A Finite Difference Method for Modeling Migration of Impurities in Multilayer Systems

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Abstract. A finite difference method to solve the one-dimensional diffusion of impurities in a multilayer system was developed for the special case in which a partition coefficient \( k \) is a ratio of the concentrations at the interface between two adjacent layers. The fictitious point method was applied to derive the algebraic equations for the mesh points at the interface, while for the non-uniform mesh points within the layers a combined method was used. The method was tested and then applied to calculate migration of impurities from multilayer systems into liquids or solids samples, in migration experiments performed for quality testing purposes. An application was developed in the field of impurities migration from multilayer plastic packaging into food, a problem of increasing importance in food industry.

Keywords: finite difference, diffusion equation, multilayer, partition coefficient, plastic packaging

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INTRODUCTION

The migration of chemicals into food products is an important safety aspect of food packaging and other food contact plastics [1]. Specific migration experiments are required in order to demonstrate compliance of a packaging with the limits. In these experiments, a multilayer (ML) plastic is brought into contact with a food simulant (e.g. vegetable oil, alcoholic or acid solution) under established time and temperature conditions, and migrant concentration (initially present in plastic) is measured as a function of time in food simulant. These migration experiments are time-consuming, expensive and often complicated to carry out, thus, the use of mathematical models to predict migration is gaining interest.

Diffusion within a ML packaging system and further substance transfer from it into a foodstuff is, in most cases, controlled by diffusion and partitioning processes. As the migrant has different solubilities in different layers, the corresponding concentrations \( c_\alpha \) and \( c_\beta \) at the interface between layers \( \alpha \) and \( \beta \) are in a ratio given by the partition coefficient \( k_\alpha = c_\alpha / c_\beta \). To handle these later cases too, numerical approximation methods must be used. Finite difference, finite element, finite volume, boundary element and semi-analytical methods have been developed to handle this problem (see [2] for a review).

In the following we will describe a finite difference method for solving the diffusion equations in a ML system. After introducing the fictitious point method used to derive algebraic equations for the interface mesh points, we will describe various configurations used in the laboratories for ML quality testing, as well as various initial conditions for the concentration distribution in order to demonstrate the importance of solving this problem.

METHOD

To illustrate the method we formulate the problem for a system made of two homogenous layers, A and B, with densities \( \rho \), diffusion coefficients \( D \), and thicknesses \( h \), \( k \cdot A, B \). Extension to three or more layers, in which one of the layers can be the food itself will become obvious after describing the method. The diffusion in the two layers is governed by the Fick’s equations:
\[ \frac{\partial c_{\alpha}}{\partial t} = D_k \frac{\partial^2 c_{\alpha}}{\partial x^2}, \quad k = A, B \]  

(1)

Initial conditions are written as \( c(x,0) = c_{\alpha 0} \), meaning a constant initial concentration of substance (impurity), usually a nonzero value in one layer and zero concentration in the other layers. This is the case of a virgin ML polymer system, however the method described here is not limited to a constant concentration but can employ a general function \( c_0(x) \), specified by values at the mesh points.

Boundary conditions impose no flux of matter through the outer wall of the system, i.e., \( \frac{\partial c_\alpha}{\partial x} \bigg|_{x=L_i} = 0 \), while two other similar conditions impose the flux continuity (no accumulation of matter) at interlayer contact. In addition the concentrations at the interface obey the condition: \( c_i = \beta_{ij} c_{ij} \) for \( x = L_i \), as imposed by the partition coefficient between the two layers.

To account for the larger concentration variations at interfaces, a non-uniform mesh was built over the ML domain, each layer having finer mesh close to the boundaries. For the mesh points inside the layers, the spatial discretization of Eq. 1 can be written as:

\[ \frac{c^{n+1}_i - c^n_i}{\delta t} = D_k \left[ \partial_i \left( g_i c^{n+1}_i + g_{i+1} c^{n+1}_{i+1} \right) + (1 - \partial_i) \left( g_i c^n_i + g_{i+1} c^n_{i+1} \right) \right] \]  

(2)

where \( n \) and \( n+1 \) indices denote concentrations at time \( t \) and \( t + \delta t \), and \( \partial_i \) is the method parameter which can take values from 0 (explicit), through 1/2 (Crank-Nicolson) to 1 (full implicit). The coefficients \( g_i \) can be derived for example from the Lagrange interpolating polynomial.

