

# 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  $\alpha$ , and there is  $\Gamma$  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  $m(r, t) := n(r, t) - c(t)$ . 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

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

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  $\varphi_k$  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

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

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  $c(0, t) = 0$ ),

$$\begin{aligned} \psi_k(t) &= K e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) \frac{1}{R} \int_{-R}^R (r/R)^2 \varphi_k(r) dr d\tau = \\ &= -2K \frac{(-1)^k}{\pi k} e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) d\tau = \\ &= -2K \frac{(-1)^k}{\pi k} \left( c(t) + e^{-\alpha \lambda_k t} c(0) - \frac{e^{-\alpha \lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c(\tau) d\tau \right). \end{aligned} \quad (23)$$

And, we remember that  $m(r, t) = n(0, t) + c(t)$ . 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

$$J = \frac{2}{R} \alpha K \sum_{k=1}^{\infty} \left( c(t) + e^{-\alpha \lambda_k t} c(0) - \frac{e^{-\alpha \lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c(\tau) d\tau \right). \quad (25)$$

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

$$\begin{aligned} \frac{\partial c}{\partial t}(x, t) &= D \frac{\partial^2 c}{\partial x^2}(x, t) - \\ &= 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} \left( c(x, t) + e^{-\alpha \lambda_k t} c(x, 0) - \frac{e^{-\alpha \lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c(x, \tau) d\tau \right), \end{aligned} \quad (26)$$

or

$$\frac{\partial c}{\partial t}(x, t) = D \frac{\partial^2 c}{\partial x^2}(x, t) - 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} e^{-\alpha \lambda_k t} \int_0^t e^{\alpha \lambda_k \tau} c'(\tau) d\tau \quad (27)$$

or still

$$\begin{aligned}\frac{\partial c}{\partial t}(x, t) &= D \frac{\partial^2 c}{\partial x^2}(x, t) - 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} (\omega_k *_t c')(x, t) \\ \omega_k(t) &= \exp\left(-\frac{\alpha \pi^2 k^2 t}{R^2}\right),\end{aligned}\tag{28}$$

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

$$\begin{aligned}\beta &:= 8\pi R \Gamma \alpha K \\ \omega &:= \sum_{k=1}^{\infty} \omega_k = \sum_{k=1}^{\infty} \exp\left(-\frac{\alpha \pi^2 k^2 t}{R^2}\right),\end{aligned}\tag{29}$$

resulting in (28) being written as

$$\frac{\partial c}{\partial t} + \beta \left( \omega *_t \frac{\partial c}{\partial s} \right) = D \frac{\partial^2 c}{\partial x^2},\tag{30}$$

or, expanding the convolution,

$$\frac{\partial}{\partial t} c(x, t) + \beta \int_0^t \omega(t - s) \frac{\partial}{\partial s} c(x, s) ds = D \frac{\partial^2 c}{\partial x^2}(x, t)\tag{31}$$

## 2.1 Cylindric precipitates, *mutatis mutandis*

If we consider the approximation by cylindric precipitates, then, defining  $\Gamma_c$  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

$$\begin{aligned}\beta &= 4\pi \Gamma \alpha K \\ \omega &= \sum_{k=1}^{\infty} \omega_k = \sum_{k=1}^{\infty} \exp\left(-\frac{\alpha u_{0,k}^2 t}{R^2}\right),\end{aligned}\tag{32}$$

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

$$\frac{\partial}{\partial t} c(t) + \beta \int_0^t \omega(t - s) \frac{\partial}{\partial s} c(s) ds.\tag{33}$$

Now, consider a discretization

$$\begin{aligned} t_0, t_1, \dots, t_n, t_{n+1} \\ c_0, c_1, \dots, c_n, c_{n+1} \\ h_i := t_i - t_{i-1} \\ t_{i+1/2} = (t_{i+1} - t_i)/2 \end{aligned} \tag{34}$$

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

$$\int_0^t \omega(t-s) \frac{\partial}{\partial s} c(s) ds \approx \sum_{i=0}^n \omega(t_{n+1} - t_{i+1/2}) (c_{i+1} - c_i). \tag{35}$$

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  $c_{n+1}$

$$\frac{c_{n+1} - c_n}{h_{n+1}} + \beta(c_{n+1} - c_n)\omega^{n+1,n} + \beta \sum_{i=0}^{n-1} (c_{i+1} - c_i)\omega^{n+1,i}, \tag{36}$$

or

$$\left( \frac{1}{h_{n+1}} + \beta\omega^{n+1,n} \right) c_{n+1} - \left( \frac{1}{h_{n+1}} + \beta\omega^{n+1,n} \right) c_n + \beta \sum_{i=0}^{n-1} (c_{i+1} - c_i)\omega^{n+1,i}. \tag{37}$$

Now, considering the space discretization <sup>1</sup>, 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)

$$\begin{aligned} (-A + (h_{n+1}^{-1} + \beta\omega^{n+1,n})I) \mathbf{c}_{n+1} = \\ -\beta \sum_{i=0}^{n-1} (\mathbf{c}_{i+1} - \mathbf{c}_i)\omega^{n+1,i} + (h_{n+1}^{-1} + \beta\omega^{n+1,n}) \mathbf{c}_n, \end{aligned} \tag{38}$$

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

- In practice,  $\omega$  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).

