

Transport of solutes undergoing a Freundlich type nonlinear and nonequilibrium adsorption process

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We investigate the behavior of solutes undergoing nonequilibrium adsorption processes that lead to a Freundlich isotherm in equilibrium. In contrast to a frequently used model we do not assume that the adsorption rate is proportional to the difference between adsorbed and equilibrium concentrations, but inspect two nonlinear laws governing the path to equilibrium. With some asymptotic considerations and numerical simulations we find that depending on the model parameters, the concentration in solution and the mass adsorbed by the matrix do not necessarily reach quasiequilibrium.

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I. INTRODUCTION

In continuum approximations, transport of solutes in porous media is usually described by the so-called advection-dispersion (or convection-diffusion) equation

$$\frac{\partial c}{\partial t} = -\mathbf{U} \cdot \nabla c + \nabla \cdot \mathbf{D} \nabla c + Q, \quad (1)$$

complemented by appropriate initial/boundary conditions. Here c denotes the concentration of the solute, \mathbf{U} is the velocity of the fluid, \mathbf{D} is the effective dispersion tensor, and Q represents sources or sinks. The latter can be used to describe interactions with the sediment, e.g., by adsorption/desorption.

In this paper we shall focus on this kind of solute-matrix interaction. If we denote by s the mass adsorbed to the solid matrix, we obtain $Q = -\partial s / \partial t$ due to mass conservation. Further we assume one spatial dimension and homogeneous U and D , such that the transport equation now reads

$$\frac{\partial c}{\partial t} = -U \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - \frac{\partial s}{\partial t}. \quad (2)$$

The simplest possible relation between s and c is a local equilibrium where s is just a function (called “isotherm”) of c ,

$$s = f(c). \quad (3)$$

In case of a linear isotherm, $s = kc$, the solutions of the transport equation can be found from the solutions of Eq. (1) with $Q = 0$ by rescaling the time by a “retardation factor” $1/(1+k)$.

In natural porous media, however, usually more complicated and nonlinear isotherms are observed, e.g., the Langmuir isotherm $s = k_1 c / (1 + k_2 c)$ taking into account that there is only a finite number of adsorption sites in the me-

dium. Frequently one observes power laws over several orders of magnitude, called “Freundlich isotherms,”

$$s = kc^n, \quad (4)$$

where k and n are constants with $0 < n \leq 1$ for many substances such as pesticides, polycyclic aromatic hydrocarbons (PAH's), or heavy metals ([1–5]).

A further complication is that in many cases the transport of substances is too fast to allow a description of the adsorption process by an equilibrium process. Unfortunately, finding an appropriate phenomenological model for the adsorption process is a very difficult and work-intensive procedure on the experimental side and an ill-posed problem on the theoretical side.

In this paper we show the following.

(i) The path to equilibrium is highly important for the asymptotic transport behavior of substances. Systems with the same equilibrium isotherm that approach the isotherm following different laws can show fundamentally different behavior if both transport and adsorption are taking place.

(ii) The concentrations in the nonequilibrium reactive transport model can differ by many orders of magnitude from concentrations predicted from an equilibrium model with the same isotherm.

(iii) Even a substance obeying a linear isotherm can show markedly nonlinear behavior if the path to the equilibrium is governed by a nonlinear relationship.

Further we rederive some well-known results for the diffusive case for illustration of the limitations and possible modifications of the form of the asymptotic solution we are assuming.

II. TWO GENERALIZED NONLINEAR NONEQUILIBRIUM MODELS

A frequently used model for the temporal change of the adsorption rate on the concentration c and the adsorbed mass s per unit volume is proportional to the deviation from the equilibrium isotherm,

$$\frac{\partial s}{\partial t} = r(kc^n - s), \quad (5)$$

with $r, k > 0$ and $0 < n \leq 1$ (e.g., Ref. [6]). This model is, like most other models, purely phenomenological and not derived from basic principles. It is interesting to note that there is a linear dependence on s , but a nonlinear dependence on c . In equilibrium, s and c are related by the Freundlich isotherm,

$$s = kc^n. \quad (6)$$

In this paper we shall investigate two nonequilibrium models that share this latter property, i.e., which lead to a Freundlich isotherm in equilibrium, but show a nonlinear dependence both on s and c . Both models are generalizations of Eq. (5) and have to our knowledge not been discussed in the literature.

Model 1:

$$\frac{\partial s}{\partial t} = r(k_p c^p - s^q), \quad (7)$$

with $r, p, q > 0$. In equilibrium ($\partial s / \partial t = 0$), adsorption in this model is described by a Freundlich isotherm with parameters $k = k_p^{1/q}$ and $n = p/q$. As the Freundlich exponent n usually lies between 0 and 1, we assume that $p < q$.

Model 2:

$$\frac{\partial s}{\partial t} = r_{\pm} |kc^n - s|^{\nu}. \quad (8)$$

In equilibrium ($\partial s / \partial t = 0$), adsorption in this model is described by a Freundlich isotherm with parameters k and n . The coefficient r_{\pm} is

$$r_{\pm} = \begin{cases} r_+ > 0 & \text{if } s < kc^n \quad (\text{adsorption phase}), \\ r_- < 0 & \text{if } s > kc^n \quad (\text{desorption phase}), \end{cases} \quad (9)$$

such that either adsorption or desorption always try to drive the system towards equilibrium.

