

6 Diffusion

In Section 4 we covered the thermodynamic basis for phase equilibrium. To further understand microstructural evolution, we need to consider **kinetic** aspects, in particular how atoms can rearrange to allow phase changes. For many (although not all) phase transformations, the key mechanism is **diffusion**.

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In this section, we cover:

- the fundamentals of diffusion and its microscopic mechanisms;
- the temperature dependence of these processes;
- how diffusion influences the rate of phase transformation;
- a constitutive model for diffusion, Fick's law and the diffusion equation.

In Section 7 models of diffusion relevant to materials processing are described, with an application to silicon doping. Later in the course the role of diffusion in other processing procedures is highlighted.

6.1 Brownian motion: the microscopic driver of diffusion

Diffusion is the **thermally assisted** random migration of atoms (or molecules) through a material. It is a familiar process in liquids or gases, where there is clearly space in the medium for atoms to migrate. A key concept in diffusion is that the net flow of atoms in a material depends on gradients in concentration. To introduce this idea, consider either a liquid or gas (though we will see later that the same idea holds for solids) where the average concentration of atoms or molecules varies spatially:

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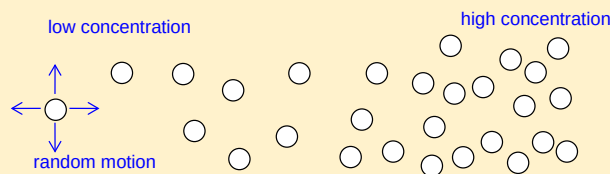


Figure 41: Concentration gradient in a material.

Each molecule undergoes random motion characterised by two parameters:

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- A length scale λ : in a gas this could represent the mean free path, in a liquid it might represent a mean atomic spacing.
- A time scale τ : in a gas this might represent the time between molecular collisions, in a liquid $1/\tau$ might be the frequency of atomic oscillations.

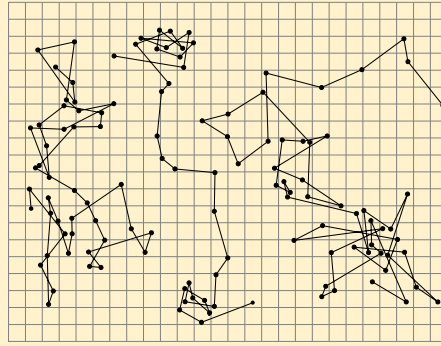


Figure 42: Reproduced from the book of Jean Baptiste Perrin, *Les Atomes*, three tracings of the motion of colloidal particles of radius $0.53 \mu m$, as seen under the microscope, are displayed. Successive positions every 30 seconds are joined by straight line segments (the mesh size is $3.2 \mu m$). Source: Wikipedia, drawing by Mirai Warren.

Brownian motion

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- The resulting random trajectory of a diffusing particle due to thermal fluctuations is called Brownian motion.
- It is this microscopic behaviour that leads to the macroscopic process of diffusion.
- How do we link the two together?

Diffusion as a random walk

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- The trajectories of diffusing particles are analogous to the configurations of polymers. Moving along a random chain one monomer at a time is like following a particle one hop at a time.
- We found in a 1D model that the end-to-end distance of a polymer with n monomers of size a was normally distributed, with mean 0 and standard deviation $\sigma^2 = na^2$.
- If we place a diffusing molecule at the origin and wait for a time t , it has made t/τ step of size λ .
- Its position at this time is random but distributed on a normal distribution centered on the origin, with standard deviation $\sigma^2 = \frac{t}{\tau}\lambda^2$.

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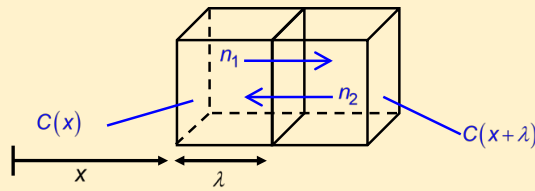
- The molecular constant $\frac{\lambda^2}{\tau}$ is a coefficient of diffusion. It captures the rate at which diffusion occurs.

- During a time t , particles move in average over a distance of the order of:

$$\sqrt{\frac{\lambda^2}{\tau} t}$$

- The exact relationship depends on the details of the model, and the dimension of the problem (1D/2D/3D).

6.2 Molecular origin of the diffusive flux



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Figure 43: Diffusion of molecules in a concentration gradient.

Consider a small cube of material of volume λ^3 at a position in space (x, y, z) . The concentration of molecules in the cube is $C(x)$ molecules / m^3 . On average, in time τ all of the molecules originally in the cube will have left through random motion.

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The number of molecules n_1 moving to the right (the positive x -direction) out of this cube in time τ will be $1/6$ of the total in the cube, as molecules are equally likely to move in any direction in space:

$$n_1 = \frac{1}{6} \lambda^3 C(x) \quad (38)$$

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Consider a second cube adjacent to the first. This has concentration $C(x + \lambda)$ molecules/ m^3 . Assuming τ and λ don't change significantly, the number of molecules n_2 moving to the left out of this cube in time τ is:

$$n_2 = \frac{1}{6} \lambda^3 C(x + \lambda) \quad (39)$$

The net **flux** of molecules J_x (molecules per second per unit area) travelling in the positive x -direction is given by:

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$$J_x = \frac{n_1 - n_2}{\lambda^2 \tau} = -\frac{\lambda}{6\tau} (C(x + \lambda) - C(x)) \quad (40)$$

But λ is a small distance, so we may consider a Taylor series expansion:

$$C(x + \lambda) = C(x) + \frac{\partial C}{\partial x} \lambda + \dots \quad (41)$$

The net **flux** of molecules J_x (molecules per second per unit area) travelling in the positive x -direction is therefore:

$$J_x = -\frac{\lambda^2}{6\tau} \frac{\partial C}{\partial x} \quad (42)$$

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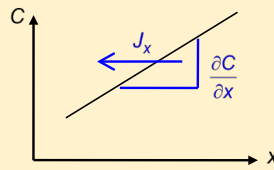


Figure 44: Diffusion of molecules in a concentration gradient.

Therefore, by random motion of atoms alone, we would expect a net flow from areas of high concentration to areas of low concentration at a rate proportional to the gradient of concentration. This is a key concept for diffusion.

