

A Differential Model of Adsorption Hysteresis with Applications to Chromatography

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In this paper we discuss a class of models that can be applied to a variety of phenomena occurring in chromatography or other related disciplines, see [21]. These models have the general form of transport equations (viscous or inviscid) complemented by some nonlinear adsorption relation in equilibrium or non-equilibrium conditions written for one or more species on a single or multiple scale. Here we are mainly interested in the presence of hysteresis in the adsorption relation and in its influence upon the solutions to the model.

In Section 1 we first introduce the basic transport model and describe the typical behavior of solutions to problems with linear, convex, or concave adsorption isotherms. This will be the basis for the discussion of the solutions corresponding to a multivalued hysteretic isotherm relationship which has a convex-concave multivalued graph. The analytical results to that problem are summarized in Section 2. They have been jointly obtained by R. E. Showalter and the author and reported in detail in [21]. In Section 3 we discuss the extensions of the basic model.

1 Modeling

Here we present the equations governing the transport of mass and adsorption phenomena in a chromatographic column. Since its rise in the beginning of 20th century, chromatography has become a wide industrial domain delivering analytical as well as production tools. A variety of chemical substances are employed as components of the chromatographic columns: they differ in phase (gaseous, liquid, solid) as well as in the type of mutual interaction (by physical forces, chemical reaction, or mechanical filtration). Because of the diversity of these processes, we do not attempt below to calibrate the models; rather, we try to emphasize the dynamics of different phenomena.

Suppose that the adsorption process is occurring in a column of length L packed with immobile particles that constitute the stationary phase through which the mobile phase is being transported. The length of the column is assumed to be considerably larger than its axial size, so that the transport is essentially one-dimensional. The

positions of the inlet and of the outlet of the column are at $x = 0, x = L$, respectively. The mobile phase, i.e., the solution, is composed of the solvent and some chemicals dissolved in it, and it moves in the direction of increasing x . The solvent itself plays no role: we assume that it does not interact directly with the stationary phase but only serves as a carrier for the travelling species. We denote by u the concentration of the species in the mobile phase, which is dependent on the position x and on the time t . The concentration in the stationary phase (in its fluid part) is denoted by $v(x, t)$. In the case of multiple species (see Section 3) we consider variables u_i, v_i .

The stationary (particle) phase (adsorber, bed) is composed of porous particles much bigger than the travelling molecules of the adsorbent; the difference in sizes can be of the order of 10 or even 1000. The predominant phenomenon accompanying the transport is the adsorption of the mobile species on the outer surface of the stationary particles. Other physico-chemical processes can also occur; see Section 3.

We assume that the velocity of the mobile phase as well as the porosity of the column are constant, and we normalize the variables u, v so that the constant coefficients are eliminated. The mass balance equation in the classical form (see [23]) then is

$$u_t + v_t + u_x = 0, \quad (1)$$

where the subscripts denote partial derivatives.

The mobile phase is inserted at one end of the column ($x = 0$) and extracted on the other ($x = L$). The output depends on the initial state of the bed. In the *elution* mode the bed is initially empty and the (possibly multicomponent) feed comes in the form of a pulse: at the column outlet one expects to recover separated components in the form of individual “peaks”. Other chromatographic modes like *displacement, frontal mode, pressure swing, temperature swing* (see [24]) are not discussed here.

The boundary and initial conditions appropriate for the elution mode are

$$u(x, 0) = v(x, 0) = 0, \quad (2)$$

$$u(0, t) = \varphi(t). \quad (3)$$

The equations (1–3) have to be complemented by a relation between u and v . In this Section we assume that it is given in the form of an equilibrium relation

$$v = m(u) \quad (4)$$

with a nonnegative nondecreasing *isotherm* $m(\cdot)$ obtained experimentally. The equation (1) together with (4) can be rewritten as a classical scalar conservation law

$$u_t + (f(u))_x = u_t + f'(u)u_x = 0$$

by setting $f(u) = (I + m)^{-1}(u)$ and as such becomes a well known problem (see for example [27]). We are interested here in the behavior of $u(x, t)$ inside the column and also in the outlet profile, $u(L, t)$, known as the *chromatogram* or the *breakthrough curve*. We shall now consider 3 main types of isotherms yielding three different shapes of the solution u . These will be the building blocks in our discussion of hysteresis.

