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A Conserving Discretization for a Stefan Problem with an Interface Reaction at the Free Boundary

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ABSTRACT

The dissolution of an Al_2Cu particle is considered. A characteristic property is that initially the particle has a non-smooth boundary. Furthermore the dissolution may be controlled by an interface reaction. The mathematical model of this dissolution process contains a description of the particle interface, of which the position varies in time. Such a model is called a Stefan problem. We use the finite element method to solve this problem numerically. The displacement of the free boundary is computed by a method based on the balance of atoms. This method leads to good results, also for non-smooth boundaries. Some numerical experiments are given for the dissolution of an Al_2Cu particle in an $Al-Cu$ alloy, with a varying rate of the interface reaction.

1991 Mathematics Subject Classification: 35A35, 35R35, 65M06, 80A22

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1. INTRODUCTION

Heat treatment of metals is often necessary to optimize their mechanical properties. During the heat treatment, the metallurgical state of the material changes. This change can either involve the phases being present or the morphology of the various phases. One of these processes, which is both of large industrial and scientific interest and amenable to modeling, is the dissolution of second phase particles in a matrix with a uniform initial composition.

To describe this particle dissolution in rigid media several physical models have been developed, incorporating the effects of long-distance diffusion [9], [2], [6] and non-equilibrium conditions at the interface [3], [1]. The long-distance diffusion models imply that the processes at the interface between particle and matrix proceed infinitely fast. Therefore, these models provide an upper bound for the dissolution rate.

Nolfi's model [3] did not include the interface migration, but as far as we know, it is the first model which incorporated non-equilibrium conditions at the interface. In the Nolfi model non-equilibrium conditions at the interface were incorporated by the introduction of a Robbins

condition, which relates the concentration gradient with the concentration at the interface. The semi-analytical solution consists of an infinite series solution for the concentration profile. Their method, however, is only accurate in the early stages of the dissolution process.

Aaron and Kotler [1] incorporated the non-equilibrium conditions at the interface too. However their approach is only applicable for those situations in which the inter-particle distance is sufficiently large, i.e. the diffusion fields do not impinge. They transformed the Robbins problem of Nolfi into a Dirichlet problem, in which the concentration is fixed at all stages of the dissolution process. Combining Whelan's [9] analytical approach for the interface velocity as a function of the annealing time, with a relation between the interface concentration and the interface position, they evaluated the interface position using a Picard-type iteration method. In their model both the interface position and the interface concentration were taken momentarily stationary during the evaluation of the interface position as a function of time.

The effects of interfacial reactions on the rate of the dissolution of spherical particles in both infinite and finite media was examined by Vermolen and Van der Zwaag numerically [7]. Using a finite difference method it was shown, that interfacial reactions can have a significant effect on the dissolution rate and hence on the concentration profiles in the matrix during particle dissolution.

All solution methods presented in the references given above are only applicable to one-dimensional problems. In [5] a method is described by Segal, Vuik and Vermolen to compute a numerical solution of a two-dimensional Stefan problem with a conserving discretization of the free boundary. This method is applied for an infinite rate of the interface reaction.

In this paper we generalize the method presented in [5] to a Stefan problem with a finite rate of reaction at the interface. The boundary conditions at the free boundary are derived in Section 2 and compared with the literature. In Section 3 the numerical method presented in [5] is summarized. The numerical discretization of the interface reaction is investigated in Section 4. In Section 5 some results are shown.

2. A MODEL FOR DISSOLUTION WITH AN INTERFACE REACTION

Consider an Al_2Cu particle in an $Al-Cu$ alloy at a given temperature. The initial concentration of Al_2Cu in the Aluminum phase is equal to c_0 (mol/m³), whereas c_{part} denotes the concentration of Al_2Cu in the particle. When the temperature is increased, dissolution of the Al_2Cu particle sets in. The equilibrium Al_2Cu concentration in the alloy is c_{sol} ($c_{part} > c_{sol} > c_0$).

