

Mathematical modeling of hydrogen diffusion in biphasic steel.

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Abstract

1 Model

The main model consists of hydrogen diffusion two-phase system, in which there is a bulk phase, with spherical precipitates in it, disperse enough so that we can do homogenization. Moreover, consider that the precipitates have a radius of R , that the bulk diffusivity is D , the precipitate diffusivity is α , and there is Γ precipitates per unit volume (we can get this statistics from the volume fraction, assuming spherical particles).

We denote by $c(x, t)$ the hydrogen concentration at the bulk phase, while we denote by $n(r, t; x)$ the concentration of hydrogen in the precipitate at x , on radius r (of the precipitate) and time t .

The interface between two phases satisfies both the continuity of chemical potential, which translates to

$$\frac{c}{n} = \frac{S_c}{S_n} = \exp\left(\frac{\mu_c - \mu_n}{RT}\right) =: K, \quad (1)$$

and the continuities of fluxes

$$J_c = J_n = J. \quad (2)$$

Now, consider an interface at (x, t) . From the point of view of the bulk, we can think of this interface as being a sink for the bulk concentration, at the boundary. Then, *each precipitate* results in a volumetric sink of strength $4\pi R^2 J$. Of course, then we have that the sink per unit volume becomes $4\pi R^2 \Gamma J$. Therefore, we can consider the bulk transport as following a diffusion equation with sink

$$\frac{\partial c}{\partial t}(x, t) = D \frac{\partial^2 c}{\partial x^2}(x, t) - 4\pi R^2 \Gamma J. \quad (3)$$

Now, from the point of view of the precipitate at x , we have that the continuity of chemical potentials makes that, at the interface *from the precipitate*

size, we can consider a time-varying inlet concentration dependant on $c(x, t)$. That is, at $r = R$ (and $r = -R$), we must have

$$n(R, t; x) = c(x, t). \quad (4)$$

As for the precipitate itself, it follows that it must obey the spherically symmetric form of the diffusion equation

$$\frac{\partial n}{\partial t}(r, t, x) = \alpha \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n}{\partial r}(r, t, x) \right) \quad (5)$$

And, of course, Fick's first law says that we can calculate the flux J from the precipitate side, given by

$$J = -\alpha \frac{\partial n}{\partial r}(R, t). \quad (6)$$

. Therefore, we end up with the model as in the next section.

2 Derivation of bulk equation

Consider then

$$\begin{aligned} \frac{\partial c}{\partial t}(x, t) &= D \frac{\partial^2 c}{\partial x^2}(x, t) - 4\pi R^2 \Gamma J; t \geq 0, 0 \leq x \leq L \\ \frac{\partial n}{\partial t}(r, t, x) &= \alpha \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n}{\partial r}(r, t, x) \right); \quad t \geq 0, -R \leq x \leq R \\ J &= -\alpha \frac{\partial n}{\partial r}(R, t) \\ n(R, t, x) &= n(-R, t, x) = Kc(x, t) \end{aligned} \quad (7)$$

First: solving n differential equation. Ommiting x , let $m(r, t) := n(r, t) - Kc(t)$. Hence,

$$\frac{\partial m}{\partial t}(r, t) = \alpha \mathcal{O}[m](r, t) + c'(t); \quad m(r, t) = m(-R, t) = 0, \quad (8)$$

with

$$\mathcal{O}(m) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial m}{\partial r} \right) \quad (9)$$

Using separation of variables, let $m(r, t) = T(t)\varphi(r)$. Hence, we have

$$T' \varphi = \alpha \mathcal{O}[\varphi] T - K c'(t) \quad (10)$$

We look then at the eigenvalue problem

$$\mathcal{O}[\varphi] = -\lambda \varphi, \quad (11)$$

or

$$r^2\varphi'' + 2r\varphi' + \lambda r^2\varphi = 0. \quad (12)$$

The above equation equals to

$$(r\varphi)'' + \lambda(r\varphi) = 0. \quad (13)$$

Considering $\varphi(R) = \varphi(-R) = 0$, for $\lambda_0 \leq 0$, $\varphi(R) = 0$, and, for $\lambda > 0$,

$$(r\varphi) = R \sin\left(\sqrt{\lambda_k} r\right); \quad \sqrt{\lambda_k} = \frac{\pi k}{R} \quad (14)$$

Hence, the eigenvalue problem is

$$\varphi_k(r) = \pi k j_0(\pi k r/R); \quad \lambda_k = \frac{\pi^2 k^2}{R^2}; \quad k = 1, 2, \dots \quad (15)$$

with $j_0(x) = \sin(x)/x$ being the zeroth spherical Bessel function of the first kind (who is also the sinc function).

