UNIVERSITÀ
DEGLI STUDI DI TRIESTE

Scienza dei Materiali
- lecture 11-

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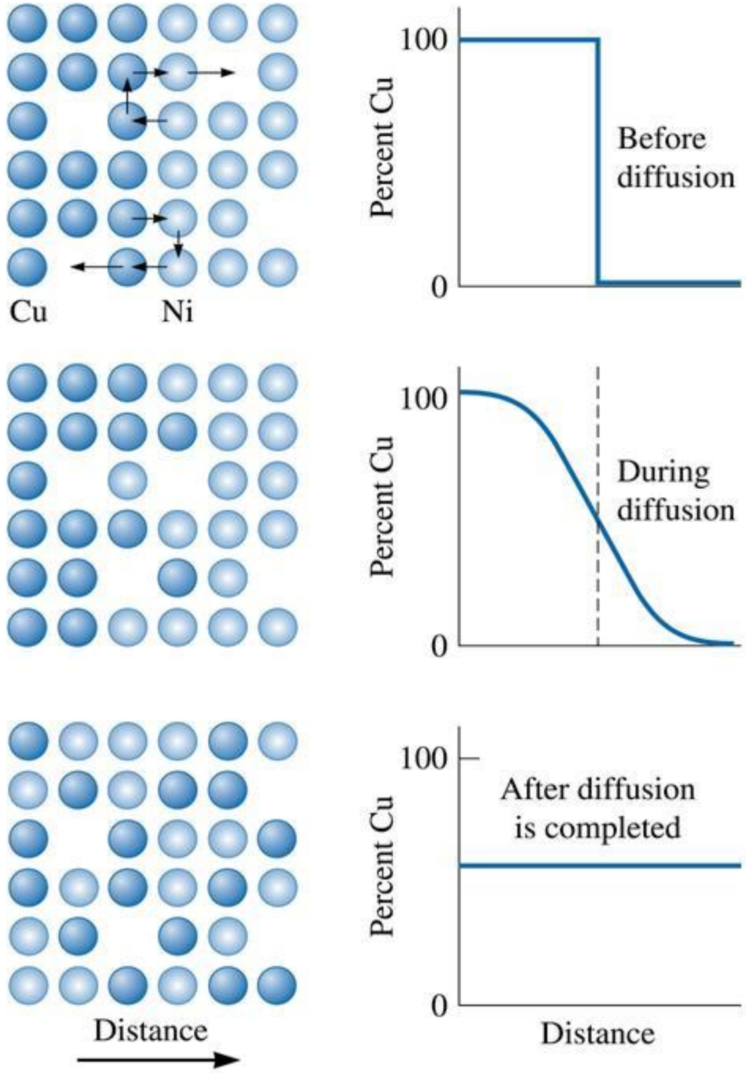
A.A. 2021-22

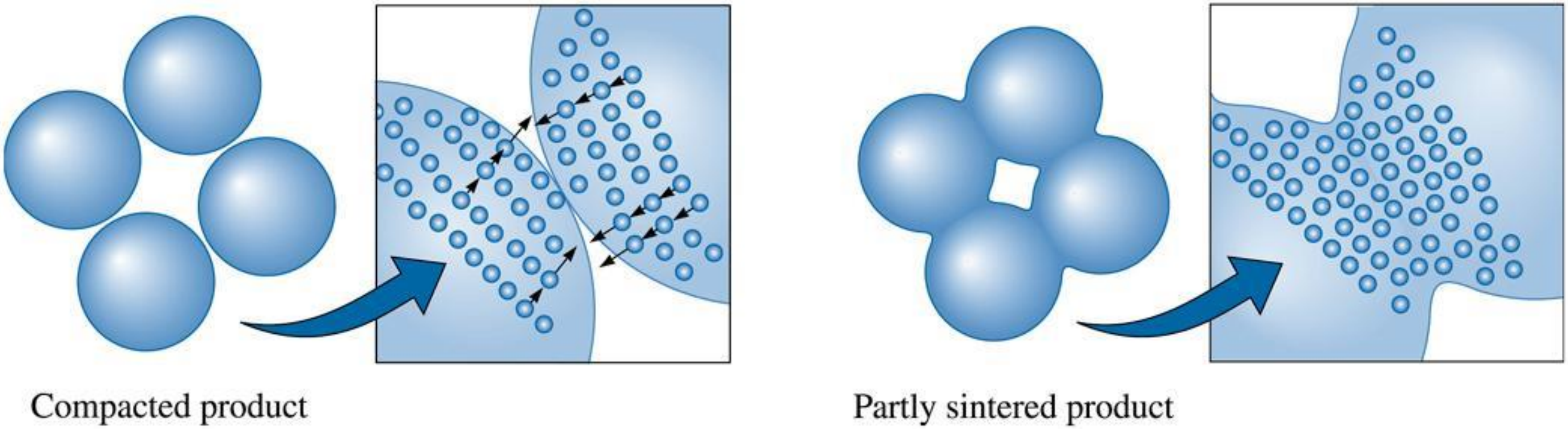
Diffusione

Di interesse per la scienza dei materiali è il trasporto di materia

La diffusione consiste in un movimento di atomi che tende a rendere omogenea la miscela



