

A COMPARISON OF CRITICAL TIME DEFINITIONS IN MULTILAYER DIFFUSION

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Abstract

There are many ways to define how long diffusive processes take, and an appropriate “critical time” is highly dependent on the specific application. In particular, we are interested in diffusive processes through multilayered materials, which have applications to a wide range of areas. Here we perform a comprehensive comparison of six critical time definitions, outlining their strengths, weaknesses, and potential applications. A further four definitions are also briefly considered. Equivalences between appropriate definitions are determined in the asymptotic limit as the number of layers becomes large. Relatively simple approximations are obtained for the critical time definitions. The approximations are more accessible than inverting the analytical solution for time, and surprisingly accurate. The key definitions, their behaviour and approximations are summarized in tables.

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1. Introduction

Diffusion through multiple layers has applications to a wide range of areas in heat and mass transport [15, 17]. For multilayer diffusion across n layers, the standard linear diffusion equation,

$$\frac{\partial U_i(x, t)}{\partial t} = D_i \frac{\partial^2 U_i(x, t)}{\partial x^2}, \quad i = 1, 2, \dots, n,$$
$$U_1(x_0) = \theta_1, \quad U_n(x_n) = \theta_2,$$

is applicable in each layer, where $x_{i-1} \leq x \leq x_i$ is distance, t is time, U_i is the diffusant in layer i , D_i is the diffusivity of layer i , and θ_1 and θ_2 are constants. The diffusant

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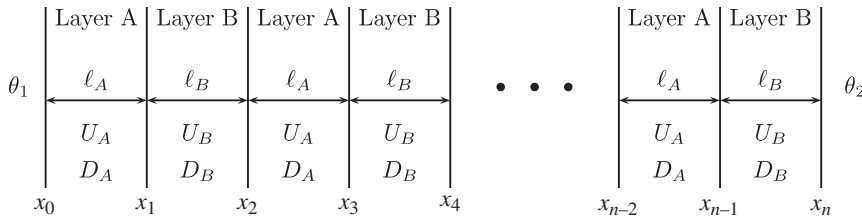


FIGURE 1. Schematic of “biperiodic layers”: repeated layers with “A” and “B” properties. The layer widths are equal, $\ell_A = \ell_B = \ell$, and Dirichlet boundary conditions $U_1(x_0, t) = \theta_1$ and $U_n(x_n, t) = \theta_2$ are used.

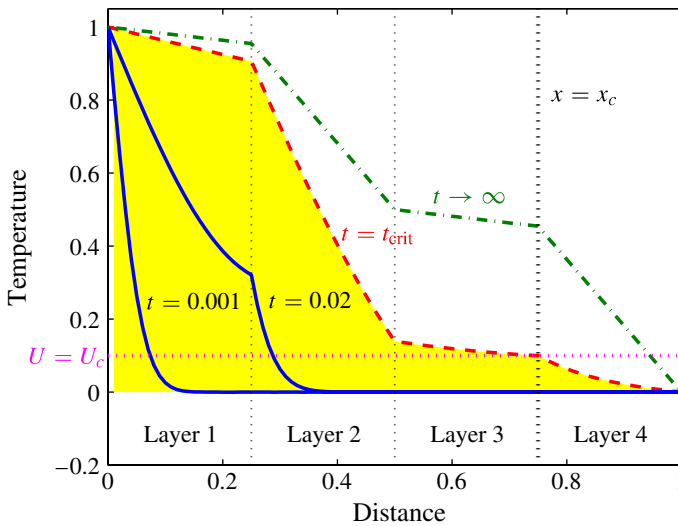


FIGURE 2. Temperature profiles. The dashed line is an example critical time, $t_{crit} \approx 0.3$, and the dot–dashed line is the steady state. Here there are $n = 4$ layers and $D = [1, 0.1]$. This t_{crit} corresponds to $\alpha = 0.8$, $\beta = 0.4$, $\gamma \approx 0.5$, and $x_c = 0.75$ and $U_c \approx 0.1$ for Definitions 1, 2, 4 and 6, respectively.

is commonly referred to as “temperature” throughout this paper to aid readability, but could be “density”. The region is assumed to consist of multiple repeating layers, as shown in Figure 1. The diffusivity is represented as either $D = [D_A, D_B]$ or $D[D_A, D_B]$. Equal layer widths ($\ell_A = \ell_B = \ell$) are assumed; a zero initial condition, $f_i(x) = 0$, is used; and Dirichlet boundary conditions $U_1(x_0, t) = \theta_1$ and $U_n(x_n, t) = \theta_2$ are used.

An important aspect of multilayer diffusion is the concept of “critical time”, which is a measure of how long the diffusive processes take. Figure 2 depicts an example “temperature” profile at a critical time. A commonly used critical time is the nondimensionalization result L^2/D_{av} , where D_{av} is calculated using the standard harmonic mean

$$\frac{L}{D_{av}} = \sum_{i=1}^n \frac{\ell_i}{D_i}, \tag{1.1}$$

where ℓ_i is the length of layer i , n the total number of layers, and $L = \sum \ell_i$ the total length of the region.

Defining a critical time is highly dependent on the specific application, so we outline the main definitions used in the literature, highlighting possible applications. The application should determine both which critical time definition is used, and the parameter value(s) for that definition. The aim of this paper is to give an overview of several definitions currently used in the literature, providing comparisons and approximations, so that the choice of definition for a given application is easier to make. To facilitate this, example applications are given for each definition at the beginning of Sections 2–7, along with a description of their strengths and weaknesses.

A comprehensive comparison of six critical time definitions is conducted in Sections 2–7, and another four definitions are briefly discussed in Section 8. The definitions are split into spatially dependent (Definitions 1–4) and independent (5–7) groups, and compared within their respective groups. To form a baseline of how the two groups compare, all definitions are also compared to Definition 1, which was used in previous publications [9, 10, 12–14]. A qualitative comparison is conducted in Section 9. A summary of the key results is given in Tables 1 and 2.

We show how the critical time varies with the number of layers for the different biperiodic orders, and compare the asymptotic equivalences for large numbers of layers for various critical time parameters. Here a biperiodic order refers to two layers with different properties alternating, as depicted in Figure 1. Quantitative comparisons are conducted at the end of each of Sections 3–7. The equivalences between the critical time parameters are only true in the asymptotic limit in the number of layers, which is evident from the various different behaviours demonstrated by the different definitions. The numerical results use the finite difference scheme presented by Hickson et al. [12], which has been verified against both the analytical solution and a commercial finite elements package, FLEXPDE. The exact analytical solutions found by Hickson et al. [9] are used, but not included here for the sake of brevity (specifically, equations (17) and (56) of Hickson et al. [9] are used for the single layer and multilayer analyses, respectively). The approximations for the critical times are all obtained by using only the leading eigenvalue, $m = 1$, in the analytical solutions for single and multiple layers. Therefore, the approximations hold when time is sufficiently large and the leading eigenvalue dominates the solution. Furthermore, all numerical results use $\theta_1 = 1$ and $\theta_2 = 0$ for the boundary conditions. Although the multilayer diffusion equation has been nondimensionalized such that $x \in [0, 1]$, we retain the total length of the region, L , in the formulas for easy comparison to other work. Where applicable, the perturbation analysis conducted by Hickson et al. [10] is repeated to find a simpler approximate expression for a definition of critical time.

This paper summarizes Chapter 5 of the thesis by Hickson [8]. The lengthy detail included in the thesis, where the critical time was considered as a function of all parameters for the different definitions, is beyond the scope of this paper. This paper is an extension of previous papers [9–13], which only considered Definitions 1 and 3 for multilayer diffusion. Definitions 1, 2 and 6 are considered in the context of single

TABLE 1. Summary of the four spatially independent definitions. The approximations are accurate to the first order in ℓ , for the sake of brevity.

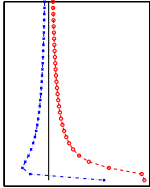
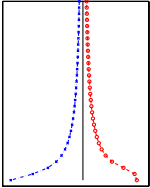
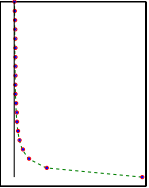
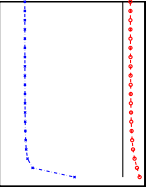
Definition	Time versus no. of layers	Approximation	Asymptotic equivalence
$t_{\text{def1}}:$ $\int_x U(x, t_{\text{def1}}) dx = \alpha \int_x w(x) dx$		$\frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{8}{\pi^2 (1 - \alpha)} \right\} - \frac{L}{\pi^2 D_{\text{av}}} \left(1 - \frac{D_{\text{av}}}{D_A} \right) \ell$	N/A
$t_{\text{def2}}:$ $\int_x U(x, t_{\text{def2}}) dx = \beta$		$\frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{8L}{\pi^2 (L - 2\beta)} \right\} - \frac{L^2}{\pi^2 D_{\text{av}}} \left(1 - \frac{D_{\text{av}}}{D_A} \right) \frac{\ell}{L - 2\beta}$	def. 1: $\alpha = \frac{2\beta}{L}$
$t_{\text{def3}}:$ $\int_0^\infty D \frac{\partial U(x, t_{\text{def3}})}{\partial x} \Big _{x_n} dt$		$\frac{L^2}{6D_{\text{av}}}$	def. 1: $\alpha \approx 0.8435$ def. 2: $\beta \approx 0.4218$
$t_{\text{def4}}:$ $\frac{\partial U(x, t_{\text{def4}})}{\partial x} \Big _{x_n} = -\gamma$		$\frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{2D_s}{D_s - \gamma L D_A} \right\}$ where $D_s = 2D_A - D_{\text{av}}$	def. 1: $\alpha = 1 + \frac{4}{\pi^2} (1 + \gamma L)$ def. 2: $\beta = \frac{L(\pi^2 - 4 + 4\gamma L)}{2\pi^2}$ def. 3: $\gamma \approx 0.6139$

TABLE 2. Summary of the three spatially dependent definitions. To aid readability, the “approximation” is for the A layer at the layer interfaces, when $x = x_{j-1}$.

