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Diffusion and binding of molecules to sites within homogeneous thin films

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In this paper we consider the process of a chemical species diffusing into a thin homogeneous film which contains fixed sites on to which the species can reversibly bind. We consider the situation in which the interaction of the diffusing species and the sites is described by the Langmuir isotherm. The differential equations that describe this nonlinear diffusion reaction problem are studied. We find that the problem may be conveniently divided into six cases. Each case is presented and approximate analytical solutions for the concentration profiles are given as a function of time for both adsorption and desorption. These solutions are relevant in situations of practical importance, including the binding of substrates to immobilized enzymes, the operation of polymeric gas sensors, and the vapour phase doping of conducting polymers.

1. Introduction

Problems of coupled diffusion and nonlinear chemical reaction are often found in practical situations. In such systems the diffusion of the chemical species into a phase is accompanied by chemical reaction either with species already present in the phase, or catalysed by species within the phase. Examples include diffusion and reaction in immobilized enzyme membranes, diffusion into living cells and micro-organisms, and chemical reactions in high polymer substances.

In this paper we present a unified treatment of coupled diffusion and reversible binding of species to immobile sites within a uniform homogeneous film. This model is appropriate to practical processes and systems, such as the dyeing of cloth or wool (Wilson 1948), the binding of substrates to immobilized enzymes (Engasser & Horvath 1976), the doping of conducting polymers (Kim *et al.* 1988), or the response of fibre-optic or surface acoustic wave chemical sensors based upon reversible binding onto immobilized sites (Seitz 1984; Ballantine & Wohltjen 1989).

Our particular interest is in the diffusion and reaction of gas molecules in thin uniform films of conducting polymers, such as poly(pyrrole) and poly(aniline). Interaction between the gas molecules and the polymer leads to changes in the film conductivity. This effect can be used in a chemoresistor configuration to construct a gas sensor. Recent work in our laboratory has shown that devices constructed by the deposition of a thin conducting polymer film across a narrow (typically 10 μm) gap show rapid reversible changes in conductivity on exposure to a variety of organic vapours (Bartlett *et al.* 1989, 1990; Bartlett & Ling-Chung 1989*a, b*). Similar results have been reported for the responses of such devices to inorganic gases such as NO_2 ,

NH_3 , and H_2S (Miasik *et al.* 1986; Hanawa *et al.* 1988). In order to understand the dynamic response of such devices it is essential to model the time-dependent concentration profile of the gas and the concomitant time-dependent fraction of occupied binding sites within the polymer film.

Although a number of particular solutions applying to certain aspects of the general problem have been reported, we are not aware of a full unified treatment of this problem. Hermans (1947) solved the problem of diffusion of a species into a semi-infinite medium containing a finite number of irreversible binding sites which were assumed to be either completely empty or completely full. This corresponds to a situation in which the kinetics of the reaction are much faster than the diffusion process and in which at equilibrium all of the sites are saturated. This model leads to the formation of a sharp boundary which propagates through the medium. Wagner (1950) addressed the problem of diffusion of a species into a bounded layer under conditions where the diffusion coefficient is proportional to the concentration of the diffusing species. This corresponds to the situation in which the occupancy of sites is linearly related to the concentration of the diffusing species (Gardner 1989*a, b*). More recently, the reversible uptake of dopants in conducting polymers has created renewed interest in this problem. Kim *et al.* (1988) have investigated the diffusion equations which describe the reversible trapping of a species diffusing into and out of a semi-infinite medium under conditions where the kinetics are fast as compared with diffusion so that local equilibrium is assumed. Numerical solutions of this problem are given in a subsequent paper by the same group (Murphy *et al.* 1988). Prock & Giering (1989*a, b*) have also addressed this problem for both semi-infinite and bounded media and provide qualitative support for these numerical solutions.

The work described above addresses different but related aspects of the same general coupled diffusion–reaction problem. Below we present a full approximate analytical solution to this general problem for both adsorption and desorption. We show that the general problem can be divided into six principal cases, for which we can obtain useful analytical solutions that can be tested by experiment and compared to the results of simulation of this problem. We describe the interrelation of these six cases and compare them to previous work. In a subsequent paper we will use the concentration and site occupancy profiles presented below to calculate the theoretical change in the electrical conductance of conducting polymer films on exposure to organic vapours, and compare it with our experimental results.

2. Preliminaries

We consider the general problem of a species A diffusing into a planar homogeneous film of constant thickness L that contains a uniform concentration of immobile reactive sites S . The local chemical reaction within the film between the diffusing species and the sites can be described by



where k_f is the second-order rate constant describing the binding of the species A at an unoccupied site S , and k_b the is the first-order rate constant describing desorption of the species A from an occupied site AS . Furthermore, we assume that there are no interactions between molecules of A on different sites, so that the adsorption

process is described by the Langmuir adsorption isotherm (Moore 1974) and the rate constants k_f and k_b are independent of coverage. The ratio of the forward and backward rate constants,

$$K = k_f/k_b, \quad (2.2)$$

is called the adsorption coefficient and has units of reciprocal concentration; it is a measure of the affinity of the sites for the species A . When K is large, the sites become saturated at low concentrations of A ; when K is small, the sites interact weakly with A and high concentrations are necessary to saturate the sites.

For the one-dimensional case, taking x as the distance in the film, t as the time, and $\theta(x, t)$ as the fraction of occupied sites, we can write the following diffusion reaction equation for the species A :

$$D \frac{\partial^2 a}{\partial x^2} - k_f a(1 - \theta)N + k_b \theta N = \frac{\partial a}{\partial t}, \quad (2.3)$$

where $a(x, t)$ is the concentration of the diffusing species A , and N is the concentration of binding sites within the film. Assuming that the species A is present in the external phase at a constant concentration a_∞ , then the boundary conditions for the adsorption transient are

$$\left. \begin{array}{l} \text{at } t = 0, \theta = 0 \text{ and } 0 \leq x \leq L, \\ \forall t > 0, \left. \frac{da}{dx} \right|_{x=0} = 0 \text{ and } a = a_\infty \text{ at } x = L. \end{array} \right\} \quad (2.4)$$

Here we assume that the partition coefficient for the species A into the film is unity and that there is no kinetic barrier at the film surface to the passage of A into the film. It should be noted that the effect of the partition coefficient is readily taken into account by replacing a_∞ by $K_a a_\infty$, where K_a is the partition coefficient. We also know, from consideration of the kinetics of the reactions at the sites, that

$$N \frac{\partial \theta}{\partial t} = k_f a(1 - \theta)N - k_b \theta N. \quad (2.5)$$

Then combining equations (2.3) and (2.5) gives

$$D \frac{\partial^2 \theta}{\partial x^2} - \frac{\partial a}{\partial t} = N \frac{\partial \theta}{\partial t}. \quad (2.6)$$

At this point it is convenient to introduce the following dimensionless parameters:

$$\chi = x/L, \quad (2.7)$$

$$\tau = Dt/L^2, \quad (2.8)$$

$$\gamma = a/a_\infty, \quad (2.9)$$

$$\kappa = k_f N L^2 / D, \quad (2.10)$$

$$\lambda = K a_\infty, \quad (2.11)$$

$$\eta = KN. \quad (2.12)$$

The dimensionless parameter κ describes the balance between the adsorption ($k_f N$) and diffusion (D/L^2) kinetics in the film; when $\kappa \gg 1$, the adsorption process is much faster than that of diffusion. The parameter λ describes the position of equilibrium: for $\lambda \ll 1$, most of the sites will be unoccupied at equilibrium; for $\lambda \gg 1$, all the

sites will be occupied at equilibrium. Finally, η is the product of the ratio of the forward and backward rate constants and the concentration of binding sites. Thus, the parameter η is a property of the material and is independent of the sample thickness or concentration of the diffusing species. Note that the ratio κ/η , which occurs in a number of the equations below, describes the balance between desorption (k_b) and diffusion (D/L^2) kinetics in the film; when $\kappa/\eta \gg 1$, the desorption process is much faster than that of diffusion.

Using these dimensionless parameters, equation (2.6) can be rewritten in the following form:

$$\frac{\partial^2 \gamma}{\partial \chi^2} - \frac{\partial \gamma}{\partial \tau} = \frac{\eta}{\lambda} \frac{\partial \theta}{\partial \tau}. \quad (2.13)$$

The corresponding boundary conditions for the adsorption transient (2.14) become

$$\left. \begin{array}{l} \text{at } \tau = 0, \theta = 0 \text{ and } \gamma = 0, \quad 0 \leq \chi \leq 1 \\ \forall \tau > 0, \quad \left. \frac{d\gamma}{d\chi} \right|_{\chi=0} = 0 \text{ and } \gamma = 1 \text{ at } \chi = 1. \end{array} \right\} \quad (2.14)$$

Similarly, we can express equation (2.5) in terms of the dimensionless parameters,

$$\eta \frac{\partial \theta}{\partial \tau} = \kappa \lambda \gamma (1 - \theta) - \kappa \theta. \quad (2.15)$$

Equations (2.13) and (2.15) are coupled nonlinear partial differential equations and do not have an exact analytical solution. However, we can identify a number of limiting cases for which we can develop approximate analytical expressions for the concentration profiles. We now derive solutions for each of these cases.

