuir isotherm.

For the purpose of this example we make some additional assumptions. We assume that the skeleton does not move which means that the velocity of the skeleton is identically zero. Also we assume that the inertial forces are small i.e. that the acceleration terms in the momentum balances vanish. A third assumption is on small changes in time of the velocity gradient. That means that the porosity balance reduces to an algebraic relation in the following way

$$\begin{aligned}\frac{\partial \Delta}{\partial t}+\frac{\Delta}{\tau} &= -n_E\frac{\partial v^F}{\partial x}\Rightarrow \Delta=-n_E\int\limits_0^t\frac{\partial v^F}{\partial x}(\eta)\,\mathrm{e}^{-\frac{t-\eta}{\tau}}\mathrm{d}\eta \\ &\simeq -n_E\frac{\partial v^F}{\partial x}(t)\int\limits_0^t\mathrm{e}^{-\frac{t-\eta}{\tau}}\mathrm{d}\eta=-n_E\tau\frac{\partial v^F}{\partial x}. \end{aligned} \tag{3.2}$$

This follows from the fact that the relaxation time of porosity is very small. In the above formal solution of the balance equation of porosity we have assumed that the characteristic macroscopic time t is much larger than τ. A further advantage of this algebraic relation for Δ is that we need no additional boundary condition for the porosity balance.

4 Governing set of equations and constitutive relations

Accounting for these assumptions and bearing in mind relations (2.2.1), (2.2.2) and (2.2.4) the source of concentration $\hat{c}$ can be specified as follows

$$\hat{c}=-\frac{\rho^A_{ad}}{\rho^L}\left\{\left[(1-\xi)\frac{cp^L}{p_0}-\xi\right]\frac{1}{\tau_{ad}}-\xi\frac{\nu}{\tau}\Delta\right\}, \tag{4.1}$$

where τ_{ad} denotes the characteristic time of adsorption, p_0 is a reference pressure of adsorption which is defined in (2.2.3) and it was measured by LANGMUIR (see: [7]), ν is a proportionality factor and $\rho^A_{ad}:=\frac{m^A f_{int}}{V}\approx$ const.

Then the balance equations have the following form

$$\begin{aligned}&\frac{\partial\rho^L}{\partial t}+\frac{\partial\rho^L v^F}{\partial x}=-\rho^A_{ad}\left\{\left[\frac{cp^L}{p_0}-\left(1+\frac{cp^L}{p_0}\right)\xi\right]\frac{1}{\tau_{ad}}-\xi\frac{\nu}{\tau}\Delta\right\}\\ &\frac{\partial c}{\partial t}+v^F\frac{\partial c}{\partial x}=-(1-c)\frac{\rho^A_{ad}}{\rho^L}\left\{\left[\frac{cp^L}{p_0}-\left(1+\frac{cp^L}{p_0}\right)\xi\right]\frac{1}{\tau_{ad}}-\xi\frac{\nu}{\tau}\Delta\right\}\\ &\frac{\partial p^L}{\partial x}+\pi v^F=0,\qquad n_E\frac{\partial v^F}{\partial x}=-\frac{\Delta}{\tau},\qquad \frac{\partial\xi}{\partial t}=\left[(1-\xi)\frac{cp^L}{p_0}-\xi\right]\frac{1}{\tau_{ad}}.\end{aligned} \tag{4.2}$$

The relations for the skeleton are not quoted, because they are not necessary to solve the problem in this form.

The constitutive relation for the pressure in the liquid phase p^L is assumed to be

$$p^L = p_0^L + \kappa\left(\rho^L - \rho_0^L\right) + \beta\Delta \tag{4.3}$$

where p_0^L and ρ_0^L are initial values of the pressure and of the mass density for the liquid phase. κ denotes the compressibility and β is a material parameter.