Definition	Time versus no. of layers	Approximation	Asymptotic equivalence
$t_{\text{def5}} = \frac{-1}{w(x_c)} \int_0^\infty v(x_c, t) dt$		$\frac{2\Theta L^3 \sin(\pi x_c/L)}{\pi^2 D_{\text{av}}(\theta_1 L + \Phi x_c)}$	def. 1: $\alpha = 1 - \frac{8}{\pi^2} \exp\left(\frac{-2L \sin(\pi x_c/L)}{\pi(L - x_c)}\right)$
$t_{\text{def6}} = U(x_c, t_{\text{def6}}) = U_c$		$\frac{L^2}{\pi^2 D_{\text{av}}} \log_\epsilon \left\{ \frac{2\Theta L \sin(\pi x_c/L)}{\pi(\theta_1 L - U_c L + x_c \Phi)} \right\}$	def. 1: $\alpha = 1 + \frac{4(U_c L - L + x_c)}{\pi L \sin(\pi x_c/L)}$ def. 5: $U_c = 1 - \frac{x_c}{L} - \frac{2}{\pi} \sin\left(\frac{\pi x_c}{L}\right) \times \exp\left(\frac{-2L \sin(\pi x_c/L)}{\pi(L - x_c)}\right)$
$t_{\text{def7}} = U(x_c, t_{\text{def7}}) = \hat{\alpha} w(x_c)$		$\frac{L^2}{\pi^2 D_{\text{av}}} \log_\epsilon \left\{ \frac{2\Theta L \sin(\pi x_c/L)}{\pi(\theta_1 L + x_c \Phi)(\hat{\alpha} - 1)} \right\}$	def. 1: $\alpha = 1 + \frac{4(\hat{\alpha} - 1)(L - x_c)}{\pi L \sin(\pi x_c/L)}$ def. 5: $\hat{\alpha} = 1 - \frac{2L}{\pi(L - x_c)} \sin\left(\frac{\pi x_c}{L}\right) \times \exp\left(\frac{-2L \sin(\pi x_c/L)}{\pi(L - x_c)}\right)$ def. 6: $\hat{\alpha} = \frac{LU_c}{L - x_c}$

layer reaction diffusion by Hickson et al. [14]. The critical time definitions were either devised or suggested by other authors, as outlined in the appropriate sections. However, with the exception of Definitions 1 and 3, this is the first time the behaviour of these definitions is explored in a multilayered material. Furthermore, the approximations of all but Definitions 1 and 3 are entirely novel. They are based on the perturbation analysis conducted by Hickson et al. [10] for Definition 1.

2. Definition 1: proportion of the average steady state

The first definition considered is the time when the spatially averaged temperature reaches a given or specified proportion of the average steady state, mentioned by Landman and McGuinness [15]. That is, the critical time is defined as the value of $t = t_{\text{def1}}$ such that

$$\int_{x=x_0}^{x_n} U_i(x, t_{\text{def1}}) dx = \alpha \int_{x=x_0}^{x_n} w_i(x) dx, \quad (2.1)$$

where $U_i(x, t)$ is the temperature in layer i , $0 < \alpha < 1$ is a chosen constant, and $w_i(x)$ is the steady state solution. For example, the temperature profile for a critical time depicted in Figure 2 was calculated using $\alpha = 0.8$ (dashed line, where the steady state is the dot-dashed line). This definition is appropriate for all types of boundary and initial conditions, and eliminates dependence on the spatial position. Overall, it allows the effect of multiple layers on the critical time to be assessed more generally than other definitions.

This definition has been thoroughly explored by Hickson et al. [9, 10]. The main results are briefly presented here for completeness and comparison with other definitions. Numerical results are shown in Section 2.1 for the critical time as a function of the number of layers; single and multiple layer approximations are also presented.

2.1. Approximations and numerical results The single layer approximation obtained by Hickson et al. [9] is

$$t_{\text{sd1}} \approx \frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{8}{\pi^2 (1 - \alpha)} \right\}, \quad (2.2)$$

where D_{av} is given by (1.1) and $0 < \alpha < 1$ is the proportion of the steady state solution. The critical time must be positive, and therefore $1 - 8/\pi^2 < \alpha < 1$.

The multilayer approximation is determined as an expansion in the layer width ℓ by Hickson et al. [10, equations 43–47]:

$$t_{\text{ad1}} = t_{\text{ad1}}^{(0)} + t_{\text{ad1}}^{(1)} \ell + t_{\text{ad1}}^{(2)} \ell^2 + t_{\text{ad1}}^{(3)} \ell^3 + O(\ell^4), \quad (2.3)$$

where

$$t_{\text{ad1}}^{(0)} = \frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{8}{\pi^2 (1 - \alpha)} \right\}, \quad (2.4)$$

$$t_{\text{ad1}}^{(1)} = \frac{L}{\pi^2 D_{\text{av}}} \left(1 - \frac{D_{\text{av}}}{D_A} \right) \Gamma, \quad (2.5)$$

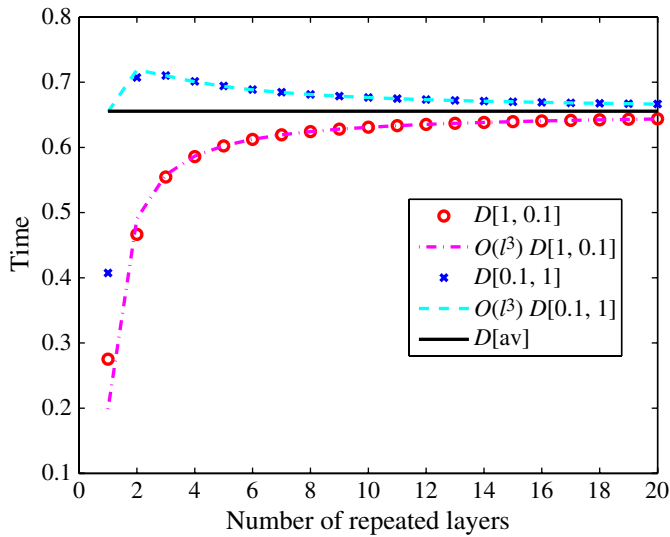


FIGURE 3. Critical time Definition 1 (equation (2.1)) versus the number of repeated layers. The circles are the critical times using $D = [1, 0.1]$, and the dot–dashed line is the corresponding approximation. The crosses use $D = [0.1, 1]$, and the dashed line is the corresponding approximation. The solid line uses $D[av] \equiv D_{av} \approx 0.18$. Here $\alpha = 0.75$.

$$t_{ad1}^{(2)} = -\frac{L^0}{\pi^2 D_{av}} \left(1 - \frac{D_{av}}{D_A}\right)^2 \left[\frac{\pi^2}{12} \log_e \left\{ \frac{8}{\pi^2(1-\alpha)} \right\} + \frac{\Gamma^2}{2} + \frac{\pi^2}{24} \right], \tag{2.6}$$

$$t_{ad1}^{(3)} = -\frac{L^{-1}}{\pi^2 D_{av}} \left(1 - \frac{D_{av}}{D_A}\right)^3 \left[\frac{\pi^2 \Gamma}{12} + \frac{\Gamma^3}{3} \right], \tag{2.7}$$

$\Gamma = (\theta_2 - \theta_1)/(\theta_2 + \theta_1)$ and $t_{ad1}^{(0)} \equiv t_{sd1}$, where t_{sd1} is defined by (2.2).

Figure 3 depicts the critical time as a function of the number of repeated layers, where a repeated layer is a combination of one A and one B layer (as shown in Figure 1), and the two different orderings of the diffusivities are considered. The third-order approximation (2.3)–(2.7) is depicted by the dashed and dot–dashed lines. The solid line uses the averaged diffusivity $D[av] \equiv D_{av} \approx 0.18$ calculated using (1.1). The circles are the critical times obtained numerically using $D = [1, 0.1]$, which corresponds to $D_A = 1$ and $D_B = 0.1$ in Figure 1. The crosses are the critical times obtained numerically using $D = [0.1, 1]$. Notably, the averaged solution is not a good approximation of the numerical solution for small numbers of layers. Of interest is the difference in behaviour for the different layer orders. This is explained mathematically by the $1 - D_{av}/D_A$ term in the approximation.

3. Definition 2: constant average temperature

Definition 2 is the time when the spatially averaged temperature reaches some constant value, β :

$$\int_{x=x_0}^{x_n} U_i(x, t_{\text{def}2}) dx = \beta. \quad (3.1)$$

This definition is closely related to Definition 1 (equation (2.1)), but does not require the existence of a steady state. This is important in cases where a steady state solution may not exist, or is not feasible to calculate [14]. For example, Figure 2 depicts temperature profiles at various times, where the dashed line is an example profile at the critical time and the shaded area corresponds to $\beta = 0.4$. This definition has applications to problems where a given amount of diffusant is required, such as the “decontamination” processes of neutralizing chemical weapons and removing graffiti [1].