III. ASYMPTOTIC CONSIDERATIONS

We are interested in the large-time behavior of substances undergoing adsorption processes described by our models 1 and 2. We assume that the time dependence of c and s in the *tail* after injection of a finite mass into the system at time $t = 0$ can be described by power laws asymptotically,

$$c(t, x) \sim t^{-\alpha} \gamma(x), \quad (10)$$

$$s(t, x) \sim t^{-\beta} \sigma(x), \quad (11)$$

with $\alpha, \beta > 0$ for $t \rightarrow \infty$. This approach is less general than the similarity solution chosen in Refs. [7] and [8] for quasiequilibrium adsorption following a Freundlich isotherm. This solution is of the form

$$c(t, x) \sim t^{-\alpha} \eta(xt^{-\delta}). \quad (12)$$

However, in the lowest-order approximation for the quasiequilibrium case, the function η can be shown to be a power law in the tail region [7] such that the similarity solution and our separation assumption lead to the same asymptotic results for large x and t [9]. In the quasiequilibrium case, one finds that the concentration decays like a power law $t^{-\alpha}$ with $\alpha = 1/(1-n)$ for $t \rightarrow \infty$.

In Sec. III B, however, we show that these approaches lead to different asymptotic behavior in the case of vanishing advection, i.e., if diffusion is the only transport process. In this limit, the concentration after injection of a mass pulse of an inert substance no longer decays exponentially. In fact, the transport equation reduces to the heat diffusion equation then, and it is well known that the solution decays proportionally to $t^{-0.5}$, i.e., it shows power law behavior even if no adsorption takes place. Depending on the spatial extent of the medium, both types of asymptotic solution can be realized in different time intervals: As long as the diffusion front has not reached the boundary of the medium, the solution approaches the similarity form. If the solute concentration becomes significant close to the boundary, the separation form takes over. Therefore, for illustration of the different kinds of asymptotic solutions discussed above, the asymptotic solution for the purely diffusive case will be discussed separately.

For nonvanishing advection speed, the power law behavior can be regarded as evidence for a nonlinear adsorption process. In the case of linearly adsorbed or inert substances obeying a convection-diffusion equation, the concentration decays exponentially (Ref. [10]) after pulse-type injection. We assume that the power law decay is also valid for the nonequilibrium models and verify this by numerical simulations. As we found a good agreement with numerical solutions and as both approaches agree to lowest order for a power law form of the spatial distribution, we worked with the simpler separation assumption rather than with the similarity solution. Note that on an infinite domain, the separation assumption (unlike the similarity solution) can only be valid for the tail and not for the propagating front of the diluted substance.

A. Nonvanishing velocity

Let us first discuss Eq. (2) for $U \neq 0$. Inserting Eqs. (10), (11) into Eq. (2), we obtain

$$-\alpha t^{-\alpha-1} \gamma(x) = -U \gamma'(x) t^{-\alpha} + D \gamma''(x) t^{-\alpha} + \beta \sigma(x) t^{-\beta-1}. \quad (13)$$

For large times, $t \rightarrow \infty$, we can neglect the terms proportional to $t^{-\alpha-1}$ compared to $t^{-\alpha}$. Thus, Eq. (13) can only be consistent if the terms proportional to $t^{-\alpha}$ are balanced by the $t^{-\beta-1}$ term, such that α and β are related by

$$\alpha = \beta + 1. \quad (14)$$

Referring back to Eq. (2), neglecting the terms proportional to $t^{-\alpha-1}$ compared to $t^{-\alpha}=t^{-\beta-1}$ is equivalent to neglecting the mobile concentration c compared to s . In other words, our assumption requires that small concentrations are favorably adsorbed, as it is the case for the Freundlich isotherm. Using this consistency relationship between α and β , we can derive the exact value for α for our nonequilibrium models.

1. Model 1

For the first model, we find from Eqs. (7) and (11),

$$-\beta\sigma(x)t^{-\beta-1}\sim r[k_p\gamma(x)^p t^{-\alpha p}-\sigma(x)^q t^{-\beta q}]. \quad (15)$$

As the signs of $r, \sigma, \gamma, \alpha, \beta, k_p$ all are non-negative, there are only two possibilities to fulfill the asymptotic equation for $t\rightarrow\infty$.

(i) For large times, the term on the left-hand side is balanced by the second term on the right-hand side, i.e.,

$$-\beta-1=-\alpha=-\beta q=(1-\alpha)q, \quad (16)$$

where we used Eq. (14), such that

$$\alpha=\frac{q}{q-1}, \quad (17)$$

irrespective of p . On the same time, the first term on the right-hand side must decay at least as fast as the second term, such that

$$\alpha\geq\beta q=(\alpha-1)q=\alpha, \quad (18)$$

due to Eq. (17), or equivalently

$$p\geq 1. \quad (19)$$

From Eq. (18) and $n=p/q<1$ we also deduce that

$$\alpha\leq 1/(1-n), \quad (20)$$

i.e., this asymptotic solution cannot decay faster than the quasiequilibrium solution.

(ii) For large times, the two terms on the right-hand side balance each other and the term on the left-hand side is of a higher order in t^{-1} , i.e.,

$$(\alpha-1)q=\alpha p, \quad (21)$$

such that

$$\alpha=\frac{1}{1-n}, \quad (22)$$

where $n=p/q$ is the exponent of the Freundlich isotherm for the equilibrium state of model 1. This is the same result that Refs. [7] and [9] obtained for reactive transport in the Freundlich quasiequilibrium case. In this case, the term on the

left-hand side (lhs) must decay at least as fast as the terms on the right-hand side (rhs), such that

$$\beta+1=\alpha\geq\alpha p, \quad (23)$$

or equivalently

$$p\leq 1. \quad (24)$$

Hence we find that there is a critical exponent $p=1$ at which there is a change in the asymptotic behavior of the concentration at a fixed position. For $p\leq 1$, the concentration decays following the same power law as in the quasiequilibrium case, with an exponent that is determined by the equilibrium Freundlich exponent $n=p/q$. For $p>1$, another power law results that is determined by the desorption exponent q rather than the equilibrium Freundlich exponent. A transport model relying on measurements of the isotherm only can, therefore, lead to vast overestimation or underestimation of the concentration. The transition at $p=1$ is continuous for n fixed, since at this point $n=p/q=1/q$ such that

$$\lim_{p\searrow 1}\alpha(p,q)=\frac{q}{q-1}=\frac{1}{1-\frac{1}{q}}=\frac{1}{1-n}=\lim_{p\nearrow 1}\alpha(p,q). \quad (25)$$

