Solutions to the diffusion equation

Numerical integration (*not tested*)

- finite difference method
- spatial and time discretization
- initial and boundary conditions
- stability

Analytical solution for special cases

- plane source
- thin film on a semi-infinite substrate
- diffusion pair
- constant surface composition
Numerical integration of the diffusion equation (I)
Finite difference method. Spatial Discretization. Internal nodes.

For 1D thermal conduction let’s “discretize” the 1D spatial domain into \( N \) small finite spans, \( i = 1, \ldots, N \):

\[
\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} V_i = J_{i-1\rightarrow i} A_L - J_{i\rightarrow i+1} A_R
\]

Balance of particles for an **internal** \((i = 2 \div N-1)\) volume \(V_i\) (change in concentration during \(\Delta t\) due to the particle exchange with adjacent cells):

First Fick’s law:

\[
J_{i-1\rightarrow i} = -D \frac{C_i^t - C_{i-1}^t}{\Delta x}
\]

\[
J_{i\rightarrow i+1} = -D \frac{C_{i+1}^t - C_i^t}{\Delta x}
\]

\[
\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} V_i = -D \frac{C_i^t - C_{i-1}^t}{\Delta x} A_L - \left( -D \right) \frac{C_{i+1}^t - C_i^t}{\Delta x} A_R
\]

\[
V_i = \Delta x \Delta y \Delta z, A_L = A_R = \Delta y \Delta z
\]

\[
\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2}
\]
Numerical integration of the diffusion equation (II)
Finite difference method. Spatial Discretization. Internal nodes.

\[ \frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2} \]

Using this equation we can calculate unknown concentration at time \( t+\Delta t \) if we know concentrations at previous timestep \( t \).

The finite difference scheme that we discussed is called the explicit Forward Time Centered Space (FTCS) method, since the unknown temperature at node \( i \) is given explicitly in terms of only known temperatures computed at the previous timestep.

There is pair by pair cancellation of terms in the FTCS equation that ensures that whatever the number of diffusing species leaves one volume is picked up by its next-door neighbor.
**Numerical integration of the diffusion equation (III)**

Finite difference method. Spatial Discretization. **End nodes.**

Let’s consider the first node, \( i = 1 \) and let’s place the node at the surface.

Balance of particles for volume \( V_I \) that is represented by the end node:

\[
\frac{C_I^{t+\Delta t} - C_I^t}{\Delta t} V_I = - J_{1\rightarrow 2} A_R
\]

First Fick’s law:

\[
J_{1\rightarrow 2} = -D \frac{C_2^t - C_1^t}{\Delta x} A_R
\]

\[
\frac{C_I^{t+\Delta t} - C_I^t}{\Delta t} V_I = D \frac{C_2^t - C_1^t}{\Delta x} A_R
\]

\[
V_I = V_N = V_i = \frac{2^{N-1}}{2}, \quad \Delta x A_R = \Delta x \Delta y \Delta z = V_i = \frac{2^{N-1}}{2} = 2V_I
\]

\[
\frac{C_I^{t+\Delta t} - C_I^t}{\Delta t} = 2D \frac{C_2^t - C_1^t}{\Delta x^2}
\]
Numerical integration of the diffusion equation (IV)
Finite difference method. Spatial Discretization. End nodes.

\[
\frac{C_{1}^{t+\Delta t} - C_{1}^{t}}{\Delta t} = 2D \frac{C_{2}^{t} - C_{1}^{t}}{\Delta x^2}
\]

\[
C_{1}^{t+\Delta t} = C_{1}^{t} + \Delta t \cdot 2D \frac{C_{2}^{t} - C_{1}^{t}}{\Delta x^2}
\]

Similarly, for another end node \( N \), one can derive:

\[
C_{N}^{t+\Delta t} = C_{N}^{t} - \Delta t \cdot 2D \frac{C_{N}^{t} - C_{N-1}^{t}}{\Delta x^2}
\]

If an initial concentration profile at time \( t = 0 \) is given, we can use the derived equations for all nodes, from 1 to \( N \), to calculate concentration profile at time \( \Delta t, 2\Delta t, 3\Delta t \), etc. up to the time that we are interested in.
Stability criterion

Assuming that the coefficients of the differential equation are constant (or so slowly varying as to be considered constant) the stability criterion for

\[ C_i^{t+\Delta t} = C_i^t + \Delta t \cdot D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2} \]

is

\[
\frac{2D\Delta t}{\Delta x^2} \leq 1
\]

This condition is referred to as the Von Neumann stability condition.