This section is divided into two parts. First, simple approximate expressions for the critical time are found for single and multiple layers in Section 3.1. These are compared to the numerical results, and the effect of the number of layers on the critical time behaviour is analysed. Second, critical time Definition 2 is compared to Definition 1 in Section 3.2, where the asymptotic equivalence between the definition parameters is found.

3.1. Approximations and numerical results The exact single layer solution of Hickson et al. [9] is used to determine a simple approximate expression for the critical time, and the single layer approximation is used to determine limitations on β . The perturbation analysis conducted by Hickson et al. [10] is used to find approximations for multiple layers, which are compared to the numerically obtained solutions as a function of the number of layers.

To find bounds on the parameter β , the single layer exact solution is substituted into the critical time definition (3.1). Only the leading eigenvalue is considered, and the equation is rearranged for the critical time and simplified, giving

$$t_{\text{sd}2} = \frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{8\Theta L}{\pi^2(L\Theta - 2\beta)} \right\}, \quad (3.2)$$

where $\Theta = \theta_1 + \theta_2$. A positive time, $t_{\text{sd}2} > 0$, requires

$$\frac{L\Theta}{2} \left(1 - \frac{8}{\pi^2} \right) < \beta < \frac{L\Theta}{2}. \quad (3.3)$$

For example, when $\theta_1 = 1$, $\theta_2 = 0$ and $L = 1$, this reduces to $0.1 \lesssim \beta < 0.5$. Note that the steady state solution for these boundary conditions is $U = 1 - x$, and hence the maximum possible area under the curve is $\beta = 0.5$ for a single layer.

An approximate multilayer critical time is found using the perturbation analysis of Hickson et al. [10]. The approximation is of the form

$$t_{\text{ad}2} = t_{\text{ad}2}^{(0)} + t_{\text{ad}2}^{(1)} \ell + O(\ell^2), \quad (3.4)$$

where the zeroth-order term reduces to the single layer solution, namely $t_{\text{ad}2}^{(0)} = t_{\text{sd}2}$, and

$$t_{\text{ad}2}^{(1)} = \frac{L^2}{\pi^2 D_{\text{av}}} \left(1 - \frac{D_{\text{av}}}{D_A} \right) \frac{\Phi}{L\Theta - 2\beta}, \quad (3.5)$$

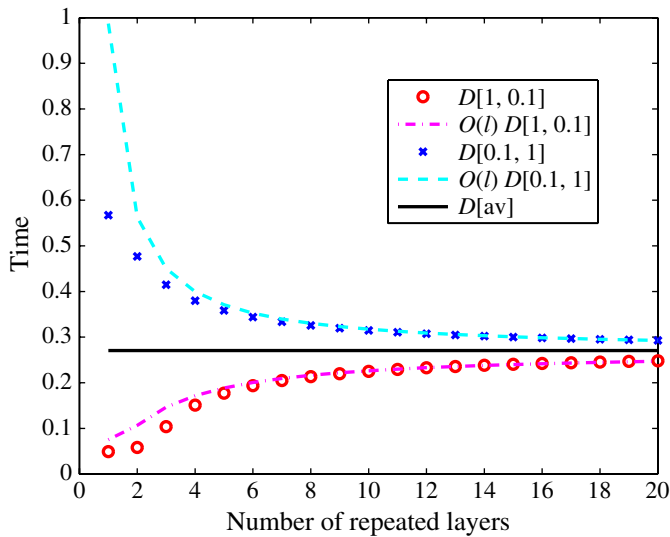


FIGURE 4. Critical time Definition 2 (equation (3.1)) versus the number of repeated layers. The circles are the critical times using $D = [1, 0.1]$, and the dot-dashed line is the corresponding approximation. The crosses use $D = [0.1, 1]$, and the dashed line is the corresponding approximation. The solid line uses $D[av] \equiv D_{av} \approx 0.18$. Here $\beta = 0.25$.

where $\Theta = \theta_1 + \theta_2$ and $\Phi = \theta_2 - \theta_1$. As expected, this approximation is similar to that of Definition 1, equations (2.3)–(2.7).

Figure 4 depicts critical time Definition 2 as a function of the number of repeated layers for $\beta = 0.25$. The value $\beta = 0.25$ was chosen so that a solution would exist for all biperiodic orders and as few as two layers. The behaviour of this critical time definition is similar to that of Definition 1 (Figure 3). Definition 2 is more symmetrical than Definition 1 for $D = [0.1, 1]$ (crosses), as there is no maximum. This is true for all values of β explored, which covers the range where $t_{sd2} > 0$. The first-order critical time approximation (3.4)–(3.5) accurately captures the behaviour, but becomes inaccurate for two or fewer repeated layers. The perturbation analysis was conducted around the number of layers $n \rightarrow \infty$, so for a first-order approximation it is surprisingly accurate.

3.2. Comparison to Definition 1 Definition 2 is spatially independent, as is Definition 1. Definitions 1 and 2 are equivalent when $\beta = \alpha S$, where S is the average of the steady state solution. The two constants in Definitions 1 and 2, α and β , can be related via the single layer approximations (2.2) and (3.2), giving

$$\alpha = \frac{2\beta}{\Theta L}. \tag{3.6}$$

Note that this is only true in the asymptotic limit for large numbers of layers, as the two definitions otherwise demonstrate different behaviour (compare Figures 3 and 4).

Substituting the α limits into the asymptotic relationship (3.6) recovers the limits determined for β . That is, $1 - 8/\pi^2 < \alpha < 1$ gives (3.3).

4. Definition 3: asymptotic quantity of diffusant through the boundary

Definition 3 considers the long-time behaviour of the total amount of diffusant to pass through the $x = x_n = L$ boundary of the region, for the configuration in Figure 1:

$$Q_t = \int_0^t -D_i \frac{\partial U_i(x, t_{\text{def3}})}{\partial x} \Big|_{x_n} dt. \quad (4.1)$$

For heat flux, D_i should strictly be κ_i , the thermal conductivity. Therefore, this form of the critical time definition is more appropriate for mass transfer. The amount of diffusant, Q_t , is plotted versus time, t , and the asymptote is used to find the time axis intercept. The single layer result,

$$t_{\text{sd3}} = \frac{L^2}{6D_{\text{av}}}, \quad (4.2)$$

is a commonly used critical time [2, 4, 6, 21]. Applications of this definition include drug delivery systems [20] and packaging of food, medical supplies, and sensitive electronic components [7].

Several authors have calculated a diffusive critical time for this definition through composites, with results summarized by Barrer [2] for some of the usual layer configurations. However, Barrer's analysis assumed that the total length of the medium, L , is increasing but that the individual layer lengths, ℓ , stay the same size. In contrast to this, we make the assumption that L stays constant and the layer widths, ℓ , change as the number of layers changes.

Reproducing the approximation for this definition gives (4.2) as the zeroth-order term, and the first-order corrections are both zero. A numerical result showing the critical time using both results as a function of the number of layers is given in Section 4.1.

4.1. Numerical results Figure 5 depicts critical time Definition 3 as a function of the number of repeated layers, for the different diffusivity orderings. The solid line is the critical time using the single layer result (equation (4.2)), found by averaging the diffusivities using (1.1). The numerically obtained critical times, given by the dashed line and crosses for $D = [1, 0.1]$ and $D = [0.1, 1]$, respectively, demonstrate identical behaviour.

The significance of Figure 5 is that the multilayer solution does not display the largely symmetrical behaviour around the critical time with the average diffusivity found for the previous definitions. This is due to the implicit averaging when the asymptote as $t \rightarrow \infty$ is taken for the total flux through the boundary. Interestingly, the behaviour typical of the $D = [1, 0.1]$ biperiodic ordering for the other spatially independent definitions dominates the multilayer behaviour.

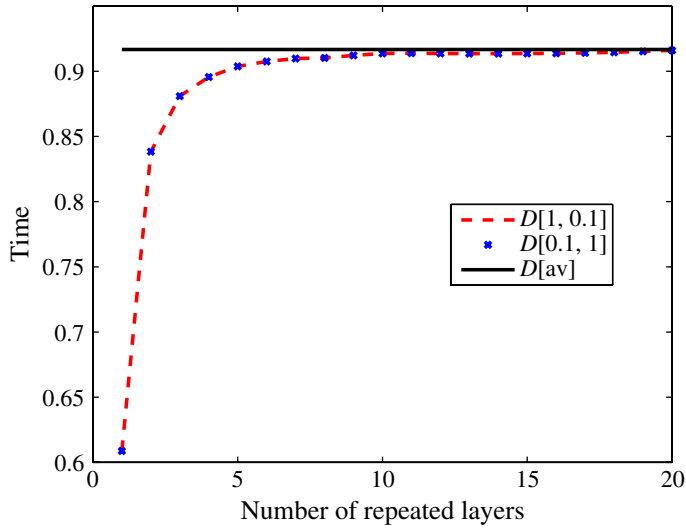


FIGURE 5. Critical time Definition 3 versus the number of repeated layers. The dashed line and crosses are for the numerically obtained critical times, using $D = [1, 0.1]$ and $D = [0.1, 1]$. The solid line corresponds to the single layer solution (4.2) using $D_{av} \approx 0.18$.