To describe the mathematical model we use the geometry as given in Figure 1. The domain filled with Aluminum is denoted by $\Omega(t)$. The boundary of this domain consists of the interface $S(t)$ and the outer boundaries Γ_i , $i \in \{1, 2, 3, 4\}$. The outer boundaries are fixed in time, except the intersections of Γ_1 and Γ_4 with $S(t)$. In the Aluminum-rich phase $\Omega(t)$, the Cu concentration $c(x, y, t)$ satisfies the (linear) diffusion equation

$$\frac{\partial c}{\partial t} = \mathbb{D}\Delta c, \quad (x, y) \in \Omega(t), \quad t \in (0, T]. \quad (2.1)$$

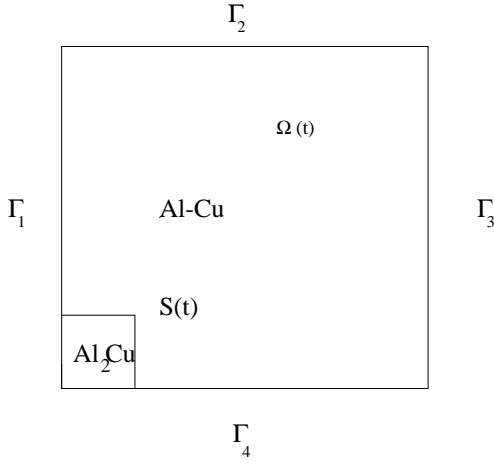


Figure 1: Geometry of an Al_2Cu particle in Aluminum

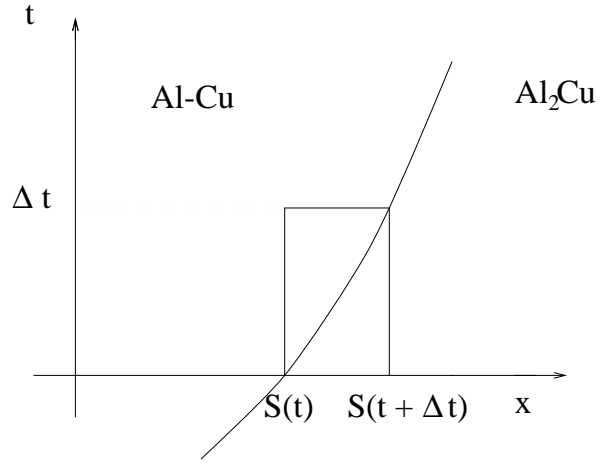


Figure 2: The control volume

The diffusion coefficient \mathbb{D} (m^2/s) is supposed to be independent of concentration. As the initial condition we use

$$c(x, y, 0) = c_0(x, y), \quad (x, y) \in \Omega(0), \quad (2.2)$$

where $\Omega(0)$ is prescribed. We assume no flux of Cu through the outer boundaries, so

$$\frac{\partial c}{\partial \mathbf{n}}(x, y, t) = 0, \quad (x, y) \in \Gamma_i, \quad i \in \{1, 2, 3, 4\}, \quad t \in [0, T]. \quad (2.3)$$

To determine the position of the interface two conditions are necessary. To derive these conditions for a spatially three dimensional problem, we consider a small part of the interface. Suppose that the interface is smooth, which means that it can locally be described by differentiable functions. For a small time step Δt the interface moves in the direction perpendicular to the interface. The x -axis is chosen along the normal. With this choice the position of the interface is locally described by the relation $x = S(t)$. We consider a control volume of width Δy and Δz . The intersection of the control volume with the surface $y = 0, z = 0$ is shown in Figure 2. The balance of Cu atoms leads to the following equation (Stefan condition):

$$(S(t + \Delta t) - S(t)) \Delta y \Delta z \cdot c_{part} = \mathbb{D} \frac{\partial c}{\partial x} \Delta y \Delta z \Delta t + (S(t + \Delta t) - S(t)) \Delta y \Delta z \cdot c_S, \quad (2.4)$$

