Monografías del Seminario Matemático García de Galdeano. **27:** 369–376, (2003).

Homogenization of heat and mass conservation equations in porous media

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Abstract

We present the modelling of several effects driving the species segregation in oil deposits. In a first part , a local model is given. Then, homogenization methods are used in order to obtain macroscopic laws. We insist on upscaling in adsorption phenomena as methods used here are slightly different from usual ones.
Keywords: Homogenization, 2-scale convergence, adsorption in a porous medium.
AMS Classification:35K55, 35B27, 65M60.

1 Local equations

In this study, Ω denotes an open part of $\mathbb{R}^n$ (n=2 or 3), which spatial basis is $(e_k)_{k\in\{1\cdots n\}}$, $Q=]0,T[\times\Omega$. We note Y the unit cube, divided in two parts, the fluid and the solid phases Y_f and Y_s. We define the medium porosity by $\phi=\frac{meas(Y_f)}{meas(Y)}$.
We consider a n-components fluid flowing in Ω. Taking into account convection, thermal diffusion and diffusion, matter and heat fluxes $\vec{J_i}$ and $\vec{J_q}$ are written

$$\vec{J_i}=\rho c_i\vec{\mathcal{U}}-\rho\sum_{j=1}^{n}\tau_{ij}\nabla c_j-\rho\delta_\theta^i c_i(1-c_i)\nabla\theta \text{ and } \vec{J_q}=\theta\vec{\mathcal{U}}-\lambda\nabla\theta.$$

Neglecting Dufour effect, conservation equations are given by

$$\left\{\begin{array}{l}\rho C_p\partial_t\theta+div(\vec{J_q})=0\\ \rho\partial_t c_i+div(\vec{J_i})=0\end{array}\right. \Longleftrightarrow \left\{\begin{array}{l}\partial_t\theta+div(\theta\vec{\mathcal{U}}-\kappa\nabla\theta)=0\\ \partial_t c_i+div(c_i\vec{\mathcal{U}}-\displaystyle\sum_{j=1}^{n}\tau_{ij}\nabla c_j-\delta_\theta^i c_i(1-c_i)\nabla\theta)=0\end{array}\right.$$

where c_i denotes the mass fraction of the i^{th} component, θ the temperature, τ_{ij} the diffusive coefficients, κ the medium thermal diffusivity. The stationary velocity field $\vec{\mathcal{U}}$ is the solution of Navier-Stokes equations which will not be studied here.

Remark 1 *The mathematical analysis of these type of equations has already been done in previous works. The reader should refer to [4] or [6].*

2 Upscaling

In this part, ε denotes a positive real parameter, denoting the ration between macro and micro scales. We are interested in studying unknowns behaviours when $\varepsilon \to 0$. In this study y denotes a local variable ($y = \frac{x}{\varepsilon}$) and x the global variable.
The treatment of flow equations has been made using asymptotic developments and will not be detailed here. This mathematical transition from a phenomenological law to an empiric one (Darcy's law) has already been studied a lot. A rigorous proof of the homogenization of permanent Navier-Stokes equation has been done by TARTAR in [7], while the homogenization of "Stokes type" equations has been studied by ANTONTSEV et *al.* in [3].

2.1 Upscaling in diffusive effects

We consider the energy equation at steady state, with some boundary conditions at free media-porous media interfaces, the temperature and the fluxes continuity, associated to respective thermal diffusivities.

$$\begin{cases} -\kappa_f \Delta\theta + \vec{\mathcal{U}}.\nabla\theta = 0 \quad \text{in the free medium,} \\ \kappa_s \Delta\theta = 0 \quad \text{in the porous structure.} \end{cases} \tag{1}$$

The variational formulation associated to this problem is the following one:

$$(E_\varepsilon^\theta) \begin{cases} \forall v \in H_0^1(\Omega),\ \int_\Omega \kappa(\frac{x}{\varepsilon})\nabla\theta_\varepsilon.\nabla v dx - \int_\Omega \chi_{\Omega_{f,\varepsilon}} \theta_\varepsilon \vec{\mathcal{U}}_\varepsilon.\nabla v dx = 0 \\ \theta_\varepsilon|_{\partial\Omega} = g \end{cases} \tag{2}$$

where g is a function in $H^{\frac{1}{2}}(\partial\Omega)$ and κ the function defined by

$$\kappa(.) = \kappa_f \chi(Y \backslash \overline{Y}_s) + \kappa_s \chi(Y_s) = \kappa_f \chi(Y_f) + \kappa_s \chi(Y_s),$$