4.2. Comparison to Definitions 1 and 2 For a single layer, equation (4.2) corresponds to Definition 1 (equation (2.1)) for $\alpha = 1 - (8/\pi^2) \exp(-\pi^2/6) \approx 0.8435$, a result calculated by Hickson et al. [9]. This value of α gives a critical time equivalent to that used by Crank [4] to quantify a “breakthrough” or “lag” time. However, equation (4.2) is only strictly valid for a single layer of material.

The single layer approximation of Definition 3 (equation (4.2)), equated to Definition 2 (equation (3.2)) and rearranged for β , gives

$$\beta = \frac{\Theta L}{2} \left[1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{6}\right) \right].$$

Recalling that $\Theta = \theta_1 + \theta_2$, we see that when $\theta_1 = 1$, $\theta_2 = 0$ and $L = 1$, $\beta \approx 0.4218$, namely half the value of α when Definitions 1 and 3 are equivalent.

These asymptotic relationships are useful for converting between definitions for a direct comparison of times, where otherwise the time comparisons are not relevant.

5. Definition 4: derivative at the boundary

Definition 4 is such that t_{def4} satisfies

$$\left. \frac{\partial U_n(x, t_{\text{def4}})}{\partial x} \right|_{x=x_n} = -\gamma, \tag{5.1}$$

where $\gamma > 0$. Since this involves the derivative at the boundary $x = x_n$, it is only applicable when the boundary condition at $x = x_n$ is held constant. This definition

is useful for applications which require the flux through the boundary to reach some minimum value, such as gas diffusion through membranes [22].

5.1. Approximations and numerical results Calculated as per the previous sections, the single layer critical time for Definition 4 is

$$t_{sd4} \approx \frac{L^2}{\pi^2 D_{av}} \log_e \left\{ \frac{-2\Theta}{\Phi + \gamma L} \right\}, \tag{5.2}$$

where $\Theta = \theta_1 + \theta_2$ and $\Phi = \theta_2 - \theta_1$. A positive time, $t_{sd4} > 0$, requires

$$\frac{-\Phi - 2\Theta}{L} < \gamma < \frac{-\Phi}{L}. \tag{5.3}$$

When $\theta_1 = 1$ and $\theta_2 = 0$, this reduces to $-1 < \gamma < 1$, but if $\theta_1 > \theta_2$ then the γ range is restricted to $0 < \gamma < 1$.

For this definition, the approximate multilayer critical time is for $x = x_n = L$, which by definition is a B layer. The approximation is of the form

$$t_{ad4} = t_{ad4}^{(0)} + t_{ad4}^{(1)} \ell + O(\ell^2), \tag{5.4}$$

where

$$t_{ad4}^{(0)} = \frac{L^2}{\pi^2 D_{av}} \log_e \left\{ \frac{-2\Theta D_s}{\Phi D_s + \gamma L D_A} \right\}, \tag{5.5}$$

$$t_{ad4}^{(1)} = 0, \tag{5.6}$$

with $\Theta = \theta_1 + \theta_2$, $\Phi = \theta_2 - \theta_1$ and $D_s = (2D_A - D_{av})$. When $D_A = D_s = D_{av}$, $t_{ad4}^{(0)} \equiv t_{sd4}$. The first-order correction being zero is understandable, given that the critical time behaviour is independent of the number of layers for all but one or two repeated layers.

Figure 6 depicts Definition 4 (equation (5.1)) as a function of the number of repeated layers for $\gamma = 0.15$. The behaviour of this definition is different from all others considered, as the three different diffusivity cases considered do not converge; they all tend to different critical time values. This difference is due to the slope of the temperature profile in the last layer being highly dependent on the diffusivity of that layer (Figure 13 shows temperature profiles at the steady state for four layers, demonstrating the difference in the slope at the boundary, which corresponds to γ). The first-order critical time approximation (5.4)–(5.6) is accurate for $D = [0.1, 1]$ (dashed line) for three or more repeated layers. However, the approximation for $D = [1, 0.1]$ (dot–dashed line) is closer to the averaged diffusivity (solid line) than the numerically obtained solution (circles). This is due to the small value of γ used, as shown in Figure 7, but a larger value of γ would have excluded the $D = [0.1, 1]$ case.

Figure 7 depicts the effect of γ on Definition 4 for $n = 10$ total layers. The value of γ is at its highest for the steady state solution, and hence there exists a maximum value of γ which cannot be exceeded. The steady state solution is different for $D = [1, 0.1]$, $D = [0.1, 1]$ and $D = D_{av}$, and therefore the lines end at different threshold values in Figure 7. That is, for 10 layers (five repeated layers), the maximum value for $D = [0.1, 1]$ is $\gamma \approx 0.2$, for $D = D_{av}$ the maximum is $\gamma \approx 1$, and for $D = [1, 0.1]$ the

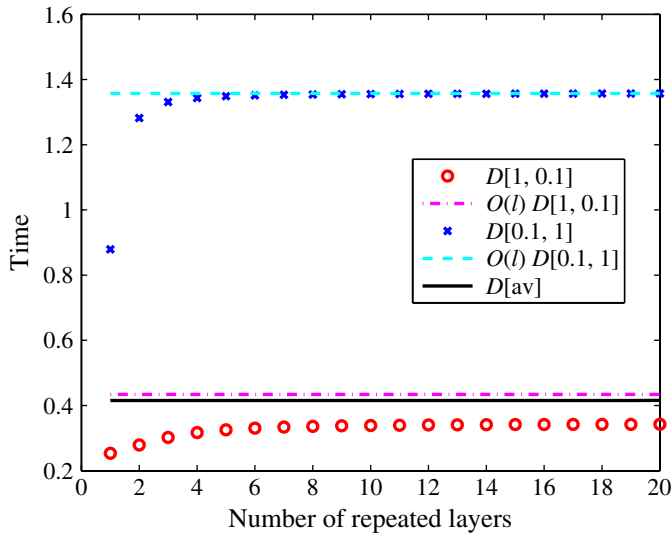


FIGURE 6. Critical time Definition 4 (equation (5.1)) versus the number of repeated layers. Here $\gamma = 0.15$, which Figure 7 demonstrates is a poor choice for $D = [0.1, 1]$, but is close to the maximum value for $D = [1, 0.1]$. Note that the different biperiodic orders do not converge.

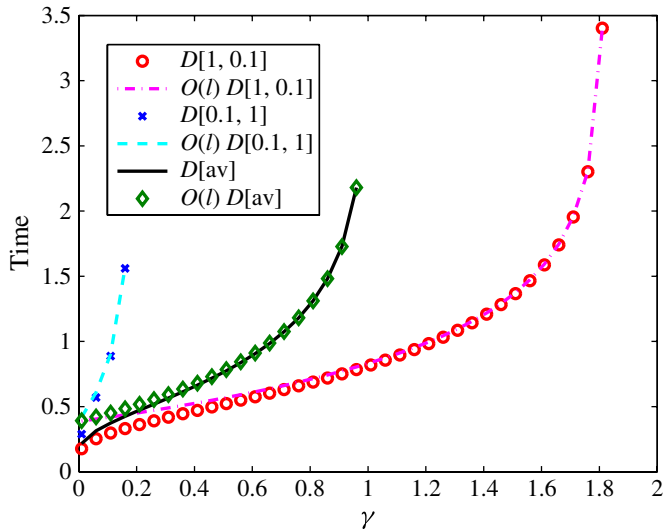


FIGURE 7. Critical time Definition 4 (equation (5.1)) versus γ . The first-order approximations are from (5.4)–(5.6). Here there are $n = 10$ layers. Note the significant variation in maximum γ values (the asymptotes) for the different biperiodic orders.

maximum is $\gamma \approx 1.8$. The first-order critical time approximation (5.4)–(5.6) is accurate for all values of γ applicable to $D = [0.1, 1]$ (crosses and dashed line). However, for the averaged diffusivity (solid line and diamonds) and $D = [1, 0.1]$ (circles and dot-dashed line), the approximate critical times only become accurate for $\gamma \gtrsim 0.2$. The accuracy above this value is impressive, particularly considering that the first-order correction is zero.

5.2. Comparison to Definitions 1, 2 and 3 Definitions 1–4 are all spatially independent, and hence compared in this section.

When the single layer approximations of Definitions 1 (equation (2.2)) and 4 (equation (5.2)) are equated,

$$\alpha = 1 + \frac{4}{\pi^2 \Theta} (1 + \gamma L).$$

The feasible range of γ is recovered. That is, $1 - 8/\pi^2 < \alpha < 1$ gives (5.3).

The two constants of Definitions 2 and 4 (β and γ , respectively) can be related via the single layer approximations (3.2) and (5.2), giving

$$\beta = \frac{L(\pi^2 \Theta + 4\Phi + 4\gamma L)}{2\pi^2},$$

which is only true in the asymptotic limit. The definitions otherwise display different behaviour, as seen from Figures 4 and 6.

The single layer approximation of Definition 3 (equation (4.2)), equated to Definition 4 (equation (5.2)) and rearranged for γ , gives

$$\gamma = -\frac{1}{L} \left[\Phi + 2\Theta \exp\left(\frac{\pi^2}{6}\right) \right].$$

Remembering that $\Theta = \theta_1 + \theta_2$ and $\Phi = \theta_2 - \theta_1$, we see that when $\theta_1 = 1$, $\theta_2 = 0$ and $L = 1$, $\gamma \approx 0.6139$.