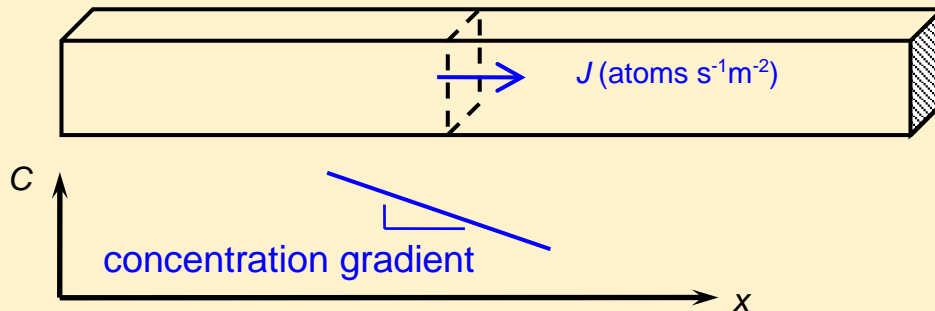
As in the previous section, we find again that the constant $\frac{\lambda^2}{\tau}$ is an important physical parameters that characterises how strong the diffusive flux will be for a given gradient.

6.3 Continuum model: the Diffusion Equation

Fick's First Law

Consider the 1D diffusion problem sketched below.

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We can generalise the simplistic model presented previously by introducing an empirical proportionality factor between the flux of atoms and the concentration gradient, which is called **Fick's first law** for the net flux of atoms J (atoms s⁻¹m⁻²):

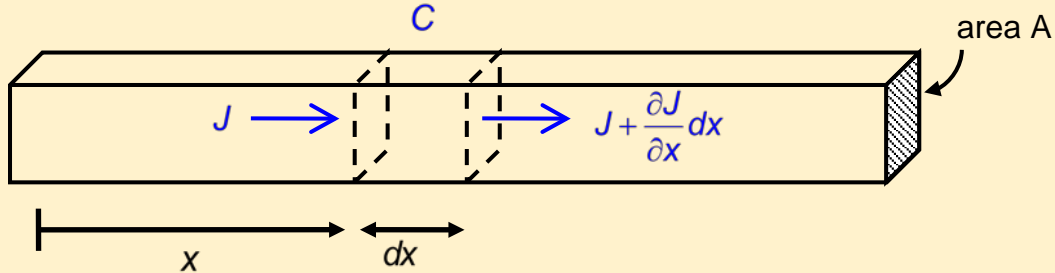
$$J = -D \frac{dC}{dx} \quad (43)$$

The direction of flow is down the concentration gradient, from high to low concentration. The constant of proportionality D is known as the diffusion coefficient (units: m²s⁻¹).

Fick's Second Law

In many problems the concentration profile $C(x, t)$ evolves with time as atoms diffuse through the material. Consider now a small control volume of length dx .

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The number of diffusing atom in the control volume is $n_{cv} = A dx C(x, t)$. During a time dt , its change is:

$$dn_{cv} = A dx dC$$

By conservation of the mass, this change must be equal to the net flow in and out of this volume at x and $x + dx$:

$$dn_{cv} = J(x, t) A dt - J(x + dx) A dt = - \frac{\partial J}{\partial x} dx A dt$$

Here, we have again applied the Taylor series expansion of J . Combining these two equations gives:

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$$\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x} \quad (44)$$

Now substitute for J from Fick's first law to obtain **Fick's second law**:

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} \left(-D \frac{\partial C}{\partial x} \right)$$

For uniform D we get the so-called diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (45)$$

6.4 Relating the continuum and microscopic behaviours**Dispersion of particles**

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- We have seen that a single particle follows a random walk, leading to its dispersion overtime that follows a normal distribution with $\sigma^2 \propto t$. Is this consistent with the diffusion equation?

- In a continuum model, we may model a set amount of material at a given location as a delta function of the concentration at $t = 0$.
- What is the solution of the diffusion equation for $C(x, t = 0) = \delta(x)$?

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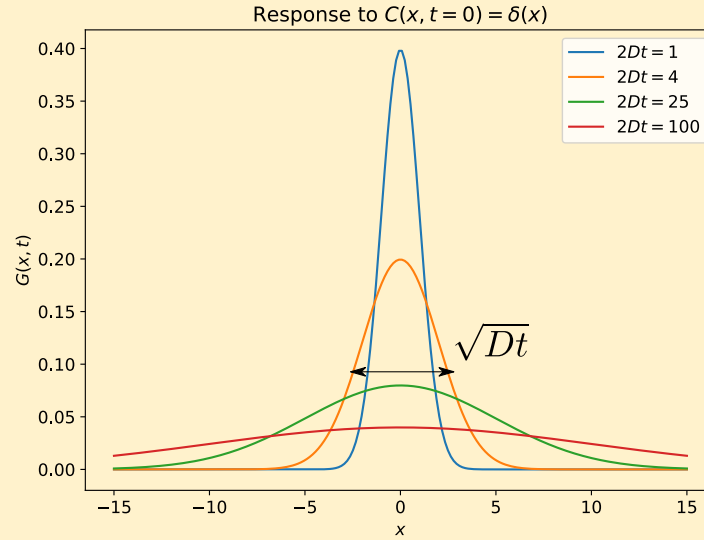


Figure 45: Evolution of the concentration profile for a point source at $t = 0$. The width of the profile is approximatively \sqrt{Dt} .

- We can show that the following function is solution (see how to prove it below):

$$C_{\delta}(x, t) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right) \text{ with } \sigma^2 = \langle x^2 \rangle = 2Dt$$

- The solution is a Normal distribution of mean $\mu = 0$ and variance $\sigma^2 = 2Dt$: $C_{\delta}(x, t) = \mathcal{N}(0, 2Dt)$.