with κ_f and κ_s the thermal diffusivities of the solid and the fluid media. Our aim here is to use a process of two scale convergence, in order to dispose of a strong enough convergence on the temperature to introduce it in the mass conservation equation and to conclude. We distinguish in the following argumentation four main parts; first, we deduce with *a priori* estimates a result of two scale convergence for the unknown θ_ε(theorem 1). Secondly, we multiply the micro state equation by appropriated test-functions in order to obtain a variational formulation at the limit state. An integration part by part allows then to determine the macroscopic problem. A last step consists in eliminating local variables in the macroscopic problem by decoupling this one from a problem posed on an elementary cell (theorem 2). We recall in a first time the following result:

Theorem 1 *The generalized sequences* $(\theta_\varepsilon)_\varepsilon$ *and* $(\nabla\theta_\varepsilon)_\varepsilon$ *two-scale converge respectively to elements* $\theta^*(x)$ *of* $H^1(\Omega)$ *and* $(\nabla_x\theta^* + \nabla_y\xi(x,y))$ *of* $H^1(\Omega) \times L^2[\Omega; H^1_\sharp(Y)\backslash\mathbb{R}]$.

The proof of this theorem has already been done in the case of perforated media by ALLAIRE in [1]. Now, we are able to determine the homogenized problem verified by the limit state θ^*:

Theorem 2 *θ^* is the unique solution in $H^1(\Omega)$ of the following homogenized problem*

$$(E^{\theta^*})\begin{cases} \forall v \in H_0^1(\Omega), \ \int_\Omega \tilde{\Lambda}\nabla\theta^*.\nabla v dx - \int_\Omega \phi\theta^*\vec{\mathcal{U}}.\nabla v dx = 0 \\ \theta^*|_{\partial\Omega} = g \end{cases} \tag{3}$$

where $\tilde{\Lambda}$ is the elliptical tensor given by

$$\begin{aligned} \Lambda_{kl} &= \int_Y \kappa(\nabla_y\sigma_k + \vec{e}_k).\vec{e}_l dy \\ &= \int_{Y_f} \kappa_f(\nabla_y\sigma_k + \vec{e}_k).\vec{e}_l dy + \int_{Y_s} \kappa_s(\nabla_y\sigma_k + \vec{e}_k).\vec{e}_l dy \end{aligned} \tag{4}$$

and (σ_k) is a family of solutions of the following problem

$$(E^\theta_{cell})\begin{cases} \sigma_k \in H^1_\sharp(Y) \\ div_y(\kappa_f[\nabla_y\sigma_k + \vec{e}_k]) = 0 \ in\, Y_f \\ div_y(\kappa_s[\nabla_y\sigma_k + \vec{e}_k]) = 0 \ in\, Y_s \\ [\kappa_f(\nabla_y\sigma_k + \vec{e}_k) - \kappa_s(\nabla_y\sigma_k + \vec{e}_k)]\,.\vec{n} = 0 \ on\, \partial Y_f \backslash \partial Y. \end{cases} \tag{5}$$

Proof

We rewrite the energy equation in free medium (1) and multiplying this one by the test function $\psi(x) + \psi_1(x, y)$ where $\psi \in D(\Omega)$ and $\psi_1 \in D[\Omega; \mathcal{C}^\infty_\sharp(Y)]$, we obtain, with a Green's formula,

$$\begin{aligned} \int_\Omega\int_Y \kappa(\frac{x}{\varepsilon})\nabla\theta_\varepsilon.\nabla(\psi(x) + \varepsilon\psi_1(x, \frac{x}{\varepsilon}))dxdy \ &- \ \int_\Omega\int_Y \chi_{\Omega_{f,\varepsilon}}\theta_\varepsilon\vec{\mathcal{U}}_\varepsilon.\nabla(\psi(x) + \varepsilon\psi_1(x, \frac{x}{\varepsilon}))dxdy \\ &= \ \int_\Omega\int_Y f_\varepsilon(\psi(x) + \varepsilon\psi_1(x, \frac{x}{\varepsilon}))dxdy. \end{aligned}$$