6. Definition 5: mean action time

Definition 5, commonly known as the mean action time, is used to measure how long it takes a disturbance introduced at a boundary to reach a spatial point in the medium [15]:

$$t_{\text{def5}}(x_c) = \frac{1}{w_i(x_c) - f_i(x_c)} \int_{t=0}^{\infty} -v_i(x_c, t) dt, \quad (6.1)$$

where $w_i(x)$ is the steady state solution, $f_i(x)$ is the initial condition, $v_i(x, t)$ is the transient solution, and x_c is the spatial position.

Unlike Definitions 1–4, the mean action time is a function of the spatial position, x_c . Applications of this definition include cooling processes [18], assessing the viability of gas fields and ore deposits for mining [17], and membrane filtration and water transport in human eye lenses [15].

The spatial dependence of this definition adds significant complexity to the results, so this section is divided into three parts. Numerical results exploring how the critical

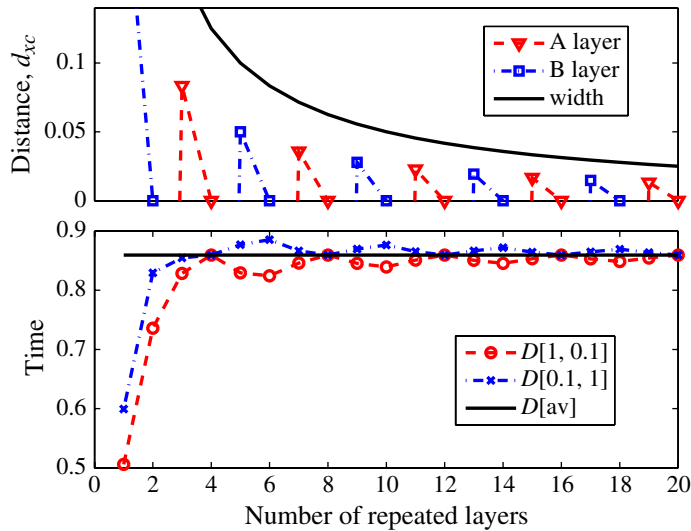


FIGURE 8. The lower subplot is critical time Definition 5 (equation (6.1)) versus the number of repeated layers, with line types as in previous figures. The upper subplot depicts the position of $x_c = 0.75$ relative to the biperiodic layer structure by showing the distance from x_c to the previous layer boundary, d_{x_c} , depicted in Figure 9.

time varies with the number of layers and the spatial position are considered in Section 6.1. Simple approximate expressions for the mean action time are found for single and multiple layers in Section 6.2. Finally, the mean action time is compared to Definition 1 in Section 6.3.

6.1. Numerical results This section explores the effect of the number of layers and the spatial position, x_c , on Definition 5, the mean action time.

The lower subplot in Figure 8 depicts the mean action time as a function of the number of repeated layers at $x_c = 0.75L \equiv 0.75$, since the region has been nondimensionalized such that $L = 1$. The oscillatory behaviour of the different biperiodic orders is a result of the position of x_c relative to the layer structure. Figure 9 demonstrates that for two layers, $x_c = 0.75$ is near the middle of a B layer, whereas for six layers, $x_c = 0.75$ is near the middle of an A layer. The upper subplot in Figure 8 depicts how this relates to the oscillatory behaviour of the critical time:

- the solid line is the layer width;
- the dashed line with triangles is the distance from x_c to the previous layer boundary when in an A layer;
- the dot-dashed line with squares is the distance from x_c to the previous layer boundary when in a B layer;
- when x_c is equal to the layer width, there is zero distance to the leftmost interface, and hence the dashed and dot-dashed lines never reach the solid line.

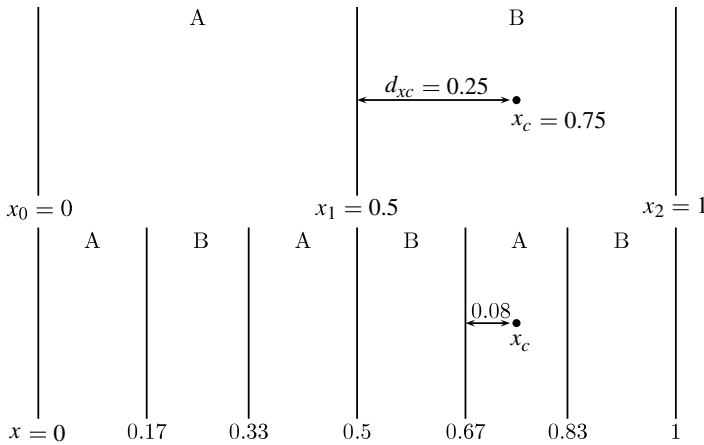


FIGURE 9. Distance, d_{x_c} , from the previous layer boundary to the critical position, $x_c = 0.75$, for two and six layers. Note that the difference in the number of layers means that x_c lies in a different biperiodic layer: B for two layers, where $d_{x_c} = 0.25$, and A for six layers, where $d_{x_c} = 0.08$. This explains the upper subplot in Figure 8.

The upper subplot thus shows that the critical time is close to the averaged solution (solid line) when in, or at the beginning of, an A layer, and further away when in, or at the beginning of, a B layer; hence the oscillations.

Figure 10 depicts the effect of the spatial position, x_c , on Definition 5 for $n = 10$ layers, or five repeated layers. The numbers at approximately -0.1 on the time axis are the layer numbers. The effect of the layers with the smaller diffusivity, $D = 0.1$, is apparent from the increased slope of the critical times over those layers. That is, since the critical times are relatively flat over the layers where $D = 1$, only a short period of time is needed to diffuse through those layers. Interestingly, both diffusivity orders converge to the same value as the averaged solution (solid line) after each biperiodic set (two layers).

6.2. Approximations Substituting the exact single layer solution into the mean action time (equation (6.1)) and simplifying gives

$$t_{sd5}(x_c) = \frac{2L^3}{\pi^3 D_{av}} \sum_{m=1}^{\infty} \frac{[\theta_1 + \theta_2(-1)^{m+1}]}{m^3(\theta_1 L + \Phi x_c)} \sin\left(\frac{m\pi x_c}{L}\right),$$

where $\Phi = \theta_2 - \theta_1$. The leading eigenvalue approximation ($m = 1$) is hence

$$t_{sd5}(x_c) \approx \frac{2\Theta L^3}{\pi^3 D_{av}(\theta_1 L + \Phi x_c)} \sin\left(\frac{\pi x_c}{L}\right), \tag{6.2}$$

where $\Theta = \theta_1 + \theta_2$. A positive critical time, $t_{sd5} > 0$, requires $0 < x_c < L$, which is already assumed.

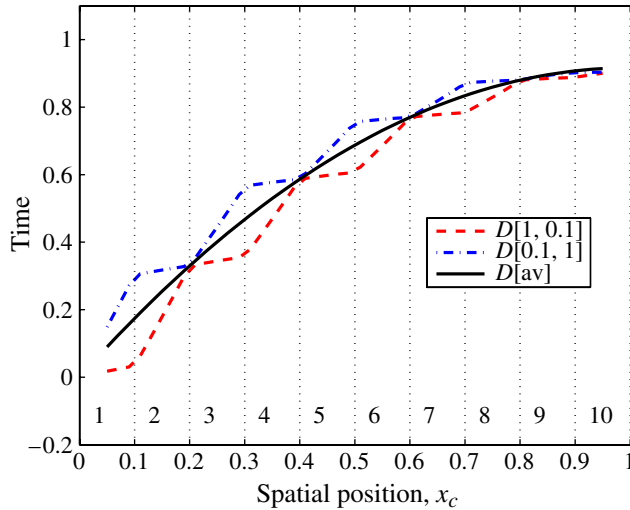


FIGURE 10. Critical time Definition 5 (equation (6.1)) versus spatial position, x_c . Here there are $n = 10$ layers.