The three types of m are a) linear, b) concave (Langmuir, Freundlich) and c) convex (anti-Langmuir). Note that, in the classical setting, the corresponding shape of f is a)

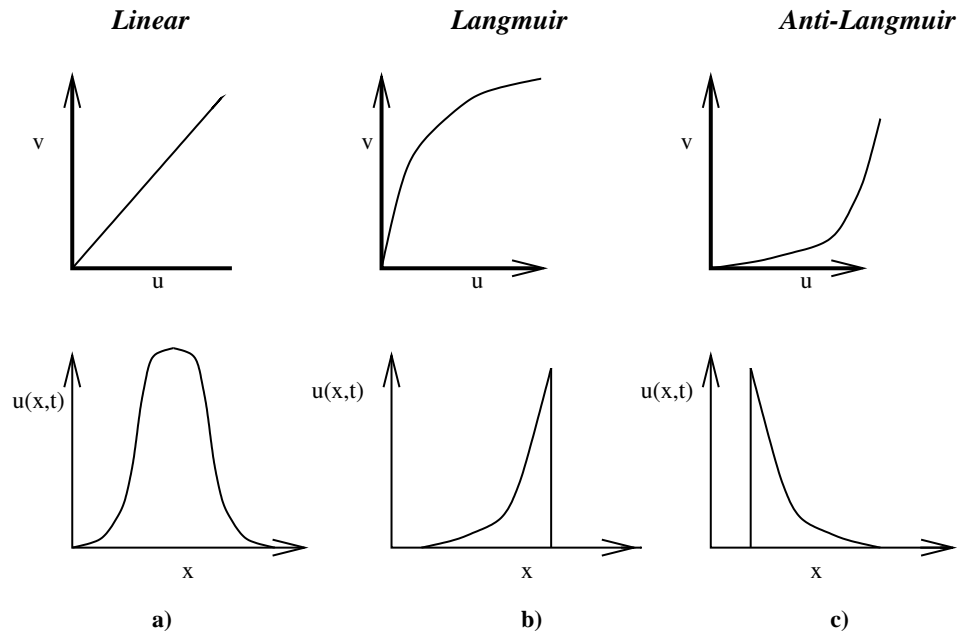


Figure 1: Typical isotherms and corresponding travelling waves

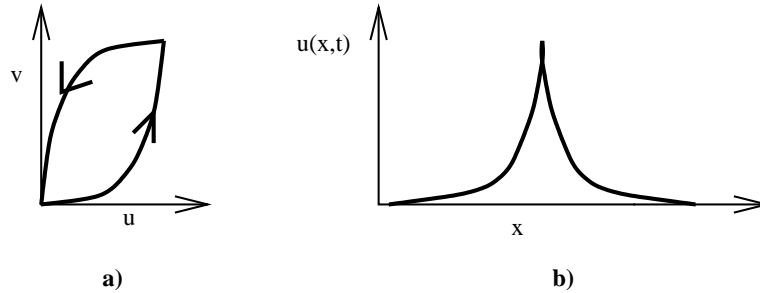


Figure 2: Convex symmetric adsorption hysteresis graph and solution

linear, b) convex and c) concave, respectively. Consider next the graph of $f'(u)$ which plays the role of velocity of the front of the travelling wave. The function $f'(u)$ is then in case a) constant, in case b) it is increasing and in case c) decreasing. Suppose the initial feed is a smooth Gaussian pulse. Then the shape of u at a given t , as a function of x is in case a) exactly the same as the initial feed, because it is a linear translate of the feed profile. In case b) a shock arises, since the velocity of the higher concentrations is larger, hence a “vertical” front arises. See [27] for the discussion of entropy solutions and shocks. The travelling shock is followed by a rarefaction which arises because smaller concentrations have decreasing velocities. Finally, in case c) we observe a situation dual to the one from b): a rarefaction is followed by a shock. The schematic picture of the three modes is presented in Figure 1.