5 Initial and boundary conditions

We assume that the inial values of the fluid-/adsorbate velocity and the change of porosity are equal to zero

$$v^F(x, t=0) = 0, \qquad \Delta(x, t=0) = 0, \tag{5.1}$$

and the mass density in the liquid phase, the pressure in the liquid phase and the concentration have the initial values

$$\begin{aligned} \rho^L(x, t=0) &= \rho_0^L, \qquad p^L(x, t=0) = p_0^L \equiv n_E p_{ext}, \\ c(x, t=0) &= c_0. \end{aligned} \tag{5.2}$$

The boundary conditions are, as usual for porous media, of third type (see: [11]). They express the fact that the flow through the boundary of the skeleton depends on the difference of the partial pressure in the liquid and the part of the external pressure which works on the fluid as well as on the permeability of the surface:

$$\begin{aligned} x &= 0: \quad -\rho^L v^F = \alpha\left(p^L - n p_l\right), \\ x &= l: \quad \rho^L v^F = \alpha\left(p^L - n p_r\right). \end{aligned} \tag{5.3}$$

The boundary of the skeleton is identified with the boundary of the whole three-component body.

6 Regular perturbation solution and Laplace transform

In order to find an approximate solution of the problem we use a regular perturbation method. Expansions with respect to a small parameter ε shall be truncated after first order contributions (linear approximation), vis.

$$\begin{gathered}
\rho^L = \rho_0^L + \varepsilon \rho_1^L, \qquad v^F = \varepsilon v_1^F, \qquad \Delta = \varepsilon \Delta_1, \\
c = c_0 + \varepsilon c_1, \qquad \xi = \xi_L + \varepsilon \xi_1.
\end{gathered} \tag{6.1}$$

Under the assumption that the pressure difference between the left and the right boundary is small, we define the small parameter as follows

$$\varepsilon = \frac{p_l - p_r}{p_r}. \tag{6.2}$$

It shall be seen that if the reference pressure in the denominator is the pressure at the right boundary we deal with an adsorption process and with a desorption process if it is the left one. However we mainly concentrate on the former case.

The zeroth step of the perturbation is trivial i.e. ρ_0^L, c_0 and ξ_L are constants. With abbreviations for combinations of constants

$$\begin{aligned}
&\iota_1 := 1 + \frac{c_0 p_0^L}{p_0}, \qquad \iota_2 := (1 - \xi_L) \frac{p_0^L}{p_0}, \qquad \iota_3 := (1 - \xi_L) \frac{c_0 \kappa}{p_0}, \\
&\iota_4 := (1 - \xi_L) \frac{c_0 \beta}{p_0}, \qquad \iota_5 := \xi_L \frac{\nu}{\tau}, \qquad \iota_6 := \xi_L - \frac{(1 - \xi_L) c_0 p_0^L}{p_0}, \\
&\iota_7 := \frac{(1 - c_0)}{\rho_0^L} \left(\xi_L - \frac{(1 - \xi_L) c_0 p_0^L}{p_0} \right)
\end{aligned} \tag{6.3}$$

we obtain for the first step the following set of equations:

$$\begin{aligned}
&\frac{\partial \rho_1^L}{\partial t} + \rho_0^L \frac{\partial v_1^F}{\partial x} = \rho_{ad}^A \left\{ \left[\iota_1 \xi_1 - \iota_2 c_1 - \iota_3 \rho_1^L - \iota_4 \Delta_1 \right] \frac{1}{\tau_{ad}} + \iota_5 \Delta_1 \right\} \\
&\frac{\rho_0^L}{\rho_{ad}^A} \frac{\partial c_1}{\partial t} = \left\{ -\iota_6 c_1 - \iota_7 \rho_1^L + (1 - c_0) \left[\iota_1 \xi_1 - \iota_2 c_1 - \iota_3 \rho_1^L - \iota_4 \Delta_1 \right] \right\} \frac{1}{\tau_{ad}} + \\
&\qquad\qquad\qquad\qquad + (1 - c_0) \iota_5 \Delta_1, \\
&\kappa \frac{\partial \rho_1^L}{\partial x} + \beta \frac{\partial \Delta_1}{\partial x} + \pi v_1^F = 0, \qquad \Delta_1 = -n_E \tau \frac{\partial v_1^F}{\partial x}, \\
&\frac{\partial \xi_1}{\partial t} = - \left[\iota_1 \xi_1 - \iota_2 c_1 - \iota_3 \rho_1^L - \iota_7 \Delta_1 \right] \frac{1}{\tau_{ad}}
\end{aligned} \tag{6.4}$$