Importanza della diffusione: processi di sinterizzazione



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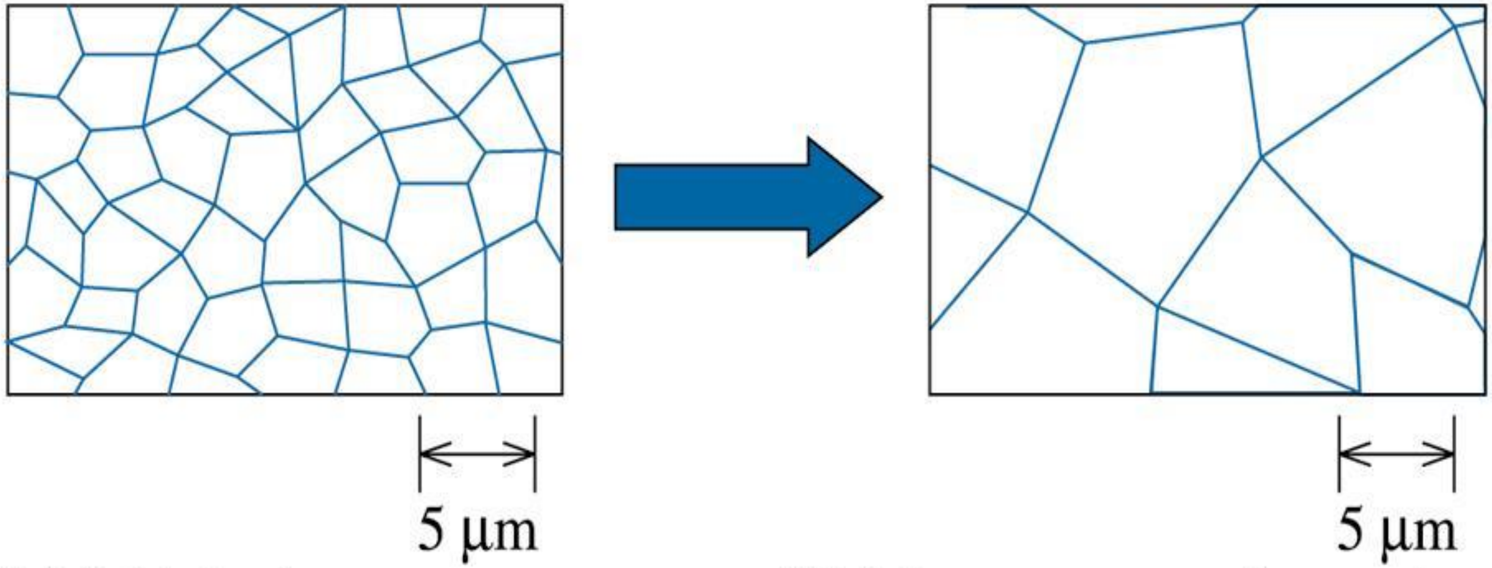
Diffusion processes during sintering and powder metallurgy. Atoms diffuse to points of contact, creating bridges and reducing the pore size