2. Model 2

For the second model, we find from Eqs. (7), (11), and (14),

$$-\beta\sigma(x)t^{-\alpha}\sim r_{\pm}|k\gamma(x)^n t^{-\alpha n}-\sigma(x)t^{-\alpha+1}|^{\nu}. \quad (26)$$

Again, there are only two possibilities to fulfill this asymptotic equation for $t\rightarrow\infty$.

(i) For large times, the term on the left-hand side is balanced by the desorption term (for adsorption, the rhs is positive and cannot balance the negative lhs), i.e.,

$$\alpha=(\alpha-1)\nu, \quad (27)$$

$$\alpha n>\alpha-1, \quad (28)$$

or equivalently

$$\alpha=\frac{\nu}{\nu-1}, \quad (29)$$

$$n>\frac{1}{\nu}. \quad (30)$$

Again, we can see from Eq. (27) that $\alpha<1/(1-n)$, i.e., this solution decays slower than the quasiequilibrium solution.

(ii) For large times, the two terms on the rhs balance each other, and the lhs is of the order of the rhs or smaller, i.e.,

$$\alpha n=\alpha-1, \quad (31)$$

$$\alpha \geq \alpha n \nu, \quad (32)$$

or equivalently

$$\alpha = \frac{1}{1-n}, \quad (33)$$

$$n \leq \frac{1}{\nu}. \quad (34)$$

In this case we obtain the result from Refs. [7] and [9] for the quasiequilibrium case again.

Hence we find a critical exponent $\nu = 1/n$, distinguishing a regime attracting the solutions towards the quasiequilibrium asymptotics ($\nu \leq 1/n$) and another regime leading to qualitatively different solutions ($\nu > 1/n$). The transition is continuous at $\nu = 1/n$, as

$$\begin{aligned} \lim_{\nu \nearrow 1/n} \alpha(\nu, n) &= \lim_{\nu \nearrow 1/n} \frac{\nu}{\nu - 1} = \lim_{\nu \nearrow 1/n} \frac{1}{1 - \frac{1}{\nu}} = \frac{1}{1-n} \\ &= \lim_{\nu \searrow 1/n} \alpha(\nu, n). \end{aligned} \quad (35)$$

3. Spatial distribution and attraction towards equilibrium

We have found in the preceding section that depending on the values of the parameters p and ν , respectively, our two models can lead to asymptotic behavior different from the quasiequilibrium solution. In those cases where $\alpha = 1/(1-n)$ as in the quasiequilibrium case, the term $\partial s/\partial t$ decayed faster than the c - and s -dependent summands on the right-hand side of Eqs. (7) and (8) such that s and c approach a quasiequilibrium state where $\partial s/\partial t = 0$. The models are chosen in a way such that this equilibrium state is equal to a Freundlich isotherm and we expect that one obtains the same asymptotic behavior as for the quasiequilibrium model, i.e., a power law in the spatial distribution

$$t^\alpha c(x, t) \sim \gamma(x) \sim \left(\frac{kn}{U}\right)^\alpha x^\alpha, \quad (36)$$

in the tail region, as shown in Refs. [7] or [9].

For parameters chosen such that $\alpha \neq 1/(1-n)$, the rhs of Eqs. (7) and (8) depends only on s for $t \rightarrow \infty$, while the c -dependent term can be neglected. This means that rather than approaching quasiequilibrium between c and s , $t^\alpha s(x, t) = \sigma(x)$ converges to a spatially constant function. If we choose, e.g., $p > 1$ in Eq. (15),

$$\beta \sigma(x) t^{-\alpha} \sim r \sigma(x)^q t^{(1-\alpha)q}, \quad (37)$$

and, therefore, [since $\alpha = (1-\alpha)q$]

$$\sigma(x) \sim \left(\frac{r}{\beta}\right)^{1/1-q}. \quad (38)$$

For model 2 with $\nu > 1/n$, we find from Eq. (26) analogously,

$$\sigma(x) \sim \sigma_0 := \left|\frac{r_-}{\beta}\right|^{1/1-\nu}. \quad (39)$$

This makes it easy to construct the spatial distribution for the concentration c . We had assumed that we could neglect c and \dot{c} compared to s and \dot{s} , respectively, so the transport equation reads for large times,

$$U \frac{d\gamma}{dx} - D \frac{d^2\gamma}{dx^2} = \beta \sigma \equiv \text{const}, \quad (40)$$

as $\sigma = \sigma(x)$ is a constant in this case, and the only power law solution of this equation is

$$\gamma = \frac{\beta \sigma}{U} x, \quad (41)$$

i.e., linear in x .

B. Vanishing velocity

An interesting modification is necessary if there is no advection, i.e., if $U = 0$, such that the only transport process is diffusion. For simplicity and illustration, we will consider only the quasiequilibrium case for the Freundlich isotherm $s = kc^n$. In this case, Eq. (2) becomes

$$(1 + kn c^{n-1}) \frac{\partial}{\partial t} c = D \frac{\partial^2}{\partial x^2} c. \quad (42)$$

This equation can be mapped to the porous media equation [11] whose asymptotics is well known. However, in order to illustrate the modifications necessary in this case, we present an elemental treatment here.