We solve this linear problem analytically by means of the Laplace transform i.e.

$$\tilde{\rho}_1^L = \int\limits_0^\infty \rho_1^L \mathrm{e}^{-st} dt \text{ and analogous for } \tilde{v}_1^F, \tilde{\Delta}_1, \tilde{c}_1, \tilde{\xi}_1. \tag{6.5}$$

The transformed quantities are functions of two variables (x, s). According to the initial data we have

$$\rho_1^L \mathrm{e}^{-st}\Big|_0^\infty = 0 \text{ and analogous for } \tilde{v}_1^F, \tilde{\Delta}_1, \tilde{c}_1, \tilde{\xi}_1, \tag{6.6}$$

provided Sommerfeld conditions for $t \to \infty$ are fulfilled. We eliminate the system (6.4) in order to obtain a differential equation for $\tilde{v}_1^F$. We get

$$\begin{aligned} \tilde{\Delta}_1 &= -n_E \tau \frac{\partial \tilde{v}_1^F}{\partial x}, \qquad \tilde{c}_1 = z_6 \frac{\partial \tilde{v}_1^F}{\partial x}, \\ \tilde{\xi}_1 &= z_7 \frac{\partial \tilde{v}_1^F}{\partial x} \quad \text{and} \quad \tilde{\rho}_1^L = z_8 \frac{\partial \tilde{v}_1^F}{\partial x}, \end{aligned} \tag{6.7}$$

where the coefficients z_i depend in a various way on the Laplace variable s :

$$\begin{aligned} z_1 &:= \frac{-\rho_0^L + \rho_{ad}^A n_E \tau \left(\iota_4 - \iota_5\right)}{s + \iota_3 \rho_{ad}^A}, \qquad z_2 := \frac{\rho_{ad}^A \iota_1}{s + \iota_3 \rho_{ad}^A}, \qquad z_3 := \frac{\rho_{ad}^A \iota_2}{s + \iota_3 \rho_{ad}^A}, \\ z_4 &:= \frac{\iota_3 z_1 - \iota_4 n_E \tau}{s + \iota_1 - \iota_3 z_2}, \qquad z_5 := \frac{\iota_2 - \iota_3 z_3}{s + \iota_1 - \iota_3 z_2}, \\ z_6 &:= \frac{-\iota_7(z_1 + z_2 z_4) + (1 - c_0)\, \iota_1 z_4 - (1 - c_0)\, \iota_3(z_1 + z_2 z_4) + (1 - c_0)\, n_E \tau \left(\iota_4 - \iota_5\right)}{\frac{\rho_0^L}{\rho_{ad}^A} s + \iota_6 + \iota_7(z_2 z_5 - z_3) - (1 - c_0)\, \iota_1 z_5 + (1 - c_0)\, \iota_2 + (1 - c_0)\, \iota_3(z_2 z_5 - z_3)}, \\ z_7 &:= z_4 + z_5 z_6, \qquad z_8 := z_1 + z_2 z_7 - z_3 z_6. \end{aligned} \tag{6.8}$$

Finally we arrive at

$$\frac{\partial^2 \tilde{v}_1^F}{\partial x^2} - \underbrace{\frac{\pi}{\beta n_E \tau - \kappa z_8}}_{a} \tilde{v}_1^F = 0, \qquad a = a(s), \tag{6.9}$$

from which we get the solution

$$\begin{aligned}
\tilde{v}_1^F &= C_1 \mathrm{e}^{\sqrt{a}x} + C_2 \mathrm{e}^{-\sqrt{a}x}, \\
\tilde{\rho}_1^L &= z_8 \sqrt{a} \left(C_1 \mathrm{e}^{\sqrt{a}x} - C_2 \mathrm{e}^{-\sqrt{a}x} \right), \\
\tilde{\Delta}_1 &= -n_E \tau \sqrt{a} \left(C_1 \mathrm{e}^{\sqrt{a}x} - C_2 \mathrm{e}^{-\sqrt{a}x} \right), \\
\tilde{c}_1 &= z_6 \sqrt{a} \left(C_1 \mathrm{e}^{\sqrt{a}x} - C_2 \mathrm{e}^{-\sqrt{a}x} \right), \\
\tilde{\xi}_1 &= z_7 \sqrt{a} \left(C_1 \mathrm{e}^{\sqrt{a}x} - C_2 \mathrm{e}^{-\sqrt{a}x} \right).
\end{aligned} \tag{6.10}$$