3. Linear diffusion–reaction ($\lambda < 1$)

We begin by considering the region where $\lambda \ll 1$. This corresponds to low adsorbate concentrations where the film is never saturated ($\theta \ll 1$). Equation (2.15) can then be simplified to give the coupled equations as

$$\frac{\partial^2 \gamma}{\partial \chi^2} - \frac{\partial \gamma}{\partial \tau} = \frac{\eta}{\lambda} \frac{\partial \theta}{\partial \tau}, \quad (3.1)$$

$$\eta \frac{\partial \theta}{\partial \tau} = \kappa \lambda \gamma - \kappa \theta. \quad (3.2)$$

This problem is now analytically soluble using the method of Laplace transforms. The inverse transform is obtained from the Heaviside expansion theorem with the roots (s_n) simplified by use of Taylor's theorem. In this way, we find the following expressions for the adsorbate concentration profile, $\gamma(\chi, \tau)$, and site occupancy, $\theta(\chi, \tau)$, as a function of dimensionless time and distance through the film:

$$\gamma(\chi, \tau) = 1 - 2\pi \sum_{n=0}^{\infty} \frac{(n + \frac{1}{2}) \cos[(n + \frac{1}{2})\pi\chi] \exp[s_n \tau]}{(-1)^n [(n + \frac{1}{2})^2 \pi^2 - s_n \kappa \ln[s_n + \kappa/\eta]]}, \quad (3.3)$$

$$\theta(\chi, \tau) = \lambda - 2\pi \kappa \lambda \sum_{n=0}^{\infty} \frac{(n + \frac{1}{2}) \cos[(n + \frac{1}{2})\pi\chi] \exp[s_n \tau]}{(\kappa + \eta s_n) (-1)^n [(n + \frac{1}{2})^2 \pi^2 - s_n \kappa \ln[s_n + \kappa/\eta]]}, \quad (3.4)$$

where

$$n = 0, 1, 2, \dots, \infty \quad \text{and} \quad s_n \approx -\frac{(n + \frac{1}{2})^2 \pi^2 \kappa}{\eta[\kappa(1 + 1/\eta) + (n + \frac{1}{2})^2 \pi^2]}. \quad (3.5)$$

Equations (3.3) and (3.4) are somewhat cumbersome. Fortunately, we can identify several approximate analytical expressions that correspond to particular physical solutions, some of which have already been reported.

(a) *Case I* ($\lambda < 1$, $\eta < 1$, $\kappa > \eta$)

When $\eta \ll 1$ and $\kappa \gg \eta$, the dominant terms of s_n reduce to $-(n + \frac{1}{2})^2 \pi^2$, and so equation (3.3) becomes

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2 \pi^2 \tau]}{(-1)^n (n + \frac{1}{2})}. \quad (3.6)$$

Under these conditions, the chemical reaction is fast when compared to the diffusion of A through the film. Consequently, equilibrium is maintained between the adsorbate and the sites, and the reaction kinetics do not appear in the final result. Equation (3.6) is identical to the result for simple diffusion with no accompanying reaction, as we would expect (Crank 1975). The occupancy of the sites θ is related to the adsorbate gas concentration γ by the Langmuir isotherm and, from equation (3.4),

$$\theta(\chi, \tau) \approx \lambda\gamma, \quad \text{as } \kappa/\eta \gg |s_n|. \quad (3.7)$$

Treatments of this case for the semi-infinite geometry (Prock & Giering 1989; Gardner 1989a) and for a thin film (Gardner 1989b) have been presented previously.

(b) *Case II* ($\lambda < 1$, $\eta > 1$, $\kappa > 1$)

When $\kappa \gg 1$ and $\eta \gg 1$, reaction at the binding sites removes a significant portion of the adsorbate as it diffuses into the film. Under these circumstances, equation (3.3) reduces to

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2 \pi^2 \tau / \eta]}{(-1)^n (n + \frac{1}{2})} \quad (3.8)$$

and

$$\theta(\chi, \tau) \approx \lambda\gamma, \quad (3.9)$$

when $\kappa \gg (n + \frac{1}{2})^2 \pi^2$.

This is identical in form to equation (3.6) but has the dimensionless time parameter τ replaced by τ/η ; this is equivalent to the diffusion coefficient D being replaced by D/η ($\equiv D/\kappa\eta$) as the effective diffusion coefficient. Thus, in this case the concentration profiles have the same form as in case I but with the adsorbate appearing to diffuse more slowly into the film, hence modifying the effective diffusion coefficient as expected (Gardner 1989a). Once again equilibrium is maintained between the adsorbate and sites (equation (3.9)).

(c) *Case III* ($\lambda < 1$, $\kappa < 1$, $\kappa < \eta$)

When $\lambda \ll 1$ and $\kappa \ll \eta$, diffusion is fast when compared to the adsorption kinetics, so that $\kappa \ll 1$ and equation (3.5) for s_n simplifies at first order to $s_n \approx -\kappa/\eta$ both for large and small values of η . Substitution of $-\kappa/\eta$ in equations (3.3) and (3.4) for

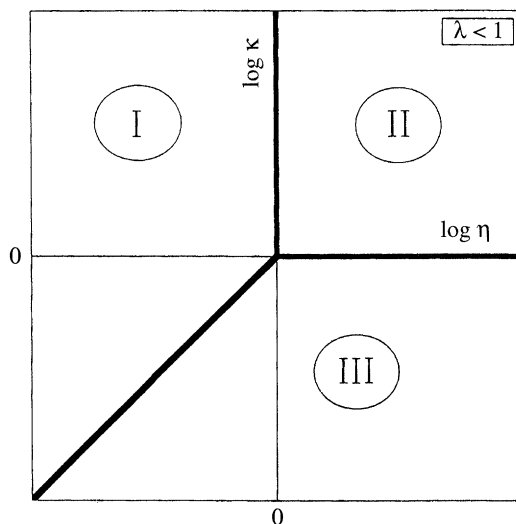


Figure 1. The relationship between the three linear diffusion–reaction cases ($\lambda < 1$). The boundaries between the cases are shown by the thick lines.

γ gives

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad (3.10)$$

$$\theta(\chi, \tau) \approx \lambda(1 - \exp(-\kappa\tau/\eta)). \quad (3.11)$$

Consequently, the diffusion of adsorbate through the film is essentially instantaneous on the time scale of reaction with the sites; the adsorbate concentration is independent of χ and depends only upon the kinetics of the adsorption reaction. The same holds true for $\eta \ll 1$ as the terms in the exponential series rapidly converge to zero. On the time-scale of the diffusion process, s_n must be expanded to second order to give a diffusion equation.

To summarise, the diffusion of the species A into the film is fast when compared with the rate of reaction of A with the sites ($\kappa/\eta \ll 1$). Thus, A diffuses into the bounded layer before any reaction can occur and so γ is described by the bounded layer diffusion equation. Reaction between the species A and the sites then takes place on a longer timescale, after γ has reached a value of 1 independent of χ . The fraction of occupied sites θ approaches its equilibrium value λ exponentially with time, as expected. This corresponds to the model used by Bartlett & Ling-Chung (1989a) to describe a thin polymeric gas-sensitive film.

Figure 1 shows a case diagram for $\lambda \ll 1$ illustrating the relationship between cases I, II and III. At the boundaries (marked by solid thick lines) between the cases, the full equations, (3.3) and (3.4), must be used.

In figure 2 we show the adsorbate concentration and site occupancy profiles calculated from the analytical solution for the three cases discussed above.