Importanza della diffusione: crescita dei grani



(a) Initial microstructure

(b) Microstructure after grain growth

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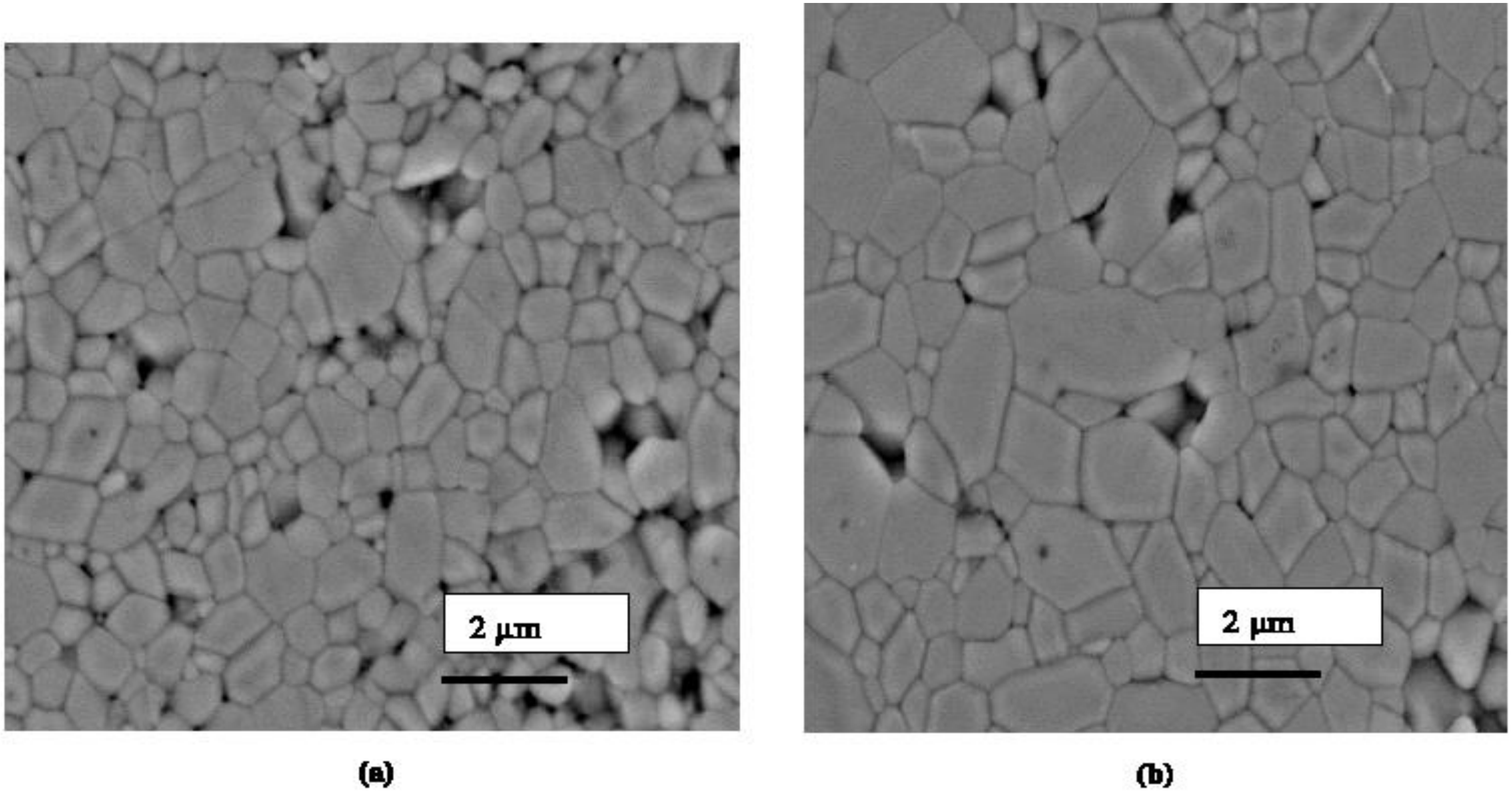
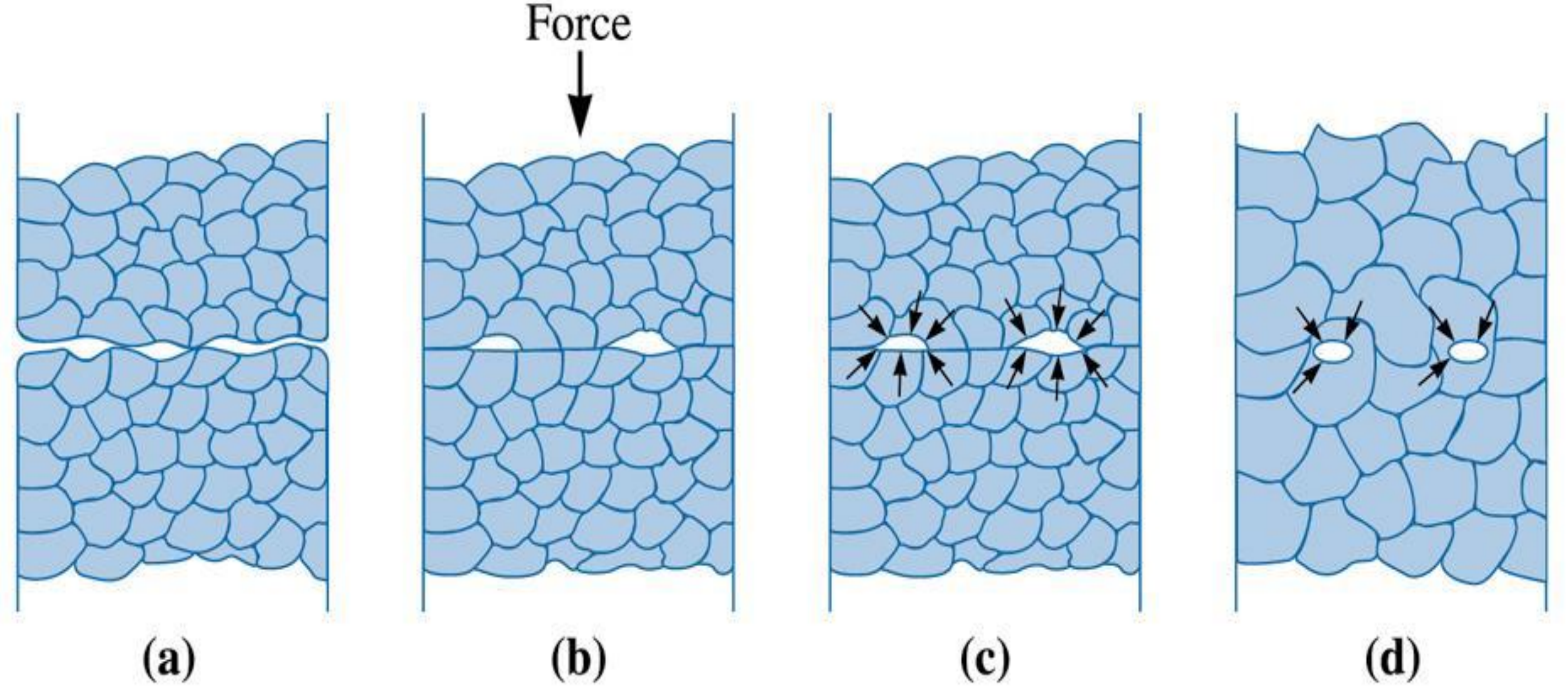
Grain growth occurs as atoms diffuse across the grain boundary from one grain to another

Importanza della diffusione: crescita dei grani



Grain growth in alumina ceramics can be seen from the SEM micrographs of alumina ceramics. (a) The left micrograph shows the microstructure of an alumina ceramic sintered at 1350°C for 150 hours. (b) The right micrograph shows a sample sintered at 1350°C for 30 hours. (*Courtesy of I. Nettleship and R. McAfee*.)