Physical interpretation: the maximum timestep is, up to a numerical factor, the diffusion time across a cell of width \( \Delta x \) (remember Einstein relation \( D = s^2/2dt \)).

Position \((C, T, \ldots)\) dependent \(D(x,t)\)

For a position-dependent diffusion coefficient, it should be evaluated at the interfaces between the volumes \(V_i\) in order to preserve the conservation of the total number of particles

\[
\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D_{i+1/2} \left( C_{i+1}^t - C_i^t \right) - D_{i-1/2} \left( C_i^t - C_{i-1}^t \right)
\]

\[
\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = \frac{D_{i+1/2} C_{i+1}^t - C_i^t}{\Delta x^2} - \frac{D_{i-1/2} C_i^t - C_{i-1}^t}{\Delta x^2}
\]

e.g., for sample with non-uniform \(T\) distribution

\[
D_{i+1/2} = \frac{1}{2} \left[ D(T_{i+1}^t) + D(T_i^t) \right]
\]

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Simple boundary conditions

No mass transfer through the boundary:

\[ \left. \frac{\partial C}{\partial x} \right|_{x=L} = 0 \]

\[ J_{N \leftrightarrow N+1} = 0 \]

Constant concentration at the boundary \( C_L = C_f \) and we can use the following boundary condition:

\[ C \bigg|_{x=L} = C_f \]
**Diffusion equation in 2D**

\[
\frac{\partial C(x,y,t)}{\partial t} = D_x \frac{\partial^2 C(x,y,t)}{\partial x^2} + D_y \frac{\partial^2 C(x,y,t)}{\partial y^2}
\]

Boundary condition: \( C(x,y,t)|_{\text{boundary}} = C_b(x,y,t) \)

Initial condition: \( C(x,y,0) = C_{\text{init}}(x,y) \)
Diffusion equation in 2D: explicit FTCS scheme

$$\frac{\partial C(x,y,t)}{\partial t} = D_x \frac{\partial^2 C(x,y,t)}{\partial x^2} + D_y \frac{\partial^2 C(x,y,t)}{\partial y^2}$$

$$\frac{C_{i,j}^{t+\Delta t} - C_{i,j}^t}{\Delta t} = \frac{D_x}{\Delta x^2} \left( C_{i+1,j}^t - 2C_{i,j}^t + C_{i-1,j}^t \right) +$$

$$+ \frac{D_y}{\Delta y^2} \left( C_{i,j+1}^t - 2C_{i,j}^t + C_{i,j-1}^t \right)$$

$$C_{i,j}^{t+\Delta t} = C_{i,j}^t + \frac{D_x \Delta t}{\Delta x^2} \left( C_{i+1,j}^t - 2C_{i,j}^t + C_{i-1,j}^t \right) +$$

$$+ \frac{D_y \Delta t}{\Delta y^2} \left( C_{i,j+1}^t - 2C_{i,j}^t + C_{i,j-1}^t \right)$$

Stability: $$\frac{D_x \Delta t}{\Delta x^2} + \frac{D_y \Delta t}{\Delta y^2} \leq \frac{1}{2}$$

$$\Delta r_{2D} \sim \sqrt{4D \Delta t}$$
Diffusion equation in 3D: explicit FTCS scheme

\[
\frac{\partial C(x,y,z,t)}{\partial t} = D_x \frac{\partial^2 C(x,y,z,t)}{\partial x^2} + D_y \frac{\partial^2 C(x,y,z,t)}{\partial y^2} + D_z \frac{\partial^2 C(x,y,z,t)}{\partial z^2}
\]

\[
\frac{C_{i,j,k}^{t+\Delta t} - C_{i,j,k}^t}{\Delta t} = \frac{D_x}{\Delta x^2} \left( C_{i+1,j,k}^t - 2C_{i,j,k}^t + C_{i-1,j,k}^t \right) + \frac{D_y}{\Delta y^2} \left( C_{i,j+1,k}^t - 2C_{i,j,k}^t + C_{i,j-1,k}^t \right) + \frac{D_z}{\Delta z^2} \left( C_{i,j,k+1}^t - 2C_{i,j,k}^t + C_{i,j,k-1}^t \right)
\]

\[
C_{i,j,k}^{t+\Delta t} = C_{i,j,k}^t + \frac{D_x \Delta t}{\Delta x^2} \left( C_{i+1,j,k}^t - 2C_{i,j,k}^t + C_{i-1,j,k}^t \right) + \frac{D_y \Delta t}{\Delta y^2} \left( C_{i,j+1,k}^t - 2C_{i,j,k}^t + C_{i,j-1,k}^t \right) + \frac{D_z \Delta t}{\Delta z^2} \left( C_{i,j,k+1}^t - 2C_{i,j,k}^t + C_{i,j,k-1}^t \right)
\]