Formally, one can use the same separation assumption as in the advection-diffusion equation, and will obtain the same kind of solution and the same asymptotic behavior in time. However, whether there is a nontrivial solution for γ or not depends on the spatial extent of the system. For an infinite system another power law is derived than for a finite system.

To show this, let us insert Eq. (10) into Eq. (42). For large times, the concentration at a given point is approaching 0 due to diffusion, such that $1 \ll kn c^{n-1}$. Multiplying by t^α , we obtain

$$\gamma''(x) = -\frac{\alpha kn}{D} \gamma(x)^n, \quad (43)$$

which is, when x is reinterpreted as a time coordinate, the equation of motion of an anharmonic oscillator (as long as $\gamma \geq 0$). This has to be supplemented by appropriate boundary conditions. For a finite system, we could for instance assume that the mass is injected at $t = 0$ and $x = 0$ and absorbed at the

boundaries $x = -L$ and $x = L$, such that $c(t, -L) = c(t, L) \equiv 0$. This would lead to the boundary conditions

$$\gamma(-L) = \gamma(L) = 0, \quad (44)$$

forming a boundary value problem together with Eq. (43) on the interval $[-L, L]$.

It is well known that for the case $n = 1$ (harmonic oscillator), this problem is a classical eigenvalue problem that has nontrivial solutions only for certain values of L . In this case, $\omega = \alpha kn/D$ is the angular frequency, and in order to obtain a positive solution on $[-L, L]$ with zero boundary values, the oscillator must perform exactly half an oscillation in a time interval of length $2L$, i.e., $\omega = \pi/2L$ or $L = (\pi/2)\sqrt{(D/\alpha k)}$. The main reason for this behavior is that for the harmonic oscillator the frequency does not depend on the amplitude of the oscillation. For $n \neq 1$ this is no longer true, and we show in the Appendix that the nonlinear problem defined by Eqs. (43) and (44) has a solution for any value of L . Thus we get a consistent solution for a finite medium.

For an infinite medium, however, this solution is no longer consistent, since we expect that the shape of the solution is smoothed out more and more with increasing time, while a nontrivial $\gamma(x)$ would mean that the shape “freezes.” This freezing can in fact be observed for the tail in the advective case, but does not apply to the front of the distribution. A more appropriate assumption on the asymptotic form of the solution is therefore provided by a *similarity solution* for the concentration

$$c(x, t) \sim t^{-\alpha} \Gamma(xt^{-\delta}) \quad \text{for } t \rightarrow \infty, \quad (45)$$

which is dispersed infinitely for $t \rightarrow \infty$. Feeding into Eq. (42) and using $1 \ll kn c^{n-1}$ for large times as the concentration goes to zero, this means that

$$-kn\Gamma(\xi)^{n-1} t^{-\alpha(n-1)-\alpha-1} [\alpha\Gamma(\xi) + \delta\xi\Gamma'(\xi)] \sim Dt^{-\alpha-2\delta}, \quad (46)$$

with $\xi := t^{-\delta}x$. If we assume that the mass pulse is injected at $x = 0$, we know from the symmetry of the problem that $\Gamma'(0) = 0$ such that the second term on the left-hand side is of second order in ξ and thus can be neglected for any fixed x , since $\xi = xt^{-\delta} \rightarrow 0$ for $t \rightarrow \infty$. Hence we find by balancing the exponents in t that

$$\alpha(n-1) - \alpha - 1 = \alpha - 2\delta. \quad (47)$$

We can find a second equation relating α and δ from the conservation of mass,

$$\frac{d}{dt} M := \frac{d}{dt} \int_{-\infty}^{\infty} (c+s) dx = \int_{-\infty}^{\infty} \left(U \frac{\partial}{\partial x} c + D \frac{\partial^2}{\partial x^2} c \right) dx = 0, \quad (48)$$

where the last line results from a partial integration assuming the boundary condition that c and its x derivative decay fast

enough for $x \rightarrow \pm\infty$. For $c \rightarrow 0$ we have $s = kc^n \gg c$ such that for large times most of the mass is in the immobile phase s and c can be neglected. Thus for $t \rightarrow \infty$,

$$\begin{aligned} M &\sim \int_{-\infty}^{\infty} s dx = \int_{-\infty}^{\infty} kc^n dx = \int_{-\infty}^{\infty} kt^{-\alpha n} \Gamma(xt^{-\delta})^n dx \\ &= kt^{-\alpha n + \delta} \int_{-\infty}^{\infty} \Gamma(\xi)^n d\xi. \end{aligned} \quad (49)$$

This can only be constant, if

$$\delta = \alpha n. \quad (50)$$

From Eqs. (47) and (50) we can conclude that

$$\alpha = \frac{1}{n+1}, \quad (51)$$

in contrast to $\alpha = 1/(1-n)$ in the advective case. Note that this result is valid for one spatial dimension, but can be generalized easily to an arbitrary number of dimensions.

IV. COMPARISON WITH NUMERICAL SIMULATIONS

Our analysis is not a rigorous derivation based only on the transport and adsorption equations, but rests on the assumption that the asymptotic form of the solution is properly described by either Eq. (10) or Eq. (45). In order to test these assumptions, we performed a number of one-dimensional numerical experiments with different parameter sets and found good agreement with the power law asymptotics derived in the previous sections, if the system could evolve for a time long enough. Depending on the value of the model parameters (e.g., for small r), the convergence to the asymptotic solution can of course be very slow. In this section, we show some exemplary results for the different cases discussed.