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- This shows that a particule would indeep diffuse with a displacement following a normal distribution.
- By comparision with the 1D derivation for random walks, we find that:

$$D = \frac{1}{2} \frac{\lambda^2}{\tau}$$

Proof (for information)

To prove that $C_\delta(x, t) = \mathcal{N}(0, 2Dt)$ is solution of the diffusion equation, the partial derivatives can be calculated:

$$\begin{aligned}\frac{\partial c}{\partial x} &= \frac{1}{2\sqrt{\pi Dt}} \frac{-x}{2Dt} e^{-x^2/4Dt} \\ \frac{\partial^2 c}{\partial x^2} &= \frac{1}{2\sqrt{\pi Dt}} \frac{x^2}{4D^2t^2} e^{-x^2/4Dt} - \frac{1}{4\sqrt{\pi}(Dt)^{3/2}} e^{-x^2/4Dt} \\ \frac{\partial c}{\partial t} &= \frac{1}{2\sqrt{\pi Dt}} \frac{x^2}{4Dt^2} e^{-x^2/4Dt} - \frac{1}{4\sqrt{\pi Dt^{3/2}}} e^{-x^2/4Dt}\end{aligned}$$

and then inserted in the diffusion equation to check that:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Summary

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- The stochastic nature of microscopic movements leads to diffusive transport at large length-scales.
- Diffusive transport can be mathematically modelled at large length scale with Fick's first and second laws. Given a concentration profile $C(x)$ (1D case) of a particular component in a given material, one can define a coefficient of diffusion D such that the diffusive flux $J(x)$ is given by:

$$J = -D \frac{\partial C}{\partial x}$$

Combined with a mass conservation argument, we get the diffusion equation:

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

- Particles spread over a distance in the order of \sqrt{Dt} over a duration t .
- The coefficient relates to the microscopic dynamics in terms of a mean-free path or jump size, and time between collisions/jumps.

6.5 Mechanisms of diffusion in solids

6.5.1 Processes involved

Diffusion is also of fundamental importance in solids. Examples where diffusion in solids plays a role appear in all sections of this course:

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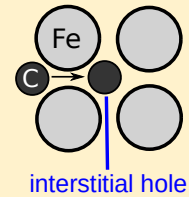
- Microstructure evolution: phase transformations, precipitation, grain growth.
- Manufacturing processes: welding, heat treatment, annealing, sintering (powder processing), “case hardening” steels, doping silicon.
- Material deformation: high temperature deformation (creep) of metals.

The mechanisms by which atoms can move through a solid are more complicated than in gases or liquids due to the tightly packed atomic structure. There are four major diffusion mechanisms in solids, two “bulk” mechanisms and two “short circuit” routes.

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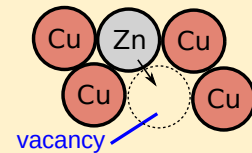
(1) **Bulk interstitial diffusion:** Small interstitial solute atoms move between the interstitial sites in a crystal lattice. The solute atom needs to have a sufficiently small atomic size compared to the bulk crystal. Example: C in Fe.

Diffusion rate: **fast** (large number of available adjacent sites)



(2) **Bulk vacancy diffusion:** Substitutional solute atoms exchange places with a vacancy in the crystal structure. Relevant to atoms of a similar atomic size. Example: Zn in Cu.

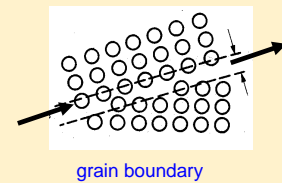
Diffusion rate: **slow** (number of free adjacent sites is relatively small)



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(3) **Short-circuit diffusion along a grain boundary:** Grain boundaries are areas where the crystal packing is more open, providing a faster route. This route is planar (2D).

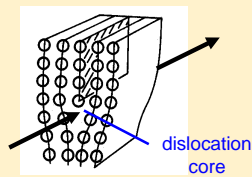
Diffusion rate: **fast** (open crystal structure)



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(4) **Short-circuit diffusion along dislocation cores:** The atom spacing around a dislocation core exceeds that in a perfect crystal. This route is linear (1D).

Diffusion rate: **fast** (open crystal structure)

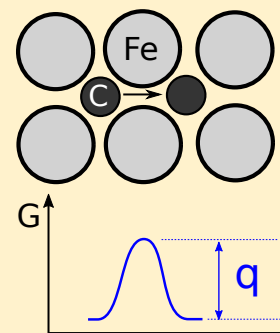


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6.5.2 Effect of temperature

Consider the interstitial bulk diffusion of carbon in iron. For the interstitial C atom to move in the Fe lattice from one interstice to another it needs to overcome an energy barrier:

- Positions A and B: favourable location in a lattice hole, minimum in G
- In between: unfavourable location for the C atom, higher free energy
- Energy barrier: q (J / atom)



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Atoms are constantly vibrating about their mean position at a frequency $\nu \approx 10^{13}$ Hz. The average energy per atom (kinetic plus potential energy):

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$$E = 3k_B T \quad (46)$$

k_B is Boltzmann's constant $1.38 \times 10^{-23} \text{ J atom}^{-1} \text{ K}^{-1}$

T is the absolute temperature (K)

However, there is a statistical distribution in the amount of energy per atom. The probability p of an atom having an energy greater than q is:

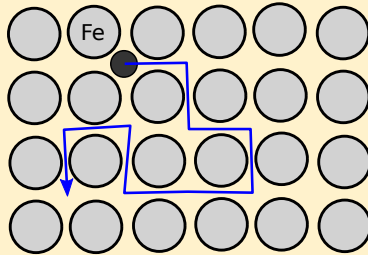
$$p = \exp\left(-\frac{q}{k_B T}\right) \quad (47)$$

Hence, as the atoms vibrate, atoms can move over the energy barrier with a probability that is strongly temperature dependent.

Transport in solids and liquids

Considering again the example of carbon atoms in iron with concentration C . There is here equal probability that an atom can jump in either direction but we expect that a concentration gradient of carbon will lead to a net flow.

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- the mean free path λ will be the distance between interstitial holes,

- the time τ between random steps will be $1/\tau \propto p = \exp(-\frac{q}{k_B T})$.