Getting already some things off the table, we have that φ_k forms an base of functions, that has the orthonormality relations

$$\frac{1}{R} \int_{-R}^R (r/R)^2 \varphi_k(r) \varphi_l(r) dr = \delta_{m,l}. \quad (16)$$

due to

$$\begin{aligned} & \frac{1}{R} \int_{-R}^R (r/R)^2 \varphi_k(r) \varphi_l(r) dr = \\ & 2\pi^2 k^2 \int_0^1 u^2 j_0(\varphi k u) j_0(\varphi l u) du = \\ & 2\pi^2 k^2 \frac{\delta_{k,l}}{2} (j_1(\pi k))^2 = \quad , \quad (17) \\ & \delta_{k,l} \pi^2 k^2 \left(\frac{-(-1)^k}{\pi k} \right)^2 = \\ & \delta_{k,l} \end{aligned}$$

with $j_1(x)$ being the first spherical Bessel function of the first kind. Hence, for any (suitable) $f(r)$, we can decompose

$$\begin{aligned} f(r) &= \sum_{k=1}^{\infty} f_k \varphi_k \\ f_k(r) &= \frac{1}{R} \int_{-R}^R (r/R)^2 f(r) \varphi_k(r) dr. \end{aligned} \quad (18)$$

. In particular, we use the decomposition

$$Kc'(t) = \sum_{k=1}^{\infty} Kc'_k(t) \varphi_k(t). \quad (19)$$

We have that, using the eigenvalue problem, decomposing

$$m(r, t) = \sum_{k=1}^{\infty} \psi_k(t) \varphi_k(r), \quad (20)$$

we have that

$$\sum_{k=1}^{\infty} (\psi'_k(t) + \lambda_k \alpha \psi_t + K c'_k(t)) \varphi(k) = 0, \quad (21)$$

Hence, we have

$$\psi_k(t) = e^{-\alpha \lambda_k t} \left(\psi_k(0) - \int_0^t e^{\alpha \lambda_k \tau} K c'_k(\tau) d\tau \right), \quad (22)$$

or, assuming $\psi_k(0) = 0$ (because we will consider $n(0, t, x) = 0$ and $c(x, 0) = 0$, although this definition *still works* for $n(r, t, x) = n(0, t, x) = Kc(x, t)$,

$$\begin{aligned} \psi_k(t) &= -K e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) \frac{1}{R} \int_{-R}^R (r/R)^2 \varphi_k(r) dr d\tau = \\ &= 2K \frac{(-1)^k}{\pi k} e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) d\tau \end{aligned} \quad (23)$$

And, we remember that $m(r, t) = n(0, t) - Kc(t)$. Finally, we can then find

$$J = \alpha \frac{\partial n}{\partial r}(t, R) = -\alpha \sum_{k=1}^{\infty} \psi_k(t) \frac{\partial \varphi_k}{\partial r}(R). \quad (24)$$

. But, we have that $\frac{\partial \varphi_k}{\partial r}(R) = (-1)^k \pi k / R$. Hence, we can join everything and find that

$$J = \frac{2}{R} \alpha K \sum_{k=1}^{\infty} e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) d\tau \quad (25)$$

Therefore, our equation for c becomes (showing again x):

$$\frac{\partial c}{\partial t}(x, t) = D \frac{\partial^2 c}{\partial x^2}(x, t) - 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(x, \tau) d\tau \quad (26)$$

or

$$\begin{aligned} \frac{\partial c}{\partial t}(x, t) &= D \frac{\partial^2 c}{\partial x^2}(x, t) - 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} (\omega_k *_t c')(x, t) \\ \omega_k(t) &= \exp\left(-\frac{\alpha \pi^2 k^2 t}{R^2}\right), \end{aligned} \quad (27)$$

with $(f *_t g)(x, t) = \int_0^t f(x, t - \tau) g(x, \tau) d\tau$ being the convolution evaluated in the t argument.

