Supplementary Information

Unexpected coupling between flow and adsorption in porous media

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A. ANALYTICAL EXPRESSION FOR THE FRACTION OF ADSORBED PARTICLES

We introduce the following quantities:

- $N_{\text{ads}}$: Number of adsorption sites
- $N_f$: Number of fluid sites
- $n_{\text{ads}}$: Number of adsorbed particles
- $n_f$: Number of free particles
- $n_{\text{tot}}$: 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:

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

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

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

$$F_a(t + \Delta t) = \frac{n_{\text{ads}}(t)}{n_{\text{tot}}} + \frac{p_a N_{\text{ads}}}{N_f} \frac{n_f(t)}{n_{\text{tot}}} - p_d \frac{n_{\text{ads}}(t)}{n_{\text{tot}}}$$

$$= (1 - p_d) F_a(t) + \frac{p_a N_{\text{ads}}}{N_f} (1 - F_a(t))$$

$$= \left(1 - p_d - \frac{p_a N_{\text{ads}}}{N_f}\right) F_a(t) + \frac{p_a N_{\text{ads}}}{N_f}$$  (3)

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

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

which is the result indicated in the main text.
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 \( p_d = k_d \Delta t/\Delta x \) and to adsorb \( p_a = k_a \Delta t \) between the bulk and the site 1 as between the bulk and the site 2. The site 1 as a probability \( p_v \) to transfer 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:

\[
\begin{align*}
    n_1(t + \Delta t) &= (1 - p_v - p_d)n_1(t) + n_f(t)p_a \\
    n_2(t + \Delta t) &= (1 - p_d)n_2(t) + n_f(t)p_a + n_1(t)p_v \\
    n_f(t + \Delta t) &= (1 - 2p_d)n_f(t) + (n_1(t) + n_2(t))p_d
\end{align*}
\]

Combining Equation 5 and Equation 6 we obtain:

\[
\frac{n_2}{n_1} = \frac{2p_v + p_d}{p_d}
\]

and,

\[
n_{tot} = n_1 + n_2 = \frac{2n.fp_a}{p_d}
\]

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 overall balance between adsorbed and free solutes.
C. RELATION BETWEEN REDUCED UNITS AND LATTICE UNITS IN LATTICE BOLTZMANN SIMULATIONS

The Lattice Boltzmann code \texttt{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). The density of the fluid is also dimensionless. It has be considered constant, corresponding 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 $\nu_r$ (in SI units). The resulting time step can then be calculated as:

$$t_r = \frac{\nu_{lb} x_{lb}^2}{\nu_r x_r^2}$$  \hspace{1cm} (10)

The real external force density $F_{ext_r}$ can be computed when we further specify the real density of the fluid $\rho_r$:

$$\frac{F_{ext_r}}{F_{ext_{lb}}} = \frac{P_r x_{lb}}{P_{lb} x_r} = \frac{f_{r} x_{lb}^3}{f_{lb} x_r^3} = \frac{m_r x_{lb}^2 t_{lb}^2}{m_{lb} x_r^2 t_r^2} = \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left( \frac{t_{lb}}{t_r} \right)^2$$  \hspace{1cm} (11)

or:

$$F_{ext_r} = F_{ext_{lb}} \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left( \frac{t_{lb}}{t_r} \right)^2$$  \hspace{1cm} (12)

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

$$\bar{v}_r = \bar{v}_{lb} \frac{x_r t_{lb}}{x_{lb} t_r}$$  \hspace{1cm} (13)

for the bulk diffusion coefficient:

$$D_{br} = D_{lb} \frac{x_{lb}^2 t_{lb}}{x_r t_r}$$  \hspace{1cm} (14)

for the adsorption coefficient:

$$k_a = k_{lb} \frac{x_{lb}}{x_r t_r}$$  \hspace{1cm} (15)

and for the desorption coefficient:

$$k_d = k_{lb} \frac{x_{lb}^2 t_{lb}}{x_r t_r}$$  \hspace{1cm} (16)

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

$$C_{tot} = \frac{D_{max} x_r^2}{D_{max_{lb}} V_p x_{lb}^3}$$  \hspace{1cm} (17)

For the external concentration of species \textit{i.e.} the contraction of species present in the fluid at the adsorption equilibrium:

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

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

$$D_{max} = D_{max_{lb}} \frac{V_p C_i x_{lb}^2}{x_r^2}$$  \hspace{1cm} (19)

\footnote{S. Succi, The Lattice Boltzmann Equation, (Oxford Science Publications), 2001}
<table>
<thead>
<tr>
<th>Description</th>
<th>Name in LB units</th>
<th>LB units</th>
<th>Name in SI units</th>
<th>SI units</th>
</tr>
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<tbody>
<tr>
<td>Distance between two nodes</td>
<td>$x_{lb}$</td>
<td>$\Delta x$</td>
<td>$x_r$</td>
<td>m</td>
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<tr>
<td>Time step</td>
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<td>$\Delta t$</td>
<td>$t_r$</td>
<td>s</td>
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<tr>
<td>Mass</td>
<td>$m_{lb}$</td>
<td>$\Delta m$</td>
<td>$m_r$</td>
<td>kg</td>
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<td>Force</td>
<td>$f_{lb}$</td>
<td>$\Delta f = \Delta m \cdot \Delta x \cdot \Delta t^{-2}$</td>
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<td>N</td>
</tr>
<tr>
<td>Pressure</td>
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<td>$\Delta p = \Delta f \cdot \Delta x^{-2}$</td>
<td>$p_r$</td>
<td>Pa</td>
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<td>Viscosity</td>
<td>$\nu_{lb}$</td>
<td>$\Delta x^{-2} \cdot \Delta t^{-1}$</td>
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<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Density</td>
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<td>$\Delta m \cdot \Delta x^{-3}$</td>
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<td>kg m$^{-3}$</td>
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<tr>
<td>External force density</td>
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<td>$\Delta p \cdot \Delta x^{-1}$</td>
<td>$F_{ext_r}$</td>
<td>Pa m$^{-1}$</td>
</tr>
<tr>
<td>Average speed</td>
<td>$\bar{v}_{lb}$</td>
<td>$\Delta x \cdot \Delta t^{-1}$</td>
<td>$\bar{v}_r$</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>Bulk diffusion coefficient</td>
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<td>$\Delta x \cdot \Delta t^{-1}$</td>
<td>$D_r$</td>
<td>m$^2$ s$^{-1}$</td>
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<tr>
<td>Adsorption coefficient</td>
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<td>$\Delta x \cdot \Delta t^{-1}$</td>
<td>$k_{a_r}$</td>
<td>m$^2$ s$^{-1}$</td>
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<tr>
<td>Desorption coefficient</td>
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<td>$\Delta t^{-1}$</td>
<td>$k_{d_r}$</td>
<td>s$^{-1}$</td>
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<td>Maximum amount of adsorbed tracers for each adsorption site</td>
<td>$D_{max_{lb}}$</td>
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<td>$D_{max_r}$</td>
<td>kg m$^{-2}$</td>
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<td>Initial concentration</td>
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<td>-</td>
<td>$C_i$</td>
<td>kg m$^{-3}$ or g L$^{-1}$</td>
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<tr>
<td>External concentration</td>
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<td>-</td>
<td>$C_{ext}$</td>
<td>kg m$^{-3}$ or g L$^{-1}$</td>
</tr>
<tr>
<td>Porous volume</td>
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<td>$V_p$</td>
<td>m$^3$</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>$Nads$</td>
<td>-</td>
<td>$S_s$</td>
<td>m$^2$</td>
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</tbody>
</table>

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