Supplementary Information

Unexpected coupling between flow and adsorption in porous media

Jean-Mathieu Vanson,[1,2] François-Xavier Coudert,[3,*] Benjamin Rotenberg,[4]
Maximilien Levesque,[2] Caroline Tardivat,[1] Michaela Klotz,[1] and Anne Boutin[2,†]

[1] *Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR 3080 Saint Gobain CREE/CNRS, 550 Avenue Alphonse Jauffret, 84306 Cavaillon, France*
[2] *École Normale Supérieure, PSL Research University, Département de Chimie, Sorbonne Universités – UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24 rue Lhomond, 75005 Paris, France*
[3] *PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France*
[4] *Sorbonne Universités, UPMC Univ. Paris 06, CNRS, UMR 8234, PHENIX, F-75005 Paris, France*

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[*] fx.coudert@chimie-paristech.fr
[†] anne.boutin@ens.fr

A. ANALYTICAL EXPRESSION FOR THE FRACTION OF ADSORBED PARTICLES

We introduce the following quantities:

- N_{ads}**:** Number of adsorption sites
- N_f**:** Number of fluid sites
- n_{ads}**:** Number of adsorbed particles
- n_f**:** Number of free particles
- n_{tot}**:** Total number of particles
- k_a**:** Adsorption coefficient (and $p_a = k_a \Delta t / \Delta x$)
- k_d**:** Desorption coefficient (and $p_d = k_d \Delta t$)
- F_a**:** Fraction of adsorbed particles

The number of adsorbed and free particles evolve according to:

$$n_{ads}(t+\Delta t) = n_{ads}(t) + \frac{p_a N_{ads}}{N_f} n_f(t) - p_d n_{ads}(t) \tag{1}$$

$$n_f(t+\Delta t) = n_f(t) - \frac{p_a N_{ads}}{N_f} n_f(t) + p_d n_{ads}(t) \tag{2}$$

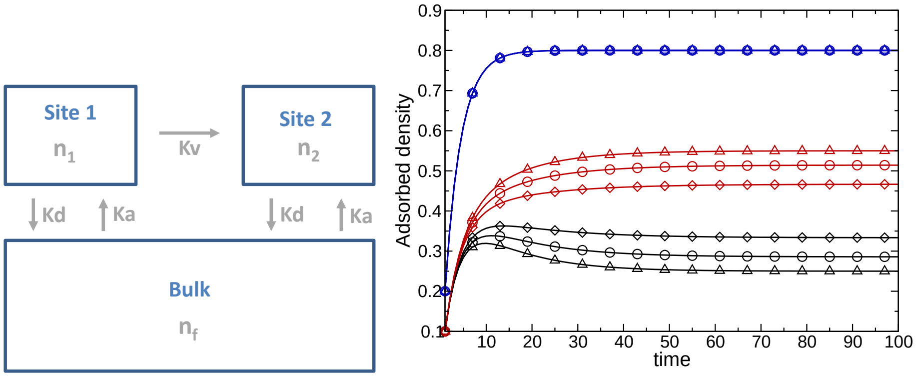
This implies that $n_{tot} = n_{ads}(t) + n_f(t)$ is conserved and that $F_a(t) = n_{ads}(t)/n_{tot}$ evolves as:

$$\begin{aligned} F_a(t+\Delta t) &= \frac{n_{ads}(t)}{n_{tot}} + \frac{p_a N_{ads}}{N_f} \frac{n_f(t)}{n_{tot}} - p_d \frac{n_{ads}(t)}{n_{tot}} \\ &= (1-p_d)\, F_a(t) + \frac{p_a N_{ads}}{N_f}\,(1-F_a(t)) \\ &= \left(1 - p_d - \frac{p_a N_{ads}}{N_f}\right) F_a(t) + \frac{p_a N_{ads}}{N_f} \end{aligned} \tag{3}$$