Of course, we can simplify things by making

$$\begin{aligned}\beta &:= 8\pi R\Gamma\alpha K \\ \omega &:= \sum_{k=1}^{\infty} \omega_k = \sum_{k=1}^{\infty} \exp\left(-\frac{\alpha\pi^2 k^2 t}{R^2}\right),\end{aligned}\tag{28}$$

resulting in (27) being written as

$$\frac{\partial c}{\partial t} + \beta \left(\omega *_t \frac{\partial c}{\partial s} \right) = D \frac{\partial^2 c}{\partial x^2},\tag{29}$$

or, expanding the convolution,

$$\frac{\partial}{\partial t} c(x, t) + \beta \int_0^t \omega(t-s) \frac{\partial}{\partial s} c(x, s) ds = D \frac{\partial^2 c}{\partial x^2}(x, t)\tag{30}$$

From (23), we can also compute $n(r, t, x)$ as

$$\begin{aligned}n(r, t, x) &= Kc(t, x) + \sum_{k=1}^{\infty} \psi_k(t) \varphi_k(r) = \\ &= Kc(t, x) + 2K \sum_{k=1}^{\infty} \frac{(-1)^k}{\pi k} e^{-\alpha\lambda_k t} \int_0^t e^{\alpha\lambda_k \tau} c'(\tau) d\tau \varphi_k(r) = \\ &= Kc(t, x) + 2K \int_0^t \sum_{k=1}^{\infty} \frac{(-1)^k}{\pi k} e^{\alpha\lambda_k(\tau-t)} \varphi_k(r) c'(\tau) d\tau,\end{aligned}\tag{31}$$

or

$$n(r, t, x) = K \left(c(x, t) - \int_0^t \xi(r, t-s) \frac{\partial}{\partial s} c(x, s) ds \right)\tag{32}$$

, where

$$\xi(r, t) := -2 \sum_{k=1}^{\infty} \frac{(-1)^k}{\pi k} e^{\alpha\lambda_k t} \varphi_k(r).\tag{33}$$

If we are interested in a more "global" information (not depending on r), we then define the mean amount of hydrogen per precipitate $c_p = \frac{1}{V} \int_V n(r) dr$, we have

$$c_p(x, t) := K \left(c(x, t) - \int_0^t \omega_p(t-s) \frac{\partial}{\partial s} c(x, s) ds \right),\tag{34}$$

with $\omega_p(t)$ being given by

$$\frac{3}{2} \sum_{k=1}^{\infty} \frac{1}{\pi^2 k^2} \exp\left(-\frac{\alpha\pi^2 k^2 t}{R^2}\right)\tag{35}$$

2.1 Cylindric precipitates, *mutatis mutandis*

If we consider the approximation by cylindric precipitates, then, defining Γ_c as the amount precipitates per cross-sectional area, we can follow the same arguments above (now using Bessel functions of the first kind), and arrive at almost the same equations, now with

$$\begin{aligned}\beta &= 4\pi\Gamma\alpha K \\ \omega &= \sum_{k=1}^{\infty} \omega_k = \sum_{k=1}^{\infty} \exp\left(-\frac{\alpha u_{0,k}^2 t}{R^2}\right) \\ c_p(x, t) &= 4\pi R^2 K \left(c(x, t) - \int_0^t \omega_p(t-s) \frac{\partial}{\partial s} c(x, s) ds \right), \\ \omega_p(t) &= \frac{1}{4} \sum_{k=1}^k \frac{1}{u_{0,k}^2} \exp\left(-\frac{\alpha \pi^2 u_{0,k}^2 t}{R^2}\right)\end{aligned}\tag{36}$$

with $u_{0,k}$ being the k-th zero of the zeroth Bessel function of the first kind.