The transport equation, Eq. (2), was solved numerically by a straightforward, explicit finite difference scheme, with an adaptive time step control ensuring that the updated concentration could not become negative. Depending on the model, the term $\partial s / \partial t$ can diverge for $s \rightarrow 0$ or $c \rightarrow 0$. In order to avoid difficulties with this term, a tiny background concentration was added in some cases, and we verified that the results were not sensitive to variations of the background, as long as the background was negligible compared to c and s .

For both of our models, one can obtain cases that do not reach quasiequilibrium for $t \rightarrow \infty$, but stay close to the quasiequilibrium solution for intermediate times (for large r_{\pm}, k as long as the concentrations do not become too small).

A. Characteristic scales

Due to the fact that there are different interesting characteristic time scales, we do not introduce new dimensionless variables, but the results will be presented in units of the following characteristic scales.

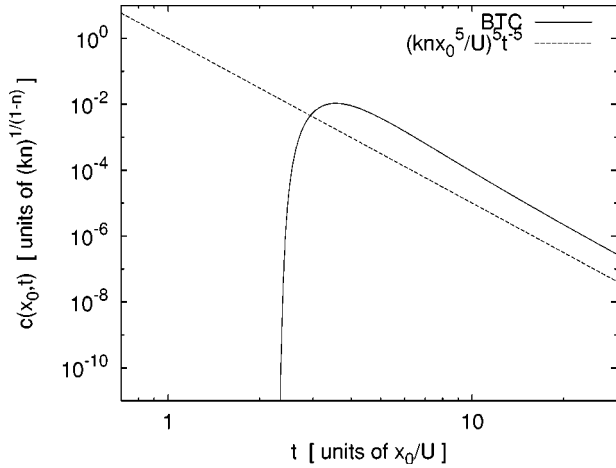


FIG. 1. Breakthrough curve, i.e., time dependence of the concentration at a fixed position x_0 , for a simulation of model 1 in a case with $p=0.64$, $q=0.8$ in a double-logarithmic plot. The concentration c is measured in units of $(kn)^{1/(1-n)}$, and time t in units of the advection time scale x_0/U . Also shown is the expected power law with exponent $\alpha=5$, predicted by the nonequilibrium model.

1. Time scales

There are several characteristic time scales involved in the problem, some of them related to transport, others, such as r^{-1} in model 1, related to adsorption. For the representation of breakthrough curves (BTC's), i.e., the concentration at a fixed position x_0 , we use the advection time scale x_0/U as a unit. Note that adsorption and desorption lead to retardation, such that the peak value of the BTC might be reached only for $t \gg x_0/U$.

For the advection free case of a finite system, another interesting time scale is the “escape time” τ_{esc} , after which a significant amount of mass has reached the boundaries. This scale can be easily estimated by dimensional analysis: τ_{esc} has dimension T (time) and can depend only on the system size L , the total mass M injected, the dispersion coefficient D (dimension L^2/T), the Freundlich coefficient k [dimension $(M/L)^{1-n}$], and the dimensionless exponent n . For large times, $c \rightarrow 0$ and the nonlinear time derivative operator on the lhs of Eq. (42) becomes $knc^{n-1} \partial/\partial t$. Therefore, scaling of k by a factor of A is the same as scaling the time variable by A^{-1} , since

$$Aknc^{n-1} \partial/\partial t = knc^{n-1} \partial/\partial(A^{-1}t). \quad (52)$$

This means that τ_{esc} depends linearly on k (in the low-concentration regime). Dimensional analysis yields, therefore,

$$\tau_{esc} = f(n) k M^{n-1} \frac{L^{3-n}}{D} =: f(n) \tau_0, \quad (53)$$

where $f(n)$ is a function only depending on n , which we expect to be of order unity. In the case $n=1$ and $k \gg 1$ (since we assumed $c \ll s$ in the analysis, which is always fulfilled

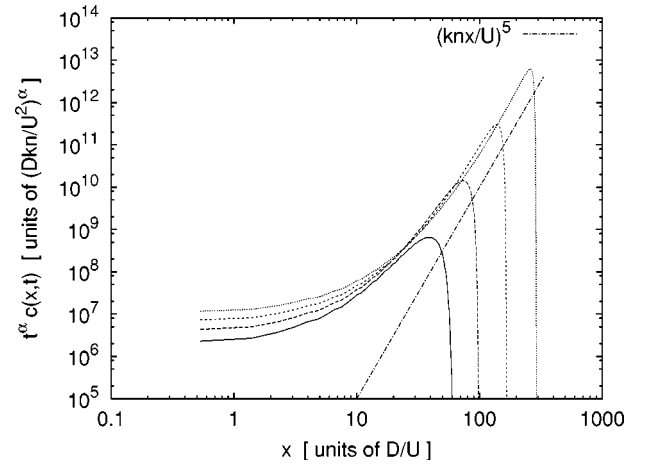


FIG. 2. Asymptotic time invariance of the rescaled mobile concentration $\gamma(x) = t^\alpha c(x, t)$ in a simulation with $p=0.64$, $q=0.8$. The figure shows $t^\alpha c(x, t)$ at different times $t = 40, 80, 160, 320 \times t_0$ (with $t_0 = 3.3D/U^2$), and the predicted power law $\gamma(x) = (nk/U)^5 x^5$ describing the tail in the quasiequilibrium case for $x \gg D/U$ (but smaller than the position of the front).

for $t \rightarrow \infty$ only for $n < 1$) this is of course consistent with the well-known result $\tau_{esc} \sim kL^2/(2D)$.

Finally, we use the characteristic time scale D/U^2 , i.e., the time at which transport begins to become dominated by advection rather than diffusion in the inert case.

2. Spatial scales

The approximations for the rescaled concentration $\gamma = t^\alpha c$ should become valid for $x \gg D/U$. For distances smaller than the spatial scale D/U , transport is dominated by diffusion.