We get:

$$J_x = -\frac{\lambda^2}{6\tau} \frac{\partial C}{\partial x} \propto \exp\left(-\frac{q}{k_B T}\right) \frac{\partial C}{\partial x} \quad (48)$$

Arrhenius Law

Processes which follow this type of exponential temperature dependence are known as thermally activated. A definition of a thermally activated process is given by the **Arrhenius law** :

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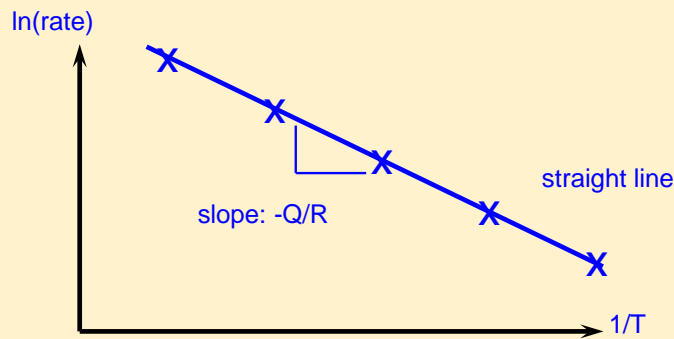
$$\text{rate of process} \propto \exp\left(-\frac{Q}{RT}\right) \quad (49)$$

$Q = \mathcal{N}_A q$ is the activation energy in J mol^{-1} for the diffusion mechanism (switching from J atom^{-1} using Avogadro's number)

$R = \mathcal{N}_A k_B$ is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, switching from Boltzmann's constant k in $\text{J atom}^{-1} \text{ K}^{-1}$ using Avogadro's number)

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To determine if a process obeys the Arrhenius law, we measure the rate at a number of different temperatures and plot the results on an Arrhenius graph:



The slope of the graph is $-Q/R$ and the measured value of Q informs us of the active mechanism of diffusion, e.g. interstitial or substitutional, and the atomic species involved:

- Interstitial diffusion of C in α -Fe (ferrite, BCC): $Q = 80$ kJ/mol
- Substitutional diffusion of Fe in α -Fe: $Q = 251$ kJ/mol
- Substitutional diffusion of Cu in Al (used in Al alloys): $Q = 136$ kJ/mol

The coefficient of diffusion in solids follows the Arrhenius law:

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$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (50)$$

D_0 is the **diffusion constant** (units: m^2s^{-1}). This is a material property which depends on the type of diffusing atom and the material through which it diffuses. Some typical values:

- Interstitial diffusion of C in α -Fe (ferrite, BCC): $D_0 = 6.2 \times 10^{-7} \text{ m}^2\text{s}^{-1}$
- Substitutional diffusion of Fe in α -Fe: $D_0 = 2.8 \times 10^{-4} \text{ m}^2\text{s}^{-1}$
- Substitutional diffusion of Cu in Al: $D_0 = 6.5 \times 10^{-5} \text{ m}^2\text{s}^{-1}$

Forces driving transport

It is also possible to get net flow as a result of a thermodynamic driving force that would tilt the energy landscape and bias the probabilities to go over an energy barrier. Possible driving forces are:

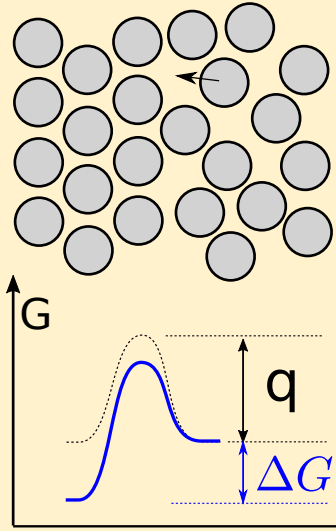
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- change of free energy due to a phase transformation (introduced in the next section),
- surface energy (the reduction of surface area and therefore the surface energy penalty, as observed in grain growth and the sintering of powders).

- stress field (observed for example in the creep of metals under stress at high temperatures).
- electric field (seen in electric resistivity or galvanic corrosion (see next lectures), driving the movement of ions).

6.6 Rates of phase transformations

6.6.1 Growth rate of a solid-liquid interface for $T < T_m$



When atoms move across a solid-liquid interface:

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- The variation of free energy per atom is $\pm \Delta G$
- The rate of transition from liquid to solid is given by:

$$p_{LS} = \exp \left(-\frac{q - \Delta G/2}{k_B T} \right) \quad (51)$$

- The rate of transition from solid to liquid is given by:

$$p_{SL} = \exp \left(-\frac{q + \Delta G/2}{k_B T} \right) \quad (52)$$

The growth rate of the solid phase will be proportional to $p_{LS} - p_{SL}$.

$$p_{LS} - p_{SL} \propto \exp \left(-\frac{q - \Delta G/2}{k_B T} \right) - \exp \left(-\frac{q + \Delta G/2}{k_B T} \right) \approx \frac{\Delta G}{k_B T} \exp \left(-\frac{q}{k_B T} \right)$$

Recalling that $\Delta G(T) \approx \Delta H \cdot \left(\frac{T_m - T}{T_m} \right)$ for $T < T_m$, we get:

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$$\text{growth rate of the solid} \propto \frac{T_m - T}{T} \exp \left(-\frac{q}{k_B T} \right)$$

The rate of growth of the solid increases with both temperature and the undercooling. These two effects oppose each other and the optimum rate is found for an intermediate temperature.

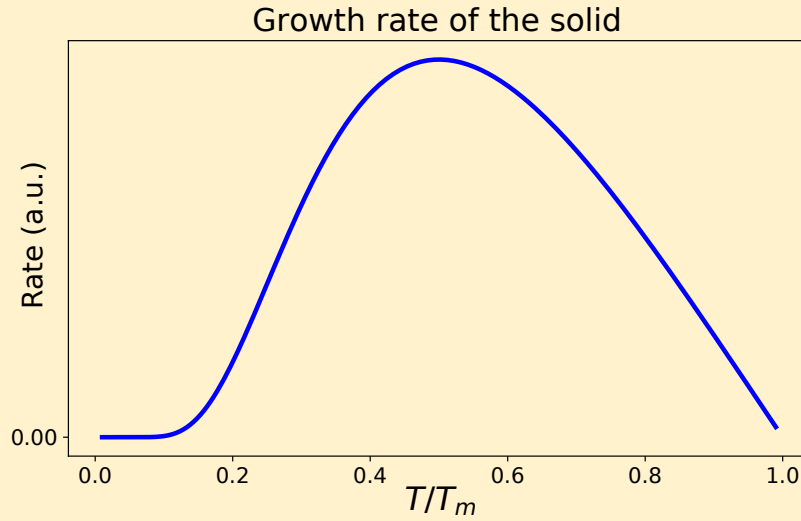


Figure 46: Growth rate of the solid (a.u.) as a function of temperature.

6.6.2 Rates of nucleation

Nucleation is another example of activated process.