In practice it is frequent that the shape of m is not uniformly concave or convex, but rather sigmoid (e.g., the *B-E-T isotherm*). The solution profiles then are composed of combined shocks and rarefactions. Another possibility is the one of hysteresis in

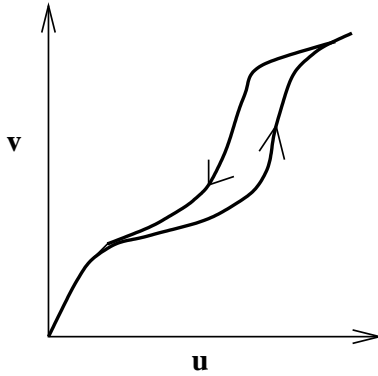


Figure 3: Example of adsorption/desorption hysteresis

which the adsorption and desorption curves are different. For example, suppose that the hysteresis loop is composed of a convex adsorption curve (increasing concentration) complemented by a concave desorption curve (decreasing concentration) as illustrated in Figure 2a. Using the above reasoning we can anticipate the shape of the solution: the profile of the travelling wave will be composed of two “rarefactions”; one following the other (see Figure 2b). This case is discussed in Section 2.

2 Convex-sided hysteresis graph

The adsorption phenomena may have irreversible character, of either rate dependent (see [17]) or rate independent type. To the latter belongs the adsorption/desorption hysteresis which has been studied already in the '40ies (see [11, 3, 16] and recent work in [25, 32, 2, 10]). In classical theories the adsorption hysteresis is compared to the one occurring in capillary condensation (contact angle theories, see [3, 16, 8, 25]). Other groups of rheological models for hysteresis are related either to the multilayer BET theories (see [32, 25]) or to the thermodynamic theories based on different enthalpies of adsorption and desorption (see [2] and references therein) or to the presence of some extra, *implicit* chemicals (see [10, 2]). Finally, adsorption may be a result of or be accompanied by irreversible changes in the adsorbing bed, for example, due to the swelling of hydrophobic clay particles (see [4, 32]).

Below we assume a general form of the adsorption/desorption curves: they are formed by two monotone graphs, coming together at certain low and high thresholds, with the one corresponding to adsorption lying below the one for desorption; see Figure 3. Such is the form documented, for example, in [16]. To describe this multivalued relationship, we write

$$v \in \mathcal{M}(u), \tag{5}$$

and this relation would replace (4) in the model. The graph \mathcal{M} is assumed to be monotone.

In the previous Section we discussed solutions to the transport problem (1–4). It was indicated that nonlinear isotherms give rise to shock discontinuities in the solution. This means that the solutions can be discussed in a very weak (L^1) sense only (see

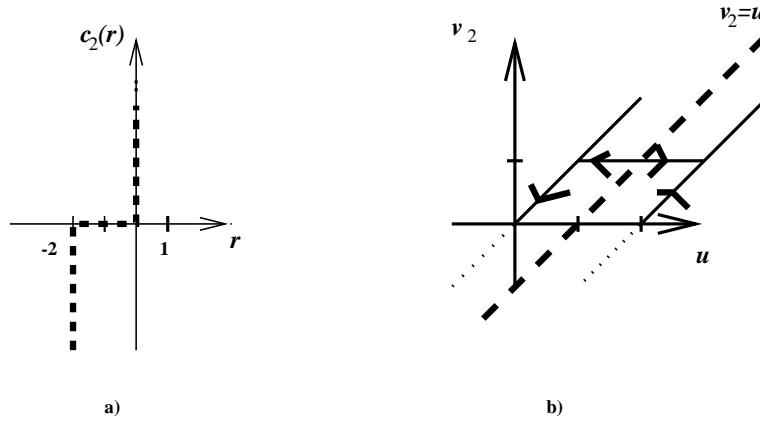


Figure 4: Preisach construction of hysteresis. Left: c_2 graph. Right: relationship between input u and output v_2 .

[5]): the dynamics of the problem is governed by a semigroup on L^1 . Suppose that we substitute (4) with (5). Then the smoothness of solutions in general cannot improve for a general (monotone) graph \mathcal{M} : this follows because $m(u)$ is just a special case of $\mathcal{M}(u)$.

However, the heuristical reasoning carried over at the end of Section 1, shows that a special class of monotone graphs will prohibit the discontinuities. Specifically, if the two sides of the adsorption/desorption graph are convex (with respect to each other), then the resulting profile of $u(x, t)$ is expected to be composed of two smooth curves and the solution remains continuous. Following the above analogy, in this case only a linear $m(u)$ can be a special case of $\mathcal{M}(u)$. The case of a convex-symmetric graph \mathcal{M} leads to an L^2 dynamics what is discussed below (details can be found in [21]).