Noticing that

$$\nabla(\psi(x) + \varepsilon\psi_1(x, y)) = \nabla_x\psi(x) + \nabla_y\psi_1(x, y) + \varepsilon\nabla_x\psi_1(x, y),$$

we get, passing to the limit when $\varepsilon \to 0$,

$$\begin{aligned} &\int_\Omega\int_Y \kappa(y)\left[\nabla_x\theta^* + \nabla_y\xi(x, y)\right].\left[\nabla_x\psi(x) + \nabla_y\psi_1(x, y)\right]dxdy \\ &- \int_\Omega\int_Y \chi_{\Omega_f}\phi\theta^*\vec{\mathcal{U}}.\left[\nabla_x\psi(x) + \nabla_y\psi_1(x, y)\right]dxdy = \int_\Omega\int_Y f\psi(x)dxdy \end{aligned}$$

for all $(\psi, \psi_1) \in D(\Omega) \times D[\Omega; \mathcal{C}^\infty_\sharp(Y)]$ and thus, by density, for all $(\psi, \psi_1) \in H_0^1(\Omega) \times L^2[\Omega; H^1_\sharp(Y)/\mathbb{R}]$. We will first have defined the function $f = div(\kappa(x)\nabla\hat{g} + \phi\chi_{\Omega_f}\hat{g}\vec{\mathcal{U}})$. The problem can then be interpreted by

$$\begin{cases} div_y\left(\kappa(y)(\nabla\theta^* + \nabla_y\xi(x, y))\right) = 0 \ in \ \Omega \times Y \\ div_x\left(-\int_Y \kappa(y)(\nabla\theta^* + \nabla_y\xi(x, y))dy + \chi_{\Omega_f}\phi\theta^*\vec{\mathcal{U}}\right) = 0 \ in \ \Omega \times Y \\ \theta^*|_{\partial\Omega} = g. \end{cases}$$

The proof relies then on the consideration of solutions $\sigma_k(x,y)$ of the problem (E^{θ}_{cell}), and the function $\xi(x,y)$ defined by the relation

$$\xi(x,y) = \sum_{k=1}^{3} \frac{\partial \theta^*}{\partial x_k} \sigma_k(x,y). \tag{6}$$

Having defined the tensor $\tilde{\Lambda}$ by

$$\Lambda_{kl} = \int_Y \kappa(y)[\vec{e}_k + \nabla_y \sigma_k(x,y)].\vec{e}_l dy,$$

one can easily get the following weak formulation

$$(E^{\theta^*}) \left\{ \begin{array}{l} \forall v \in H^1_0(\Omega),\ -\int_\Omega \tilde{\Lambda} \nabla \theta^* . \nabla v dx + \int_\Omega \phi \theta^* \vec{\mathcal{U}} . \nabla v dx = 0 \\ \theta^*|_{\partial\Omega} = g. \end{array} \right.$$

The homogenized problem has been entirely determined. We remark that it is a problem very similar to the one posed in a free medium. The study of such a problem is not necessary as soon as the tensor introduced has properties (symmetry, pseudo-ellipticity) that allow to conclude immediately, using analysis done for the free medium problem. The complete determination of the thermal field in the porous medium *via* the homogenized equation requires to solve the problem (E^{θ}_{cell}) and the knowledge of the functions (σ_k) and more precisely the estimation of energies relative to these functions (the term Λ_{kl}), less expensive in terms of computations.

2.2 Soret effect equations

In this part, we are interested in the homogenization of mass conservation equations of each component of the mixture. The sorption effects are not considered here as they will be treated in a next part. This model is mainly different from the energy one as the quantities $c_{i,\varepsilon}$ are defined on a domain $\Omega_{\varepsilon,f}$ depending on the parameter ε. This difficulty is overcame by introducing an extension operator.
We consider the convective-diffusive equations with Soret effect in $\Omega_{f,\varepsilon}$

$$\forall\, i \in \{1..n\},\ \partial_t c_{i,\varepsilon} + \vec{\mathcal{U}}_\varepsilon . \nabla c_{i,\varepsilon} - \sum_{j=1}^{n} \tau_{ij} \Delta c_{j,\varepsilon} - \delta^i_\theta div(c_{i,\varepsilon}(1-c_{i,\varepsilon})\nabla \theta_\varepsilon) = 0 \tag{7}$$

associated to initial and boundary conditions

$$\left\{ \begin{array}{l} \sum_{j=1}^{n} \tau_{ij} \frac{\partial c_{j,\varepsilon}}{\partial n} + \delta^i_\theta c_{i,\varepsilon}(1-c_{i,\varepsilon}) \frac{\partial \theta_\varepsilon}{\partial n} = 0 \\ c_{i,\varepsilon}(x,0) = c^0_i. \end{array} \right.$$