The spatial meshes built to solve the diffusion equations in the two layers may have different step sizes. In Fig. 1 the meshes at the boundary between two domains are presented. To simplify the notation, the concentrations are denoted by \( a_i \) in layer A and by \( b_i \) in layer B. Two fictitious points, \( a_{i-1} \) and \( b_{i+1} \), are also introduced, like for boundary conditions [3]. The step sizes left and right of node \( i \) will be denoted by \( \delta x_a \) and \( \delta x_b \) respectively. As one can note, at the interface there are two different values of the concentrations \( a_i \) and \( b_i \) for the same nodal point \( i \).

This describes in fact the jump in substance concentration at the interface, as imposed by a non-unitary partition coefficient due to different solubility of the substance in domain A and respectively B. The physical reality is a bit more complicated than this description. The jump in substance concentration at the interface takes place in a very thin but spatially finite region of both layers. More elaborated numerical techniques, like finite element method, can describe more accurately this jump. However the FD method presented above is simple enough to show the results of the physical process of diffusant partitioning at any interface of a ML structure. Moreover, from the reliability tests made it was found that, if at the interface region the discretization mesh is fine enough, this FD method produces correct and reliable data.

Discretization of the diffusion equation at node \( i \) for \( a_i \) yields:

\[ \frac{a^{n+1}_i - a^n_i}{\delta t} = \frac{1}{\delta x_a} \left[ g_a \frac{a^{n+1}_{i+1} - 2a^n_i + a^{n+1}_i}{\delta x_a^2} + (1 - g_a) \frac{a^n_i - 2a^n_{i-1} + a^n_{i+1}}{\delta x_a^2} \right] \]

Similar equation can be written for \( b_i \) concentration. The two fictitious concentrations, \( a_{i-1} \) and \( b_{i+1} \), which we introduced are eliminated by using the expression for the flux of matter through the boundary [4], and by writing the interface conditions for time \( t \) and \( t + \delta t \), after some algebraic manipulations, one gets eventually:

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\[-2r_\alpha \delta \partial \alpha^{n+1} + (1 + 2r_\alpha \delta - 2p_\alpha \delta) \alpha^{n+1} + 2p_\alpha \delta \delta \alpha^{n+1} = 2r_\alpha \delta \delta \alpha^{n+1} \left[1 - 2r_\alpha \delta (1 - p_\alpha) \right] \alpha^{n} - 2p_\alpha \delta \delta \alpha^{n} \]

for \( \alpha \) concentration and

\[-2p_\beta \delta \delta \beta^{n+1} + (1 + 2r_\beta \delta - 2p_\beta \delta) \beta^{n+1} - 2p_\beta \delta \delta \beta^{n+1} - 2p_\beta \delta \delta \beta^{n+1} = -2p_\beta \delta \delta \beta^{n+1} + (1 - 2r_\beta \delta (1 - p_\beta) \left) \beta^{n} + 2p_\beta \delta \delta \beta^{n} \]

for \( \beta \) concentration. Here \( \delta = 1 - \beta \cdot \rho \), \( D/\delta \delta \alpha \) and \( p_\alpha = \frac{\delta \beta}{\delta \alpha \delta \alpha} \).

Equation 2 for interior mesh points combined with Eqs. (3-4) for interface form a system of equation which, in matrix form, can be written \( \mathbf{\Lambda} \mathbf{\alpha}^{n+1} = \mathbf{B} \cdot \mathbf{e}^{n} \). One can easily observe that Eqs. (3-4) preserve the tridiagonal form of the system matrices. The extension of the method to three and more layers is quite straightforward.