where c_S is the limit of the concentration in Ω in the neighborhood of the interface. The left-hand side of (2.4) is equal to the amount of atoms transferred from the particle to the alloy. Assuming a first order reaction at the interface the second equation is (Robbins condition):

$$K (c_{sol} - c_S) \Delta y \Delta z \Delta t = \mathbb{D} \frac{\partial c}{\partial x} \Delta y \Delta z \Delta t + (S(t + \Delta t) - S(t)) \Delta y \Delta z \cdot c_S, \quad (2.5)$$

where K (m/s) is a measure of the rate of the interface reaction. For K large the problem is diffusion controlled, whereas for K small the problem is reaction controlled. Dividing (2.4) and (2.5) by $\Delta y \Delta z \Delta t$ and taking the limit $\Delta t \rightarrow 0$ one obtains

$$c_{part} v_n(x, y, t) = \mathbb{D} \frac{\partial c}{\partial \mathbf{n}}(x, y, t) + c_S v_n(x, y, t), \quad (x, y) \in S(t), \quad t \in (0, T], \quad (2.6)$$

$$K(c_{sol} - c_S) = \mathbb{D} \frac{\partial c}{\partial \mathbf{n}}(x, y, t) + c_S v_n(x, y, t), \quad (x, y) \in S(t), \quad t \in (0, T]. \quad (2.7)$$

where \mathbf{n} is the unit normal vector on the interface pointing outward with respect to $\Omega(t)$ and v_n is the normal velocity of the interface.

In the references [3], [7] and [8] comparable boundary conditions are used. In [3] and [7] the final term in (2.7) is not taken into account. This approximation is reasonable because in their applications $c_{sol} \ll c_{part}$, which implies that the neglected term is small.

3. A CONSERVING COMPUTATION OF THE FREE BOUNDARY FOR INFINITE RATE OF REACTION

In the literature (see [5] for a short overview) one can find various numerical methods to solve Stefan problems. These methods can be distinguished in the following categories: front-tracking, front-fixing and fixed-domain methods. We shall restrict ourselves to front-tracking since it allows first order reaction at the interface.

The algorithm for an infinite rate of reaction can be described as follows. In each time-step we solve the (ALE) convection-diffusion equation

$$\frac{Dc}{Dt} - \mathbb{D}\Delta c - \mathbf{u}_{mesh} \cdot \nabla c = 0, \quad (3.1)$$

with $\frac{Dc}{Dt}$ the so-called material derivative and $\mathbf{u}_{mesh} = \frac{\mathbf{x}(t+\Delta t) - \mathbf{x}(t)}{\Delta t}$ the mesh velocity. After that, the boundary is updated according to

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + v_n \Delta t \mathbf{n} = \mathbf{x}(t) + \frac{\mathbb{D}}{c_{part} - c_{sol}} \frac{\partial c}{\partial \mathbf{n}} \Delta t \mathbf{n}. \quad (3.2)$$

The straight-forward way to update the free boundary is to compute the gradient of the concentration in the elements connected to the free boundary (normal_velocity method). Using an averaging procedure for the gradient as well as an averaging procedure to compute the normals in the vertices of the boundary, equation (3.2) can be evaluated.