The variational formulation associated to this problem is the following one:

$$\begin{array}{l} \int_\Omega \chi_{\Omega_{f,\varepsilon}} \partial_t c_{i,\varepsilon} v dx - \int_\Omega \chi_{\Omega_{f,\varepsilon}} c_{i,\varepsilon} \vec{\mathcal{U}}_\varepsilon . \nabla v dx \\ + \sum_j \tau_{ij} \int_\Omega \chi_{\Omega_{f,\varepsilon}} \nabla c_{j,\varepsilon} . \nabla v dx + \int_\Omega \chi_{\Omega_{f,\varepsilon}} \delta^i_\theta c_{i,\varepsilon}(1-c_{i,\varepsilon}) \nabla \theta_\varepsilon . \nabla v dx = 0 \end{array} \tag{8}$$

2.2.1 Behaviour of $\bar{c}_{i,\varepsilon}$

One can easily prove (*cf.* for example [4]) that unknowns $c_{i,\varepsilon}$ are bounded in $H^1(Q_\varepsilon)$, independently of ε. The method consists in searching an extension operator on $H^1(Q)$ for the unknowns that allows to conserve such a property. Thus, we introduce the extension operator P_ε

$$P_\varepsilon : \left| \begin{array}{l} H^1(Q_\varepsilon) \longrightarrow H^1(Q) \\ c_{i,\varepsilon} \longmapsto P_\varepsilon(c_{i,\varepsilon}) = \bar{c}_{i,\varepsilon} \end{array} \right.$$

which is continue, with a continuity constant C_p independent of ε. This operator allows to conserve *a priori* estimates, independently of ε. As a direct consequence, we have

$$\|\bar{c}_{i,\varepsilon}\|_{1,Q} \leq C_p \|c_{i,\varepsilon}\|_{1,Q_\varepsilon} \leq C' \tag{9}$$

C' being independent of ε. Since Q is a bounded lipschitzian part, we can apply the Rellich Kondrachoff theorem which ensures us of the compacity of $H^1(Q)$ in $L^2(Q)$. The inequality (9) allows to prove the existence of an extracted subsequence of $\bar{c}_{i,\varepsilon}$ that converges weakly in $H^1(Q)$. The injection of $H^1(Q)$ in $L^2(Q)$ being compact, there exists an extracted subsequence -again denoted by $(\bar{c}_{i,\varepsilon})$- which converges strongly in $L^2(Q)$ and almost everywhere in Q to a limit c_i. The sequel of the proof is not detailed here (*cf.* [6]) and remains similar to the one given for energy equation. The final result is given in

Theorem 3 *The sequence $\bar{c}_{i,\varepsilon}$ converges to the solution of a problem associated with the variational formulation*

$$\begin{array}{l} \int_\Omega \phi \partial_t c_i v dx - \int_\Omega \phi c_i \vec{\mathcal{U}}.\nabla v dx \\ + \sum_j \tau_{ij} \int_\Omega \left[\tilde{\Upsilon} \nabla c_j \right].\nabla v dx + \int_\Omega c_i(1-c_i)[\tilde{\Sigma}_i \nabla \theta^*].\nabla v dx = 0 \end{array} \tag{10}$$

where $\tilde{\Upsilon}_i$ and $\tilde{\Sigma}_i$ are the tensors defined by

$$(\tilde{\Sigma}_i)_{kl} = \delta_\theta^i (\tilde{\Upsilon})_{kl} \tag{11}$$

$$= \frac{\delta_\theta^i}{\mathcal{L}^3 - meas(Y)} \int_{Y_f} (\nabla_y \omega_k + \vec{e_k})(\nabla_y \omega_l + \vec{e_l}) dy \tag{12}$$

with $(\omega_k)_{k=1,2}$ is a family of functions, solutions of problems on the elementary cell Y

$$\left\{ \begin{array}{l} \omega_k \in H^1_\sharp(Y) \\ -div_y(\nabla_y \omega_k + \vec{e}_k) = 0 \;\; in \, Y_f \\ (\nabla_y \omega_k + \vec{e}_k).\vec{n} = 0 \; on \, \partial Y_f \backslash \partial Y. \end{array} \right. \tag{13}$$

Remark 2 *The main difficulty in the proof of the convergence remains in the fact that quantities $c_{i,\varepsilon}$ are defined on a part $\Omega_{\varepsilon,f}$. Other techniques can be used, as the proof of the compacity of the injection of $H^1(\Omega_{\varepsilon,f})$ in $L^2(\Omega_{\varepsilon,f})$, which is uniform in ε (this is a suited version of Rellich theorem to the perforated media).*