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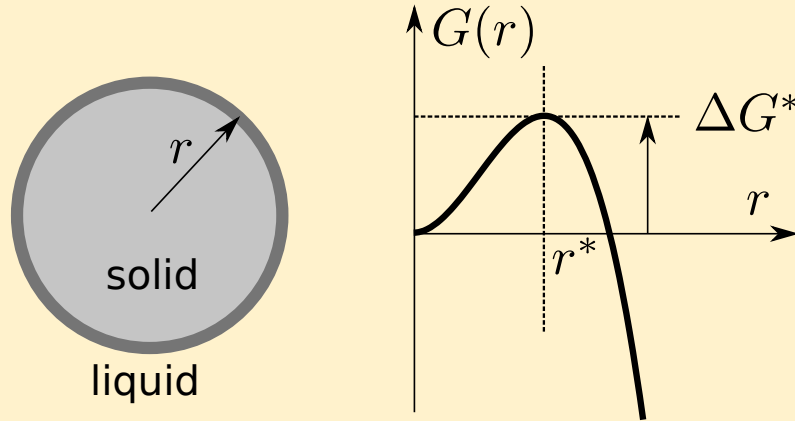


Figure 47: The Gibbs Free energy curve defines the activation energy required to create a stable nucleus.

We have seen that a nucleus of a radius larger than a critical radius r^* is required to initiate solidification. For this to happen, a free energy $\Delta G^* = G(r^*)$ is needed:

$$\Delta G^* = G(r^*) = \frac{16\pi\gamma^3 T_m^2}{3\Delta H_v^2 (T_m - T)^2} \propto \frac{1}{(T_m - T)^2}$$

We can see that ΔG^* becomes very large near the melting temperature T_m . At a qualitative level, nucleation requires:

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- some small scale fluctuations to get atoms to move around (as in the previous sections),

- the fluctuations of energy of the order of ΔG^* , bringing together a nucleus of size r^*

The rate is therefore expected to vary with temperature as:

$$\text{rate of nucleation} \propto \exp\left(-\frac{\Delta G^*}{k_B T}\right) \cdot \exp\left(-\frac{q}{k_B T}\right) \quad (53)$$

As in the case of the growth of the solid phase in the previous section, we see that the optimum rate corresponds to a balance between maximising atomic fluctuations (large T) and minimising r^* or ΔG^* . This is achieved by using large temperatures but not too close to the melting temperature as nucleation becomes very difficult in this region.

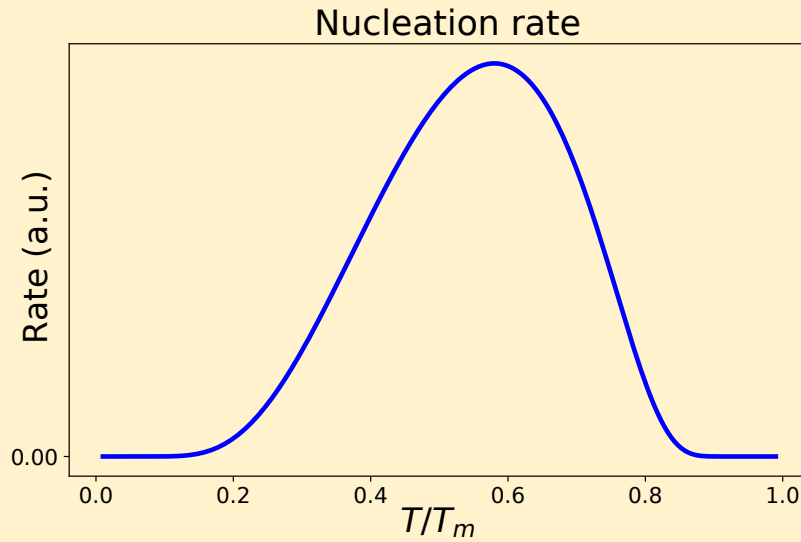


Figure 48: Nucleation rate (a.u.) as a function of temperature.

Summary

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- In solids, different mechanisms lead to transport, in the bulk (interstitial or vacancy) or along specific short-circuit paths due to grain boundaries or dislocations.
- Microscopic rearrangements in solids require thermal fluctuations to overcome a energy barrier. At temperature T , the probability to overcome an energy barrier q is:

$$p = \exp\left(-\frac{q}{k_B T}\right)$$

- This causes the rate of many transport processes to follow the same dependence with temperature, called Arrhenius law:

$$\text{rate of process} \propto \exp\left(-\frac{Q}{RT}\right)$$

- Considering the rate of phase transformations, a trade-off is observed. Temperature should be large enough to promote atomic movements, and not too close to T_m so that there is a sufficient thermodynamic driving force.

7 Diffusion in materials processing - Case study

7.1 Silicon doping

In order to illustrate the most relevant solutions of the diffusion equation in material sciences, we will look at an important industrial process, silicon doping.

Semiconductor behaviour

Electrical materials can be divided into three classes:

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- **Conductors** e.g. metals. Contain large concentrations of free, mobile conduction electrons which transport charge by moving in an electric field: resistivities are low.
- **Insulators** e.g. ceramics. Contain almost no free electrons: high resistivities.
- **Semiconductors** e.g. silicon. Contain some mobile charge carriers: resistivities are intermediate between metals and insulators. At $T = 0\text{ K}$, each atom in pure silicon is covalently bonded to four others, and there are no free conduction electrons. As the temperature is increased, an increasing number of atoms become ionised, freeing an electron to move through the lattice: the conductivity increases. A “hole”, effectively a positive charge, is left in the covalent bond, which can also migrate through the lattice.

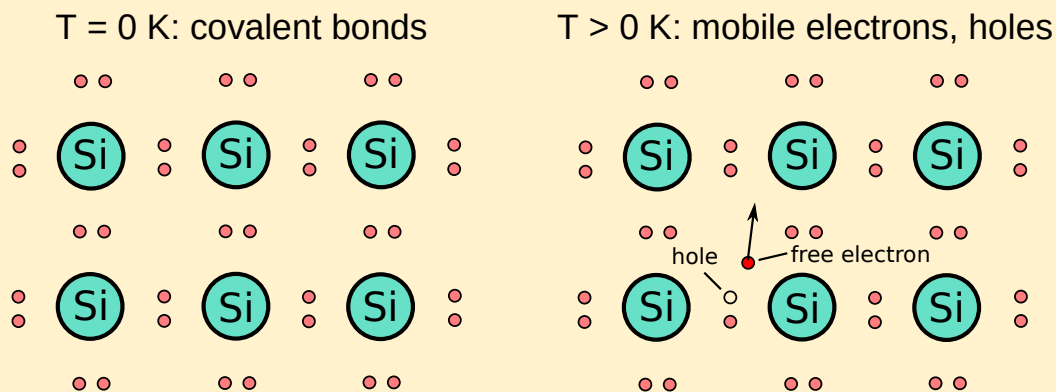


Figure 49: Atomic structure and electronic configuration of silicon at $T = 0\text{ K}$ and $T > 0\text{ K}$.