4. Reaction kinetics ($\kappa < \eta/(1 + \eta)$)

We now turn our attention to the region where the reaction kinetics are slow so that diffusion is more rapid than chemical reaction and equilibrium is no longer

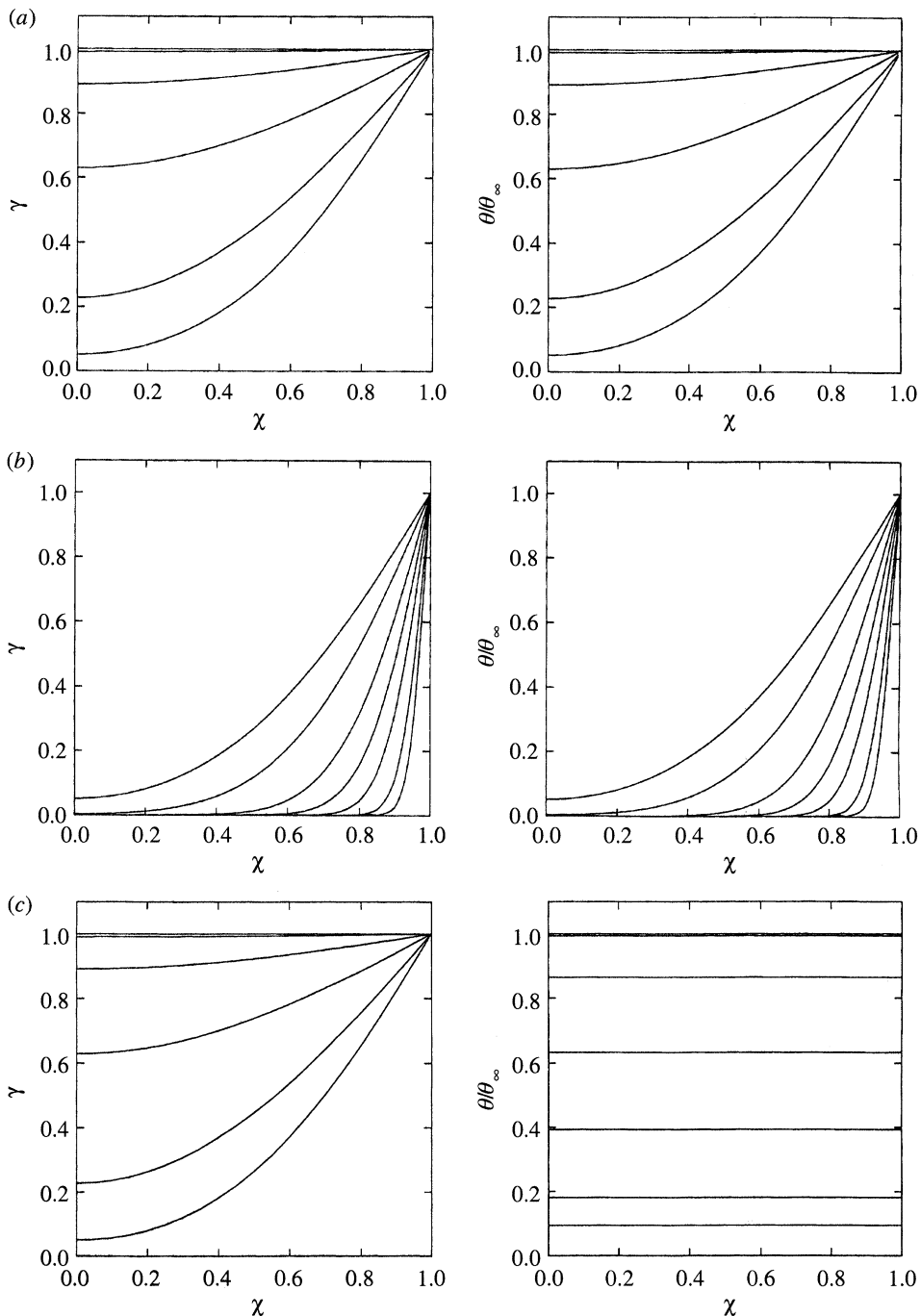


Figure 2. Plots of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ , for cases I–III calculated for $\tau = 0.1, 0.2, 0.5, 1.0, 2.0, 5.0$ and 10.0 . The curves for case I (a) are calculated from equations (3.6) and (3.7) with $\kappa = 100$, $\lambda = 0.01$ and $\eta = 0.01$; for case II (b), from equations (3.8) and (3.9) with $\kappa = 100$, $\lambda = 0.01$ and $\eta = 100$; for case III (c), from equations (3.10) and (3.11) with $\kappa = 0.01$, $\lambda = 0.01$ and $\eta = 1.0$. For each calculation, θ_∞ is 0.0099 .

maintained. This requires diffusion to be faster than either the forward or backward reaction, whichever is the slower process. In dimensionless terms, this corresponds to the condition that $\kappa \ll \eta/(1+\eta)$. Consequently, the fractional occupancy of the sites $\theta(\chi, \tau)$ is determined by the chemical kinetics. Under these conditions the time-scales for diffusion and reaction are different and, hence, we can decouple the differential equations. Equation (2.15) can be rewritten in the form

$$\frac{\eta}{\lambda} \frac{\partial \theta}{\partial \tau} = \kappa(\gamma - \theta(1/\lambda + \gamma)). \quad (4.1)$$

Now, $0 \leq \gamma \leq 1$ and $0 \leq \theta \leq \lambda/(1+\lambda)$, and thus $-1 \leq (\gamma - \theta(1/\lambda + \gamma)) \leq 1$, so that, with $\kappa \ll \eta/(1+\eta)$,

$$\frac{\eta}{\lambda} \frac{\partial \theta}{\partial \tau} \ll 1,$$

and equation (2.13) becomes

$$\frac{\partial^2 \gamma}{\partial \chi^2} - \frac{\partial \gamma}{\partial \tau} \approx 0. \quad (4.2)$$

This is equivalent to applying the steady state approximation to the site occupancy θ ; in effect, we assume that the diffusion of A into the film occurs on a much faster time scale than the change in occupancy of the sites. Equation (4.2) is now the simple diffusion equation and so we get

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2 \pi^2 \tau]}{(-1)^n (n + \frac{1}{2})}. \quad (4.3)$$

Then assuming that γ is constant because the time scales of diffusion and reaction are now different, solution of equation (2.15) for θ gives

$$\theta(\chi, \tau) = \frac{\lambda\gamma}{1 + \lambda\gamma} \left(1 - \exp\left(-\frac{(1 + \lambda\gamma)\kappa\tau}{\eta}\right) \right). \quad (4.4)$$

The diffusion of A into the film occurs before there is any significant reaction to fill the sites, so that it follows simple bounded diffusion. The reaction with the sites occurs subsequently when the concentration of A is close to its equilibrium value within the film ($\gamma \approx 1$). Equation (4.4) for θ has two limiting forms depending on the magnitude of λ . We now present these two limiting cases.

(a) *Case III* ($\kappa < \eta/(1+\eta)$, $\lambda < 1$)

When $\lambda \ll 1$ we can simplify equation (4.4), with $\gamma \sim 1$, to obtain

$$\theta(\chi, \tau) \approx \lambda[1 - \exp(-\kappa\tau/\eta)] \quad (4.5)$$

It is satisfactory that this is identical to the result which we obtained for case III above (§ 3c) as a special case of equation (19) derived for $\lambda \ll 1$.

(b) *Case IV* ($\kappa < \eta/(1+\eta)$, $\lambda > 1$)

When $\lambda \gg 1$ and $\gamma \sim 1$ in equation (4.4), we can replace $(1 + \lambda\gamma)$ by $\lambda\gamma$ to give

$$\theta(\chi, \tau) \approx 1 - \exp(-\lambda\gamma\kappa\tau/\eta). \quad (4.6)$$

This corresponds to the situation in which the sites are fully occupied at equilibrium, hence as $\tau \rightarrow \infty$, θ approaches 1. The curves are similar to those in case III, except for a factor of γ in the exponential, and are therefore not shown.

5. Nonlinear kinetics with slow diffusion ($\kappa > \eta/(1 + \eta)$)

So far we have developed solutions for all $\lambda \ll 1$, and for all $\kappa \ll \eta/(1 + \eta)$. We now consider the final region where $\kappa \gg \eta/(1 + \eta)$. Since $\kappa \gg \eta/(1 + \eta)$ we can assume that equilibrium is maintained between the diffusing species A and the sites, so that

$$\theta = \lambda\gamma/(1 + \lambda\gamma) \quad (5.1)$$

and

$$\frac{\partial\theta}{\partial\tau} = \frac{\lambda}{(1 + \lambda\gamma)^2} \frac{\partial\gamma}{\partial\tau}. \quad (5.2)$$

Substitution in equation (2.13), followed by rearrangement, gives

$$\frac{\partial^2\gamma}{\partial\chi^2} = \frac{(1 + \lambda\gamma)^2 + \eta}{(1 + \lambda\gamma)^2} \frac{\partial\gamma}{\partial\tau}. \quad (5.3)$$

It is clear from inspection of equation (5.3) that in this case the problem is nonlinear. When $\lambda \ll 1$, equation (5.3) neatly reduces to the modified diffusion equation,

$$\frac{\partial^2\gamma}{\partial\chi^2} = (1 + \eta) \frac{\partial\gamma}{\partial\tau}. \quad (5.4)$$

The solution to this equation, with suitable boundary conditions (Gardner 1989*a*), produces the results for case I when $\eta \ll 1$, and for case II when $\eta \gg 1$, given above.