We first discuss the model of \mathcal{M} . There exist many ways to describe hysteresis relations, see [19] for review. Here we consider a *Preisach* model of hysteresis in which some auxiliary differential equations are defined, see [29, 20] for discussion of Preisach models. For our purposes here (the hysteresis graph is symmetric and convex-sided) the construction following the one in [21] will be used.

We use the sgn^{-1} graph defined for $|r| \leq 1$ as $sgn^{-1}(r) = 0$ if $|r| < 1$, $sgn^{-1}(-1) = (-\infty, 0]$, $sgn^{-1}(1) = [0, \infty)$. The model is built with the use of graphs from a family of rescaled signum inverse. Consider a set of parameters $A \subset \mathcal{R}$, and for a parameter $\alpha \in A$ define

$$c_\alpha(r) = sgn^{-1}\left(\frac{2}{\alpha}r + 1\right).$$

For example, if $\alpha = 2 \in A$, then $c_2(r)$ is the signum inverse graph translated by 1 to the left and so its domain is $[-2, 0]$. See Figure 4a for the graph of c_2 .

Suppose that for a given x, t we have the value of $u(x, t)$ which is our input. Then for every α we consider $v_\alpha(x, t)$ that solves the equation

$$v_{\alpha,t} + c_\alpha(v_\alpha - u) \ni 0. \quad (6)$$

This equation specifies that at all instants of x, t the value of $v_\alpha - u$ must be in the domain of c_α (the interval $[0, -\alpha], \alpha < 0$ or $[-\alpha, 0], \alpha > 0$). Furthermore, whenever

this value reaches the left or the right end of the domain, then the time derivative of the solution may take any positive or any negative value, respectively. For example, for $\alpha = 2$, the solution v_2 remains constant (so that $v_{2,t} = 0$) as long as $u - 2 < v_2 < u$. It is allowed to increase (at an arbitrary rate) provided v_2 equals $u - 2$ or is allowed to decrease, if v_2 equals u . See Figure 4b for the sketch of the u versus v_2 relationship.

The above describes v_α as an output for given data u . The feedback is realized by inserting the collection of v_α into the transport equation in the form of an integral

$$\int_A v_\alpha d\mu_\alpha.$$

In the above the family of measures μ_α is associated with A so that $\{A, \mu\}$ is a positive finite measure space. If $\{A, \mu\}$ is discrete, then \mathcal{M} is piecewise linear, otherwise smooth curves can be constructed by way of second derivatives of the isotherms, see [21]. The integral above can be understood as the value of some v which then must satisfy (5).

In summary, the system to be solved now is

$$(u + \int_A v_\alpha d\mu_\alpha)_t + u_x = 0 \tag{7}$$

$$v_{\alpha,t} + c_\alpha(v_\alpha - u) \ni 0, \alpha \in A \tag{8}$$

$$u(0, t) = \varphi(t) \tag{9}$$

$$u(x, 0) = 0 = v_\alpha(x, 0). \tag{10}$$

The problem (7–10) is an evolution equation in t . The non-evolution terms of the equation are associated with an operator which can be proved to be m-accretive. This leads to an existence–uniqueness result:

If $\varphi \in W^{2,1}(0, T)$ and $\varphi(0) = 0$, then there is a unique solution of (7–10) with $u, v_\alpha \in W^{1,\infty}(0, T; L^2(0, L))$ for almost every $\alpha \in A$. This solution satisfies $u_t, u_x, v_{\alpha,t} \in L^\infty(0, T; L^2(0, L))$.

This result can be extended to the problems with diffusion terms and some of the other models discussed in Section 3.

However, it turns out that, because of the similar role that the variables x and t play in the above system, the use of x instead of t as the evolution variable leads to optimal results as far as the regularity requirements on the boundary feed φ are concerned:

If $\varphi \in W^{1,2}(0, T) = H^1(0, T)$, then there is a unique solution of (20) with $u_x \in L^\infty(0, L; L^2(0, T))$, and for all x , $u(x, \cdot) \in H^1(0, T)$, $u(x, 0) = 0$.