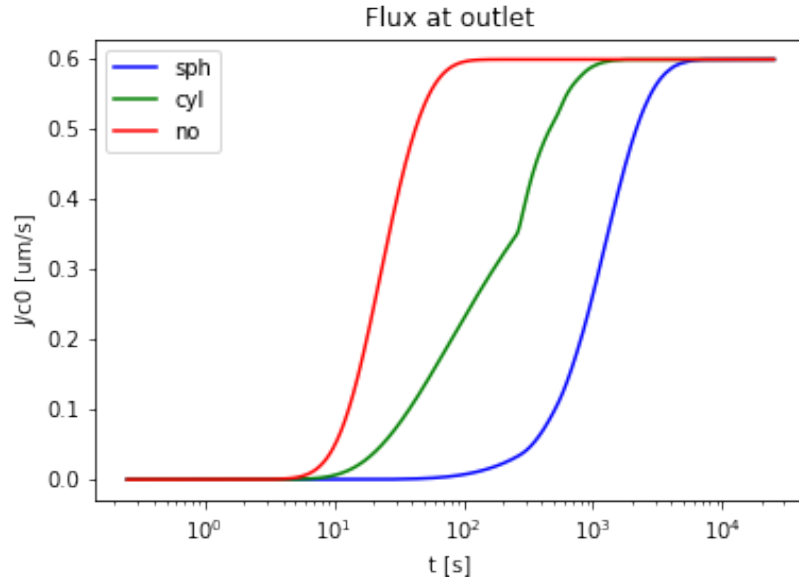
## 4 Results

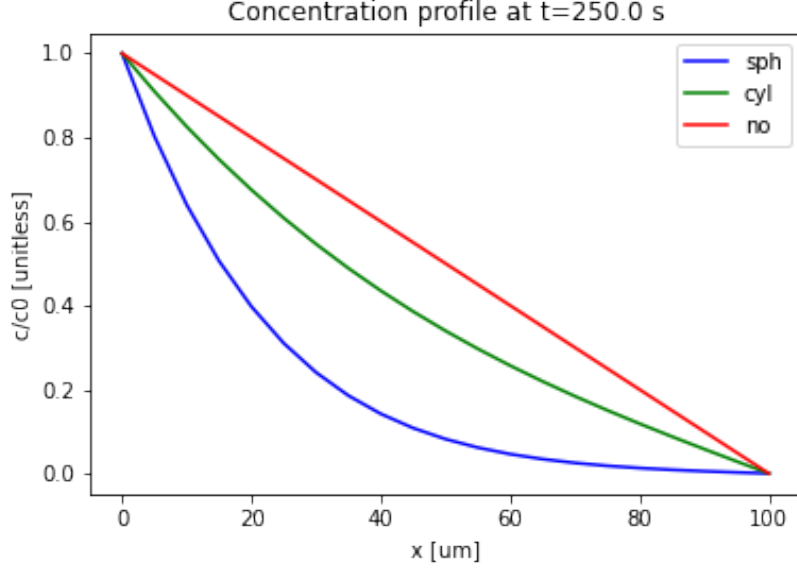
There are the results of a simulation of this model, with unit concentration at the inlet and zero concentration at the outlet.

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<sup>1</sup>can be finite differences, elements, or whatever

- Physical parameters (some taken from Olden)
  - $D - 6.0 \cdot 10^{-1} \mu m^2/s$
  - $\alpha - 1.4 \cdot 10^{-4} \mu m^2/s$
  - $K - 32.51/0.033$
  - $R = 5 \mu m$
  - $\Gamma - 0.0007639437268410977 \mu m^{-3}$  (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





## A Transform approaches

### A.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

$$\mathcal{F}_t\left(\frac{\partial}{\partial t}c(x, t)\right)(s) = 2\pi isC(x, s) \quad (39)$$

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_{\text{t}} c')(x, t)\right) = C(x, s) \sum_{k=1}^{\infty} \frac{1}{1 - i \frac{\alpha \pi^2 k^2}{2R^2 \pi s}}, \quad (40)$$

or

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_{\text{t}} c')(x, t)\right) = C(x, s) \sum_{k=1}^{\infty} \frac{1}{1 + \left(\frac{\alpha \pi^2 k^2}{2R^2 \pi s}\right)^2} \left(1 + i \frac{\alpha \pi^2 k^2}{2R^2 \pi s}\right), \quad (41)$$