Finally, since for $t \to \infty$ we have $F_a(t+\Delta t) = F_a(t)$, we obtain in this limit:

$$\lim_{t\to\infty} F_a(t) = \left(1 + \frac{p_d N_f}{p_a N_{ads}}\right)^{-1} , \tag{4}$$

which is the result indicated in the main text.



a b

Figure 1. Simple model showing the effect of the flux on the adsorbed density. a. Scheme of the modele and exchanges between the bulk, site 1 and site 2. b. Evolution with time of the adsorbed quantity ($p_a = 0.1, p_d = 0.05$). Black curves correspond to n_1, red curves correspond to n_2 and blue curves correspond to $n_1 + n_2$. Diamonds correspond to $p_v = 0.01$, circles to $p_v = 0.02$ and triangles to $p_v = 0.03$

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B. RESULTS ON A 3 SITES ANALYTICAL MODEL SHOWING THE DISPARITY OF ADSORBED DENSITY IN VERY SIMPLE CASE

In order to understand well the behaviour influence of transport on adsorption we want to know if a transport parameter can modify the local quantity adsorbed without modifying the total fraction adsorbed.

We consider the system shown on Figure 1a having two adsorption sites 1 and 2 and a bulk reservoir representing the fluid. We assume that the bulk reservoir is homogeneous and the transport is set on the surface. The particles has the same probability to desorb ($p_a = k_a\Delta t/\Delta x$) and to adsorb ($p_d = k_d\Delta t$) between the bulk and the site 1 as between the bulk and the site 2. The site 1 as a probabilty p_v to transfert particles to the site 2. We call n_1 the population of site 1, n_2 the population of site 2, n_f the population of the bulk and $n_{tot} = n_1 + n_2$). The populations evolve according to:

$$n_1(t + \Delta t) = (1 - p_v - p_d)n_1(t) + n_f(t)p_a \tag{5}$$

$$n_2(t + \Delta t) = (1 - p_d)n_2(t) + n_f(t)p_a + n_1(t)p_v \tag{6}$$

$$n_f(t + \Delta t) = (1 - 2p_a)n_f(t) + (n_1(t) + n_2(t))\,p_d \tag{7}$$

Combining Equation 5 and Equation 6 we obtain:

$$\frac{n_2}{n_1} = \frac{2p_v + p_d}{p_d} \tag{8}$$

and,

$$n_{tot} = n_1 + n_2 = \frac{2n_f p_a}{pd} \tag{9}$$

Figure 1b shows the evolution of n_1, n_2 and n_{tot} for different values of p_v. When p_v increases, n_1 decreases and n_2 increases. However, regardless to the value of p_v, n_{tot} has always the same value. This result is an agreement with the Equation 9 where n_{tot} does not depend on p_v. This mechanism therefore results in local heterogeneities without modifying the overal balance between adsorbed and free solutes.

C. RELATION BETWEEN REDUCED UNITS AND LATTICE UNITS IN LATTICE BOLTZMANN SIMULATIONS

The Lattice Boltzmann code `laboetie` runs in reduced units (also called LB units). We present below the relation to transform the adimensional results in scientific international units (SI units). The Table I summarize the symbols and their units used here. In LB units the distance between two nodes of the grid corresponds to x_{lb}. The time step corresponds to t_{lb}. In the algorithm, the viscosity of the fluid is constant ($\nu_{lb} = 1/6$ in lattice units)[1]. The density of the fluid is also dimentionless. It has be considered constant, correponding to an incompressible fluid ($\rho_{lb} = 1$ lattice units). Translating to real units first requires defining the real distance between two nodes x_r and the real viscosity of the fluid ν_r (in SI units). The resulting time step can then be calculated as:

$$t_r = t_{lb} \frac{\nu_{lb} x_r^2}{\nu_r x_{lb}^2} \, . \tag{10}$$

The real external force density $Fext_r$ can be computed when we further specify the real density of the fluid ρ_r:

$$\frac{Fext_r}{Fext_{lb}} = \frac{P_r x_{lb}}{P_{lb} x_r} = \frac{f_r x_{lb}^3}{f_{lb} x_r^3} = \frac{m_r x_{lb}^2 t_{lb}^2}{m_{lb} x_r^2 t_r^2} = \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left(\frac{t_{lb}}{t_r}\right)^2 \tag{11}$$

or:

$$Fext_r = Fext_{lb} \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left(\frac{t_{lb}}{t_r}\right)^2 \tag{12}$$