Next we formulate the boundary conditions for the first step. To describe an adsorption (not a desorption) process we define the pressure on the left hand side of the channel p_l with a given pressure on the right hand side p_r

$$p_l := p_r + \varepsilon p_r, \qquad \varepsilon > 0. \tag{6.11}$$

We insert the constitutive relation (4.3) for p^L into the boundary conditions (5.3). It follows

$$\begin{aligned}
-\rho_0^L v_1^F &= \alpha \left(\kappa \rho_1^L + \beta \Delta_1 - p_r \Delta_1 - n_E p_r \right)\Big|_{x=0}, \\
\rho_0^L v_1^F &= \alpha \left(\kappa \rho_1^L + \beta \Delta_1 - p_r \Delta_1 \right)\Big|_{x=l}.
\end{aligned} \tag{6.12}$$

After applying the Laplace transform and inserting the solution (6.10) we have

$$\begin{gathered}
-\rho_0^L \left(C_1 + C_2 \right) = z_9 \left(C_1 - C_2 \right) - \frac{\alpha n_E p_r}{s}, \\
\rho_0^L \left(C_1 \mathrm{e}^{\sqrt{a}l} + C_2 \mathrm{e}^{-\sqrt{a}l} \right) = z_9 \left(C_1 \mathrm{e}^{\sqrt{a}l} - C_2 \mathrm{e}^{-\sqrt{a}l} \right), \\
z_9 = \alpha \left[\kappa z_8 - n_E \tau \left(\beta - p_r \right) \right] \sqrt{a}.
\end{gathered} \tag{6.13}$$

and finally for the integration constants

$$\begin{aligned}
C_1 &= -\frac{\alpha n_E p_r \left(z_9 + \rho_0^L \right)}{s \left[\left(z_9 - \rho_0^L \right)^2 \mathrm{e}^{2\sqrt{a}l} - \left(z_9 + \rho_0^L \right)^2 \right]}, \\
C_2 &= -\frac{\alpha n_E p_r \left(z_9 - \rho_0^L \right) \mathrm{e}^{2\sqrt{a}l}}{s \left[\left(z_9 - \rho_0^L \right)^2 \mathrm{e}^{2\sqrt{a}l} - \left(z_9 + \rho_0^L \right)^2 \right]}.
\end{aligned} \tag{6.14}$$

We use a FORTRAN-solver to get numerical solutions for the inverse Laplace transform.

7 Results and conclusions

In order to illustrate the above presented solution we choose the following values of parameters

Initial mass density ρ_0^L	$2.3 \cdot 10^2 \ \frac{\mathrm{kg}}{\mathrm{m}^3}$	Equilibrium porosity n_E	0.23
Length of the body l	1 m	Initial concentration c_0	10^{-3}
Langmuir pressure p_0	10 kPa	Initial pressure p_0^L	23 kPa
Pressure on right h. s. p_r	100 kPa	Proportionality factor ν	10
Coupling constant β	1 GPa	Compressibility κ	$2.25 \cdot 10^6 \ \frac{\mathrm{m}^2}{\mathrm{s}^2}$
Permeability of solid π	$10^9 \ \frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{s}}$	Permeability of surface α	$4 \cdot 10^{-8} \ \frac{\mathrm{s}}{\mathrm{m}}$
Relaxation time τ	10^{-3} s	Charact. time of adsorp. τ_{ad}	1 s
Fraction of occupied sides in equilibrium ξ_L	$2.3 \cdot 10^{-2}$	mass density of adsorbate on internal surface ρ_{ad}^A	$40 \ \frac{\mathrm{kg}}{\mathrm{m}^3}$

For mass density and porosity we have chosen typical values for rocks and soils. The values of material parameters β and τ have been chosen on the basis of estimates of the attenuation of acoustic waves. The influence of permeability is described by two constants π and α. The first one reflects the resistence of the skeleton to the flow of the fluid/adsorbate mixture. The second one describes the surface resistance to the outflow of the mixture from the solid. Its appearance is connected with a boundary layer between the porous body and the external world.