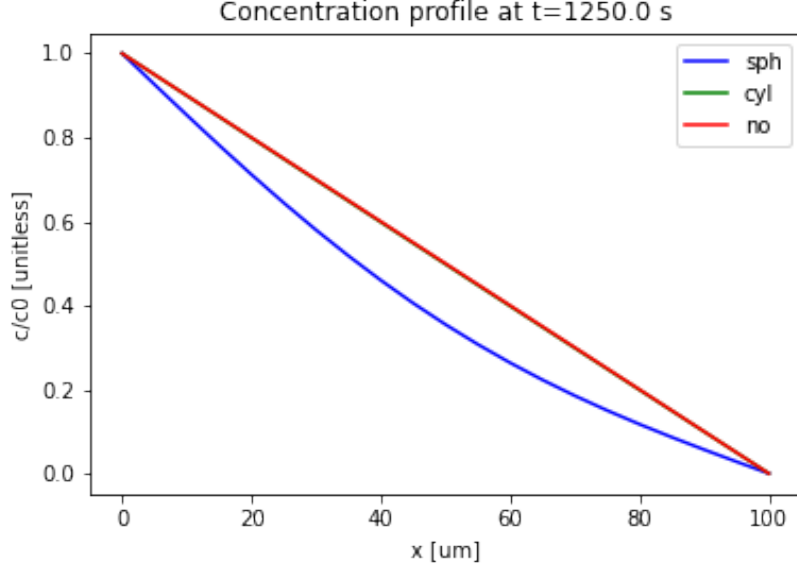
and the diffusive term stays the same. Hence, joining everything

$$C(x, s)\zeta(s) = D \frac{\partial^2 C}{\partial x^2}(x, s), \quad (42)$$

with

$$\zeta(s) = 2\pi is + 8\pi R\Gamma\alpha K \sum_{k=1}^{\infty} \frac{1}{1 - i \frac{Ak^2}{s}}; \quad A = \frac{\alpha \pi}{2R^2} \quad (43)$$





## A.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

$$\mathcal{L}_t \left( \frac{\partial}{\partial t} c(x, t) \right) (s) = s\mathcal{C}(x, s) - c(x, 0), \quad (44)$$

and

$$\mathcal{L}_t \left( \sum_{k=1}^{\infty} (\omega_k *_{t} c')(x, t) \right) = (s\mathcal{C}(x, s) - c(x, 0)) \sum_{k=1}^{\infty} \frac{1}{1 + \frac{\alpha \pi^2 k^2}{R^2} s} \quad (45)$$

$$\sum_{k=1}^{\infty} \frac{1}{1 + \frac{\alpha \pi^2 k^2}{R^2} s} = \frac{1}{2} \left( \sqrt{\frac{R}{\alpha}} s^{-1/2} \coth \left( \sqrt{\frac{R}{\alpha}} s^{-1/2} \right) - 1 \right). \quad (46)$$

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

$$\begin{aligned} \mathcal{C}(x, s) \xi(s) &= \frac{\partial^2 \mathcal{C}}{\partial x^2}(x, s) \\ \xi(s) &= \frac{s}{D} \left( 1 + \frac{\beta}{2} \left( \sqrt{\frac{R}{\alpha s}} \coth \left( \sqrt{\frac{R}{\alpha s}} \right) - 1 \right) \right). \end{aligned} \quad (47)$$

We must have

$$\mathcal{C}(x, s) = A(s)e^{\sqrt{\xi(s)}x} + B(s)e^{-\sqrt{\xi(s)}x} \quad (48)$$

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

$$\begin{bmatrix} 1 & 1 \\ e^{\sqrt{\xi(s)}L} & e^{-\sqrt{\xi(s)}L} \end{bmatrix} \begin{bmatrix} A(s) \\ B(s) \end{bmatrix} = \begin{bmatrix} c_0/s \\ 0 \end{bmatrix}, \quad (49)$$

We have that

$$\begin{aligned} A(s) &= \frac{e^{-\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \\ B(s) &= -\frac{e^{\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \end{aligned} \quad (50)$$

Then, we have that

$$\mathcal{C}(x, s) = \frac{c_0}{s \left( e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L} \right)} \left( e^{-\sqrt{\xi(s)}(L-x)} - e^{\sqrt{\xi(s)}(L-x)} \right) \quad (51)$$

Or, simplifying

$$\frac{c_0}{s} \frac{\sinh\left(\sqrt{\xi(s)}(L-x)\right)}{\sinh\left(\sqrt{\xi(s)}L\right)} \quad (52)$$

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