Stability:

\[
\frac{D_x \Delta t}{\Delta x^2} + \frac{D_y \Delta t}{\Delta y^2} + \frac{D_z \Delta t}{\Delta z^2} \leq \frac{1}{2}
\]

\[
\Delta r_{3D} \sim \sqrt{6D\Delta t}
\]
Possible algorithm for solving 1D diffusion equation

1. Initialize diffusion constant $D$, system size $L$, step of spatial discretization $\Delta x$, time-step $h$, and the total time of the simulation. You can use $N \sim 100$ steps in spatial discretization. Make sure that stability criterion is satisfied.

2. Define an initial concentration profile, $C_i^{0}$. Use an array to represent the concentration at discrete points $x_0, x_1, \ldots, x_N$ and set the value at each point equal to the initial concentration at that point.

3. At each node position except the two surface nodes calculate new concentration using the finite difference method described in the lecture notes, use a dummy array to store new concentration.

   $$C_{i}^{t+\Delta t} = C_{i}^{t} + \Delta t \cdot D \frac{C_{i+1}^{t} - 2C_{i}^{t} + C_{i-1}^{t}}{\Delta x^2}$$

   for $i = 2, \ldots, N-1$

4. Calculate concentration for the two surface nodes using boundary conditions appropriate for the problem of your choice. For example, for zero-flux surfaces we have:

   $$C_{1}^{t+\Delta t} = C_{1}^{t} + 2\Delta t \cdot D \frac{C_{2}^{t} - C_{1}^{t}}{\Delta x^2} \quad C_{N}^{t+\Delta t} = C_{N}^{t} - 2\Delta t \cdot D \frac{C_{N}^{t} - C_{N-1}^{t}}{\Delta x^2}$$

   Note, that 2 in the right term of these formulas result from the fact that the thickness of the first and last slices is $\Delta x/2$ rather than $\Delta x$.

5. Copy the dummy array into your concentration array.

6. Update current time = time + $h$

7. If the time is less than the time of the simulation, go to 3 and repeat.

8. Write data for plotting final concentration profile versus position. You can also write data several time during the simulation if you want to see the evolution of the concentration profile with time.
Analytical Solutions of the Diffusion Equation

While the numerical method described above can be applied to solve the diffusion equation for any initial and boundary conditions, in many special cases it is possible to derive analytic solutions as well. The advantage of analytical solution – does not involve long computations, gives clear picture of the dependence of the solution on different parameters in the whole range of $x$ and $t$.

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2}$$

Let’s consider the simple case of solute atoms initially inserted into the middle of an infinite one-dimensional system (plane source).

All solute is in one plane initially

With time the solute atoms will diffuse from the plane. The redistribution of the atoms can be described by the following solution of the diffusion equation:

$$C(x, t) = \frac{A}{\sqrt{t}} \exp \left( -\frac{x^2}{4Dt} \right)$$
Analytical solution for plane source

We can show by differentiation that for the plane source in an infinite system

\[ C(x, t) = \frac{A}{\sqrt{t}} \exp \left( -\frac{x^2}{4Dt} \right) \]

is the solution of the diffusion equation

\[ \frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \]
Analytical Solutions of the Diffusion Equation

\[ C(x, t) = \frac{A}{\sqrt{t}} \exp \left( - \frac{x^2}{4Dt} \right) \]
Analytical solution for plane source

Coefficient $A$ we can find from the condition that the total quantity of solute per unit of the cross-section area $S$ is

$$\frac{M}{S} = \int_{-\infty}^{+\infty} C(x, t) dx = \int_{-\infty}^{+\infty} \frac{A}{\sqrt{t}} \exp \left(-\frac{x^2}{4Dt}\right) dx$$

Using substitution of variable $y = \frac{x}{\sqrt{4Dt}}$ we have $dx = \sqrt{4Dt} dy$

$$M = \frac{AS}{\sqrt{t}} \int_{-\infty}^{+\infty} \exp \left(-y^2\right) dy = AS \sqrt{4D} \times \sqrt{\pi}$$

$$A = \frac{M}{S \sqrt{4\pi D}}$$

$$C(x, t) = \frac{M}{S \sqrt{2\pi Dt}} \exp \left(-\frac{x^2}{4Dt}\right)$$

The solution is a Gaussian concentration profile whose width increases with time.
Side-note: Derivation of Einstein relation for 1D case (not tested)

Let’s consider diffusion of particles that are initially concentrated at the origin of our coordination frame, \( C(x,0) = \delta(x) \) – Dirac delta function