For systems of finite extent $[-L, L]$, the system radius L plays a natural role.

3. Concentration

In quasiequilibrium, the local retardation factor is $(1 + knc^{n-1})$ as in Eq. (42). Therefore, we expect nonlinear effects to become important for

$$knc^{n-1} \geq 1$$

$$c \leq (kn)^{1/(1-n)}, \quad (54)$$

and use $(kn)^{1/(1-n)}$ as a natural concentration scale.

B. Results for nonvanishing velocity

1. Model 1

For $p \leq 1$, we observe the same behavior as in the quasiequilibrium case. Figure 1 shows the breakthrough curve (i.e., the concentration c at a fixed position) for a case with $p=0.64, q=0.8$, i.e., $n=p/q=0.8$. As predicted, this curve shows a power law dependence with an exponent of $\alpha = 1/(1-n) = 5$ for large times. The shape of the rescaled spatial distribution $t^\alpha c(x, t)$ should approach $\gamma(x)$ in the tail region, i.e., become time independent. In Refs. [7] and [9] it is shown that for $x \gg D/U$, this distribution is proportional to

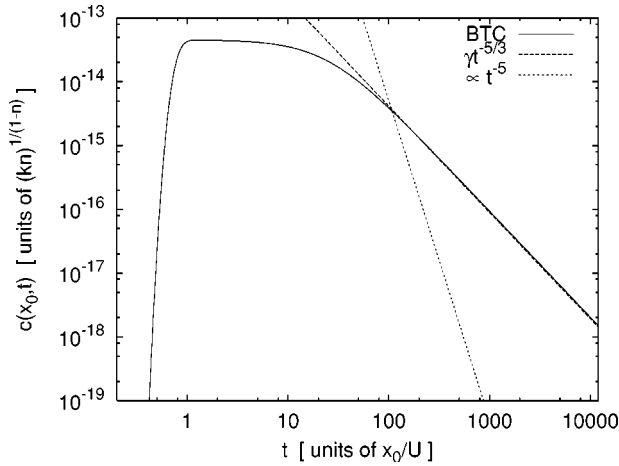


FIG. 3. Breakthrough curve, i.e., time dependence of the concentration at a fixed position x_0 , for a simulation of model 1 in a case with $p=2$, $q=2.5$ in a double-logarithmic plot. Also shown are the power laws with the exponent $\alpha=5/3$, predicted by the nonequilibrium model and exponent $\alpha=5$, predicted by a quasi-equilibrium model with the same equilibrium Freundlich isotherm.

a power law $\gamma(x) \propto x^\alpha$. This behavior was also observed in our simulations for $p < 1$. Figure 2 shows an example.

For $p > 1$, our asymptotic consideration led to the prediction that breakthrough curves decay asymptotically like $t^{-q/(q-1)}$. This prediction could be verified in our numerical simulations. Figure 3 shows a breakthrough curve for the case $p=2, q=2.5$. The exponent of the power law is $\alpha = q/(q-1) = 5/3 \approx 1.667$, and thus the breakthrough curves decay considerably slower than in the corresponding equilibrium case for $n=p/q=0.8$ where $\alpha=1/(1-n)=5$.

Furthermore, we predicted that the rescaled adsorbed mass distribution $\sigma(x) = t^\beta s(x, t)$ converges towards a spatial constant distribution in this case $\sigma(x) \equiv \sigma_0 = (r/\beta)^{1/(1-q)}$. This behavior is shown in Fig. 4.

Based on this result, we derived that the mobile concentration c increases linearly in x . For model 1, Eq. (41) reads

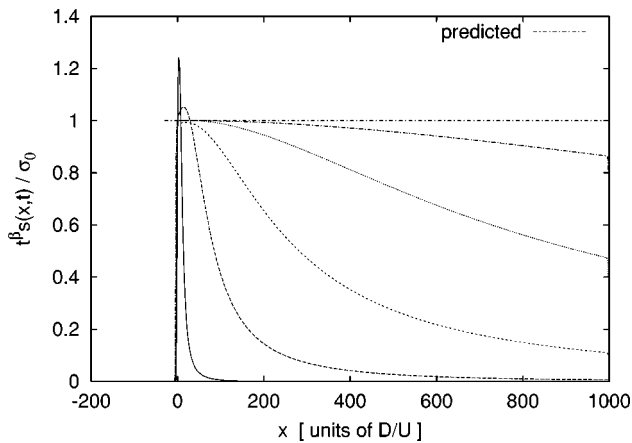


FIG. 4. Convergence of the rescaled adsorbed mass density $\sigma(x) = t^\beta s(x, t)$ towards a constant value σ_0 in a simulation with $p=2, q=2.5$. The figure shows $t^\beta s(x, t)$ at different times $t = 200, 3200, 25\ 600, 204\ 800, 1\ 638\ 400 \times t_0$ (with $t_0 = D/U^2$), normalized to the predicted asymptotic value $\sigma_0 = (r/\beta)^{1/(1-q)}$.