The following results have to be multiplied by ε, the normalized difference between the pressures on the left and the right hand side of the body. For flow processes in soil we assume that $\varepsilon = 0.1$. This means that the pressure difference between both sides is one tenth of an atmosphere.

In the figures below we present various fields as functions of place x and time t. The results are illustrated in a pointwise manner. We have chosen 100 points in the x-direction and 100 points in the t-direction. For the value of characteristic time of adsorption τ_{ad} of 1 second (see: table) we obtain a total time of app. 10 seconds for the whole nonstationary adsorption process. However in reality the characteristic time of adsorption is of order of hours or days. This means that the characteristic time of adsorption should be chosen much larger than one second.

Figure 7.1 shows the change of the mass density of the liquid phase. Of course, for every place of the body, it begins with the value zero at $t = 0$. The mass density increases in all points of the body. However these increments are rapid and parabolic at $x = 0$ (on the back of the diagram) and they are lower and nearly linear at $x = l$ (on the front side of the diagram). At the left hand side of the body (the highest point) it reaches a maximum value of about $1.5 \cdot 10^{-3} \ \frac{\mathrm{kg}}{\mathrm{m}^3}$ and on the other side it is about a half of this value. Certainly these results depend on the pressure difference between both sides.

In Figure 7.2 we show the x-component of the common velocity of the fluid and of the adsorbate v^F. Also for this field the value is equal to zero at the beginning of the process. The values of velocity reach rather fast a steady state, i.e. it is nearly constant in time and linearly decreasing in place. The maximum value of the velocity is about $4{\cdot}10^{-6}\ \frac{\mathrm{m}}{\mathrm{s}}$. This value is somewhat smaller than the value which VOGELSANG in [12] obtained in flow experiments of the groundwater. He measured how long some substances (e.g. paints or plants) needed to come from one place to another. In this way he determined a flow velocity of the ground water of about $10^{-4}\ \frac{\mathrm{m}}{\mathrm{s}}$.

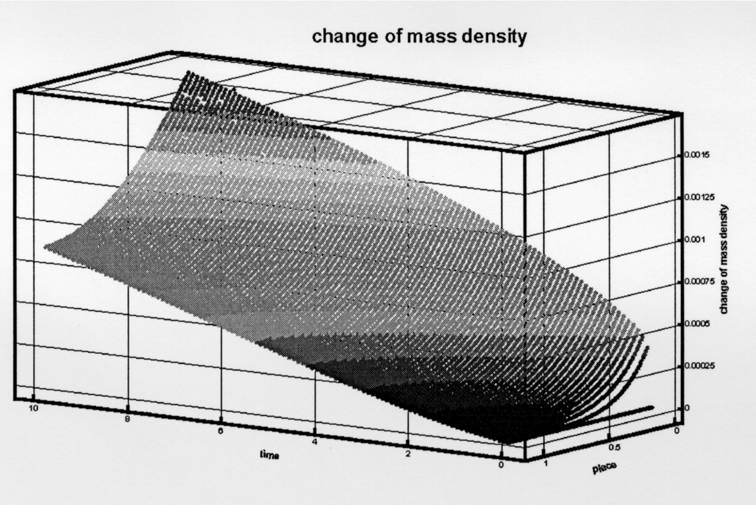


Fig. 7.1: Change of mass density of the liquid phase.