Importanza della diffusione: processi di giunzione per diffusione (diffusion bonding)



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The steps in diffusion bonding: (a) Initially the contact area is small; (b) application of pressure deforms the surface, increasing the bonded area; (c) grain boundary diffusion permits voids to shrink; and (d) final elimination of the voids requires volume diffusion

Importanza della diffusione: indurimento superficiale per cementazione o nitrurazione

Furnace for heat treating steel using the carburization process. (Courtesy of Cincinnati Steel Treating).

Importanza della diffusione: drogaggio nei semiconduttori

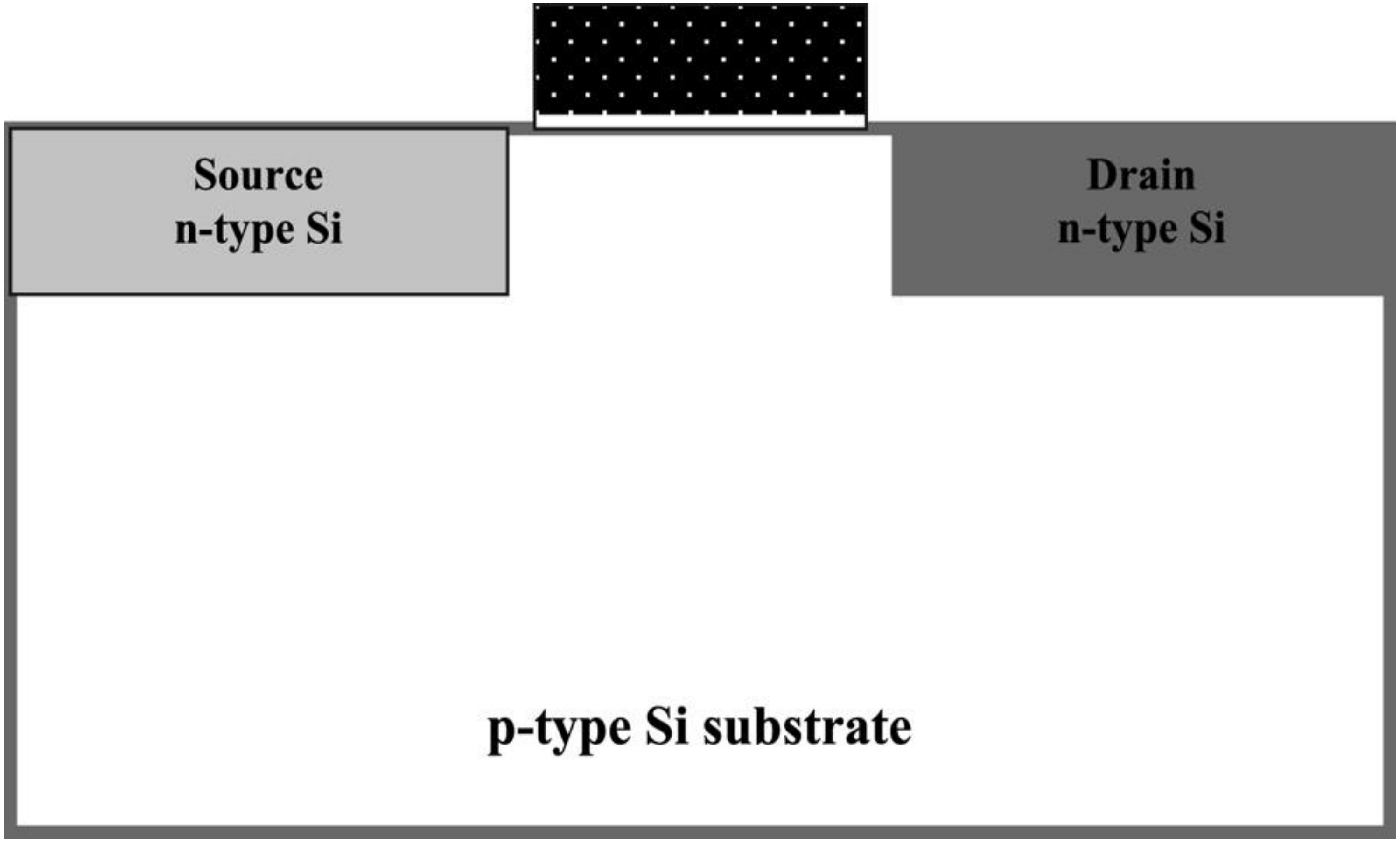