When $\lambda \gg 1$ we can identify two new cases from equation (5.3) which depend upon the value of η . We now consider these cases in turn.

(a) Case V ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 > \eta$)

When $\lambda^2 \gg \eta$ and $\lambda \gg 1$, equation (5.3) reduces to the simple diffusion equation. Thus, γ is described by the simple bounded diffusion result

$$\gamma(\chi, \tau) = 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad (5.5)$$

and, because equilibrium is maintained, θ is given by equation (4.4).

It is satisfactory that for $\lambda \ll 1$ the equations reduce to those for case I. Equations (5.1) and (5.5) describe the propagation of a reaction profile through the film. In general, at the outside of the film $\lambda\gamma \gg 1$, and so $\theta = 1$ and the sites are saturated; on the inside of the film $\lambda\gamma \ll 1$ and $\theta = 0$, the sites are empty. As A diffuses into the film, described by equation (5.5), the boundary between the saturated and unsaturated regions moves from the outside to the inside of the film (figure 3).

(b) Case VI ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 < \eta$)

So far we have considered the situation for $\lambda \ll 1$ and $\lambda^2 \gg \eta$ for $\kappa \gg \eta/(1 + \eta)$. We now consider the final region where $1 \ll \lambda^2 \ll \eta$. In this case we cannot linearize the nonlinear diffusion equation (5.3).

In this case we have an example of a 'moving boundary' problem. The problem of diffusion with a moving boundary has been of great interest for many years. Hermans (1947) discussed the penetration of sulphide ions into a gel containing heavy metal ions. In order to tackle the problem, he made the simplifying assumption that the sites were either empty or full, which led to a discontinuous solution. In 1969, Paul claimed that an analytical solution is not feasible for the sorption problem

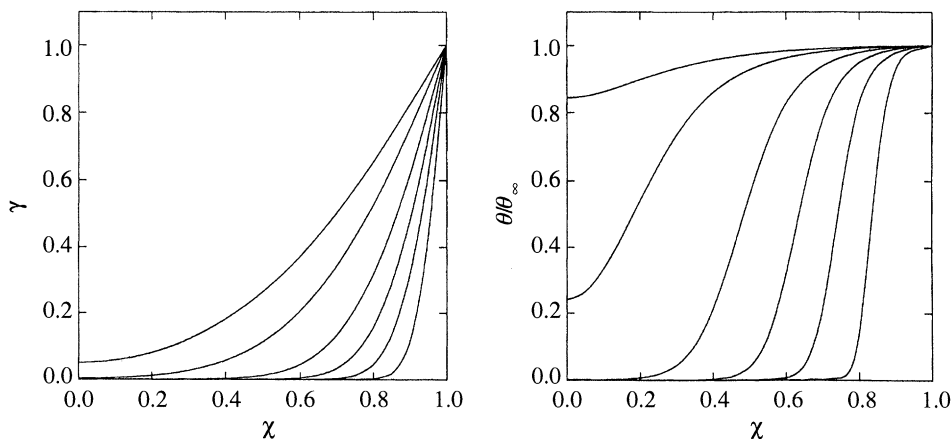


Figure 3. Plot of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ for case V: nonlinear fast kinetics with normal diffusion. The curves are calculated from equations (5.5) and (4.4) with $\kappa = 100$, $\lambda = 100$ and $\eta = 1$ for $\tau = 0.002, 0.005, 0.010, 0.020, 0.050$ and 0.100 . For this calculation, θ_∞ is 0.99.

and that the requirements of a numerical solution are too cumbersome. Instead, he used the method of Frisch (1957) to derive analytical expressions for the time lags on adsorption and desorption. More recently Murphy *et al.* (1988) have obtained numerical solutions of a ‘stiff’ nonlinear diffusional boundary-value problem, where the diffusing material can be reversibly bound to fixed traps. The solutions show, as expected, a difference in the adsorption and desorption times and a sharp step in the concentration profiles. Finally Kim *et al.* (1988) have addressed the problem of doping electroactive polymer films and produced a nonlinear partial differential equation identical to that given here (see equation (5.3)).

It is instructive to begin by considering a very simple model. For case VI the reaction kinetics are fast compared to diffusion and at equilibrium a significant amount of the diffusing species is bound to the immobile sites within the film. Under these circumstances, as the species A diffuses in to the film, a reaction front will be established at some position χ_* within the film. Ahead of this reaction front (for $\chi < \chi_*$) the sites will be empty, behind the reaction front (for $\chi > \chi_*$) the sites will be full. At the boundary, corresponding to $\chi = \chi_*$, we assume that the sites are half full so that, from equation (5.1), $\gamma_* = 1/\lambda$. The velocity with which the reaction front moves into the film is determined by the requirement that the flux of material reacting at the front balances the flux of material diffusing through the film to the reaction front

$$\frac{d\chi_*}{d\tau} = \frac{\lambda}{\eta} \frac{d\gamma}{d\chi}. \quad (5.6)$$

Assuming that the gas profile in the outside saturated region is linear, we can substitute into equation (5.6) for $d\gamma/d\chi$ and obtain the following equation for the velocity of the boundary:

$$\frac{d\chi_*}{d\tau} = \frac{\lambda(1 - \gamma_*)}{\eta(1 - \chi_*)}. \quad (5.7)$$

Given that $\chi_* = 1$ at $\tau = 0$, and that γ_* is constant until the reaction front hits the impermeable region at $\chi = 0$, then equation (5.6) may be solved to produce a quadratic in χ_* . Its solution (taking the negative root as the only physical solution)

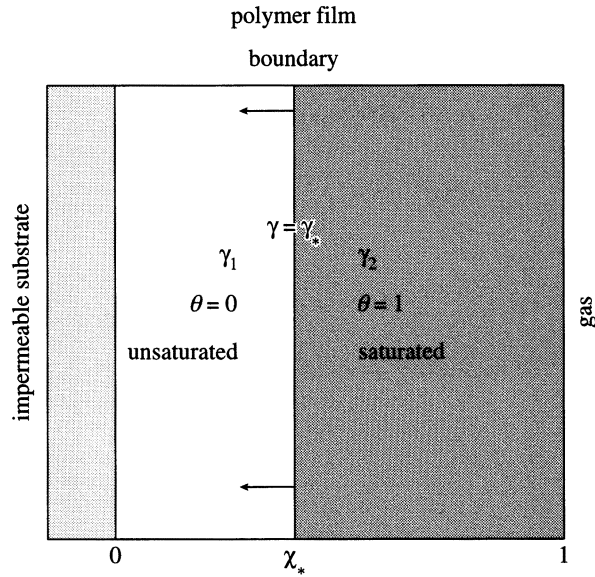


Figure 4. Schematic of the moving boundary problem.

gives the time dependency of the wavefront as

$$\chi_* = 1 - [2(1 - \gamma_*)\tau\lambda/\eta]^{1/2}. \quad (5.8)$$

Equation (40) describes the position of the boundary as it moves through the film. Note that the position of the boundary depends on $\tau^{1/2}$, because, as time progresses, the distance over which the material must diffuse in order to reach the reaction front increases and hence the flux decreases.

We can also approach this problem in a different manner. Again we begin by dividing the film at $\chi = \chi_*$, where $\gamma = \gamma_* = 1/\lambda$, into two regions; an inner region where the sites are unsaturated and an outer region in which the sites are saturated (figure 4). We then proceed to solve the problem by adapting Neumann's solution for the propagation of a boundary between two phases in a semi-infinite medium (Carslaw & Jaeger 1959). In terms of Neumann's formulation of the problem, the transient describing the diffusion of the gas into the polymer (the adsorption transient) corresponds to melting.