2.3 Upscaling in sorption effects

2.3.1 Statement of the problem

In this part, we are interested in adsorption phenomena occurring on the porous surface. The notations used here are similar to the previous part ones. Adsorption phenomena occurring on fluid-solid interface Γ, we have to define $\Sigma_\varepsilon = \Gamma_\varepsilon \times]0, T[$, where $\Gamma_\varepsilon = \partial\Omega_{\varepsilon,f} \setminus \partial\Omega_\varepsilon$. The repartition of the species into the fluid is modelized by a classic "convecto-diffusive" equation

$$\partial_t c_\varepsilon + div(c_\varepsilon \vec{\mathcal{U}}_\varepsilon - \tau \nabla c_\varepsilon) = 0 \ \text{ in } \ \Omega_{f,\varepsilon}. \tag{14}$$

The adsorption effects are translated by a boundary condition on the fluid-solid interface of the type

$$-\tau \frac{\partial c_\varepsilon}{\partial n} = \varepsilon \lambda(\frac{x}{\varepsilon}) \varphi(c_\varepsilon) \ \text{ on } \ \Gamma_\varepsilon \tag{15}$$

where λ is an element of $L^\infty_\sharp(\Gamma)$ and D the diffusion coefficient of the component in the fluid. The initial and the complete boundary conditions remain similar to the ones considered in the first part. Thus, with a Green's formula and equality (15) we obtain the variational formulation with a sink term

$$\begin{aligned} \int_{\Omega_{f,\varepsilon}} \partial_t c_\varepsilon v dx \ &- \ \int_{\Omega_{f,\varepsilon}} c_\varepsilon \vec{\mathcal{U}}_\varepsilon . \nabla v dx \\ &+ \ \tau \int_{\Omega_{f,\varepsilon}} \nabla c_\varepsilon . \nabla v dx = -\varepsilon \int_{\Gamma_\varepsilon} \lambda(\frac{x}{\varepsilon}) \varphi(c_\varepsilon) v d\sigma_\varepsilon \end{aligned} \tag{16}$$

for "regular enough" functions v defined on $\bar{Q}$. One can easily verify that the problem (16) admits a unique solution (evolutive parabolic problem with a non linear sink term).

2.3.2 Irreversible case: The Langmuir isotherm

We are interested in the case of full irreversible adsorption, given by the Langmuir's model, one of the most classically used isotherm. The flux at the interface is then described by

$$\varphi : \ r \in \mathbb{R} \ \longmapsto \ \varphi(r) = \left(\frac{\alpha r}{1 + \beta r} - c_{sat} \right)^+ . \tag{17}$$

c_{sat} being a saturation value.

Proposition 1 *We have the following estimates:*

$$\exists C_1 > 0, \ \|c_\varepsilon\|_{H^1(Q_\varepsilon)} \leq C_1, \quad \exists C_2 > 0, \ \|\varphi(c_\varepsilon)\|_{H^1(Q_\varepsilon)} \leq C_2.$$

The function φ being lipschitzian and vanishing at $r = 0$, with a Lipschitz constant $Lip(\varphi)$, we get that $\varphi(c_\varepsilon)$ is bounded in $H^1(Q_\varepsilon)$ and

$$\|\varphi(c_\varepsilon)\|_{H^1(Q_\varepsilon)} \leq Lip(\varphi) \|c_\varepsilon\|_{H^1(Q_\varepsilon)}. \tag{18}$$

Proposition 2 (Langmuir's isotherm)

The generalized sequence $(c_\varepsilon)_\varepsilon$ converges to an element c, solution of the equation

$$\phi\partial_t c + div\left(\phi c\vec{\mathcal{U}} - \tau\tilde{\Upsilon}\nabla c\right) + \left[\int_\Gamma \lambda(y)d\sigma(y)\right]\varphi(c) = 0 \text{ in } Q. \tag{19}$$

Proof

Considering the variational formulation verified by c_ε, and integrating the inequality (16) on $[0,T]$, we have

$$\int_0^T\int_{\Omega_{f,\varepsilon}} \partial_t c_\varepsilon v dxdt \quad - \quad \int_0^T\int_{\Omega_{f,\varepsilon}} c_\varepsilon \vec{\mathcal{U}}_\varepsilon.\nabla v dxdt$$
$$+ \quad \tau\int_0^T\int_{\Omega_{f,\varepsilon}} \nabla c_\varepsilon.\nabla v dxdt = -\varepsilon\int_0^T\int_{\Gamma_\varepsilon} \lambda(\frac{x}{\varepsilon})\varphi(c_\varepsilon)vd\sigma_\varepsilon dt.$$