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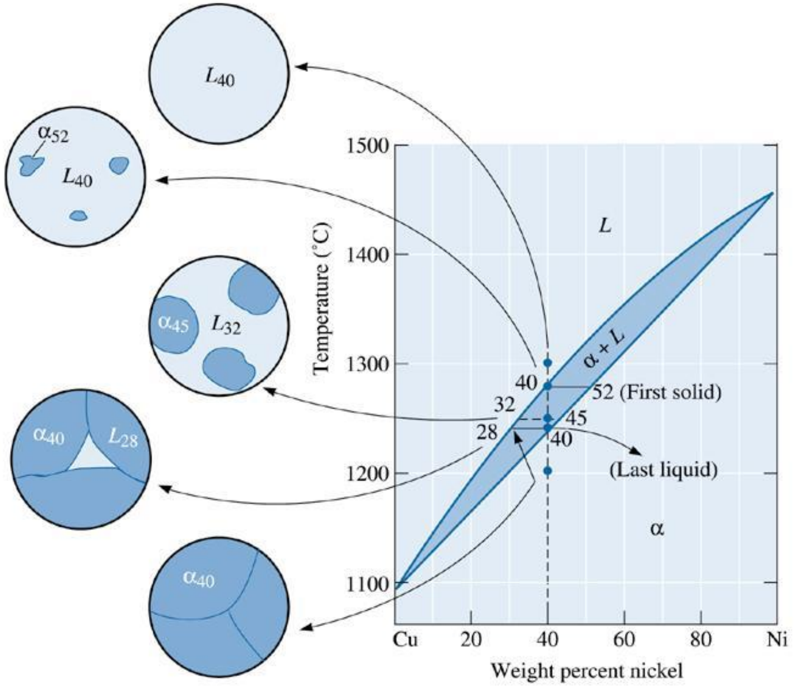
Figure 5.2 Schematic of a n-p-n transistor. Diffusion plays a critical role in formation of the different regions created in the semiconductor substrates. The creation of millions of such transistors is at the heart of microelectronics technology

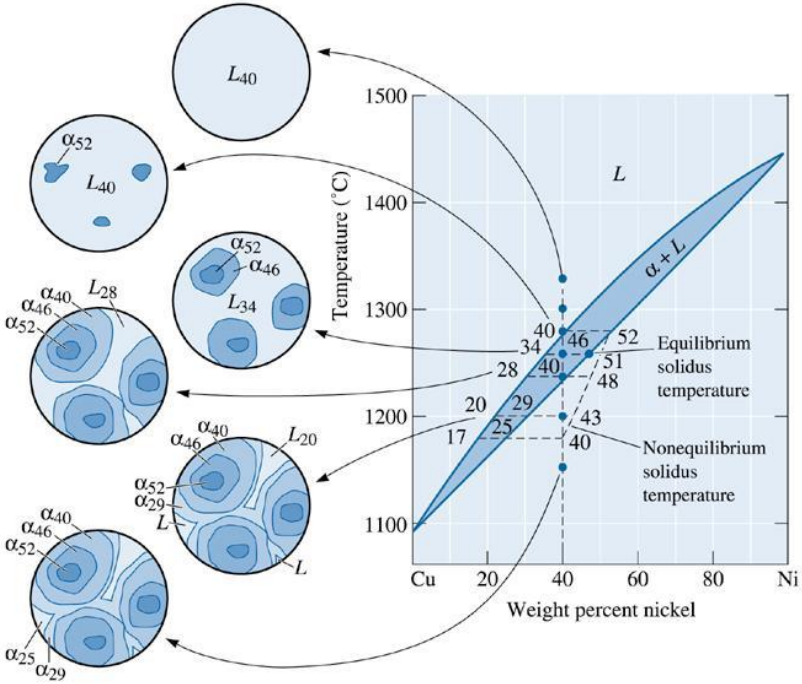
Importanza della diffusione:
influenza sulla microstruttura nei processi di solidificazione

Raffreddamento in condizioni di equilibrio



Raffreddamento in condizioni di non equilibrio

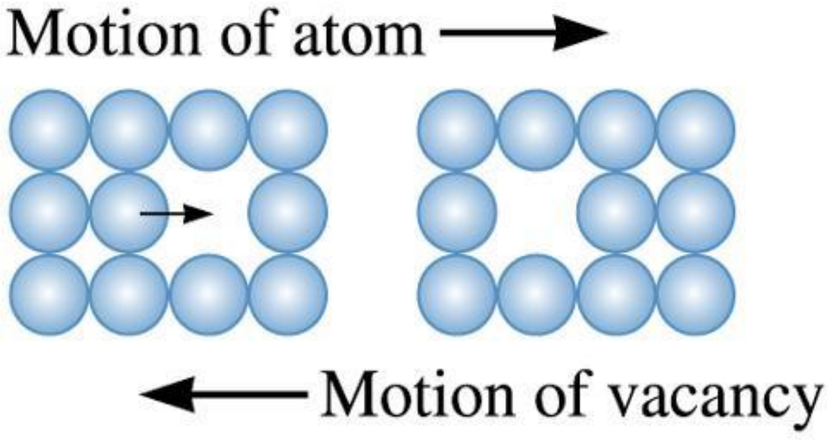
- Ridistribuzione atomica limitata dalla diffusione
- Microstruttura diversa