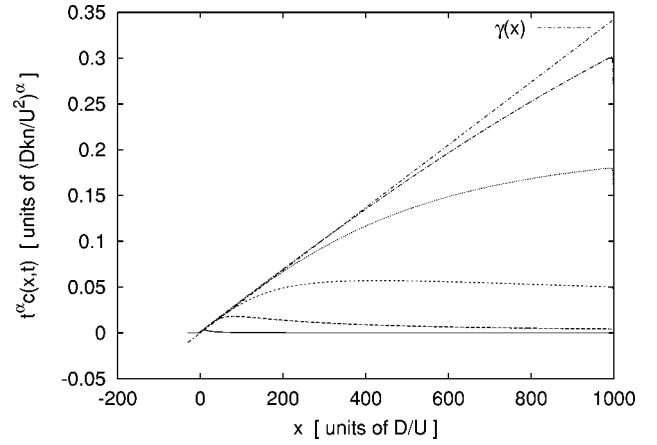


FIG. 5. Convergence of the rescaled mobile concentration $\gamma(x) = t^\alpha c(x, t)$ towards a linear function in a simulation with $p=2$, $q=2.5$. The figure shows $t^\alpha c(x, t)$ at different times $t = 200, 3200, 25\ 600, 204\ 800, 1\ 638\ 400 \times t_0$ (with $t_0 = D/U^2$), and the predicted asymptotic linear function $\gamma(x) = U/\beta(r/\beta)^{1/(1-q)}x$ describing the tail.

$$t^\alpha c(x, t) \sim \gamma(x) = \frac{\beta\sigma}{U}x. \quad (55)$$

This is illustrated in Fig. 5.

It is interesting to note that for the model that does not reach quasiequilibrium, the “comet shape” from Fig. 2 is inverted. In contrast to the quasiequilibrium case with its self-sharpening front, in Fig. 5 the front is propagating and dispersing rapidly while the position of the maximum concentration moves slowly towards infinity. The shape does of course depend on the parameters and for fast adsorption and desorption rate constants the front can look self-sharpening for a long time and breakthrough curves can stay close to the quasiequilibrium solutions before approaching the asymptotic solution for $t \rightarrow \infty$.

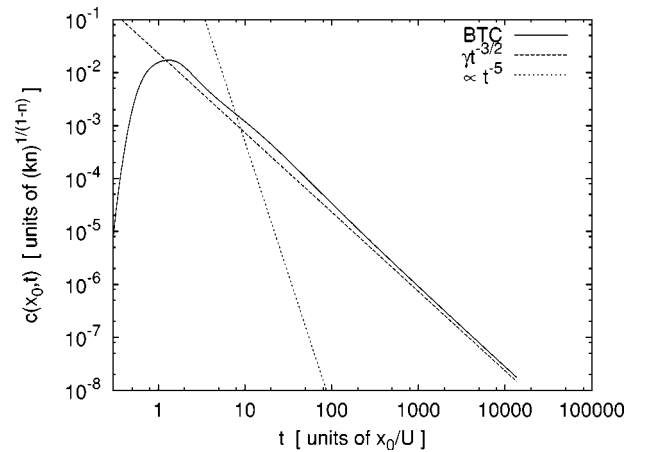


FIG. 6. Breakthrough curve for a simulation of model 2 in a case with $n=0.8$, $\nu=3$ in a double-logarithmic plot. Also shown are the power laws with exponent $\alpha=3/2$, predicted by the nonequilibrium model, and exponent $\alpha=5$, predicted by a quasiequilibrium model with the same equilibrium Freundlich isotherm.

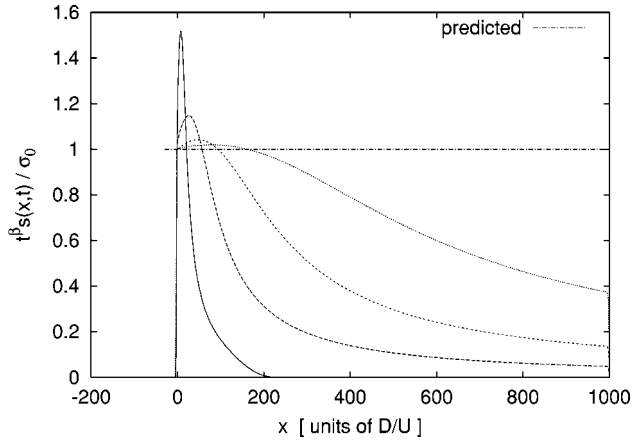


FIG. 7. Convergence of the rescaled adsorbed mass density $\gamma(x) = t^\beta s(x, t)$ to its asymptotic value in a simulation of model 2 with $n=0.8$, $\nu=3$. The figure shows $t^\beta s(x, t)$ at different times $t = 100, 200, 400, 32\,000, 25\,600, 204\,800 \times t_0$ (with $t_0 = D/U^2$) and the predicted asymptotic value from Eq. (39).

2. Model 2

For $\nu \leq 1/n$, we observed again that the solutions approached the quasiequilibrium asymptotics. We don't present a figure here, the results look very similar as in model 1.

For $\nu > 1/n$, the results of the simulations agreed with our asymptotic results as they did for model 1. Figure 6 shows the breakthrough curves for a case with $n=0.8$ and $\nu=3$. As predicted from our asymptotic considerations, the concentrations decays following a power law in time with an exponent of $\nu/(\nu-1) = -3/2$ rather than $1/(n-1) = -5$ as predicted by the corresponding quasiequilibrium model. Figure 7 shows the spatial distribution of s , rescaled by t^β , which slowly approaches the constant value predicted in Eq. (39).

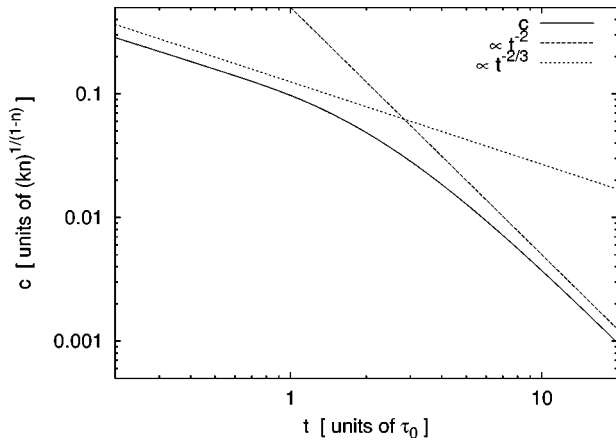


FIG. 8. Time behavior of the concentration at the origin for purely diffusive propagation with quasiequilibrium Freundlich adsorption for $n=0.5$ for a finite system. As long as no significant part of the total mass has diffused to the boundary, the concentration decays proportional to $t^{-1/(1+n)}$, as predicted by the similarity solution for an infinite system. As soon as the distribution reaches the boundary, the asymptotic behavior changes to $\approx t^{-1/(1-n)}$, predicted for a finite system. Time t is measured in units of the time scale $\tau_0 = kM^{n-1}L^{3-n}/D$, proportional to the escape time.