Silicon doping

The real value of semiconductors lies in the ability to modify their conductivity through a process called doping. The aim of doping is to add an impurity in order to generate additional free electrons or holes. There are two types:

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- n-type: replacing a Si atom with a phosphorous (P) atom leaves the covalent bond with one extra electron, which is free to migrate.
- p-type: replacing a Si atom with a boron (B) atom leaves the covalent bond short of one electron, generating a hole.

Production of doped semiconductors is achieved by solid state diffusion of dopant atoms into high purity Si. This occurs in two steps:

- pre-deposition: **sets the amount of dopant;**
- drive-in: **spreads the dopant across the material.**

Pre-deposition

Dopant is diffused into the surface by maintaining a high concentration of dopant at the surface (from a gas, or a surface deposit). Diffusion depths are small compared to the treated area.

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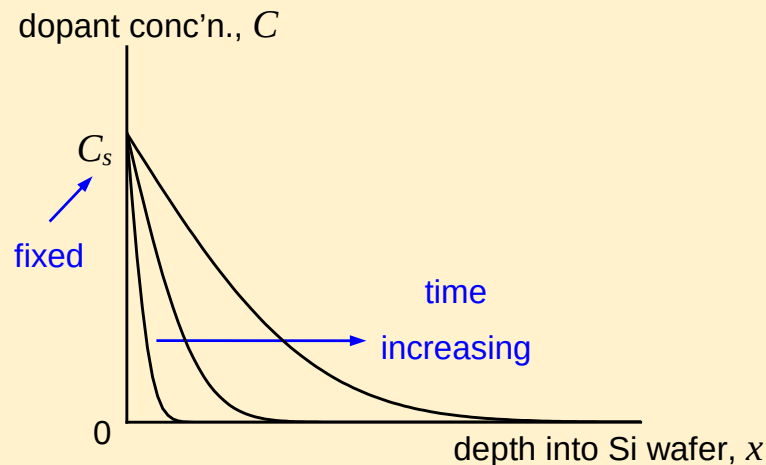


Figure 50: Qualitative evolution of the dopant concentration profile over time.

The process is conducted at high temperature ($> 900^\circ\text{C}$) to give a viable rate of diffusion.

How long should pre-deposition last to insert a controlled amount N of dopant in the silicon?

Drive-in

In this stage, the surface supply of dopant is removed, and the temperature is increased, to diffuse the pre-deposited atoms much further into the material. The aim is to produce a near-uniform distribution of dopant.

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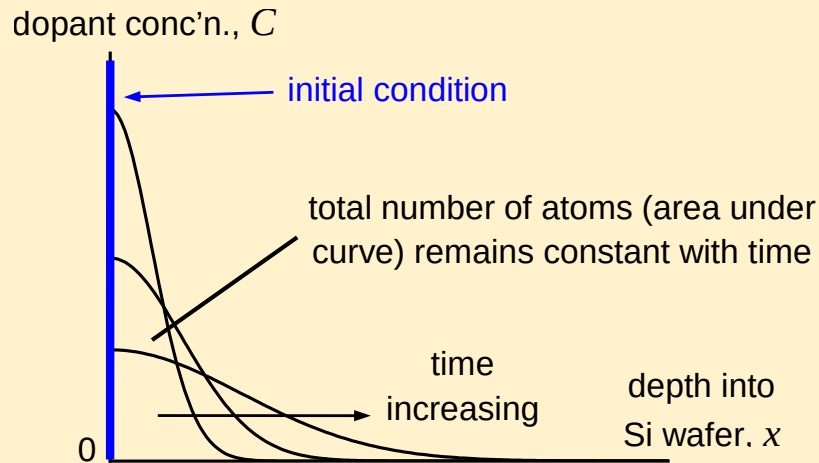


Figure 51: Qualitative evolution of the concentration profile during the drive-in phase.

How long do we need to wait for the dopant to spread over a given distance?

Time required for drive-in phase

This case is relatively straight-forward given what we know already, so we look at it first.

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- We have seen already that particles localised in a narrow region will disperse following a normal distribution that spreads over time.

$$C_{\delta}(x, t) = \mathcal{N}(0, 2Dt)$$

- If D is the diffusion coefficient of the dopant in silicon, the time t taken to spread over a depth x into the wafer is of the order of \sqrt{Dt} , as an order of magnitude.

7.2 Diffusion from a fixed surface concentration

The case of pre-deposition is more complex. The amount of diffusing material is not constant, but increasing over time. We look for solutions of the diffusion equation that satisfy a fixed concentration value at $x = 0$, $C(x = 0, t) = C_s$, and an initial condition that is $C(x > 0, t = 0) = 0$.

You'll study in IB Maths the exact form of this solution. I'll give it to you in the lecture. Another derivation is provided later in the handouts for your convenience too. But it is also important to gain a qualitative understanding of the process.

The process of predeposition is also relatively easy to model numerically, as demonstrated in the iPython notebook available on Moodle.

Semi-quantitative analysis

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- The profile of concentration in the case of pre-deposition are intuitively monotonically decreasing from the surface to the bulk.
- How far could dopant molecules penetrate over a time t ? Wherever they go, they need to get there by diffusion.
- During a time t , the typical distance travelled is \sqrt{Dt} .
- We therefore expect the amount pre-deposited to be of the order of $C_s \sqrt{Dt}$.

Numerical analysis

This process can also be modelled numerically. This allows us to evaluate the concentration profile and verify the approximations based on qualitative arguments we made earlier.