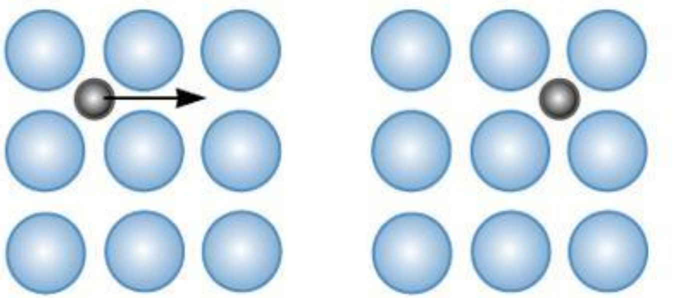
Possibili meccanismi di diffusione

Meccanismi sostituzionali

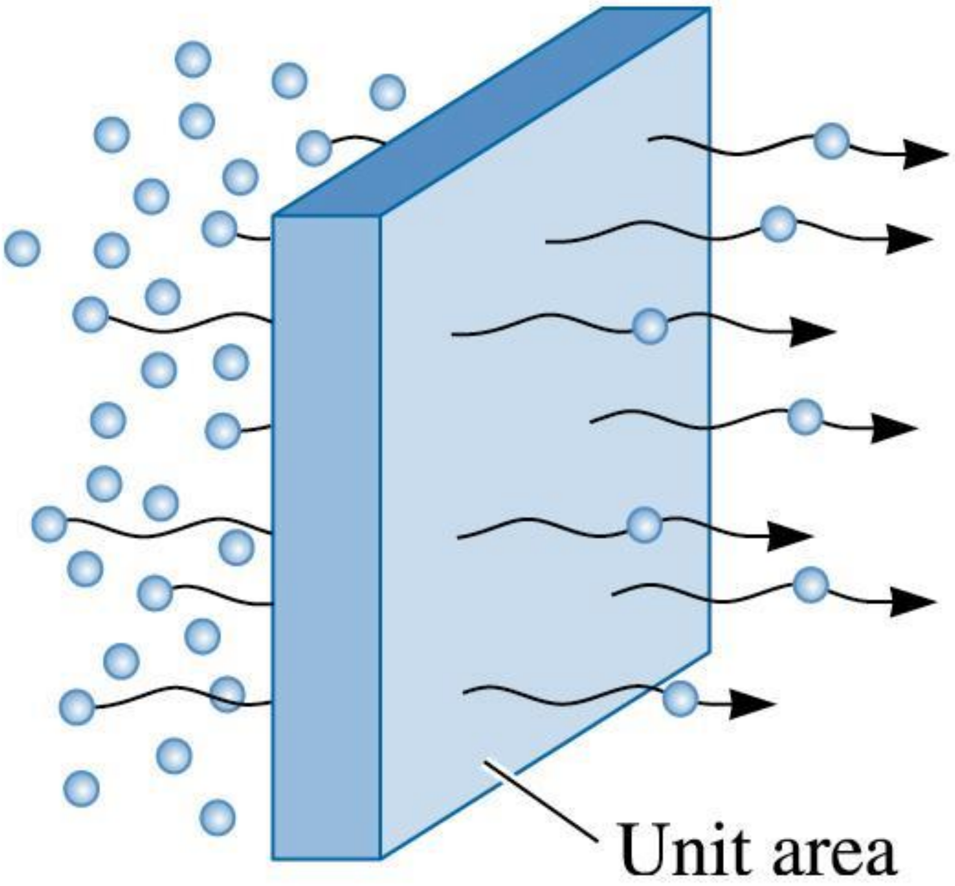
È necessaria la presenza di vacanze



Meccanismi interstiziali



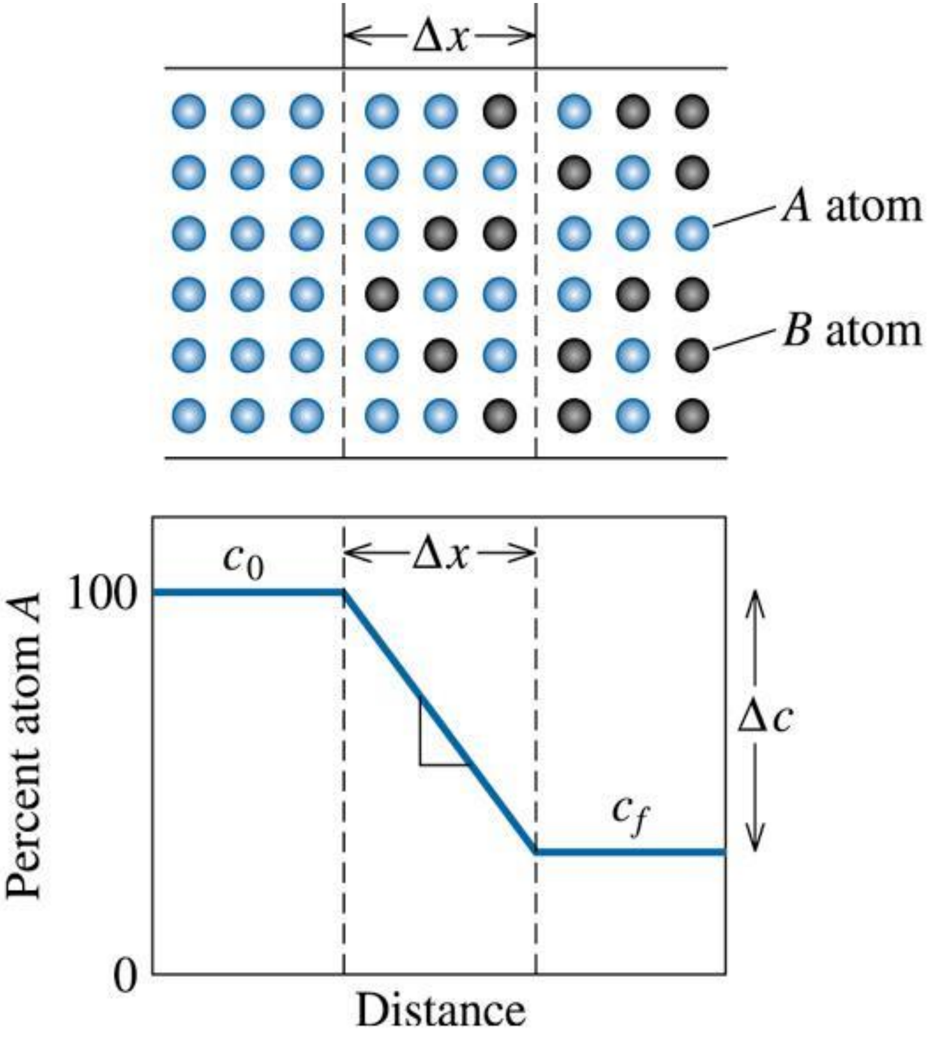
La prima legge di Fick



$$J = -D \frac{\Delta c}{\Delta x}$$

J: flusso
D: coefficiente di diffusione
c: concentrazione
x: coordinata spaziale

La prima legge di Fick



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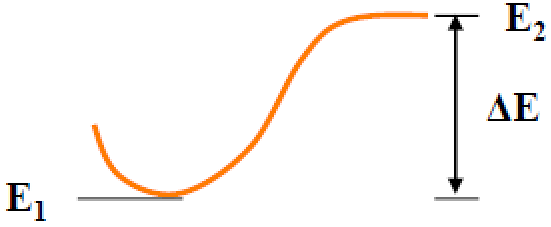
Gradiente di concentraizione nella legge di Fick

La prima legge di Fick: giustificazione statistico-microscopica

STOCHASTIC DIFFUSION

Problem: particle diffusing in a solid.

First take on it:



This is an energy barrier **ΔE** and the

$$\frac{P(E_2)}{P(E_1)} = e^{-\beta \Delta E} \quad \text{with} \quad \beta = \frac{1}{k_b T}$$

from what we know.

However: (1) There could be **more then one** barrier

(2) The instantaneous barrier “oscillates” with time as the atoms move!

How to take this into account?

(1) Two barriers (already seen) accessible from the same, single stable site

$P(E_2)/P(E_1)$ is **twice** as big!

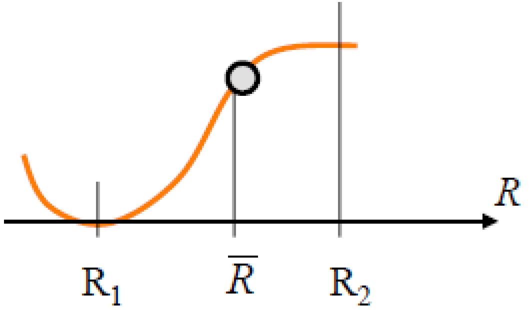
Here $W = 2$, so if $\Delta S_{conf} = k_b \ln W \Rightarrow 2 = e^{\frac{\Delta S_{conf}}{k_b}}$