The application of this last result is restricted to the system above, with no extra terms (discussed in the last Section) allowed. This is because the “symmetry” of the role of x and t has to be preserved.

3 Extensions

The transport model presented in Section 1 was built under several implicit assumptions. In particular, any effects of compressibility, viscosity and temperature have been

ignored; see [25, 31, 4, 2] for discussion of thermal waves and the effect of temperature on the isotherms (Arrhenius law). Below we discuss some extensions of the model and indicate mathematical problems related to them. We consider separately the diffusion, the kinetics, multiple scales and the case of multiple species. We indicate which extensions can be mixed.

Diffusion. The (Fickian) diffusion terms can complement the transport equation (1) so that it becomes

$$u_t + u_x + v_t - ku_{xx} = 0. \quad (11)$$

The diffusion term (k is a diffusion–dispersion coefficient, for simplicity assumed constant) has a regularizing effect here. In fact, its presence is frequently used as a tool in the analysis of the conservation law (1), where one lets $k \rightarrow 0$ in (11) to recover (1). The equation (11) is formally parabolic and if the isotherm is nonlinear, it is known as a *porous medium equation* whose solutions can have a finite speed of propagation but no sharp fronts are to be expected, see [1] and references therein.

The diffusion terms can accompany virtually all of the extensions described below and they are expected to occur for sure at the microscopic level. The analysis of hysteresis accompanied by diffusion only (without transport) has been studied for example in [26]. However as it was presented in Section 2, the inclusion of the diffusion terms would not change the results for the problem.

Kinetics. The isotherm relationship (4) is established in equilibrium. In other words, it is assumed that the *relaxation time* is small or that the *kinetics* of the adsorption process is very fast with respect to the mass transport velocity. In order to describe the adsorption process which is not in equilibrium, the character of transient behavior (the *order* of kinetics) must be known (see [28, 9, 25]). For example, the *first order kinetics* (right-hand-side linearly dependent on v) can be modeled by (c is a constant)

$$v_t = c(v_\infty - v) = c(m(u) - v), \quad (12)$$

where, by setting $v_t = 0$ or letting $c \rightarrow \infty$ for fast processes, we recover the equilibrium relation $v = v_\infty = m(u)$. In the *second order kinetics*, the right-hand-side functions are polynomials of second degree in u, v . The asymptotics of solutions is similar to the one for the first-order case and is given by the equilibrium relation. For example, in order to recover the Langmuir isotherm, we can use the second order kinetic relation given by (see [12, 25])

$$\frac{\partial}{\partial t}v = c_a u(v_\infty - v) - c_d v. \quad (13)$$

where c_a, c_d are constants.

In general, solutions to nonequilibrium problems, when compared to the equilibrium ones, exhibit relaxation in the form of exponential smoothing. The nonequilibrium profiles asymptotically tend to the (sharper) equilibrium ones. The analysis here involves the study of extra Lipschitz functionals in the equation. It is worth mentioning that the introduction of a non-equilibrium relation is used as a proof technique in parallel to the use of vanishing diffusion terms.

The hysteresis relation is an equilibrium relation established in experiments in which the state of the system was measured after a sufficiently long time to eliminate disturbances. Therefore the presence of hysteresis in the system should be accompanied by non-equilibrium relation only if they concern different species or different length scales.

Multiple species. The main goal of chromatography, the separation of species present in the solution, is due to differing sorption characteristics for the species and to their mutual competition for the adsorption sites. The species that get adsorbed better remain longer attached to the stationary phase, and so the remaining ones move faster through the system.

The modelling in the case of multiple chemicals present in the mobile phase involves writing down balance equations for each species in the form of equation (1). These equations are complemented by appropriate isotherm, kinetic, or hysteresis relations which usually involve cross-dependence of the isotherms between species. For example, the two-component Langmuir second order kinetics are described by the pair of equations

$$\frac{\partial}{\partial t} v_1 = c_{1,a} u_1 (v_{\infty,1} - v_1 - v_2) - c_{1,d} v_1 \quad (14)$$

$$\frac{\partial}{\partial t} v_2 = c_{2,a} u_2 (v_{\infty,2} - v_1 - v_2) - c_{2,d} v_2 \quad (15)$$

If $v_{\infty,1} = v_{\infty,2}$ (necessary for thermodynamic consistency, see [Ruthven]), then at the equilibrium one obtains

$$v_i = c_i \frac{u_i}{1 + u_1 + u_2}, \quad i = 1, 2. \quad (16)$$

The mathematical analysis of the resulting system of equations for u_i, v_i is complex, see [27], and we will not discuss it here.