To move the boundary between the saturated and unsaturated regions through a distance $d\chi$, a quantity of adsorbate $\eta d\chi/\lambda$ per unit area must be supplied by diffusion. This requires

$$\frac{1}{\eta} \frac{\partial \gamma_1}{\partial \chi} - \frac{\partial \gamma_2}{\partial \chi} = \frac{\eta}{\lambda} \frac{d\chi_*}{d\tau}, \quad (5.9)$$

where $\gamma_1(\chi, \tau)$ and $\gamma_2(\chi, \tau)$ are the concentrations of gas in the unsaturated and saturated regions, respectively (equation (5.9) corresponds to equation (2) on p. 284 of Carslaw & Jaeger (1959)). For linear diffusion, γ_1 and γ_2 have to satisfy

$$\frac{\partial^2 \gamma_1}{\partial \chi^2} - \eta \frac{\partial \gamma_1}{\partial \tau} = 0, \quad (5.10)$$

$$\frac{\partial^2 \gamma_2}{\partial \chi^2} - \frac{\partial \gamma_2}{\partial \tau} = 0, \quad (5.11)$$

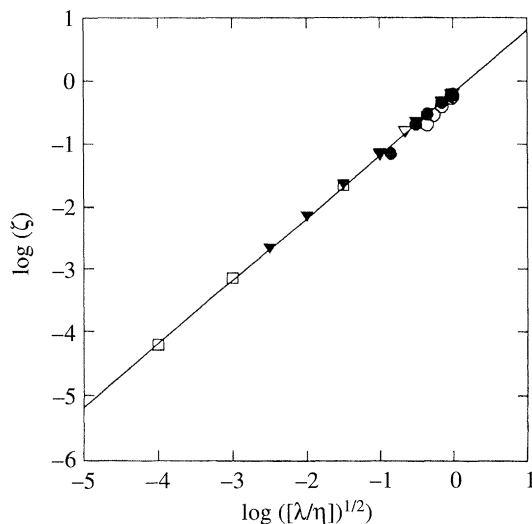


Figure 5. Plot of $\log(\zeta)$ values calculated for adsorption transients from equation (5.13) against $\log([\lambda/\eta]^{1/2})$ for values of η of: 10, (\circ); 10^2 , (\bullet); 10^3 , (∇); 10^6 , (\blacktriangledown); 10^9 , (\square). A range of λ values are shown.

and the appropriate boundary conditions.

Following Carslaw & Jaeger (1959), the position of the boundary between the two regions for the adsorption transient case is given by

$$(1 - \chi_*) = 2\zeta\tau^{1/2}, \quad (5.12)$$

where ζ is the root of

$$\frac{\exp(-\zeta^2)}{\operatorname{erf} \zeta} - \frac{\gamma_* \exp(-\zeta^2\eta)}{\eta^{1/2}(1 - \gamma_*) \operatorname{erfc}(\zeta\eta^{1/2})} = \frac{\eta\pi^{1/2}\zeta}{\lambda(1 - \gamma_*)}, \quad (5.13)$$

and the concentrations of adsorbate on the two sides of the boundary for the adsorption transient are given by

$$\gamma_1 = \frac{\gamma_*}{\operatorname{erfc}(\zeta\eta^{1/2})} \operatorname{erfc} \left\{ \frac{\eta^{1/2}(1 - \chi)}{2\tau^{1/2}} \right\} + \varepsilon(\chi, \tau), \quad (5.14)$$

$$\gamma_2 = 1 - \frac{1 - \gamma_*}{\operatorname{erf} \zeta} \operatorname{erf} \left\{ \frac{1 - \chi}{2\tau^{1/2}} \right\} + \varepsilon(\chi, \tau), \quad (5.15)$$

where we have added a correction term, $\varepsilon(\chi, \tau)$, to take into account the effects of the finite thickness of the film.

Equation (5.13) for ζ was solved numerically using the Van Wijngaarden–Dekker–Brent method (Press *et al.* 1986). A good approximation for ζ is found to be $\zeta = 0.65(\lambda/\eta)^{1/2}$ (figure 5). Thus, to a good approximation, the position of the boundary is

$$(1 - \chi_*) = 1.3(\tau\lambda/\eta)^{1/2}. \quad (5.16)$$

It is pleasing that this result is identical in form to that given in equation (5.8) for the very simple model of a propagating boundary.

Neumann's treatment assumes semi-infinite linear diffusion. This is not true of our problem. A better approximation to γ is achieved by folding in the semi-infinite

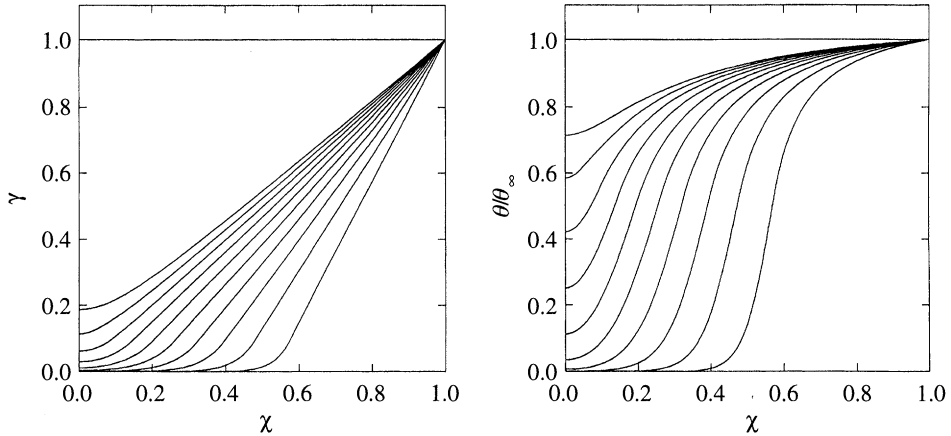


Figure 6. Plot of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ for case VI: the moving boundary problem. The curves are calculated from equations (5.1), (5.12)–(5.15) and (5.17) with $\kappa = 100$, $\lambda = 10$ and $\eta = 1000$ for $\tau = 10, 15, 20, \dots, 60$. For this calculation, θ_∞ is 0.909.

linear diffusion profile at the impermeable boundary (i.e. $\chi = 0$). Folding in the external profile twice increases γ_1 and γ_2 with

$$\varepsilon(\chi, \tau) \approx \frac{\gamma_*}{\operatorname{erfc}(\zeta\eta^{1/2})} \left[\operatorname{erfc} \left\{ \frac{\eta^{1/2}}{2\tau^{1/2}}(1 + \chi) \right\} - \operatorname{erfc} \left\{ \frac{\eta^{1/2}}{2\tau^{1/2}}(3 - \chi) \right\} \right]. \quad (5.17)$$

At some point the moving boundary will encounter the inside edge of the film. To deal with this we calculate the time at which the boundary reaches the inside of the film, τ_* . From equation (5.16), $\tau_* = 0.59\eta/\lambda$. For times greater than this critical time we assume that the process is dominated by simple diffusion. The solution for diffusion into a bounded layer starting from a general concentration profile has been given by Crank (1975). Modifying this equation to apply to our problem gives

$$\begin{aligned} \gamma(\chi, \tau) = & 1 + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos(n\pi) - 1}{n} \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) \exp\left(-\frac{1}{4}n^2\pi^2(\tau - \tau_*)\right) \\ & + 2 \sum_{n=1}^{\infty} \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) \exp\left(-\frac{1}{4}n^2\pi^2(\tau - \tau_*)\right) \\ & \times \int_0^1 \gamma_2(\chi', \tau_*) \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) d\chi', \end{aligned} \quad (5.18)$$

where $\gamma_2(\chi', \tau_*)$ is given by equation (5.15) with $\chi = \chi'$ and $\tau = \tau_*$. Profiles calculated using equations (5.1), (5.12)–(5.15) and (5.16) are shown in figure 6.

The profiles calculated for this case show a well developed reaction front in the plots of θ as the saturated region spreads from the outside into the film. It is noticeable in the profiles for γ that, to a good approximation, these are linear in the saturated outer region, as assumed in the very simple analysis which lead to equation (5.8). Notice, also, that because the material diffusing into the film must fill the sites, the time scale for the process is significantly longer, by a factor of the order of η/λ , than that for simple linear diffusion.