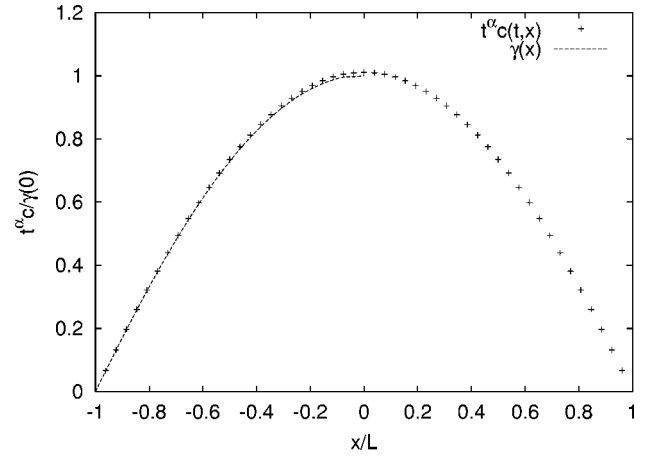


FIG. 9. Concentration for the system from Fig. 8, rescaled by t^α at $t = 11.6\tau_0$, and the solution for $\gamma(x)$ derived in the Appendix.

As in model 2, the shape of the distribution depends on the parameters and one can obtain solutions with an inverted comet shape as well as solutions that stay close to the quasiequilibrium solutions for a long time, depending on the value of the adsorption/desorption rate parameters.

C. Results for vanishing velocity

Figure 8 shows the behavior for a large, but finite system. As long as the solute has not diffused to the boundary, the concentration at a fixed position ($x=0$) decays proportional to $t^{-1/(n+1)}$. As soon as a significant amount of mass has reached the boundaries, the distribution “freezes,” as shown in Fig. 9, and concentrations decay with $t^{-1/(1-n)}$.

V. SUMMARY AND CONCLUSIONS

We discussed the large-time asymptotic behavior of substances transported by advection and diffusion and undergoing reversible adsorption. We generalized a kinetic model leading to a Freundlich isotherm in equilibrium by two different models with paths towards equilibrium that are nonlinear both in the mobile and immobile concentrations c and s . For both models there exists a critical parameter whose value decides whether the solution will reach quasiequilibrium locally or not.

The critical values and the exponents can be derived from a simple separation assumption and are in a good agreement with numerical simulations. The separation assumption is inappropriate for the case of vanishing advection in an infinite system. In this case, the asymptotic behavior can be obtained using a similarity solution approach. However, for finite systems, the separation approach leads to correct results.

If the parameter is larger than its critical value, the concentrations at fixed positions decay following power laws with an exponent different from the value predicted by the quasiequilibrium model. Hence predictions of pollutant concentrations from isotherms determined from batch experiments can lead to overestimation or underestimation by many orders of magnitude.

APPENDIX: SOLUTION OF THE ANHARMONIC OSCILLATOR BVP FOR THE PURELY DIFFUSIVE CASE

In this appendix, we show that there is a solution for γ in the case of vanishing advection for any finite size L of the system. From Eqs. (43) and (44), we have to solve the following boundary value problem:

$$\gamma''(x) = -\frac{\alpha kn}{D} \gamma(x)^n, \quad (\text{A1})$$

$$\gamma(-L) = \gamma(L) = 0. \quad (\text{A2})$$

The “energy”

$$E := \frac{1}{2} \gamma'(x)^2 + \kappa \gamma(x)^{n+1}, \quad (\text{A3})$$

with $\kappa = \alpha kn/D(n+1)$ is conserved. From the symmetry of the problem we expect that the solution has a maximum at $x_0=0$ and is symmetric around this point. From the energy conservation we then know that

$$\gamma'(-L) = \sqrt{2E}, \quad (\text{A4})$$

$$\gamma(0) = (\kappa^{-1}E)^{1/n+1}, \quad (\text{A5})$$

and integrating Eq. (A4) we obtain

$$\begin{aligned} L &= \int_0^L dx = \int_{\gamma(-L)}^{\gamma(0)} \frac{d\gamma}{\sqrt{2(E - \kappa\gamma^{n+1})}} \\ &= \int_0^{(E/\kappa)^{1/(n+1)}} \frac{d\gamma}{\sqrt{2(E - \kappa\gamma^{n+1})}} \\ &= \frac{1}{\sqrt{2}\kappa^{1/(n+1)}} E^{(1-n)/(2n+2)} \int_0^1 \frac{d\xi}{\sqrt{1 - \xi^{n+1}}}, \quad (\text{A6}) \end{aligned}$$

with the simple substitution $\xi := E^{-1/(n+1)}\gamma$. As the integral over ξ is finite, we see that we can find an energy E for any L , and a solution corresponding to this energy $E(L)$, for any $n \neq 1$. [The solution can be found by integration of Eq. (A3) with the initial condition determined by Eq. (A5).] For $n = 1$, $E^{(1-n)/(2n+2)} = 1$ and we recover the well-known result that the period $4L$ of the harmonic oscillator is independent of its energy, such that a solution exists only for discrete values of L .

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