The convergence of convective, diffusive and evolutive terms has already been proved in the previous parts. In a first time we use a suitable extension $\tilde{c}_\varepsilon$ of the unknowns c_ε in order to obtain a constant $C > 0$, independent of ε, such that

$$\|\tilde{c}_\varepsilon\|_{H^1(Q_\varepsilon)} \leq C\ \|c_\varepsilon\|_{H^1(Q_\varepsilon)}. \tag{20}$$

The tricky point consists in passing to the limit in the term $\varepsilon\int_{\Gamma_\varepsilon} \lambda(\frac{x}{\varepsilon})\varphi(c_\varepsilon)vd\sigma_\varepsilon$.

With this aim in view, we use results of two scale convergence for the expressions on the boundaries. These results, introduced by Allaire, Damlamian and Hornung in [2], are the generalization to the boundaries of the two scale convergence notion introduced in [1] and have been applied to diffusive equations with Fourier type boundary conditions. In the following, we will denote this type of convergence by $u_\varepsilon \overset{2-scale}{\underset{\Gamma}{\rightharpoonup}} u_0$. Similar problems of reactions at fluid-solid interfaces had been studied in [5].

The adaptation of this notion to our model does not give any difficulty with the help of proposition (1). Thus, taking for test function $v = \varphi(c_\varepsilon)$ in the variational formulation (16), we easily obtain the inequality

$$\varepsilon\int_0^T\int_{\Gamma_\varepsilon} |\lambda(\frac{x}{\varepsilon})\varphi(x)|^2 d\sigma_\varepsilon(x) \leq C. \tag{21}$$

Therefore, as mentioned in [2], there exists a function $\varphi(x,y) \in L^2(\Omega; L^2(\Gamma))$ such that $\varphi_\varepsilon \overset{2-scale}{\underset{\Gamma}{\rightharpoonup}} \varphi$. We have the following convergence properties:

$$\varepsilon'\int_0^T\int_{\Gamma_{\varepsilon'}} \lambda(\frac{x}{\varepsilon'})\varphi(c_{\varepsilon'})\phi(t,x,\frac{x}{\varepsilon'})d\sigma_{\varepsilon'}(x)dt \overset{\varepsilon'\to 0}{\longrightarrow} \int_Q\int_\Gamma \lambda(y)\varphi(c)\phi(t,x,y)d\sigma(y)dxdt \tag{22}$$

for each continuous function $\phi(x,y) \in \mathcal{C}[\bar{\Omega}; \mathcal{C}_\sharp(Y)]$. Moreover, with the compacity of the injection from $H^1(Q)$ in $L^2(Q)$, it comes

$$\tilde{c}_{\varepsilon'} \rightharpoonup c \text{ in } H^1(Q) \text{ weakly}, \quad \tilde{c}_{\varepsilon'} \to c \text{ in } L^2(Q) \text{ strongly}.$$

and then $\varphi(\tilde{c}_{\varepsilon'}) \longrightarrow \varphi(c)$ in $L^2(Q)$ strongly.

The previous proof remains true for all lipschitzian function φ, which is non decreasing and which vanishes at 0, that allows to consider a wide set of natural behaviours.

2.3.3 The reversible case: the Freundlich isotherm

We consider here the reversible case which can be modelized by the Freundlich isotherm:

$$\varphi : \ r \in \mathbb{R} \longmapsto \varphi(r) = r^p \ \ (0 < p < 1) \tag{23}$$

which is translated by a condition on the fluid-solid interface

$$-\frac{\partial c_\varepsilon}{\partial n} = \varepsilon \lambda |c_\varepsilon - c_{sat}|^{p-1}(c_\varepsilon - c_{sat}) \ \text{ on } \ \Gamma_\varepsilon. \tag{24}$$

Proposition 3 (Freundlich isotherm)

The macroscopic conservative equation is the following one:

$$\phi \partial_t c + div\left(\phi c \vec{\mathcal{U}} - \tau \tilde{\Upsilon} \nabla c\right) = -\lambda\, meas(\Gamma)|c - c_{sat}|^{p-1}(c - c_{sat}) \ \ in\ Q. \tag{25}$$

The proof of such a result has already been established in the case of the homogenization of chemical reactions between fluid and solid phases at the interface.

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