An approximate multilayer mean action time is found using the perturbation analysis of Hickson et al. [10]. The analysis considered A and B layers separately, and since this definition is dependent on the spatial position, separate approximations are found for A and B layers. The A layer approximation is of the form

$$t_{Ad5} = t_{Ad5}^{(0)} + t_{Ad5}^{(1)}\ell + O(\ell^2), \tag{6.3}$$

where

$$\begin{aligned} t_{Ad5}^{(0)} &= \frac{2\Theta L^3 d_A \Upsilon}{\pi^3 D_{av} y}, \\ t_{Ad5}^{(1)} &= \left(1 - \frac{D_{av}}{D_A}\right) \frac{\Theta L^2 d_A}{\pi^2 d_{av} y} \sin\left(\frac{\pi x_{i-1}}{L}\right) \sin\left(\frac{\pi z d_{av}}{L d_A}\right), \end{aligned} \tag{6.4}$$

with

$$\begin{aligned} z &= x_c - x_{i-1}, \quad \Theta = \theta_1 + \theta_2, \quad \Phi = \theta_2 - \theta_1, \\ y &= \theta_1 L D_A + \Phi(x_{i-1} D_A + z D_{av}), \\ \Upsilon &= d_A \sin\left(\frac{\pi x_{i-1}}{L}\right) \cos\left(\frac{\pi z d_{av}}{L d_A}\right) + d_{av} \cos\left(\frac{\pi x_{i-1}}{L}\right) \sin\left(\frac{\pi z d_{av}}{L d_A}\right), \end{aligned}$$

where $d_A = \sqrt{D_A}$. The B layer approximation is of the same form:

$$t_{Bd5} = t_{Bd5}^{(0)} + t_{Bd5}^{(1)}\ell + O(\ell^2), \tag{6.5}$$

where

$$\begin{aligned}
 t_{\text{Bd5}}^{(0)} &= \frac{2\Theta L^3 d_A \Upsilon^*}{\pi^3 D_{\text{av}} y^*}, \\
 t_{\text{Bd5}}^{(1)} &= \frac{\Theta L^2 BC(2\Upsilon^* D_A L \Phi + \pi y^* \Xi)}{\pi^3 D_{\text{av}} d_A y^{*2}},
 \end{aligned}
 \tag{6.6}$$

with

$$\begin{aligned}
 y^* &= \theta_1 L D_A + \Phi(x_{i-1} D_A + z D_s), \\
 \Upsilon^* &= d_A \sin\left(\frac{\pi x_{i-1}}{L}\right) \cos\left(\frac{\pi z d_s}{L d_A}\right) + d_s \cos\left(\frac{\pi x_{i-1}}{L}\right) \sin\left(\frac{\pi z d_s}{L d_A}\right), \\
 \Xi &= d_s \sin\left(\frac{\pi z d_s}{L d_A}\right) \sin\left(\frac{\pi x_{i-1}}{L}\right) - 2d_A \cos\left(\frac{\pi z d_s}{L d_A}\right) \cos\left(\frac{\pi x_{i-1}}{L}\right),
 \end{aligned}$$

where $d_s = \sqrt{2D_A - D_{\text{av}}}$. The first-order A layer approximation simplifies more than the first-order B layer approximation, which is interesting as the critical times for different biperiodic orders were closer to the averaged solution in A layers (see Figure 8). The key difference between the A and B layer zeroth-order approximations is the substitution of d_s for d_{av} .

This spatially dependent approximation is more complex than the spatially independent approximations of Definitions 1–4. It is a nontrivial exercise to obtain these simplifications, even with the aid of MAPLE, and for the sake of brevity only the results are shown.

Figure 10 demonstrates that the critical time converges to the zeroth-order solution (averaged diffusivity) every two layers. This corresponds to the beginning of an A layer and end of a B layer. By considering $x_c = x_{i-1}$ ($z = 0$), the approximation for A layers simplifies to

$$t_{\text{Ad5}} \approx \frac{2\Theta L^3}{\pi^2 D_{\text{av}}(\theta_1 L + \Phi x_c)} \sin\left(\frac{\pi x_c}{L}\right).$$

Similarly, the B layer approximation simplifies to

$$\begin{aligned}
 t_{\text{Bd5}}^{(0)} &= t_{\text{Ad5}}, \\
 t_{\text{Bd5}}^{(1)} &= \frac{2\Theta L^2}{\pi^2 D_{\text{av}}(\theta_1 L + x_c \Phi)} \left(1 - \frac{D_s}{D_A}\right) \left[\cos\left(\frac{\pi x_c}{L}\right) - \frac{\Phi L \sin(\pi x_c/L)}{\pi(\theta_1 L + x_c \Phi)}\right],
 \end{aligned}$$

where $D_s = 2D_A - D_{\text{av}}$. These simplified approximations are calculated with respect to the previous layer interface. The A layer expression is simpler as the critical time converges at the beginning of the layer, as shown in Figure 10. For example, when x_c is at the start of layer 3 (an A layer), the critical time corresponds to the average value $D[\text{av}]$; however, when x_c corresponds to the start of layer 4, the critical time is significantly different from the $D[\text{av}]$ value, requiring a first-order correction.

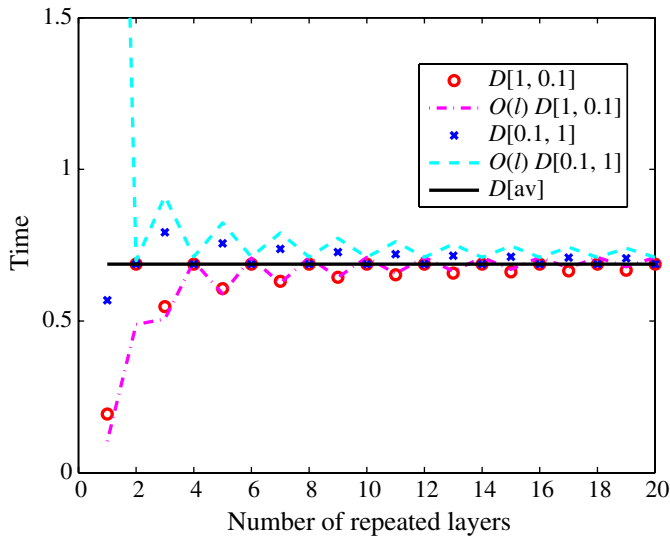


FIGURE 11. Critical time Definition 5 (equation (6.1)) versus the number of repeated layers. The first-order approximations are from equations (6.3)–(6.6). Here $x_c = 0.5$. Note the convergence at the interface between every second layer.

Figure 11 depicts the first-order critical time approximation (6.3)–(6.6) as a function of the number of repeated layers for $x_c = 0.5$. The approximation successfully captures the oscillatory behaviour, only becoming inaccurate for one, two or three repeated layers. The approximation is surprisingly accurate, considering that the analysis is only first-order accurate in ℓ .

6.3. Comparison to Definition 1 The mean action time is spatially dependent, whereas Definitions 1–4 are not. However, all definitions are being compared to Definition 1 as a baseline. Comparing the single layer approximations of the mean action time (equation (6.2)) and Definition 1 (equation (2.2)) gives

$$\alpha = 1 - \frac{8}{\pi^2} \exp\left(\frac{-2\Theta L \sin(\pi x_c/L)}{\pi(\theta_1 L + \Phi x_c)}\right).$$

An abrupt change in the value of α occurs at $x_c = L$. This is due to the mean action time not being defined at this point, since $\alpha \neq 1$.

7. Definition 6: temperature threshold at a set position

Petrovskii and Shigesada [19] mention a definition commonly used to determine the area occupied by invasive species:

$$U_i(x_c, t_{\text{def6}}) = U_c, \tag{7.1}$$

where x_c is some spatial position, U_c is a threshold value of the diffusant, and $t = t_{\text{def6}}$ is the time taken to reach the threshold at that position. This definition is spatially

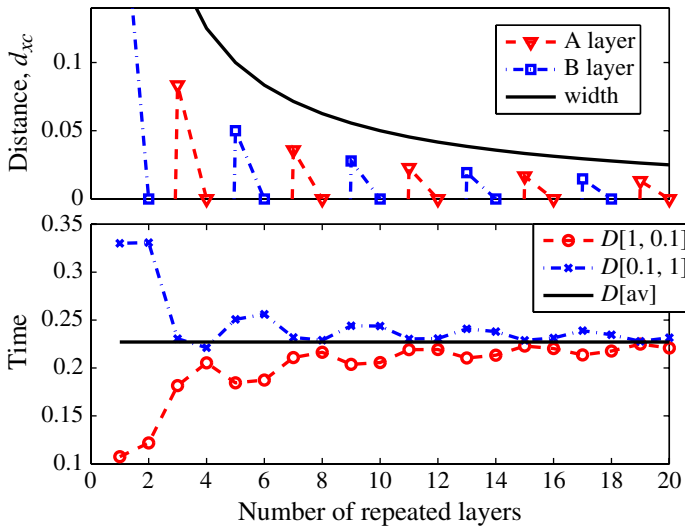


FIGURE 12. The lower subplot is critical time Definition 6 (equation (7.1)) versus the number of repeated layers, with line types as in previous figures. The upper subplot depicts the position of $x_c = 0.75$ relative to the biperiodic layer structure by showing the distance from x_c to the previous layer boundary, d_{x_c} , depicted in Figure 9. Here $U_c = 0.01$.

dependent. Figure 2 depicts temperature profiles at various times, where the dashed line is an example profile of Definition 6. The horizontal dashed line is the temperature threshold, $U_c \approx 0.1$, and a vertical dashed line at $x_c = 0.75$ is the spatial position which is on the interface between layers 3 and 4.

As done for previous definitions, this section is divided into two parts. Simple approximate expressions for the critical time are presented in Section 7.1, and Definition 6 is compared to Definitions 1 and 5 in Section 7.2.

7.1. Approximations and numerical results The lower subplot in Figure 12 depicts Definition 6 as a function of the number of repeated layers at $x_c = 0.75$ and for $U_c = 0.01$. As discussed for Definition 5, the oscillatory behaviour is the result of the position of x_c relative to the layer structure. A notable difference in behaviour is that Definition 6 is approximately symmetrical for small numbers of layers, whereas Definition 5 is not.