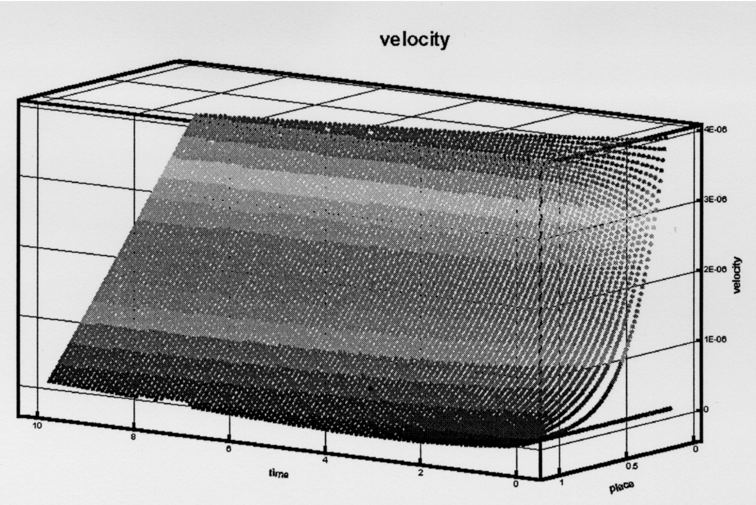


Fig. 7.2: Velocity of fluid and adsorbate.

The algebraic form of the porosity balance yields the change of porosity from its equilibrium value proportional to the velocity gradient. Therefore this change is nearly constant after a short time. Whereas the increments according to the result presented in Fig. 7.2 are very steep on the left side of the body they are almost neglectigible on the right hand side.

As we can see in Fig. 7.4 the concentration of the adsorbate in the liquid phase starts with a value of 10^{-3} and decreases for this adsorption process both in time and over the length of the body. The maximum change is $4{\cdot}10^{-5}$. If the concentration decreases, of course, the fraction of occupied sides on the surface of the solid increases as we show in Fig. 7.5. The largest deviation from the Langmuir value $\xi_L = 2.3{\cdot}10^{-2}$ is app. $2 \cdot 10^{-4}$.

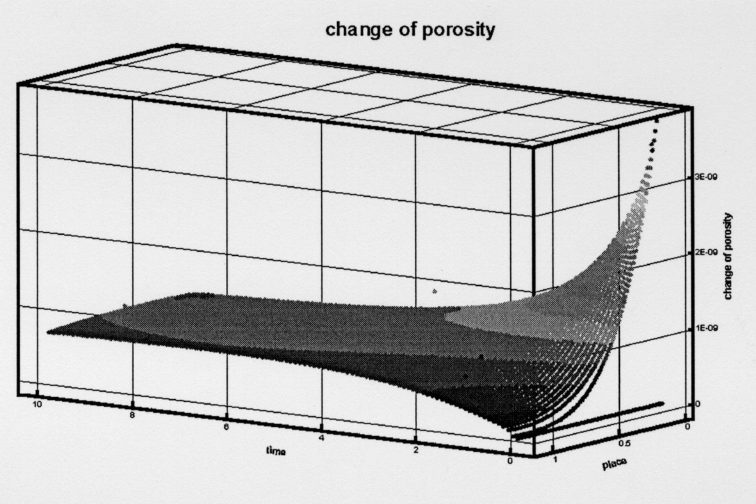


Fig. 7.3: Change of porosity.

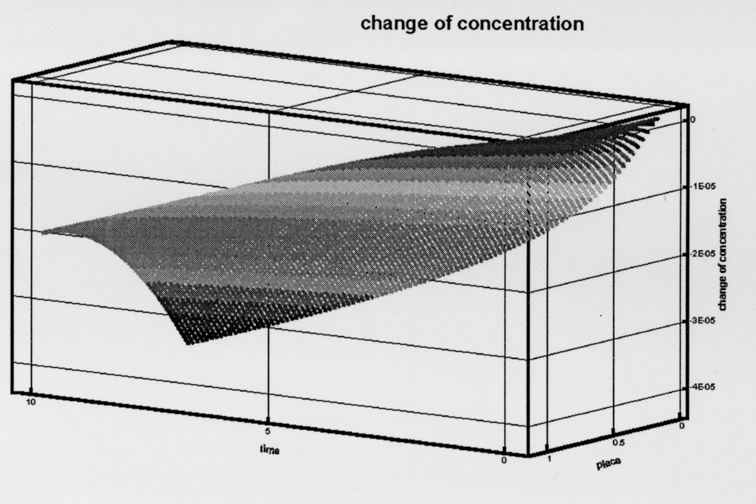


Fig. 7.4: Change of concentration.