However, in case of sharp corners this may lead to a strange behavior as is shown in Figure 3. In order to get rid of this phenomenon we have developed a new algorithm (Stefan) based on the integral representation of the Stefan boundary condition. This implies that the area of the particle that has been dissolved is equal to the amount of diffused material. The flux through the element (x_{i-1}, x_i) is approximately equal to:

$$\mathbb{D} \frac{\partial c}{\partial \mathbf{n}}(x_{i-\frac{1}{2}}) l_i \Delta t, \quad (3.3)$$

with l_i the length of the line element (x_{i-1}, x_i) . Hence the amount of diffused material through the boundary $(x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}})$ is equal to

$$\frac{\Delta t}{2} \left(\mathbb{D} \frac{\partial c}{\partial \mathbf{n}}(x_{i-\frac{1}{2}}) l_i + \mathbb{D} \frac{\partial c}{\partial \mathbf{n}}(x_{i+\frac{1}{2}}) l_{i+1} \right). \quad (3.4)$$

The amount M of material dissolved, is approximately equal to $(c_{part} - c_{sol})O$, where O is the area defined in Figure 5. Due to the balance of atoms M must be equal to the amount

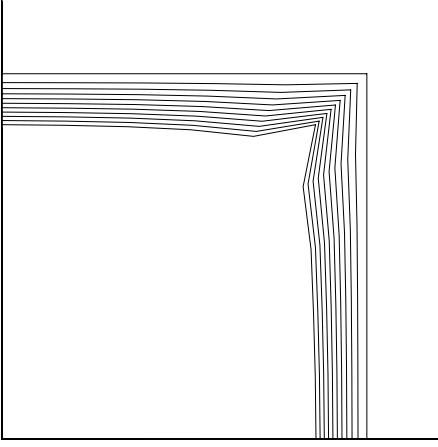


Figure 3: Position of free boundary at first 10 time-steps using the normal_velocity method for infinite rate of reaction

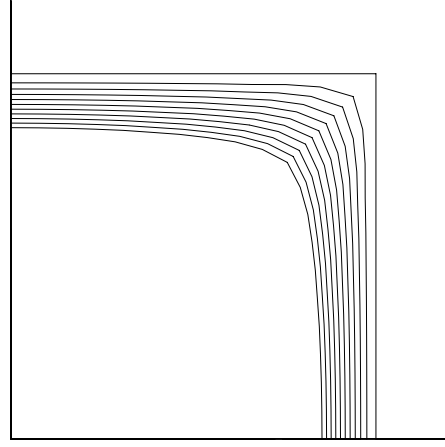


Figure 4: Position of free boundary at first 10 time-steps using the Stefan method for infinite rate of reaction

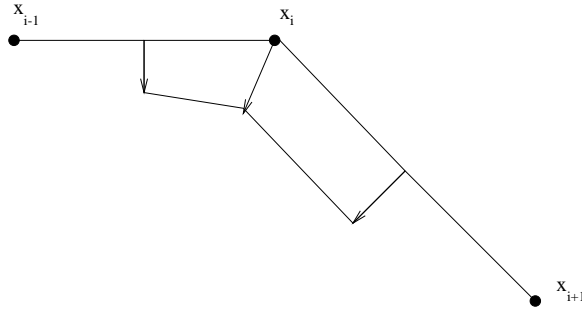


Figure 5: Area occupied by the region defined by the displacement of the vertex

of diffused material given in Equation (3.4). Consider two adjacent line elements (x_{i-1}, x_i) , and (x_i, x_{i+1}) , with length l_i and l_{i+1} respectively (Figure 5). The mid-side points of these elements are denoted by $x_{i-\frac{1}{2}}$ and $x_{i+\frac{1}{2}}$. Let the from formula (3.2) computed displacement in the mid-side points, be equal to $\delta x_{i-\frac{1}{2}}$ and $\delta x_{i+\frac{1}{2}}$. The new position of vertex x_i is denoted by \hat{x}_i . The length of the displacement is given as $\Delta x_i = \|\hat{x}_i - x_i\|$. Once the displacement in the vertices is computed, also the displacements in the mid-side points change. In order to get both a local and global equilibrium in the amount of dissolved material, it is necessary, that the new area is equal to

$$\frac{1}{2}l_i\delta x_{i-\frac{1}{2}} + \frac{1}{2}l_{i+1}\delta x_{i+\frac{1}{2}}. \quad (3.5)$$

The area O depends on Δx_i , $\Delta x_{i-\frac{1}{2}}$ and $\Delta x_{i+\frac{1}{2}}$, where $\Delta x_{i-\frac{1}{2}}$ is the adapted length of the displacement in $x_{i-\frac{1}{2}}$. Since $\Delta x_{i-\frac{1}{2}}$ and $\Delta x_{i+\frac{1}{2}}$ depend on Δx_{i-1} , Δx_i and Δx_{i+1} the relation is non-linear.