For the leading eigenvalue, the single layer critical time for Definition 6 is

$$t_{sd6} = \frac{L^2}{\pi^2 D_{av}} \log_e \left\{ \frac{2\Theta L \sin(\pi x_c/L)}{\pi[L(\theta_1 - U_c) + \Phi x_c]} \right\}, \tag{7.2}$$

where $\Theta = \theta_1 + \theta_2$ and $\Phi = \theta_2 - \theta_1$. A positive time, $t_{sd6} > 0$, requires

$$\theta_1 + \frac{\Phi x_c}{L} - \frac{2\Theta}{\pi} \sin\left(\frac{\pi x_c}{L}\right) < U_c < \theta_1 + \frac{\Phi x_c}{L}. \tag{7.3}$$

When $\theta_1 = 1$, $\theta_2 = 0$ and $L = 1$, this becomes

$$1 - x_c - \frac{2}{\pi} \sin(\pi x_c) < U_c < 1 - x_c,$$

though it should be noted that $U_c > 0$. The upper bound for U_c comes from the steady state solution, $w(x) = 1 - x$.

Since this definition is dependent on the spatial position, separate approximations are found for A and B layers, as done for Definition 5. For the sake of clarity and brevity, the full approximations are not shown here. The approximations are further simplified as done for Definition 5, since the critical time converges to the zeroth-order solution (averaged diffusivity) every two layers. This corresponds to the beginning of an A layer, where $x_c = x_{i-1}$ ($z = 0$). The approximation for A layers is thus

$$t_{\text{Ad6}} \approx \frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{2\Theta L \sin(\pi x_c/L)}{\pi(\theta_1 L - U_c L + x_c \Phi)} \right\}.$$

Similarly, the B layer approximation is

$$t_{\text{Bd6}}^{(0)} = t_{\text{Ad6}},$$

$$t_{\text{Bd6}}^{(1)} = \frac{L}{\pi D_{\text{av}}} \left(1 - \frac{D_s}{D_A} \right) \left[\cot\left(\frac{\pi x_c}{L}\right) - \frac{\Phi L}{\pi(\theta_1 L - U_c L + x_c \Phi)} \right].$$

Similar to Definition 5, the approximation for Definition 6 successfully captures the oscillatory behaviour of the critical time versus the number of layers.

The effect of the spatial position, x_c , on the critical time approximation was also considered, and yielded much the same result as found for Definition 5. That is, the approximation is accurate until near the end of the region, where the threshold becomes larger than the steady state and the approximation becomes inaccurate. A notable difference between Definitions 5 and 6 is the existence of asymptotes for Definition 6, near the end of the region.

7.2. Comparison to Definitions 1 and 5 Definition 6 is first compared to Definition 1 as the baseline. Equating the single layer approximations of Definitions 6 (equation (7.2)) and 1 (equation (2.2)) gives

$$\alpha = 1 + \frac{4(U_c L - \theta_1 L - \Phi x_c)}{\pi \Theta L \sin(\pi x_c/L)}.$$

Note that this relationship is dependent on U_c and the spatial position, x_c .

Definitions 5 and 6 are both spatially dependent, showing the oscillatory behaviour for the critical time as a function of the number of repeated layers with different biperiodic orders. Equating the single layer approximations of Definitions 6 (equation (7.2)) and 5 (equation (6.2)) gives

$$U_c = \theta_1 + \frac{\Phi x_c}{L} - \frac{2\Theta}{\pi} \sin\left(\frac{\pi x_c}{L}\right) \exp\left(\frac{-2\Theta L \sin(\pi x_c/L)}{\pi(\theta_1 L + \Phi x_c)}\right).$$

8. Other definitions

Definitions 1–6 are commonly used. This section briefly outlines other possible definitions, including extensions of those already discussed.

8.1. Definition 7 A spatially dependent version of Definition 1 was also considered by Hickson [8, 115–123], where $t = t_{\text{def7}}$ is such that

$$U_i(x_c, t_{\text{def7}}) = \hat{a}w_i(x_c), \quad (8.1)$$

$U_i(x, t)$ is the temperature in layer i , $w_i(x)$ is the steady state solution, and $0 < \hat{a} < 1$ is the proportion of the steady state. Definition 7 is considered by Petrovskii and Shigesada [19] for determining the inhabited domain radius for invasive plant spread scenarios. The analysis of this definition is not included here for the sake of brevity, although the outcomes are included in Table 2. The behaviour of this definition as a function of the number of layers is very similar to that of Definition 5. An important difference is that the approximation becomes more accurate towards the end of the region, whereas the mean action time (Definition 5) becomes less accurate.

8.2. Definition 8 Definition 4 (equation (5.1)) can be altered to consider the flux through $x = x_n$, such that $t = t_{\text{def8}}$ satisfies

$$D_n \left. \frac{\partial U_n(x, t_{\text{def8}})}{\partial x} \right|_{x=x_n} = -\hat{\gamma}.$$

The resulting single ($D \equiv D_{\text{av}}$) and multiple layer approximation is

$$t_{\text{def8}} \approx \frac{L^2}{\pi^2 D_{\text{av}}} \log_e \left\{ \frac{2\Theta D_{\text{av}}}{\Phi D_{\text{av}} + \hat{\gamma}L} \right\}.$$

This definition displays behaviour very similar to Definition 3, shown in Figure 5. It matches Definition 3 when

$$\hat{\gamma} = \frac{D_{\text{av}}}{L} \left[2\Theta \exp\left(\frac{-\pi^2}{6}\right) - \Phi \right].$$

It could be further extended to consider the flux through any chosen location, and thus be less dependent on the boundary condition.

8.3. Definition 9 A definition appropriate to the annealing of steel coils [3, 16, 23] is when the coldest point in the coil reaches a given temperature. Definition 6 (equation (7.1)) is well suited to this application. The minimum temperature is found by setting $\partial U/\partial x = 0$, and the corresponding position and the annealing temperature can be substituted into Definition 6 to find the critical (annealing) time.

8.4. Definition 10 As discussed by Hickson et al. [14], Definition 6 is equivalent to the “penetration time” when $U_c = 10^{-k}U(x_0)$, where $k = 1, 2, \dots, 10$ [5]. The penetration time is defined by de Monte et al. [5] as the time it takes for an interior

point ($x = x_c$) to be affected at the level 10^{-k} by an imposed boundary condition at $x = x_0$. A value of $k = 2$ is useful for engineering and visual purposes, whereas $k = 10$ is useful for verification of numerical code [5]. The result of de Monte et al. [5],

$$t_{\text{def}10} = \frac{L^2}{10kD} \left(\frac{x_c}{L} \right)^2, \quad k = 1, 2, \dots, 10,$$

is a good approximation for short times ($k > 2$), whereas the approximations found here are good for large times ($k \leq 1$).

9. Discussion

This section discusses the qualitative differences in the various definitions, splitting the definitions into two groups: spatially dependent and independent. The significant difference is that the spatially dependent definitions demonstrate oscillatory critical time behaviour as a function of the number of layers, whereas the spatially independent definitions do not. The spatially independent definitions are discussed in Section 9.1, and the spatially dependent definitions in Section 9.2.

9.1. Spatially independent This section considers the behaviour of the spatially independent critical times, Definitions 1–4, namely equations (2.1), (3.1), (4.1) and (5.1). In general, these spatially independent definitions have “smooth” behaviour as a function of the number of repeated layers.

Definitions 1 and 2 demonstrate symmetry of the $D = [1, 0.1]$ versus $D = [0.1, 1]$ cases around the averaged diffusivity, D_{av} , in Figures 3 and 4. However, Definition 1 has a maximum for a small number of repeated layers, and the one repeated layer time defies the symmetry.

For Definition 3, the behaviour changes for single versus multiple layers, but not for the different biperiodic orders (see Figure 5). That is, Definition 3 demonstrates the same behaviour as Definition 1 for $D = [1, 0.1]$, but does not change for $D = [0.1, 1]$.

Definition 4 displays behaviour very different than any other definition. There is no convergence of the different biperiodic orders, and hence no symmetrical behaviour. After a small number of repeated layers, the critical time becomes independent of the number of layers. Another interesting feature of this definition is the large difference in maximum γ values, shown in Figure 7, for the different biperiodic orders.

The similarities between Definitions 1 and 2 are expected, as the definitions are almost identical. Upon inspection of Figures 3 and 4, the black solid lines have the same values for the critical times, demonstrating the equivalence between the definitions for a single layer when $\beta = \alpha/2$, $\theta_1 = 1$ and $\theta_2 = 0$. The critical time values of the averaged diffusivities (solid lines) are equal, where $\alpha = 0.5$ for Figure 3 and $\beta = 0.25$ for Figure 4.

The zeroth-order or single layer approximations of Definitions 1, 2 and 4 are all of the same form: $L^2/(\pi^2 D_{\text{av}}) \times \log_e\{\dots\}$, but Definition 3 is $L^2/(6D_{\text{av}})$. That is, it has “6” as opposed to “ π^2 ” in the denominator, and has no logarithm term. The various

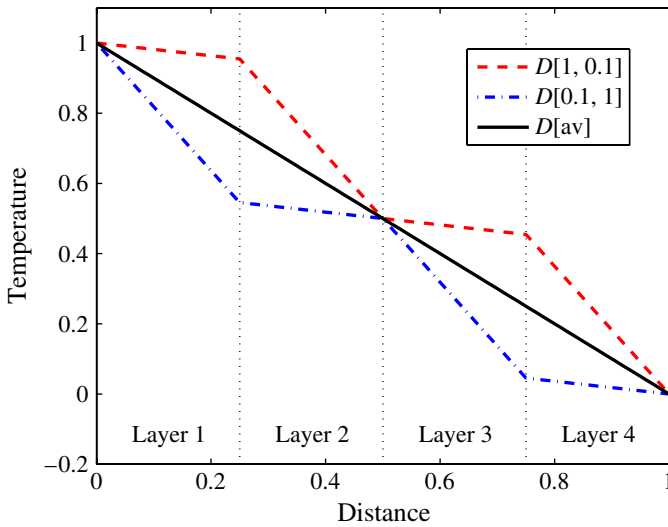


FIGURE 13. Steady state temperature profile for $n = 4$ layers. Here $D_{av} \approx 0.18$. Note the difference in slopes of the profiles in layer 4.

parameters can be “tuned” to obtain the same critical time value in the asymptotic limit; the definitions otherwise demonstrate distinct behaviour.