3 Discretization

Let's discretize this. Forgetting about x for now, consider only the operator

$$\frac{\partial}{\partial t} c(t) + \beta \int_0^t \omega(t-s) \frac{\partial}{\partial s} c(s) ds.\tag{37}$$

Now, consider a discretization

$$\begin{aligned}t_0, t_1, \dots, t_n, t_{n+1} \\ c_0, c_1, \dots, c_n, c_{n+1} \\ h_i := t_i - t_{i-1} \\ t_{i+1/2} = (t_{i+1} - t_i)/2\end{aligned}\tag{38}$$

Then, we can discretize the integral at time t_{n+1} by

$$\int_0^t \omega(t-s) \frac{\partial}{\partial s} c(s) ds \approx \sum_{i=0}^n \omega(t_{n+1} - t_{i+1/2}) (c_{i+1} - c_i).\tag{39}$$

Separating the c_{n+1} from the rest, and defining $\omega^{n+1,i}$ as $\omega(t_{n+1} - t_{i+1/2})$, we have the discretization as a function of c_{n+1}

$$\frac{c_{n+1} - c_n}{h_{n+1}} + \beta(c_{n+1} - c_n)\omega^{n+1,n} + \beta \sum_{i=0}^{n-1} (c_{i+1} - c_i)\omega^{n+1,i},\tag{40}$$

or

$$\left(\frac{1}{h_{n+1}} + \beta\omega^{n+1,n}\right) c_{n+1} - \left(\frac{1}{h_{n+1}} + \beta\omega^{n+1,n}\right) c_n + \beta \sum_{i=0}^{n-1} (c_{i+1} - c_i)\omega^{n+1,i}.\tag{41}$$

Now, considering the space discretization ¹, let the discretized operator matrix be A letting \mathbf{c} be the space discretization vector, we have that, using the implicit Euler method, the above problem translates to (rewritten so that we guarantee a positive diagonal)

$$\begin{aligned} & (-A + (h_{n+1}^{-1} + \beta\omega^{n+1,n})I) \mathbf{c}_{n+1} = \\ & -\beta \sum_{i=0}^{n-1} (\mathbf{c}_{i+1} - \mathbf{c}_i) \omega^{n+1,i} + (h_{n+1}^{-1} + \beta\omega^{n+1,n}) \mathbf{c}_n, \end{aligned} \quad (42)$$

which we can then solve at each time step. Some notes here

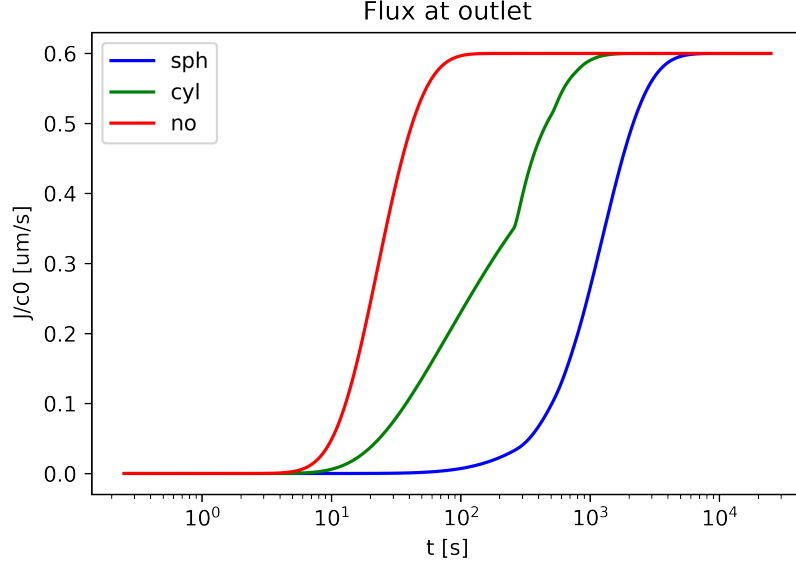
- In practice, ω decays as $t_{n+1} - t_i$ grows large. Can probably do some cutoff here.
- If we use a constant time step, we can define $\hat{\omega}^j := \omega^{n+1,n-j} = \omega(h(j + 1/2))$. We just calculate beforehand for some values of j and hold the values (remembering the cutoff note above).

4 Results

There are the results of a simulation of this model, with unit concentration at the inlet and zero concentration at the outlet.