we can thus write $$2 \cdot e^{-\beta \Delta E} = e^{\frac{\Delta S_{conf}}{k_b}} \cdot e^{-\beta \Delta E} = e^{-\beta\left(\Delta E - T S_{conf}\right)}$$

i.e., same expression as before, but the **barrier** is a **free energy one**.

STOCHASTIC DIFFUSION

(2) Suppose we define a reaction coordinate ***R***.



We ca still look at the behaviour of the entire system if we **fix** $R=\overline{R}$ for a generic $\overline{R}$ along the reaction path.

the distribution will be $\rho_R = \dfrac{e^{-\beta H}}{Z(\overline{R})}$ $\quad H = E_{pot} + E_{kin}$

where the Potential Energy of the system has that degree of freedom fixed and the Partition Function $Z(\overline{R})$ will just be:

$$Z(\overline{R}) = \int e^{-\beta H}\, d\boxed{\Gamma_{-R}}$$

phase space without ***R*** as a variable.

$$\mathrm{E}(R) = \int \rho_R H \, d\Gamma_{-R}$$

We can define $S(R)$ as well: $\mathrm{S}(R) = -k_b \int \rho_R \ln \rho_R d\Gamma_{-R}$

From here $\quad F(R) = E(R) - TS(R)$

➡ $F(R) = -k_b T \ln Z(R)$ as already seen.

STOCHASTIC DIFFUSION

$$F(R) = -k_bT \ln Z(R)$$

Now in $F(R)$ is the real barrier, the force at point $\overline{R}$ should be $-\frac{\partial}{\partial R} F(R)$.