Similarly, the average velocity of the fluid is computed using:

$$\bar{v}_r = \bar{v}_{lb} \frac{x_r t_{lb}}{x_{lb} t_r} \, , \tag{13}$$

for the bulk diffusion coefficient:

$$Db_r = Db_{lb} \frac{x_r^2 t_{lb}}{x_{lb}^2 t_r} \, , \tag{14}$$

for the adsorption coefficient:

$$ka_r = ka_{lb} \frac{x_r t_{lb}}{x_{lb} t_r} \, , \tag{15}$$

and for the desorption coefficient:

$$kd_r = kd_{lb} \frac{x_r^2 t_{lb}}{x_{lb}^2 t_r} \, . \tag{16}$$

The pore volume and specific surface area are simply given by $V_p = N_f x_r^3$ and $S_s = N_{\text{ads}} x_r^2$, respectively.
For the total concentration of species in the fluid:

$$C_{tot} = \frac{Dmax_r x_r^2}{Dmax_{lb} V_p x_{lb}^2} \tag{17}$$

For the external concentration of species *i.e.* the contration of species present in the fluid at the adsorption equilibrium:

$$C_{ext} = C_{tot}(1 - F_a) \tag{18}$$

For the maximum amount of adsorbed tracers for each adsorption site:

$$Dmax_r = Dmax_{lb} \frac{V_p C_i x_{lb}^2}{x_r^2} \tag{19}$$

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[1] S. Succi, The Lattice Boltzmann Equation, (Oxford Science Publications), 2001

Description	Name in LB units	LB units	Name in SI units	SI units
Distance between two nodes	x_{lb}	Δx	x_r	m
Time step	t_{lb}	Δt	t_r	s
Mass	m_{lb}	Δm	m_r	kg
Force	f_{lb}	$\Delta f = \Delta m.\Delta x.\Delta t^{-2}$	f_r	N
Pressure	P_{lb}	$\Delta p = \Delta f.\Delta x^{-2}$	m_r	Pa
Viscosity	ν_{lb}	$\Delta x^2.\Delta t^{-1}$	ν_r	m^2. s^{-1}
Density	ρ_{lb}	$\Delta m.\Delta x^{-3}$	ρ_r	kg.m^{-3}
External force density	$Fext_{lb}$	$\Delta p.\Delta x^{-1}$	$Fext_r$	Pa.m^{-1}
Average speed	$\bar{v}_{lb}$	$\Delta x.\Delta t^{-1}$	$\bar{v}_r$	m.s^{-1}
Bulk diffusion coefficient	Db_{lb}	$\Delta x^2.\Delta t^{-1}$	Db_r	m^2.s^{-1}
Adsorption coefficient	ka_{lb}	$\Delta x.\Delta t^{-1}$	ka_r	m.s^{-1}
Desorption coefficient	kd_{lb}	Δt^{-1}	kd_r	s^{-1}
Maximum amount of adsorbed tracers for each adsorption site	$Dmax_{lb}$	-	$Dmax_r$	kg.m^{-2}
Initial concentration	-	-	C_i	kg.m^{-3} or g.L^{-1}
External concentration	-	-	C_{ext}	kg.m^{-3} or g.L^{-1}
Porous volume	N_f	-	V_p	m^3
Specific surface area	$Nads$	-	S_s	m^2

Table I. Description of the different variables used in LB units and SI units