- Physical parameters (some taken from Olden)
 - D - $6.0 \cdot 10^{-1} \mu m^2/s$
 - α - $1.4 \cdot 10^{-4} \mu m^2/s$
 - K - $32.51/0.033$
 - $R = 5 \mu m$
 - Γ - $0.0007639437268410977 \mu m^{-3}$ (from 0.1 of volumetric fraction)
 - L - $100 \mu m$
- Solver parameters
 - Space discretization points = 21
 - Maximum kernel expansion = 1000
 - Time step = 0.25
 - Decay limit = 0.01
 - Memory's maximum size = 1000

¹can be finite differences, elements, or whatever



5 Transform approaches

5.1 Fourier transforming bulk equation

We can do other things. Let's try to Fourier transform this (in t). Let $C(x, s) = \mathcal{F}_t(c(x, t))(s)$. Hence, we have that

$$\mathcal{F}_t \left(\frac{\partial}{\partial t} c(x, t) \right) (s) = 2\pi i s C(x, s) \quad (43)$$

$$\mathcal{F}_t \left(\sum_{k=1}^{\infty} (\omega_k *_{\mathbf{t}} c')(x, t) \right) = C(x, s) \sum_{k=1}^{\infty} \frac{1}{1 - i \frac{\alpha \pi^2 k^2}{2R^2 \pi s}}, \quad (44)$$

or

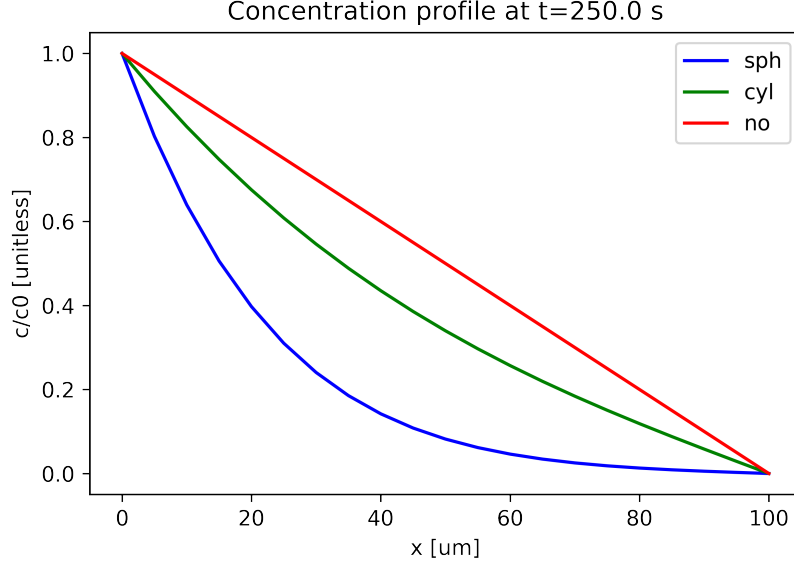
$$\mathcal{F}_t \left(\sum_{k=1}^{\infty} (\omega_k *_{\mathbf{t}} c')(x, t) \right) = C(x, s) \sum_{k=1}^{\infty} \frac{1}{1 + \left(\frac{\alpha \pi^2 k^2}{2R^2 \pi s} \right)^2} \left(1 + i \frac{\alpha \pi^2 k^2}{2R^2 \pi s} \right), \quad (45)$$

and the diffusive term stays the same. Hence, joining everything

$$C(x, s) \zeta(s) = D \frac{\partial^2 C}{\partial x^2}(x, s), \quad (46)$$

with

$$\zeta(s) = 2\pi i s + 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} \frac{1}{1 - i \frac{A k^2}{s}}; \quad A = \frac{\alpha \pi}{2R^2} \quad (47)$$



5.2 Laplace transforming bulk equation

In a similar manner, we try Laplace transform then. Let $\mathcal{C}(x, s) = \mathcal{L}_t(c(x, t))(s)$. He have that

$$\mathcal{L}_t \left(\frac{\partial}{\partial t} c(x, t) \right) (s) = s\mathcal{C}(x, s) - c(x, 0), \quad (48)$$

and

$$\mathcal{L}_t \left(\sum_{k=1}^{\infty} (\omega_k *_{t} c')(x, t) \right) = (s\mathcal{C}(x, s) - c(x, 0)) \sum_{k=1}^{\infty} \frac{1}{1 + \frac{\alpha \pi^2 k^2}{R^2} s} \quad (49)$$