Multiple scales. The difference in size of the particles of the mobile and of the stationary phase gives rise to several multiscale phenomena which may be the most interesting and difficult to model of all those considered in this Section.

First, it may be possible that the molecules of the mobile phase not only get adsorbed on the outer surface of the bed pellets, but that they also penetrate inside the porous structure, diffuse into the stagnant fluid phase residing in the *micro pores* of the pellets, and interact with their solid part. That interaction can be of physical or chemical nature, and it can involve the adsorption mechanism on the surface of the micro pores. In the case of multiple species, some (smaller) particles could penetrate inside the porous skeleton, whereas the others would remain in the outside mobile phase, thereby leading to the separation induced by different sizes (*size exclusion*, used in *molecular sieves* of gases on zeolites). The process of migration of molecules inside the bed particles is called *partition* ([31]), and it could include the surface migration and/or Knudsen diffusion of molecules into the capillaries on the surface of the pellets and/or Poiseuille flow.

In order to deal with multiple scales (size of the micro pores versus the size of the particles versus the length of the bed) one can use the technique of REV or averaging

or *homogenization*; see e.g. development of models in [30, 14, 18] or explicit models from engineering literature in [25, 12]. The model we propose here is already a limiting model in the sense of the homogenization and is similar in nature to the one given in [12]; see the development of *double porosity models* in [7] and classical references therein. We assume that at each point x there is a (microscopic) particle Ω_x whose surface Γ_x provides the site for the exchange between $u(x, t)$ and $v(x, y, t)$ governed by a dynamic boundary condition. The changes in the input $u(x, t)$ applied on the boundary Γ_x drive the diffusion inside the particle where we consider a microscopic position variable $y \in \Omega_x$. The microscopic balance equation and the dynamic boundary condition are (the variables are again normalized)

$$(v + w)_t - K \Delta_y v = 0, \quad y \in \Omega_x \quad (17)$$

$$K \frac{\partial v}{\partial \eta} + \frac{1}{\sigma}(v - u) = 0, \quad y \in \Gamma_x \quad (18)$$

Above K is the (microscopic) diffusion coefficient, and σ controls the exchange relaxation time. Note that there is no convection term in (17): this is because on the microscopic scale locally only the diffusion is significant. Now the macroscopic balance equation (11) has to be modified, and it is given by

$$u_t + \frac{1}{|\Omega_x|} \int_{\Gamma_x} K \frac{\partial v}{\partial \eta} dS_y + u_x - k \Delta u = 0. \quad (19)$$

With $\sigma \rightarrow 0, K \rightarrow \infty$, the last equation reduces to the classical one (11) (if $k = 0$ the (1) is obtained) in which $v(x, t)$ takes the meaning of the (average) concentration in the (*lumped*) particle phase.

The equations have to be complemented by a counterpart of (4) which now must be written for w and v . It could be an equilibrium or non-equilibrium adsorption isotherm or hysteresis relation. In the case of multiple species present, we could write equations for some of the species involving microscale, while the others (for example, those subject to the size exclusion process) would be considered only in the “macroscopic, lumped” form. It is important though to realize that by introducing microscopic equations we change the time scale of the problem and so all the variables should then be considered practically as being in non-equilibrium. Therefore, for example, the appearance of hysteresis (observed in equilibrium) has to be carefully matched to other relations, preferably of equilibrium type.

The analysis of problems with multiple scales suggests that their solutions are expected to be smoother than the ones to the original (nonlinear) transport problems. The coupling integral term in (19) together with the boundary condition (18) can be asymptotically represented as a convolution of v_t with a weakly singular kernel. Such a term introduces smoothing effects. See [6] and the previous work [22] done in the context of viscoelasticity equations.

The analytical results corresponding to the extensions discussed in this Section will be reported in a forthcoming paper.

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