To solve this non-linear system we had to use an under-relaxation parameter. Choosing this parameter equal to 0.5 gave a fast convergence. The results of the Stefan algorithm are shown in Figure 4. The results in Figure 4 are more reliable than those in Figure 3 since from

physical point of view we expect a large diffusion of the atoms at the angular free boundary point. This gives locally larger free boundary velocities. For more details we refer to [5].

4. THE DISCRETIZATION FOR A FINITE RATE OF REACTION

The method summarized in Section 3 has been developed for a Stefan problem with an infinite fast interface reaction, so the concentration at the free boundary is equal to c_{sol} . To generalize this method to a finite rate of reaction one has to discretize the boundary conditions (2.6) and (2.7). Both conditions contain the normal velocity of the interface. In our implementation we use the Robbins condition (2.7) to solve the diffusion equation and the Stefan condition (2.6) to adapt the free boundary. In order to get rid of the normal velocity in (2.7) equation (2.6) is substituted into (2.7):

$$K(c_{sol} - c_S) = \mathbb{D} \frac{c_{part}}{c_{part} - c_S} \frac{\partial c}{\partial \mathbf{n}}(x, y, t), \quad (x, y) \in S(t), \quad t \in (0, T]. \quad (4.1)$$

This equation is linearized by taking c_S in the right-hand side of (4.1) at the old time level.

Experiments with boundary condition (4.1) in combination with the Stefan algorithm to adapt the free boundary, showed inaccuracies for a finite rate of reaction. The computed shapes of the free boundary resemble the shapes shown in Figure 3. The approximation of the normal gradient of c used in (3.3) may be the cause of these instabilities. To avoid this approximation, (2.7) is subtracted from (2.6) which yields:

$$v_n(x, y, t) = K \frac{c_{sol} - c_S}{c_{part}}, \quad (x, y) \in S(t), \quad t \in (0, T]. \quad (4.2)$$

Note that for $K \rightarrow \infty$, v_n is bounded since $c_S \rightarrow c_{sol}$. However when the difference between c_S and c_{sol} is very small it is not practical to use (4.2) because cancellation can occur.

To adapt the free boundary the Stefan algorithm (3.5) combined with (4.2) is used. In this algorithm the velocities are used in the mid-side points of the element boundaries, whereas the concentrations are given in the vertices of the elements. Therefore $c_S(x_{i-\frac{1}{2}})$ is approximated by averaging the c_S in the vertices and substitute this value into equation (4.2).

5. NUMERICAL EXPERIMENTS

An algorithm has been developed to investigate the dissolution kinetics for a two-dimensional case with a first order reaction at the interface. This algorithm has been implemented in our finite element code SEPRAN [4]. As an example we consider the dissolution of a needle shaped particle in a bar. Due to the symmetry of this two-dimensional problem, we restrict the simulation to one quarter of the real geometry. First we investigate the influence of the rate of the interface reaction (K) on the shape of the dissolving particle. Thereafter we compare the influence of the extra terms used in (2.6) and (2.7). In all our examples we have chosen the following parameters:

diffusion coefficient	\mathbb{D}	=	0.04858,
concentration in the particle	c_{part}	=	54,
initial concentration	c_0	=	0.0011.