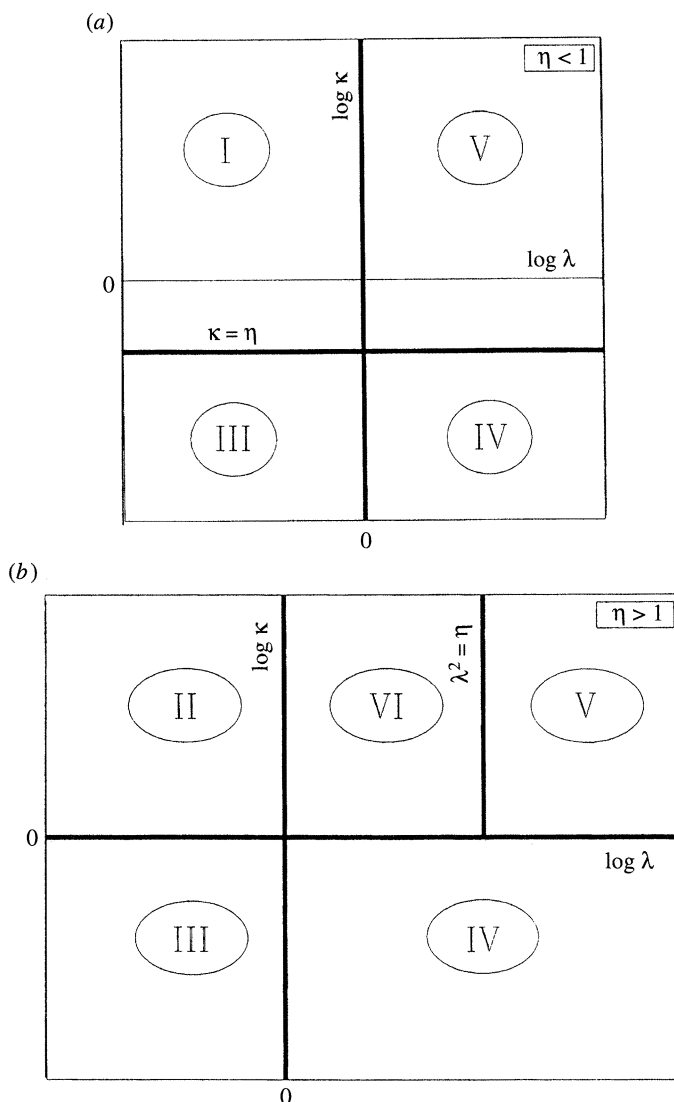


Figure 7. Full case diagram for all six cases showing the regions of dominance for the different cases as a function of κ , λ and η .

6. The case diagram

We now collect our results. Figure 7 shows the relation between the six cases in (κ, λ, η) space. The corresponding approximate analytical expressions for $\gamma(\chi, \tau)$ and $\theta(\chi, \tau)$ are collected together in Appendix A. At the boundaries between the cases, the approximate solutions will be most in error and a more complex expression should be used. These are gathered together in Appendix B. It is satisfactory that there is a good match between the cases at the boundaries. We now discuss each case in turn.

In case I, the film is unsaturated at equilibrium and the kinetics of the reaction are fast when compared to diffusion. Consequently, the occupancy of the sites follows the diffusion of the species A into the film. The amount of A bound on sites is small

compared to the amount of free A in the film and thus the diffusion of A is not affected by the reaction.

In case II, the film is unsaturated at equilibrium and the reaction kinetics are fast when compared to diffusion. However, this case differs from case I because a large proportion of A is now bound to sites in the film. This leads to a reduced diffusion coefficient, and hence the characteristic time for A to diffuse into the film is greater by a factor η than in case I.

In case III, the film is unsaturated at equilibrium, but now the reaction kinetics are slow when compared to diffusion. Thus, A diffuses into the film and attains a constant concentration before reaction occurs. The reaction then proceeds on a slower timescale homogeneously throughout the film.

In case IV, the film is saturated at equilibrium, but the reaction kinetics are still slow when compared to diffusion. Thus, again, A diffuses into the film and attains a constant concentration before the sites are filled. The reaction then proceeds homogeneously throughout the film to completely fill the sites.

In case V, the sites are saturated at equilibrium and the kinetics are fast so that the occupancy of the sites follows the diffusion of the species A into the film. The reaction does not significantly perturb the diffusion because only a small fraction of A ends up in the bound form. As a result, the region of occupied sites spreads into the film from the outside at a rate governed by the diffusion of A .

Finally, in case VI, the situation is more complex. Once again the sites are fully occupied at equilibrium and the reaction kinetics are fast but now the fraction of the species A bound to sites is significant. Thus, the reaction slows down diffusion of A into the film. The region of occupied sites spreads through the film as a moving boundary from the outside in, but now this is slower than for case V because a significant quantity of A is bound to the immobile sites at equilibrium.

7. Desorption

So far we have considered the problem of the simultaneous diffusion into and reaction of an adsorbate with a uniform homogeneous film. The boundary conditions for this adsorption process are given by equation (2.14). Clearly, there is the complimentary problem in which the adsorbate is initially distributed uniformly throughout the film and subsequently diffuses out into the external phase. Under these circumstances the boundary conditions are

$$\left. \begin{array}{l} \text{at } \tau = 0, \theta = \lambda/(1 + \lambda) \text{ and } \gamma = 1, 0 \leq \chi \leq 1, \\ \forall \tau > 0, \left. \frac{d\gamma}{d\chi} \right|_{\chi=0} = 0 \text{ and } \gamma = 0 \text{ at } \chi = 1. \end{array} \right\} \quad (7.1)$$

Provided the diffusion–reaction equation describing the process is linear, it is easy to show that the solutions derived for adsorption can be readily modified to describe the desorption process. We simply need to replace the variables γ by $(1 - \gamma)$ and θ by $(\theta_\infty - \theta)$ to obtain the desorption solutions. Thus, for cases I–III, the solutions for the desorption process are readily obtained from the results given above. The appropriate expressions are given in Appendix C. For cases IV–VI, the diffusion reaction equation is nonlinear and, hence, the desorption process is not simply derived from the solutions for the adsorption transients.

(a) Case IV ($\kappa < \eta/(1 + \eta)$, $\lambda > 1$)

In case IV, the reaction kinetics are slow when compared to diffusion, hence diffusion of the unbound species from the film is unaffected and is described by equation (3.6). The fixed sites in the film do not start to empty until γ falls to a value of $1/\lambda$. The time τ_d required to reach this condition can be found from the solution of the simple bounded diffusion problem (case I, equation (3.6)). Using the first term in the series, and setting $\chi = 0$, gives

$$\gamma(\chi = 0, \tau = \tau_d) = \frac{4}{\pi} \exp(-\frac{1}{4}\pi^2\tau_d). \quad (7.2)$$

Rearranging and substituting for $\gamma = 1/\lambda$ gives

$$\tau_d \approx \frac{4}{\pi^2} \ln(4\lambda/\pi). \quad (7.3)$$

The effect of this time delay on the profile for θ can then be taken into account by modifying equation (4.6) to give

$$\theta = \frac{\exp(-\kappa(\tau - \tau_d)/\eta)}{1 + \exp(-\kappa(\tau - \tau_d)/\eta)}. \quad (7.4)$$

Now when $\tau \ll \tau_d$, $\theta \approx 1$ and when $\tau \gg \tau_d$, $\theta \approx \exp(-\kappa(\tau - \tau_d)/\eta)$ as required. Figure 8 shows examples of the adsorption and desorption transients for case IV.

(b) Case V ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 > \eta$)

In case V, at $\tau = 0$ the sites are saturated ($\lambda \gg 1$) and the kinetics are fast so that equilibrium is maintained between the free and bound species ($\kappa \gg \eta/(1 + \eta)$). In addition, the conditions are such that only a small fraction of the total amount of gas is bound to the sites at $\tau = 0$ ($\lambda^2 \gg \eta$). Thus, the diffusion of the free species out of the film is essentially unperturbed by the bound material and is described by the simple bounded diffusion equation (from equation (3.6))

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad (7.5)$$

and then, since the kinetics are fast, θ is given by equation (5.1). Because the sites cannot empty until the concentration of free gas falls sufficiently low ($\gamma \ll 1/\lambda$) so as to shift out of the saturated region, the desorption transient for θ is slower than the corresponding adsorption transient. Figure 9 illustrates the difference between the adsorption and desorption transients in case V.

(c) Case VI ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 < \eta$)

Case VI is similar to case V but with one crucial difference; now the amount of bound gas is significant and so we can no longer assume that it does not perturb the diffusion of the unbound gas out of the film. In fact, in this case, it is the desorption of the bound gas which is dominant. As a result, the problem in this case is highly nonlinear. Expressions for the time lag in desorption under these conditions have been presented (Paul 1969), but expressions for the concentration profiles are not readily available.