Diffusion equation: \[ \frac{\partial}{\partial t} C(x,t) = D \frac{\partial^2}{\partial x^2} C(x,t) \]

Solution: \[ C(x,t) = \frac{1}{2 \sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \]

Let’s multiply the diffusion equation by \( x^2 \) and integrate over space:

\[ \frac{\partial}{\partial t} \int x^2 C(x,t) \, dx = D \int x^2 \frac{\partial^2 C(x,t)}{\partial x^2} \, dx \]

\[ \langle x^2(t) \rangle \]

\[ \frac{\partial \langle x^2(t) \rangle}{\partial t} = D \int x^2 \frac{\partial^2 C(x,t)}{\partial x^2} \, dx = D \int \frac{\partial}{\partial x} \left( x^2 \frac{\partial C(x,t)}{\partial x} \right) \, dx - \]

\[ - D \int \frac{\partial x^2}{\partial x} \frac{\partial C(x,t)}{\partial x} \, dx = D x^2 \frac{\partial C(x,t)}{\partial x} \bigg|_{-\infty}^{+\infty} - 2D \int x \frac{\partial C(x,t)}{\partial x} \, dx = \]

\[ = 0 - 2D \int \frac{\partial}{\partial x} (xC(x,t)) \, dx + 2D \int \frac{\partial x}{\partial x} C(x,t) \, dx = \]

\[ = - 2DxC(x,t) \bigg|_{-\infty}^{+\infty} + 2D \int C(x,t) \, dx = 2D \]

\[ \langle x^2(t) \rangle = 2Dt + A \quad \text{for 1D diffusion} \]
### Side-note: Derivation of Einstein relation for $d$ dimensions (not tested)

Let’s consider diffusion of particles that are initially concentrated at the origin of our coordination frame, $C(r,0) = \delta(r)$ - Dirac delta function

**Diffusion equation:**
\[
\frac{\partial C(r,t)}{\partial t} = D \nabla^2 C(r,t)
\]

**Solution:**
\[
C(r,t) = \frac{1}{(4\pi D t)^{d/2}} \exp \left( -\frac{r^2}{4Dt} \right)
\]

Let’s multiply the diffusion equation by $r^2$ and integrate over space:

\[
\frac{\partial}{\partial t} \left\langle r^2(t) \right\rangle = D \int r^2 \nabla^2 C(r,t) d\tilde{r} = D \int \nabla \cdot (r^2 \nabla C(r,t)) d\tilde{r} -
\]

\[
- D \int \nabla r^2 \cdot \nabla C(r,t) d\tilde{r} = D \int r^2 \nabla C(r,t) dS - 2D \int r \cdot \nabla C(r,t) d\tilde{r} =
\]

\[
= 0 - 2D \int \nabla \cdot (rC(r,t)) d\tilde{r} + 2D \int \nabla \cdot \tilde{r} C(r,t) d\tilde{r} =
\]

\[
= -2D \int \tilde{r} C(r,t) dS + 2dD \int C(r,t) d\tilde{r} = 2dD
\]

\[
\left\langle r^2(t) \right\rangle = 2dDt + A \quad \text{for diffusion in d-dimensional space}
\]
Side-note: Review of calculus used in previous page (not tested)

Gradient: \[ \vec{\nabla} \equiv \frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} + \frac{\partial}{\partial z} \hat{z} \]

Laplacian: \[ \nabla^2 \equiv \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]

Gradient of a scalar function: \[ \vec{\nabla} \Phi (\vec{r}) \equiv \frac{\partial \Phi}{\partial x} \hat{x} + \frac{\partial \Phi}{\partial y} \hat{y} + \frac{\partial \Phi}{\partial z} \hat{z} \]

Divergence of a vector function: \[ \vec{\nabla} \cdot \vec{F} (\vec{r}) \equiv \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \]

\[ \vec{\nabla} \cdot \left( \Phi (\vec{r}) \vec{F} (\vec{r}) \right) = \Phi (\vec{r}) (\vec{\nabla} \cdot \vec{F} (\vec{r})) + \left( (\vec{\nabla} \Phi (\vec{r})) \cdot \vec{F} (\vec{r}) \right) \]

The divergence theorem: \[ \int_V \vec{\nabla} \cdot \vec{F} (\vec{r}) d\vec{r} = \int_S \vec{F} (\vec{r}) d\vec{S} \]

L’Hôpital’s rule: if \( \lim \frac{g(x)}{f(x)} \) result in the indeterminate form \( 0/0 \) or \( \infty/\infty \), then
\[ \lim \frac{g(x)}{f(x)} = \lim \frac{dg}{dx} \]