5.1 The influence of the interface reaction

We consider a square dissolving in a square for $c_{sol} = 3.88$ and various choices of K . In Figure 6 we present the results as given in ([5], Fig. 21) for the Dirichlet condition at the interface. The next figures contain the results for $K = 1000$, 10, and 0.1. For K large we expect that

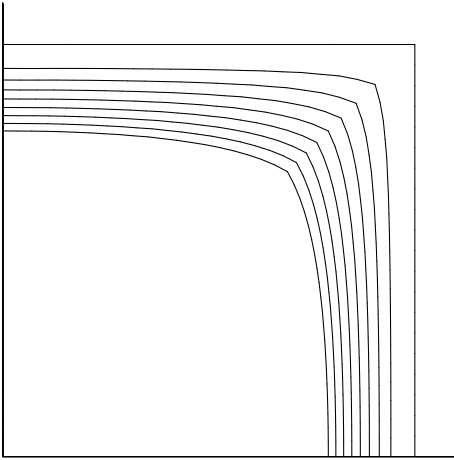


Figure 6: Free boundary of a bar dissolving in a bar using a Dirichlet boundary condition

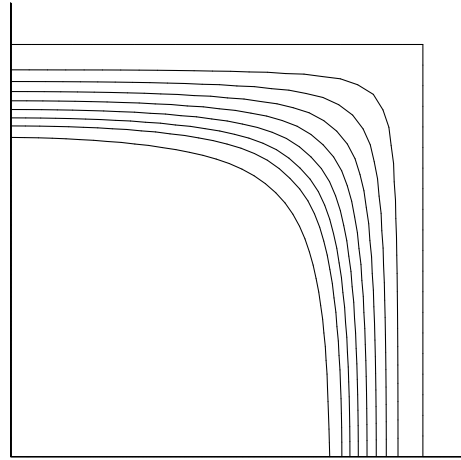


Figure 7: Free boundary of a bar dissolving in a bar with $K = 1000$

the solution converges to the solution of the Dirichlet problem. However comparing Figure 6 and 7 it appears that the latter figure shows a more rounded profile of the particle. The reason for this is that in Figure 6 the fluxes are approximated by the normal derivative of the concentration in the mid-side points. In the vicinity of the corner these derivatives appear to be underestimated. For $K = 1000$ the fluxes are approximated by equation (4.2), which is based only on the concentration. When the grid is refined we observe that the Dirichlet solution converges to the solution as given in Figure 7. So we expect that this solution is more accurate than the solution of the Dirichlet problem for the same grid size.

For small values of K the evolution of the position of the interface is completely determined by the rate of the interface reaction. Therefore one expects that the particle remains square-like. This is in accordance with the results as given in Figure 8 and 9. Also the velocity of the interface decreases when K decreases.

5.2 The influence of the term $c_S v_n$

In the derivation of the model we have already noted that in some references the term $c_S v_n$ is deleted from equation (2.7). For the problem as considered in Section 5.1 we have compared the solution with and without this term and it appears that its influence is negligible. On the other hand when c_{sol} is closer to c_{part} the differences may be large. Therefore we consider an academic problem where c_{sol} is 10 times as large: $c_{sol} = 38.8$ and take $K = 0.1$. The results of the correct boundary conditions are given in Figure 10. Since c_{sol} is much larger the velocity of the interface is much higher. Therefore the time-steps used in these problems are equal to the time-steps of the previous problem divided by 10. The results given in Figure 11 are obtained when the term $c_S v_n$ is deleted from equation (2.7). There are considerable differences between both results. Neglecting $c_S v_n$ leads to an overestimate of the position of