The difference in Definition 4 makes sense since the slope of the temperature profile in the final layer is highly dependent on the diffusivity. Obtaining the same slope subsequently requires different profiles for each biperiodic order. Temperature profiles at steady state for $n = 4$ layers are shown in Figure 13. The steady state profiles of the different biperiodic orders are also significantly different; hence the large difference in maximum γ values.

9.2. Spatially dependent The spatially dependent definitions are considered in this section. These are Definitions 5–7, namely equations (6.1), (7.1) and (8.1), respectively. As noted previously, the defining feature of these definitions is the oscillatory critical time behaviour as the number of layers is varied.

Using the values in Figure 8, for one, two or three repeated layers Definition 5 is asymmetrical for $D = [1, 0.1]$ and $D = [0.1, 1]$, where the times are all smaller (and hence the disturbance reaches the observation point more quickly) than the averaged diffusivity case (solid line). Definition 7 demonstrates the same behaviour [8]. However, Definition 6 is symmetrical for all numbers of repeated layers for the parameter values used by Hickson [8].

When considering the critical time as a function of spatial position, Definitions 5 and 7 again show similar behaviour, whereas Definition 6 displays an exponential increase in time as $x_c \rightarrow 0.9$. This is due to the temperature threshold, U_c , becoming equal to (or larger than) the steady state temperature near the boundary condition $U(x_n, t) = 0$, which forces the limits in (7.3).

Definitions 6 and 7 have limitations on the parameter values, required for $t > 0$, given in (7.3) for Definition 6. Definition 5 has no critical time parameter other than x_c , which naturally has the limitations $0 \leq x_c \leq 1$ in nondimensionalized space.

Definitions 6 and 7 have similar single layer approximations, as shown in Table 2. The difference in the denominator of the logarithm is due to the different definition parameters. However, the single layer approximation for Definition 5 (equation (6.2)) is different since there is no logarithm. Intriguingly, if the logarithm is ignored in Definition 7, the terms are identical.

The first-order corrections for A layers for all definitions are very similar, with all containing $1 - D_{av}/D_A$ and the $\sin(\dots) \times \sin(\dots)$ terms. The first-order A layer corrections of Definitions 6 and 7 are exactly equal, but the denominator of Definition 5, in particular, is simpler. The first-order corrections for B layers are slightly different for each definition, though notably the substitution parameters are largely the same. That is, B , C , Υ^* and Ξ are identical for all five definitions, and the variation in y^* is minimal.

9.3. Summary The spatially independent definitions are summarized in Table 1, and the spatially dependent definitions in Table 2. To keep the summary approximations as simple as possible, the spatially dependent definitions in Table 2 use the A layer approximations at the layer interfaces, when $x = x_{i-1}$. The asymptotic equivalence between the definitions (the last column in both tables) assumes that $\theta_1 = 1$ and $\theta_2 = 0$.

In conclusion, the critical time definition should be chosen according to the application. Indeed, our aim is to give an overview of several definitions with comparisons and approximations, so that the most appropriate choice is easier to determine. However, Definition 2 is the most versatile form, as it does not depend on the form of the boundary conditions and does not require the existence of a steady state solution. The approximation (equations (3.2), (3.4) and (3.5)) represents the numerical solution well and illustrates that layer order is important (Figure 4).

References

- [1] D. Allwright, M. Blount, H. Gramberg and I. Hewitt, Reaction–diffusion models of decontamination. Study group report (ESGI 2009, Southampton), Smith Institute, 2009, <http://www.smithinst.ac.uk/Projects/ESGI68/ESGI68-DSTL/Report>.
- [2] R. M. Barrer, “Diffusion and permeation in heterogeneous media”, in: *Diffusion in polymers* (eds J. Crank and G. S. Park), (Academic Press, London, 1968) 165–217.
- [3] S. I. Barry and W. L. Sweatman, “Modelling heat transfer in steel coils”, *ANZIAM J. (E)* **50** (2009) C668–C681.
- [4] J. Crank, *The mathematics of diffusion* (Oxford University Press, London, 1957).
- [5] F. de Monte, J. V. Beck and D. E. Amos, “Diffusion of thermal disturbances in two-dimensional cartesian transient heat conduction”, *Int. J. Heat Mass Tran.* **51** (2008) 5931–5941; doi:10.1016/j.ijheatmasstransfer.2008.05.015.
- [6] H. L. Frisch, “The time lag in diffusion”, *J. Phys. Chem.* **62** (1957) 401–404; doi:10.1021/j150547a018.
- [7] G. L. Graff, R. E. Williford and P. E. Burrows, “Mechanisms of vapor permeation through multilayer barrier films: lag time versus equilibrium permeation”, *J. Appl. Phys.* **96** (2004) 1840–1849; doi:10.1063/1.1768610.

- [8] R. I. Hickson, "Critical times of heat and mass transport through multiple layers", Ph.D. Thesis, PEMS, UNSW@ADFA, April 2010.
- [9] R. I. Hickson, S. I. Barry and G. N. Mercer, "Critical times in multilayer diffusion. Part 1: Exact solutions", *Int. J. Heat Mass Tran.* **52** (2009) 5776–5783; doi:10.1016/j.ijheatmasstransfer.2009.08.013.
- [10] R. I. Hickson, S. I. Barry and G. N. Mercer, "Critical times in multilayer diffusion. Part 2: Approximate solutions", *Int. J. Heat Mass Tran.* **52** (2009) 5784–5791; doi:10.1016/j.ijheatmasstransfer.2009.08.012.
- [11] R. I. Hickson, S. I. Barry and G. N. Mercer, "Exact and numerical solutions for effective diffusivity and time lag through multiple layers", *ANZIAM J. (E)* **49** (2009) C324–C340.
- [12] R. I. Hickson, S. I. Barry, G. N. Mercer and H. S. Sidhu, "Finite difference schemes for multilayer diffusion", *Math. Comput. Model.* **54** (2011) 210–220; doi:10.1016/j.mcm.2011.02.003.
- [13] R. I. Hickson, S. I. Barry and H. S. Sidhu, "Critical times in one- and two-layered diffusion", *AJEE* **15** (2009) 77–84; http://www.engineersmedia.com.au/journals/aace/pdf/AJEE_15_2_Hickson.pdf.
- [14] R. I. Hickson, S. I. Barry, H. S. Sidhu and G. N. Mercer, "Critical times in single-layer reaction diffusion", *Int. J. Heat Mass Tran.* **54** (2011) 2642–2650; doi:10.1016/j.ijheatmasstransfer.2009.08.012.
- [15] K. Landman and M. McGuinness, "Mean action time for diffusive processes", *J. Appl. Math. Decis. Sci.* **4** (2000) 125–141; doi:10.1155/S1173912600000092.
- [16] M. McGuinness, W. Sweatman, D. Boawan and S. Barry, "Annealing steel coils", in: *Proceedings of the 2008 MISG* (eds T. Marchant, M. Edwards and G. Mercer), 2009, <http://www.uow.edu.au/content/groups/public/@web/@inf/@math/documents/doc/uow053938.pdf>.
- [17] A. McNabb, "Mean action times, time lags and mean first passage times for some diffusion problems", *Math. Comput. Model.* **18** (1993) 123–129; doi:10.1016/0895-7177(93)90221-J.
- [18] A. McNabb and G. C. Wake, "Heat conduction and finite measures for transition times between steady states", *IMA J. Appl. Math.* **47** (1991) 193–206; doi:10.1093/imamat/47.2.193.
- [19] S. Petrovskii and N. Shigesada, "Some exact solutions of a generalized Fisher equation related to the problem of biological invasion", *Math. Biosci.* **172** (2001) 73–94; doi:10.1016/S0025-5564(01)00068-2.
- [20] R. A. Siegel, "A Laplace transform technique for calculating diffusion time lags", *J. Membr. Sci.* **26** (1986) 251–262; doi:10.1016/S0376-7388(00)82110-9.
- [21] R. A. Siegel, "Algebraic, differential, and integral relations for membranes in series and other multilaminar media: permeabilities, solute consumption, lag times, and mean first passage times", *J. Phys. Chem.* **95** (1991) 2556–2565; doi:10.1021/j100159a083.
- [22] A. W. Thornton, T. Hilder, A. J. Hill and J. M. Hill, "Predicting gas diffusion regime within pores of different size, shape and composition", *J. Membr. Sci.* **336** (2009) 101–108; doi:10.1016/j.memsci.2009.03.019.
- [23] W. Y. D. Yuen, "Transient temperature distribution in a multilayer medium subject to radiative surface cooling", *Appl. Math. Model.* **18** (1994) 93–100; doi:10.1016/0307-904X(94)90164-3.