**Preliminary tests**

The numerical algorithm based on this FD method is relatively simple and was implemented into a computer program which can be run on a PC. Preliminary tests were conducted to check the model and the application. We checked for example that the solution has the correct jump at the interface, as given by the partition coefficients. This quantity was found to be dependent on the number \( V \) of mesh points used in a layer, the relative deviation \( c_i - c_{i+1}/k_{i+1} \), being 0.04% for \( V = 100 \), and 0.02% for \( V = 400 \). Also, integrating the solution over the spatial domain one obtains the total mass of migrant, which, in an isolated ML system, must be conserved in time. When one starts from the most unfavorable case, namely an initial step distribution of the concentration, the relative deviation of the integrated solution from the correct value is \( 6 \times 10^{-5} \) for the first time step, then drops sharply to less than \( 10^{-7} \) for later time steps. This is due to the errors in integrating a function with sharp variations at the interfaces.

In another series of tests a ML system made of \( n \) homogenous layers, \( 2 < n < 10 \), with different thicknesses \( L_1 = L_2 = \ldots = L_n \), was considered. All \( n \) layers are homogenous and exhibit the same density, diffusion coefficient and initial concentration of migrant. The partition coefficients at the interfaces between the layers were taken unity, \( K_n = 1 \). This ML was assumed to be in contact with a non-contaminated, \( c_{i,0} = 0 \), liquid food of finite volume, \( V_L \), and density, \( \rho_L \). The partition coefficient \( K_n \) between the contact-layer \( n \) and \( F \) was also taken unity, \( K_{1,F} = 1 \). The ML structure defined above is in fact a homogenous monolayer "sliced" in \( n \) layers in contact with a liquid of volume, \( V_L \), and density, \( \rho_L \). We already know [5] that for such a system the diffusion/migration equation admits an analytical solution, and migration values can be computed. Comparison between the solution computed numerically and analytically was satisfactory, the relative variation never exceeding 0.1%.

**APPLICATIONS**

Standard laboratory tests are performed daily for compliance assessment purposes, to measure the amount of a specific substance migrated from a ML packaging into food or food simulants. The configurations most frequently used in measurements are one side configuration, when one side of the ML is in contact with liquid, and two sides configuration, when one or more MLs are fully immersed in liquid, or the equivalent configuration in which two additional plastic receptors are added on both sides of the ML system and kept under tight contact. These methods yield the time dependence of the substance migrated from the ML system. An alternative (see Fig. 2) is to use a source of migrant and a series of virgin polymer layers in tight contact. The concentration in each layer gives the spatial distribution of the migrant in this ML system, from which the diffusion and/or partition coefficients can be derived. From the modeling point of view each configuration can be formulated in the same framework, by specifying appropriate initial and/or boundary conditions.

There are many parameters which determine the diffusion in these experiments: physical-geometrical parameters (thickness and density) of the sample and contact medium, chemical parameters (initial concentration and type of migrant), diffusion coefficients in sample and contact medium, and partition coefficients between two adjacent layers. Not all these parameters are well known, for example diffusion and partition coefficients of some layers of the sample. The result of the measurement, as illustrated in Fig. 3, can be the amount of migrated substance as a function of time or the spatial profile of the concentration. The experimental data are then fitted using the model described here, the fitting parameter being one of the migration parameters of the ML system. In case modeling serves as an additional expertise instrument which complements the measurements [6].

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FIGURE 2. Laboratory methods used for migration experiments

FIGURE 3. Time dependent migration data or spatial profile of the migrant concentration can be fitted to yield migration parameters like diffusion or partition coefficients

One important aspect within the European Union’s public healthcare is the exposure of consumers to undesirable chemicals originating from food-contact materials like packaging. Because of the complex, heterogeneous and variable nature of foodstuffs, no general tools for modelling migration into foods are yet available. European Union adopted Directive 2002/72/EC which allows establishing the value of the specific migration “by an adequate experimentation or by an application of generally recognized diffusion models based on scientific evidence”. However the diffusion model accepted up to now by the legislators is limited to cases where an analytical solution of the problem can be derived. Monolayer packaging in contact with a finite amount of food can be treated analytically while ML systems under real contact conditions only admit a numerical solution. The EU project “Foodmigrosure” developed a first approach to a migration model for foods [7] but only for monolayers. Refinement and extension of such models probably represent the only practical way to accurately describe the foodstuffs as eaten by European consumers. Developing a migration model for multilayer systems is one necessary step for reaching this goal.

REFERENCES


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