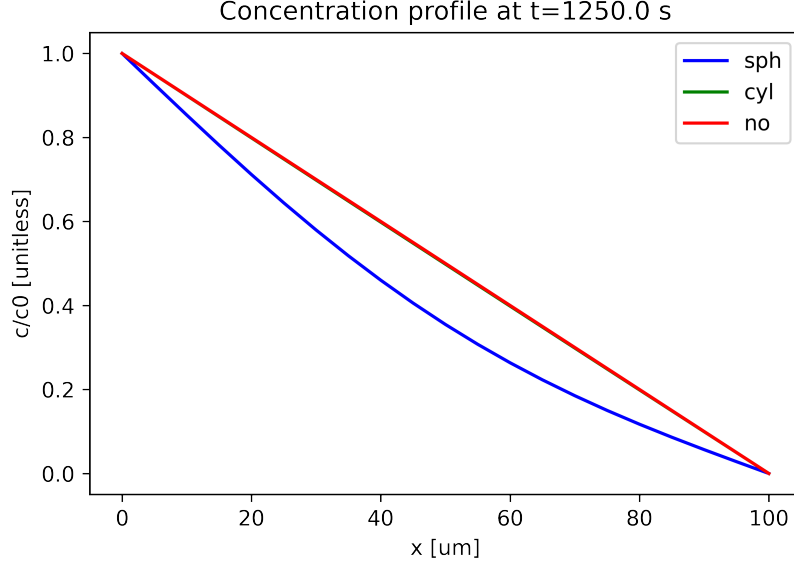
$$\sum_{k=1}^{\infty} \frac{1}{1 + \frac{\alpha \pi^2 k^2}{R^2} s} = \frac{1}{2} \left(\sqrt{\frac{R}{\alpha}} s^{-1/2} \coth \left(\sqrt{\frac{R}{\alpha}} s^{-1/2} \right) - 1 \right). \quad (50)$$

Since we assumed $c(x, 0) = 0$, the equation for \mathcal{C} becomes

$$\begin{aligned} \mathcal{C}(x, s) \xi(s) &= \frac{\partial^2 \mathcal{C}}{\partial x^2}(x, s) \\ \xi(s) &= \frac{s}{D} \left(1 + \frac{\beta}{2} \left(\sqrt{\frac{R}{\alpha s}} \coth \left(\sqrt{\frac{R}{\alpha s}} \right) - 1 \right) \right). \end{aligned} \quad (51)$$

We must have

$$\mathcal{C}(x, s) = A(s)e^{\sqrt{\xi(s)}x} + B(s)e^{-\sqrt{\xi(s)}x} \quad (52)$$



Using Dirichlet conditions $c(0, s) = c_0$, $c(L, s) = 0$, we have that $\mathcal{C}(0, s) = c_0/s$, $\mathcal{C}(L, 0) = 0$, and we find $A(s), B(s)$ solving the system

$$\begin{bmatrix} 1 & 1 \\ e^{\sqrt{\xi(s)}L} & e^{-\sqrt{\xi(s)}L} \end{bmatrix} \begin{bmatrix} A(s) \\ B(s) \end{bmatrix} = \begin{bmatrix} c_0/s \\ 0 \end{bmatrix}, \quad (53)$$

We have that

$$\begin{aligned} A(s) &= \frac{e^{-\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \\ B(s) &= -\frac{e^{\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \end{aligned} \quad (54)$$

Then, we have that

$$\mathcal{C}(x, s) = \frac{c_0}{s(e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L})} \left(e^{-\sqrt{\xi(s)}(L-x)} - e^{\sqrt{\xi(s)}(L-x)} \right) \quad (55)$$

Or, simplifying

$$\frac{c_0}{s} \frac{\sinh(\sqrt{\xi(s)}(L-x))}{\sinh(\sqrt{\xi(s)}L)} \quad (56)$$

For each x , Laplace-invert $\mathcal{C}(x, s)$. Have no idea how tough this is numerically.