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The concentration profile $c(x, t)$ in the half space $x \geq 0$ is modelled as a 1D array where the index represents space. The spatial discretisation step i represents the step size/mean free path λ . Furthermore, each time step represents the physical time τ .

$$c_{i,n} = c(x = i\lambda, t = n\tau)$$

Based on this, we can assume that, from one time step to the next, half of the particles at location i went to the location on the left, and the other half on the right. This allows us to iteratively calculate the evolution of the concentration profile.

$$c_{i,n+1} = \frac{1}{2} (c_{i-1,n} + c_{i+1,n})$$

The boundary condition at $x = 0$, $c(x = 0, t) = C_0$ implies that at each time step we must reassign the value of $c_{0,n}$ to C_s .

Analytical solutions

The exact solution of our problem is:

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$$C(x, t) = c_s \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$

Where: $\operatorname{erf}(x) = \int_{-x}^x \mathcal{N}(\mu = 0, \sigma^2 = 1/2) = \int_{-x}^x \frac{1}{\sqrt{\pi}} e^{-x'^2} dx' = 2 \int_0^x \frac{1}{\sqrt{\pi}} e^{-x'^2} dx'$

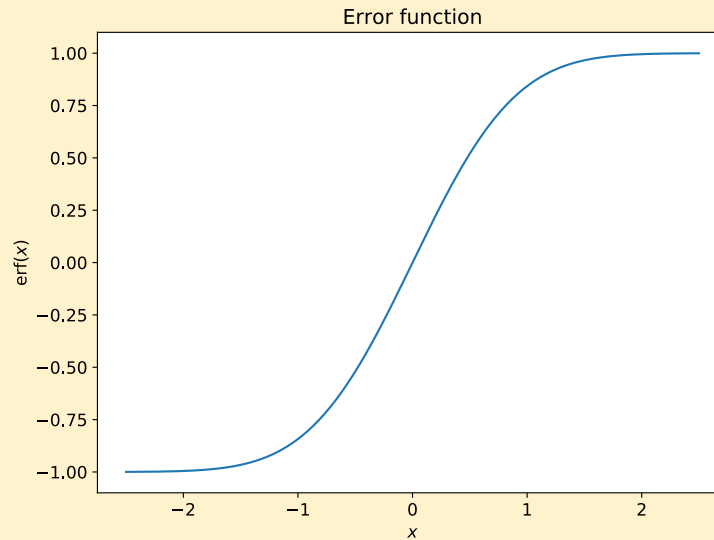
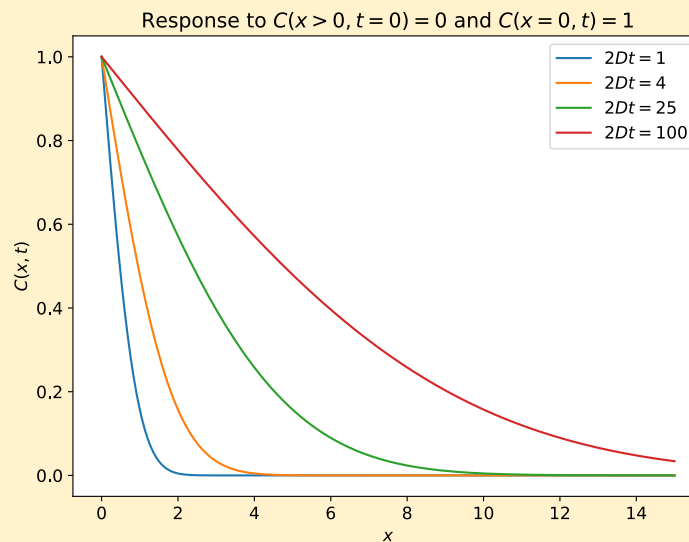


Figure 52: Graph of the error function.



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Figure 53: Evolution of the concentration profiles for the pre-deposition step. .

We can see from the resulting profiles that the penetration distance is approximately \sqrt{Dt} .

Diffusive flux from the surface

The amount $N(t)$ of atoms/molecules that entered in the semi-infinite block can be evaluated by calculating:

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$$N(t) = \int_0^\infty C(x, t) dx = c_s \int_0^\infty \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) dx$$

Graphically, we can see that the area under the curve is roughly the area of a triangle of height c_s and width \sqrt{Dt} . An exact result would use the identity:

$$\int_0^\infty (1 - \operatorname{erf}(x)) dx = \frac{1}{\sqrt{\pi}}$$

$$N(t) = c_s 2\sqrt{Dt} \int_0^\infty \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) \frac{dx}{2\sqrt{Dt}} = \frac{2c_s\sqrt{Dt}}{\sqrt{\pi}}$$

The relationship above allows us to estimate the duration of the pre-deposition stage of silicon doping.

Qualitatively, the amount of introduced material grows like \sqrt{t} - a classical signature of processes driven by diffusion.

7.3 To go further: Using a linear systems approach for the pre-deposition curve equations

This section demonstrates how to derive the analytical expression of the solution of the diffusion equation in the context of pre-deposition. This is an alternative approach to what is presented in the IB Maths course.

To understand how to tackle our specific problem, we need to study first the case of a step in concentration. Then we can use the symmetry of the solution to identify the solution for our problem. And finally derive the final solution.

7.3.1 Step response of the diffusion equation

If two materials with different concentrations of the diffusing particles are placed in contact, the concentration profile contains a discontinuity (step) at the interface at the time of contact. This can be modelled as a step function $H(t)$. What would be the concentration profile over time?

We consider first the case of an initial concentration profile that is 0 for $x < 0$ and 1 for $x > 0$.

$$C_H(x, t = 0) = H(x) = \int_{-\infty}^x \delta(x') dx'$$

The step, which is the integral of the delta function, can therefore be expressed as an infinite sum of impulses, as you have seen in linear systems. Because the diffusion equation is linear, we can immediately write the solution at any time:

$$C_H(x, t) = \int_{-\infty}^x C_\delta(x', t) dx'$$

More generally, if the concentration profile at $t=0$ is $C = c_1$ for $x < x_0$ and $C = c_2$ for $x > x_0$:

$$C = c_1 + (c_2 - c_1)H(x - x_0)$$

then the solution writes:

$$C(x, t) = c_1 + (c_2 - c_1)C_H(x - x_0, t)$$

It is worth noting that in this case, there is a net transport of particles across the interface between the materials.

7.3.2 Cumulative Gaussian integrals and error function

Because the solution of the diffusion equation to a delta function as initial concentration is a normal distribution, or Gaussian function, we now need to study the integrals of this function.