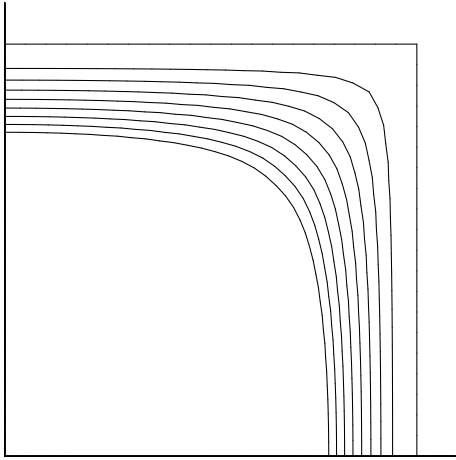


Figure 8: Free boundary of a bar dissolving in a bar with $K = 10$

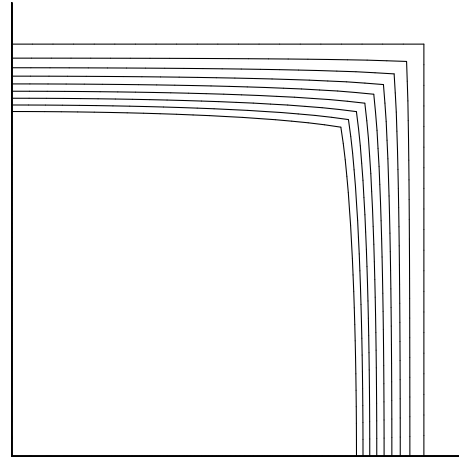


Figure 9: Free boundary of a bar dissolving in a bar with $K = 0.1$

the free boundary.

6. CONCLUSIONS

Particle dissolution in binary alloys is investigated by numerical techniques. The mathematical model used is that of a free boundary problem of Stefan type with a parameter which allows to switch between "diffusion controlled" and "interface controlled" migration. The problem is solved by a two-dimensional finite element method. It has been shown that this approach leads to an accurate solution of the problem.

It appears that the solution of the model with a fast reaction on the interface leads to better results than the model with a Dirichlet condition at the interface. Therefore we recommend to use the numerical solution of the model with an interface reaction with K sufficiently large to approximate the solution of the model with the Dirichlet boundary condition. As expected the influence of the diffusion disappears when the reaction is slow. In such a case the shape of the dissolving particle remains the same during dissolution.

In some references the boundary conditions are only approximately true. It has been shown that this approximation is allowed for the problems considered. However in other applications where c_{sol} and c_{part} have the same order of magnitude all terms should be included in the boundary conditions.

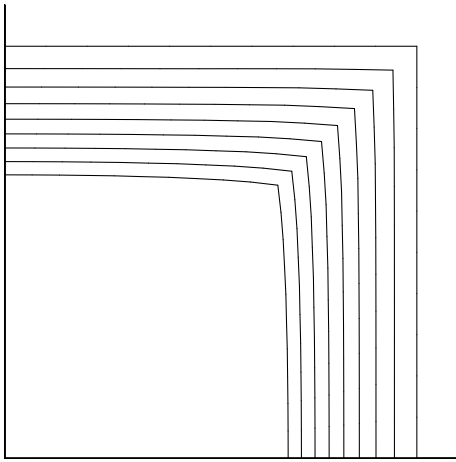


Figure 10: Free boundary of a bar dissolving in a bar with $K = 0.1$ and $c_{sol} = 38.8$

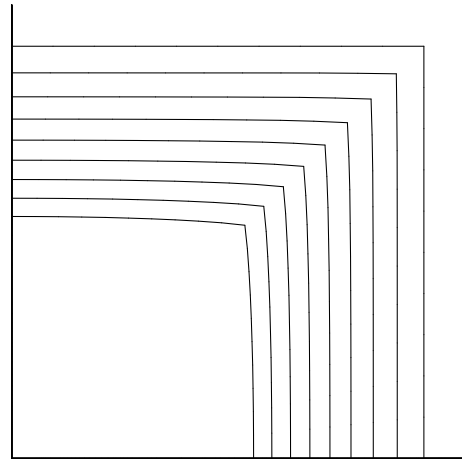


Figure 11: Free boundary of a bar dissolving in a bar with $K = 0.1$ and $c_{sol} = 38.8$ without the term $c_S v_n$

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