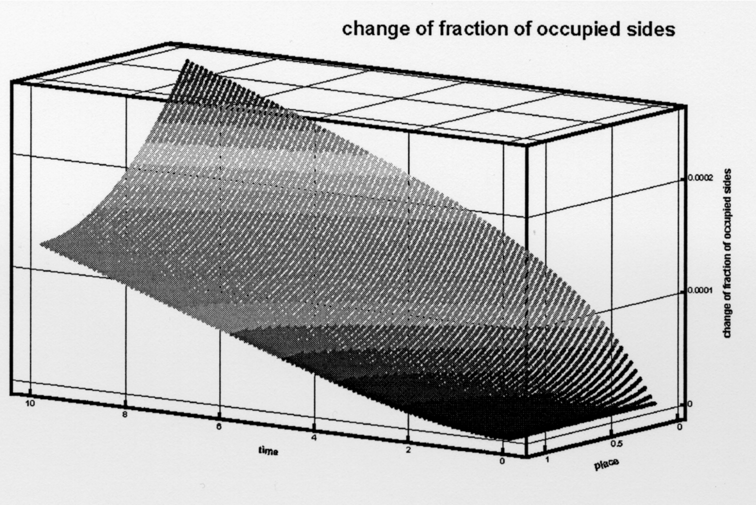


Fig. 7.5: Change of fraction of occupied sides.

The above presented results do not show clearly contributions to the rate of adsorption separated between two physical mechanisms: evolution of the number of bare sides $\frac{d\xi}{dt}$, and the change of the internal surface $\frac{df_{int}}{dt}$. What we could not observe at all is the influence of the explicit changes of porosity $\frac{dn}{dt}$ because these are driven by a very short relaxation time τ of porosity. Consequently the change of the internal surface is solely related to the divergence of relative velocity – in our example, to $\frac{\partial v^F}{\partial x}$. Under constant pressure difference this quantity is always different from zero (a constant in our example after some 10 s.). Hence the rate of adsorption cannot go to zero as it would be the case with the Langmuir mechanism for steady-state processes (ξ would reach a local equilibrium value ξ_L corresponding to $p^A(x, t = \infty)$).

Acknowledgement: I appreciate very much numerous discussions with my teacher Prof. Dr. K. Wilmanski and other colleagues of the research group "Continuum Mechanics" of WIAS during the work on this paper.

References

[1] S. J. Gregg, K. S. W. Sing: Adsorption, Surface Area and Porosity, *Academic Press*, London (1982).

[2] B. Albers, K. Wilmanski: Modeling of Adsorption and Diffusion in Multicomponent Continua, *Transport in Porous Media* (1999, in preparation).

[3] K. Wilmanski: On a Homogeneous Adsorption in Porous Materials, *ZAMM* (1999, in print).

[4] J. Bear: Dynamics of Fluids in Porous Media, *American Elsevier Publishing Company* (1972), also: *Dover Publications* (1988).

[5] I. LANGMUIR: The Constitution and Fundamental Properties of Solids and Liquids. Part 1, *J.Am.Chem.Soc.*,**38**, 2221-2295 (1916).

[6] I. LANGMUIR: The Constitution and Fundamental Properties of Solids and Liquids. Part 2, *J.Am.Chem.Soc.*, **39**, 1848 (1917).

[7] I. LANGMUIR: The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J.Am.Chem.Soc.,* **40,** 1361-1403 (1918).

[8] KNABNER, P.: Mathematische Modelle für Transport und Sorption gelöster Stoffe in porösen Medien, *Verlag Peter Lang*, Frankfurt (1991).

[9] K. WILMANSKI: Porous Media at Finite Strains. The New Model With the Balance Equation For Porosity, *Arch. Mech.*, **48**, 4, 591-628 (1996).

[10] K. WILMANSKI: A Thermodynamic Model of Compressible Porous Materials with the Balance Equation of Porosity, *Transport in Porous Media*, **32:**, 21-47 (1998).

[11] B. ALBERS: Randbedingungen für den zweikomponentigen Körper auf dem Rand des Skeletts, *WIAS-Preprint* No. 360, Berlin (1997).

[12] D. VOGELSANG: Grundwasser, *Springer* (1998).