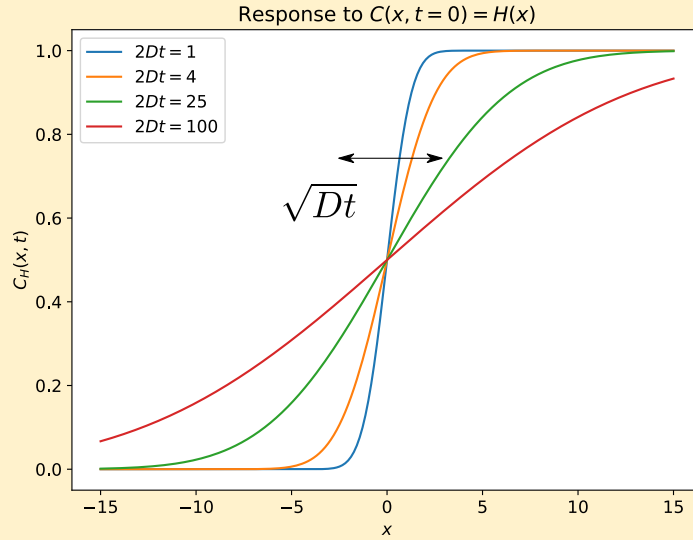


Figure 54: Evolution of the concentration profile $C_H(x, t)$ for a step distribution at $t = 0$. The width of the step is approximatively \sqrt{Dt} .

A number of mathematical functions exist to characterise integrals of Gaussian functions (or normal distributions). A common example used here is the Error function:

$$\text{erf}(x) = \int_{-x}^x \mathcal{N}(\mu = 0, \sigma^2 = 1/2) = \int_{-x}^x \frac{1}{\sqrt{\pi}} e^{-x'^2} dx' = 2 \int_0^x \frac{1}{\sqrt{\pi}} e^{-x'^2} dx'$$

We can now write the solution of the diffusion with a step function as initial state using the error function:

$$C_H(x, t) = \int_{-\infty}^x C_\delta(x', t) dx' = \int_{-\infty}^0 C_\delta(x', t) dx' + \int_0^x C_\delta(x', t) dx'$$

$$C_H(x, t) = \frac{1}{2} + \int_0^x \frac{1}{2\sqrt{\pi Dt}} \exp\left(-\frac{x'^2}{4Dt}\right) dx' = \frac{1}{2} \left(1 + \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

The relationship above uses a change of variable $z = \frac{x}{2\sqrt{Dt}}$ in the integration:

$$\int_0^x \frac{1}{2\sqrt{\pi Dt}} \exp\left(-\frac{x'^2}{4Dt}\right) dx' = \int_0^x \frac{1}{\sqrt{\pi}} \exp\left(-\frac{x'^2}{4Dt}\right) \frac{dx'}{2\sqrt{Dt}} = \int_0^z \frac{1}{\sqrt{\pi}} \exp(-z'^2) dz'$$

7.3.3 Diffusion from a fixed surface concentration

In a number practical situations such as the pre-deposition of dopant atoms in silicon, a material is in contact with a reservoir of particles at a fixed concentration for a certain amount of time, and we need to know how many of these particles entered the material.

Mathematically, assume we have a material that fills the half-space $x \geq 0$, with the initial condition:

- $C(x > 0, t = 0) = 0$: no dopant in the material;
- $C(x = 0, t) = c_s$: material exposed to a set concentration of dopant at the interface.

What would happen over time?

We can see that this condition is satisfied for one half space of the step response previously calculated. Looking at the solution $C_H(x, t)$ for step in concentration at $t = 0$ ($C_H(x, t = 0) = H(x)$), one can see indeed that the concentration value at $x = 0$ remains constant over time, half way between the initial values in each domain (see figure 54). This is consistent with what we need for $x \geq 0$.

Our problem is therefore equivalent to finding the solution for this initial condition: $C(x > 0, t = 0) = 0$, and $C(x < 0, t = 0) = 2c_s$

$$C(x, t) = 2c_s (1 - C_H(x, t)) = 2c_s \left(1 - \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) \right)$$

$$C(x, t) = c_s \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$

Summary

The example of silicon doping gave us a good opportunity to demonstrate how diffusion influences a number of materials-related processes, with application to a broad range of engineering areas - in this case electronic engineering. A few more examples will follow in this lecture series.

At a qualitative level, we learn from this analysis that diffusion blurs the concentration profile, spreading smoothly particles over a distance given by \sqrt{Dt} , with a coefficient that would depend on specific aspects of the problem, such as the dimension (our analysis was only 1D). A drop of ink would therefore spread by diffusion such that the patch size increases like \sqrt{Dt} . Two balls of ice-cream with different flavours would, when in contact, mix at the interface such that the thickness of the mixed region would be \sqrt{Dt} ; different chemicals may have different coefficients of diffusion - pick the largest maybe. Once you get used to working with these approximations, many problems can be tackled without too much mathematical work. But if you want an exact solution - then you need to get your computer ready and do a bit of modelling as most often real problems don't have analytical solutions.

Intended Learning Outcomes

The intended learning outcomes of this section are:

- Explain the microscopic origin of Fick's first law through a minimal model, and provide an estimation of the coefficient of diffusion in terms of mean free path and time between collision or particle speed. Students should be able to explain how random motion of the individual particles is consistent with directed net diffusive flux.
- Integrate Fick's first law with mass conservation to derive the diffusion equation.
- Describe a number of microscopic processes related to particle diffusion in solid and explain why some are expected to be faster than others.
- Explain qualitatively why diffusive processes and many other kinematic processes have rates that follow the Arrhenius law. Students should be able to use Arrhenius law to model the dependence of the diffusion coefficient on temperature.
- Sketch and explain the qualitative dependence of the rate of nucleation and solid phase growth with temperature. Understand the interplay between thermodynamic and kinetic considerations.
- Use the fact that the mean diffusive displacement of particles is approximately given by \sqrt{Dt} to predict the evolution of simple diffusive processes. Draw the analogy between the statistics of random particle motion and random polymer configurations to interpret this relationship.

You can test yourself against these to make sure you have covered the relevant content, and return to your notes if necessary. The week 3 quiz and examples paper questions may now be fully attempted and will also cover most of these learning outcomes.