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Thin film deposited on a semi-infinite piece of material

\[ \frac{\partial C}{\partial x} \bigg|_{x=0} = 0 \]

Using the same solution we have a different condition for coefficient A:

\[ M = S \int_{0}^{+\infty} \frac{A}{\sqrt{t}} \exp \left( - \frac{x^2}{4Dt} \right) dx \]

Using substitution of variable \( y = \frac{x}{\sqrt{4Dt}} \)

\[ M = \frac{AS \sqrt{4Dt}}{\sqrt{t}} \int_{0}^{+\infty} \exp \left( - y^2 \right) dy = AS \sqrt{4D} \times \frac{\sqrt{\pi}}{2} \]

\[ A = \frac{M}{S \sqrt{\pi} \ D} \]

\[ C(x, t) = \frac{M}{S \sqrt{\pi} \ D t} \exp \left( - \frac{x^2}{4Dt} \right) \]

The solution is a half of a Gaussian concentration profile.

At the surface, the boundary condition

\[ \frac{\partial C}{\partial x} \bigg|_{x=0} = 0 \]

is satisfied
Think of the block of B as being made up of many thin layers of thickness $\Delta x$ and cross-sectional area $S$. Each layer initially contains $C_1 S \Delta x$ of B atoms. We know that if the areas surrounding a layer are initially B-free, the distribution of solute atoms that originate from a thin layer can be described by the Gaussian profile. Assuming that the presence of other solutes (atoms of type B) do not affect the diffusion of atoms that originate from the layer, the overall solution can be found as superposition of the Gaussian profiles from the layers.

\[
C(x, t) = \sum_{i=1}^{n} \frac{C_1 \Delta x S}{S 2 \sqrt{\pi} Dt} \exp \left( - \frac{(x + x_i)^2}{4Dt} \right)
\]
Analytical solutions: Pair of Semi-infinite Solids (II)

\[
C(x, t) = \sum_{i=1}^{n} \frac{C_1 \Delta x S}{S 2\sqrt{\pi} Dt} \exp\left(-\frac{(x + x_i)^2}{4Dt}\right)
\]

In the limit of \( n \) going to infinity and \( \Delta x \) going to zero we can go from the sum to an integral.

\[
C(x, t) = \frac{C_1}{2\sqrt{\pi} Dt} \int_{0}^{\infty} \exp\left(-\frac{(x + w)^2}{4Dt}\right)dw
\]

Substituting \( \frac{x + w}{2\sqrt{Dt}} = u \) we can rewrite the integral:

\[
C(x, t) = \frac{C_1}{\sqrt{\pi}} \int_{x/2\sqrt{Dt}}^{\infty} e^{-u^2} du = \frac{C_1}{\sqrt{\pi}} \left( \int_{x/2\sqrt{Dt}}^{0} e^{-u^2} du + \int_{0}^{\infty} e^{-u^2} du \right)
\]

Using definition of the error function:

\[
\text{erf} (z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} \exp \left(- y^2 \right) dy
\]

and taking into account that \( \text{erf} (\infty) = 1 \) and \( \text{erf} (-z) = -\text{erf} (z) \)

\[
C(x, t) = \frac{C_1}{2} \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right]
\]
Analytical solutions: Constant surface composition (I)

\[ C\bigg|_{x=0} = C_s \quad \text{and} \quad C\bigg|_{x=\infty} = C_0 \]

A similar solution of the diffusion equation can be derived for a constant surface concentration. If the initial concentration of solute atoms in the specimen is \( C_0 \) and concentration at the surface is \( C_s \), the analytical solution of the Fick’s second law is

\[
C = C_s - (C_s - C_0) \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

where \( \operatorname{erf} \) is the error function defined by the following equation:

\[
\operatorname{erf} (z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp \left(-y^2\right)dy
\]

The error function is tabulated in books of standard mathematical functions and is defined as an internal function in some of programming languages.

\[
\begin{align*}
\operatorname{erf} (z) &= 1 \quad \text{for } z = \infty \\
\operatorname{erf} (z) &= 0 \quad \text{for } z = 0 \\
\operatorname{erf} (z) &= 0.5 \quad \text{for } z = 0.5
\end{align*}
\]
Summary

Make sure you understand language and concepts:

Numerical integration of the diffusion equation \textit{(not tested)}

- Finite difference method
- Spatial and time discretization
- Initial and boundary conditions
- Stability criterion

Analytical solutions for special cases

- plane source
- thin film on a semi-infinite substrate
- diffusion pair
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