We begin our analysis by going back to the basic differential equation appropriate for this case, i.e. equation (5.3). We note for case VI, that $\eta \gg \lambda^2$ and so we simplify

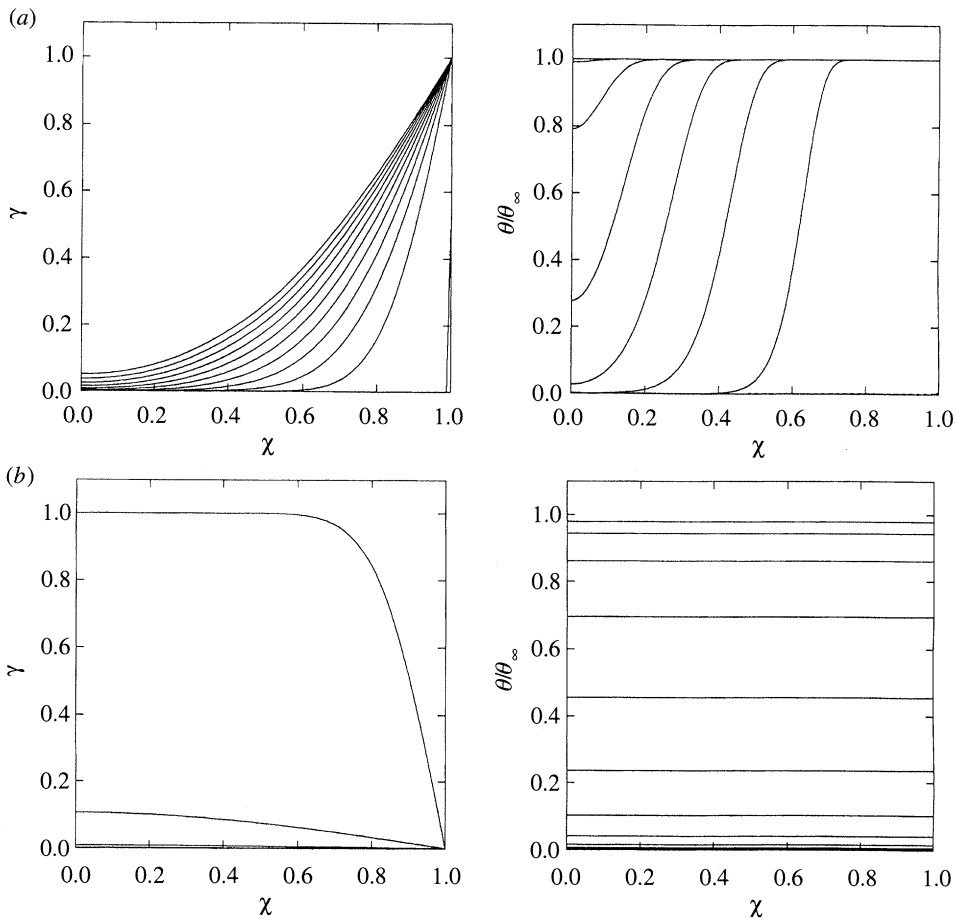


Figure 8. Plot of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ for the adsorption and desorption transients for case IV calculated for $\kappa = 0.01$, $\lambda = 10^4$, $\eta = 0.01$. Note the difference in the timescales for the θ transient (a) adsorption, $\tau = 10^{-6}$, 0.01, 0.02, 0.03 etc. up to 0.1; (b) desorption, $\tau = 0.01, 1, 2, 3$, etc. up to 10. In both cases, θ_∞ is 0.9999.

(5.3) and write

$$\frac{\partial^2 \gamma}{\partial \chi^2} = \frac{\eta}{(1 + \lambda \gamma)^2} \frac{\partial \gamma}{\partial \tau}. \tag{7.6}$$

Our approach is then to substitute an approximate expression for $\gamma(\chi, \tau)$ in the denominator on the right-hand side of equation (7.6) and then to solve it. First, we put $\gamma = 1$ in the denominator of equation (7.6), and hence obtain a linear equation which we solve. We choose to use the form of the expression given in terms of the complementary error function (erfc) which is a good approximation at short times. Following Crank (1975) and using our notation, for the desorption transient we obtain

$$\gamma = \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \left(\frac{((2n+1) - \chi)\eta^{1/2}}{2(1+\lambda)\tau^{1/2}} \right) + \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \left(\frac{((2n+1) + \chi)\eta^{1/2}}{2(1+\lambda)\tau^{1/2}} \right). \tag{7.7}$$

We can now obtain a better approximation for γ by taking the leading term in

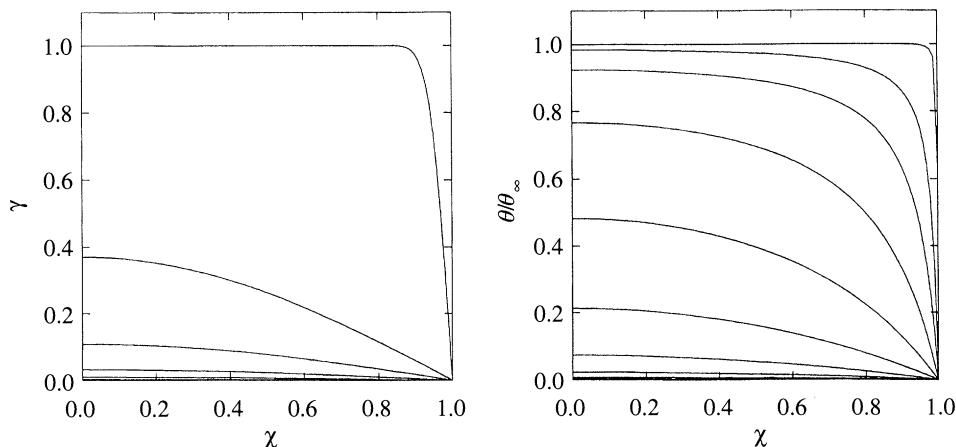


Figure 9. Plot of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ for desorption in case V. The curves were calculated from equations (7.4) and (5.1) with $\kappa = 100$, $\lambda = 100$ and $\eta = 1$ for $\tau = 0.001, 0.5, 1, 1.5, \text{etc.}$, up to 5. Note that the time scale is much longer than that for the corresponding case V adsorption transient shown in figure 3. For this calculation, θ_∞ is 0.99.

equation (7.6) for γ at $\chi = 0$. This gives

$$\gamma = \text{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})]. \tag{7.8}$$

We then substitute this expression for γ in the denominator of equation (7.6) to give

$$\frac{\partial^2 \gamma}{\partial \chi^2} = \frac{\eta}{(1 + \lambda \text{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})])^2} \frac{\partial \gamma}{\partial \tau}. \tag{7.9}$$

To solve this we introduce the new variable ζ , such that

$$\frac{\partial \gamma}{\partial \zeta} = (1 + \lambda \text{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})])^2, \tag{7.10}$$

and hence (7.9) becomes

$$\frac{\partial^2 \gamma}{\partial \chi^2} = \eta \frac{\partial \gamma}{\partial \zeta}. \tag{7.11}$$

Solution of (7.11), with the boundary conditions for desorption given in equation (7.1), gives equation (7.12) for γ :

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2 \pi^2 \chi / \eta]}{(-1)^n (n + \frac{1}{2})}, \tag{7.12}$$

where, from integration of (7.10),

$$\zeta = \tau + 2\lambda \int_0^\tau \text{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})] d\tau + \lambda^2 \int_0^\tau \text{erf}^2[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})] d\tau, \tag{7.13}$$

and since the kinetics are fast and equilibrium is maintained, θ is again given by equation (5.1).

The evaluation of the integral in equation (7.13) leads to other integrals (Prudnikov *et al.* 1986) and it is more convenient to evaluate these numerically. When $\eta^{1/2}/[2(1 + \lambda)]$ is greater than unity, the following approximation is good:

$$\zeta \approx \tau + 2\lambda\tau \text{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})] + \lambda^2 \tau \text{erf}^2[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})]. \tag{7.14}$$

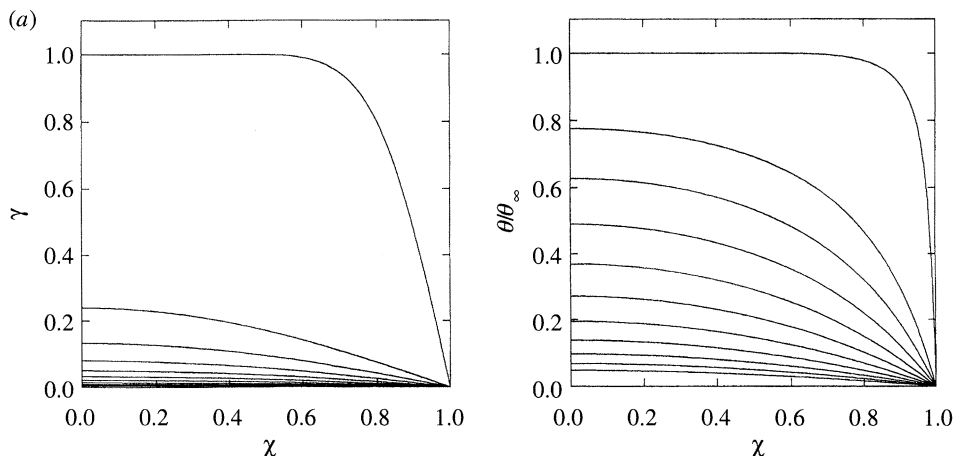


Figure 10. Plot of the adsorbate concentration γ and the site occupancy divided by its equilibrium value θ/θ_∞ for desorption in case VI. The curves are calculated from equations (5.1), (7.12) and (7.13) with $\kappa = 100$, $\lambda = 10$ and $\eta = 1000$ for $\tau = 0.1, 100, 200, 300$, etc., up to 1000. For this calculation, θ_∞ is 0.909.

