# Adsorption and Desorption

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# 1 Theory

The reactive transport module of MOOSE[1] solves quite general advection-dispersion-reaction equations. Such equations are found in porous media, for example. The adsorption/desorption kernels described herein are a small addition to such scenarios. They can also be used to describe adsorption and desorption in systems governed by the multi-phase Richards' equation.

The adsorption/desorption equation is

$$\dot{C} = \begin{cases} -(C - C_e)/\tau_d & \text{for} \quad C \geq C_e \\ -(C - C_e)/\tau_a & \text{for} \quad C < C_e \, . \end{cases} \tag{1.1}$$

In this equation:

- $C = C(x,t)$ is the adsorbed concentration of a fluid (mass/volume, usually kg.m$^{-3}$). In the porous-media setting, $C$ is the concentration of the fluid within the matrix of the porous medium, for example, the concentration of methane adsorbed into the coal matrix. Note the units: experiments often quote concentration as mass-of-fluid-at-standard-temperature-and-pressure divided by mass-of-matrix. To convert such an experimental value to $C$, the experimental value must be multiplied by the density of the fluid at standard temperature and pressure.

- $\tau_d$ is the time-constant for desorption.

- $\tau_a$ is the time-constant for adsorption.

- $C_e$ is the equilibrium concentration, described more fully below

The governing equation is therefore free of spatial derivatives, and is just a Newton-cooling equation.

In many cases the fluid is desorbed from the matrix into the porespace (and adsorbed from the porespace back to the matrix), and there is another equation governing the mass of the fluid in the porespace:

$$\dot{\rho} = \frac{1}{\tau}(C - C_e) + \ldots \, . \tag{1.2}$$

Here $\rho$ is the mass density of the fluid in the porespace (which is usually the product of porosity, density and saturation of the fluid). The $(C - C_e)/\tau$ term is the rate of desorption (with $\tau = \tau_d$) or adsorption (with $\tau = \tau_a$) from the matrix to the porespace. The final "..." represent other physics, such as advection or dispersion which are unimportant here.

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[1]L Guo, H Huang, DR Gaston, CJ Permann, D Andrs, GD Redden, C Lu, DT Fox, Y Fujita, "A parallel, fully coupled, fully implicit solution to reactive transport in porous media using the preconditioned Jacobian-Free Newton-Krylov Method" Advances in Water Resources 53 (2013) 101–108

Finally, $C_e$ must be defined, and there are many different possible forms. So far I have only coded the Langmuir version, which is defined by

$$C_e = \frac{\rho_L P}{P + P_L} \ . \tag{1.3}$$

In this equation $\rho_L$ is the "Langmuir density" (measured in mass/volume, usually kg.m$^{-3}$). Usually the Langmuir *volume* is used, which is the volume of adsorbed gas at standard temperature and pressure, divided by the volume of the matrix. This is inconvenient in MOOSE as everything else is measured in mass/volume. Therefore, the usual Langmuir volume must be multiplied by the density of gas at standard temperature and pressure to yield the "Langmuir density":

$$\rho_L = V_L \times \rho_{stp} \ . \tag{1.4}$$

$P_L$ is the "Langmuir pressure" (with the same units as $P$). $P$ is the (partial) pressure of the fluid in the porespace that appears in Eqn (**??**).

# 2 MOOSE implementation

The RHSs of Eqn (**??**) and Eqn (**??**) (without the ... terms) have been coded as two Kernels. The reason for having two, rather than one, is to make the Jacobian contributions simple.

The Langmuir equilibrium concentration, Eqn (**??**), has been coded into a Material class, which stores $\rho_L$ and $P_L$, and calculates $C_e$ as well as its derivative with respect to $P$. By doing this, rather than getting the Kernels to calculate $C_e$, I hope future developers will be able to more easily code different forms for $C_e$.

# 3 Tests

It is sufficient to test the following system of equations

$$
\begin{aligned}
\dot{C} &= -(C - C_\mathrm{e})/\tau\,, \\
\dot{P} &= (C - C_\mathrm{e})/\tau\,, \\
C_\mathrm{e} &= \frac{\rho_L P}{P_L + P}\,.
\end{aligned}
\tag{3.1}
$$

These equations are not supposed to be physically meaningful (for instance, $P_L$ has dimensions mass/volume), but they have simple solutions. I have used $\tau = \tau_d = \tau_a$.

## 3.1 A test of the Jacobian

The Jacobians of the two Kernels both involve diagonal terms (derivatives wrt the variable) and off-diagonal terms (derivatives wrt the other variable). The automatic test suite uses PETSc's `snes_type=test` (a finite-difference) to test that these Jacobian entries are correct.

## 3.2 A test of the dynamics

A single-element model is initialised with $C = 1 = P$, and $\tau = 1.1$, $\rho_L = 0.88$ and $P_L = 1.23$. The simulation is run to $t = 2$, and compared with an Excel solution of Eqns (**??**). Good agreement is shown in Figure **??**. This test is part of the automatic test suite that is run every time the MOOSE core code is updated.
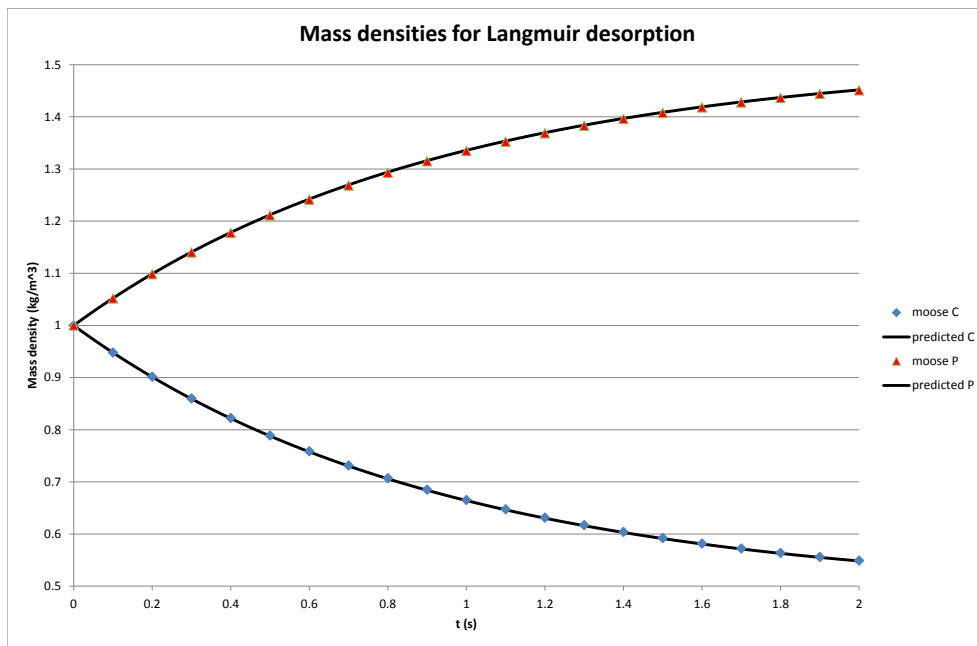
Figure 3.1: Comparison of the MOOSE solution (dots) to Eqn (**??**) and an Excel solution (lines) demonstrating that MOOSE's implementation of the equations is correct.