This approximation is valid for most of case VI as $\lambda \gg 1$ and $\lambda^2 \ll \eta$.

Figure 10 shows typical profiles for desorption in case VI. It is notable that the time scale for desorption in this case is much slower, by a factor of about 2λ , than the time scale for adsorption. This is because in the adsorption process the large concentration difference between the outside of the film, where $\gamma = 1$, and the reaction front, where $\gamma = 1/\lambda$ (remember, for this case $\lambda \gg 1$), drives the flux of material into the film by diffusion to fill the fixed sites. In contrast, in the desorption process, the concentration difference between the inside of the film, where $\gamma = 1/\lambda$, and the outside, where $\gamma = 0$, is small and hence the flux of material leaving the film is much smaller.

8. Conclusions

In this paper we have presented approximate analytical expressions for the transient concentration profiles for a species diffusing into a bounded film containing a number of fixed sites which bind the diffusing species according to the Langmuir isotherm. We have shown that we can distinguish six different limiting cases and we have shown how these are related by means of a case diagram. We have considered both the adsorption and desorption transient behaviours for each case. The results are summarized in Appendix A and Appendix C. We find that for the linear kinetic cases (I–III), the adsorption and desorption transients are simply related. For the nonlinear kinetic cases (IV–VI), the situation is more complex and the adsorption and desorption transients are different and occur on different time scales. In case IV, there is a time delay, until γ falls to a value of approximately $1/\lambda$, before the sites begin to empty. Thus, the adsorption and desorption transients for γ are on the same time scale, but the corresponding θ transients are on different time scales. In case V, the adsorption and desorption transients for γ are again simply related, but the θ transients are on very different time scales because equilibrium is maintained between the bound and the unbound material. In case VI, both γ and θ adsorption and desorption transients are on different time scales.

We have compared our approximate analytical solution presented here with the results of digital simulation of the adsorption and desorption processes using finite difference techniques and we find good agreement. We have also used our approximate analytical expressions for the concentration profiles to model the transient responses for gas sensor devices, based on adsorption of a gas into a thin film. Full details of this work will be given in a subsequent paper.

We thank Mr Keith Pratt for helpful discussions.

Appendix A. Approximate analytical expressions for adsorbate concentration and site occupancy for adsorption

Case I: ($\lambda < 1$, $\eta < 1$, $\kappa > \eta$)

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma.$$

Case II: ($\lambda < 1$, $\eta > 1$, $\kappa > 1$)

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau/\eta]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma.$$

Case III: ($\lambda < 1$, $\kappa < \eta/(1 + \eta)$)

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda[1 - \exp(\kappa\tau/\eta)].$$

Case IV: ($\kappa < \eta/(1 + \eta)$, $\lambda > 1$)

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx 1 - \exp(-\lambda\gamma\kappa\tau/\eta).$$

Case V: ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 > \eta$)

$$\gamma(\chi, \tau) \approx 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma/(1 + \lambda\gamma).$$

Case VI: ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 < \eta$)

$$\gamma(\chi, \tau) \approx \tau_* = 0.59\eta/\lambda, \quad \chi_* = 1 - 2\zeta\tau^{1/2},$$

$$\theta(\chi, \tau) \approx \lambda\gamma/(1 + \lambda\gamma)$$

$$\frac{\exp(-\zeta^2)}{\operatorname{erf} \zeta} - \frac{\gamma_* \exp(-\zeta_*\eta)}{\eta^{1/2}(1 - \gamma_*) \operatorname{erfc}(\zeta\eta^{1/2})} = \frac{\eta\pi^{1/2}\zeta}{\lambda(1 - \gamma_*)},$$

$$\varepsilon(\chi, \tau) \approx \operatorname{erfc} \left\{ \frac{\eta^{1/2}}{2\tau^{1/2}}(1 + \chi) \right\} - \operatorname{erfc} \left\{ \frac{\eta^{1/2}}{2\tau^{1/2}}(3 - \chi) \right\}.$$

For $\tau < \tau_*$,

$$\chi < \chi_*, \quad \gamma_1 = \frac{\gamma_*}{\operatorname{erfc}(\zeta\eta^{1/2})} \operatorname{erfc} \left\{ \frac{\eta^{1/2}(1 - \chi)}{2\tau^{1/2}} \right\} + \varepsilon(\chi, \tau),$$

$$\chi > \chi_*, \quad \gamma_2 = 1 - \frac{1 - \gamma_*}{\operatorname{erf} \zeta} \operatorname{erf} \left\{ \frac{1 - \chi}{2\tau^{1/2}} \right\} + \varepsilon(\chi, \tau).$$

For $\tau > \tau_*$,

$$\begin{aligned} \gamma(\chi, \tau) = & 1 + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos(n\pi) - 1}{n} \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) \exp\left(-\frac{1}{4}n^2\pi^2(\tau - \tau_*)\right) \\ & + 2 \sum_{n=1}^{\infty} \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) \exp\left(-\frac{1}{4}n^2\pi^2(\tau - \tau_*)\right) \\ & \times \int_0^1 \gamma_2(\chi', \tau_*) \sin\left(\frac{1}{2}n\pi(\chi + 1)\right) d\chi'. \end{aligned}$$

Appendix B. Exact analytical expressions for gas concentration and site occupancy (adsorption transients)

Cases I–III:

$$\gamma(\chi, \tau) = 1 - 2\pi \sum_{n=0}^{\infty} \frac{(n + \frac{1}{2}) \cos[(n + \frac{1}{2})\pi\chi] \exp[s_n\tau]}{(-1)^n [(n + \frac{1}{2})^2\pi^2 - s_n\kappa \ln[s_n + \kappa/\eta]]},$$

$$\theta(\chi, \tau) = \lambda - 2\pi\kappa\lambda \sum_{n=0}^{\infty} \frac{(n + \frac{1}{2}) \cos[(n + \frac{1}{2})\pi\chi] \exp[s_n\tau]}{(\kappa + \eta s_n)(-1)^n [(n + \frac{1}{2})^2\pi^2 - s_n\kappa \ln[s_n + \kappa/\eta]]},$$

where

$$n = 0, 1, 2, \dots, \infty, \quad \text{and } s_n \approx -\frac{(n + \frac{1}{2})^2\pi^2\kappa}{\eta[\kappa(1 + 1/\eta) + (n + \frac{1}{2})^2\pi^2]}.$$

Cases III, IV:

$$\gamma(\chi, \tau) = 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n (n + \frac{1}{2})},$$

$$\theta(\chi, \tau) = \frac{\lambda}{1 + \lambda} \left(1 - \exp\left(-\frac{(1 + \lambda\gamma)\kappa\tau}{\eta}\right) \right).$$

Appendix C. Approximate analytical expressions for adsorbate concentration and site occupancy for desorption

Case I: ($\lambda < 1$, $\eta < 1$, $\kappa > \eta$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n (n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma.$$

Case II: ($\lambda < 1$, $\eta > 1$, $\kappa > 1$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau/\eta]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma.$$

Case III: ($\lambda < 1$, $\kappa < \eta/(1 + \eta)$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx 1 - \lambda[1 - \exp(-\kappa\tau/\eta)].$$

Case IV: ($\kappa < \eta/(1 + \eta)$, $\lambda > 1$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})},$$

$$\theta \approx \frac{\exp(-\kappa(\tau - \tau_d)/\eta)}{1 + \exp(-\kappa(\tau - \tau_d)/\eta)}, \quad \text{with } \tau_d = \{4 \ln(4\lambda/\pi)\}/\pi^2.$$

Case V: ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 > \eta$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\tau]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma/(1 + \lambda\gamma).$$

Case VI: ($\kappa > \eta/(1 + \eta)$, $\lambda > 1$, $\lambda^2 < \eta$)

$$\gamma(\chi, \tau) \approx \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi\chi] \exp[-(n + \frac{1}{2})^2\pi^2\zeta/\eta]}{(-1)^n(n + \frac{1}{2})}, \quad \theta(\chi, \tau) \approx \lambda\gamma/(1 + \lambda\gamma),$$

where

$$\zeta = \tau + 2\lambda \int_0^\tau \operatorname{erf}[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})] d\tau + \lambda^2 \int_0^\tau \operatorname{erf}^2[\eta^{1/2}/(2(1 + \lambda)\tau^{1/2})] d\tau.$$

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