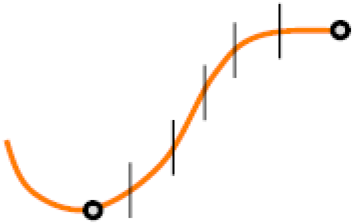
$$-\frac{\partial}{\partial R|_{R=\overline{R}}} F(R) = k_bT \frac{\partial}{\partial R} \ln Z(R)$$

$$= k_bT \frac{1}{Z(\overline{R})} \frac{\partial}{\partial R} \int e^{-\beta H}\, d\Gamma_{-R} = \cancel{k_bT} \int \frac{e^{-\beta H}}{Z(\overline{R})} \left(-\cancel{\beta} \frac{\partial E_{pot}(R)}{\partial R|_{\overline{R}}} \right) d\Gamma_{-R}$$

$$F(\overline{R}) = \left\langle -\frac{\partial E_{pot}}{\partial R|_{\overline{R}}} \right\rangle$$

This is the thermodynamic average (while the lattice oscillates) of the "**force against**"!

This makes it very plausible that barriers for diffusion are, effectively, free energy barriers.

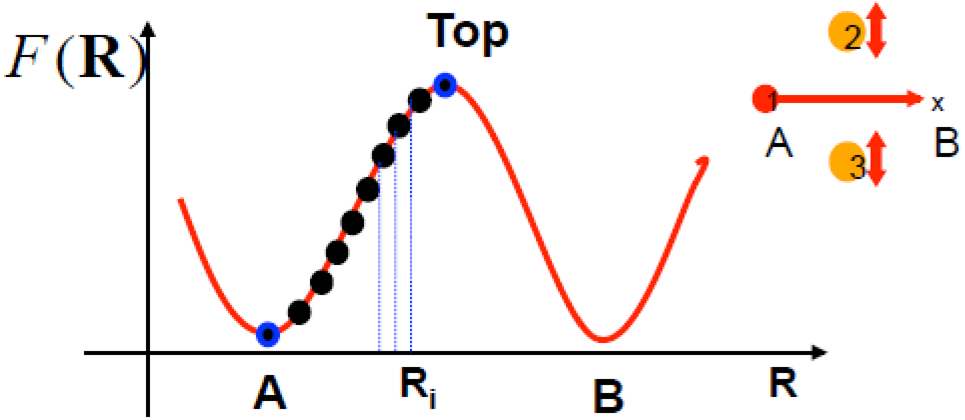


We could run a *molecular dynamics simulation* at fixed $\overline{R}$ and average over time this "force against climbing the barrier". If we do it for a sequence of positions R_i we can calculate the barrier ⇨ **Thermodynamic Integration**

From now on, we will write the barrier as **ΔE**, but it's understood that it's really **a free energy barrier**

“Thermodynamic integration” of the free energy barrier

So: the idea is to compute the force on a set of closely spaced points placed on the diffusion path. The average in the expression



$$-\left(\frac{\partial F}{\partial \mathbf{R}}\right)_{\mathbf{R}_1=\mathbf{R}_i} = \left\langle -\left(\frac{\partial E_{pot}}{\partial \mathbf{R}_1}\right)_{\mathbf{R}_1=\mathbf{R}_i}\right\rangle$$

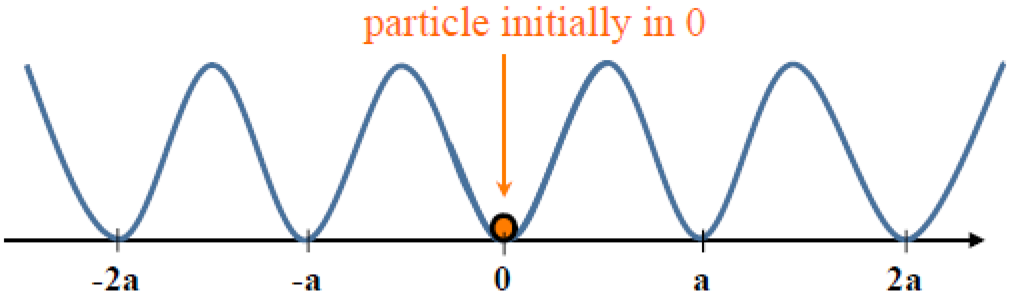
would seem to require an integration over the whole configuration space. However, we know that this corresponds to a time average over any long-enough molecular dynamics (MD: a theoretical modelling technique) trajectory of the system! For each $\mathbf{R}_i$ we can just evaluate the force $\mathbf{f}_i = -dF/d\mathbf{R}$ (which is just minus the gradient of the barrier). At the end we can integrate numerically the free energy barrier value as a sum:

$$\mathbf{f}_i = -\left(\frac{\partial F}{\partial \mathbf{R}}\right)_{\mathbf{R}_1=\mathbf{R}_i} = \left\langle -\left(\frac{\partial E_{pot}}{\partial \mathbf{R}_1}\right)_{\mathbf{R}_1=\mathbf{R}_i}\right\rangle = \lim_{t\to\infty}\frac{1}{t}\int_0^t -\left(\frac{\partial E_{pot}(\mathbf{R}_1,\mathbf{R}_2(t),\ldots,\mathbf{R}_n(t))}{\partial \mathbf{R}_1}\right)_{\mathbf{R}_1=\mathbf{R}_i} dt$$

$$\Delta F = -\int_{\mathrm{A}}^{\mathrm{Top}} \mathbf{f}\cdot d\mathbf{R} \cong -\sum_i \mathbf{f}_i\cdot\Delta\mathbf{R}_i$$

← Barrier for diffusion: integral of the work done against the *average force* which the rest of the system exerts on the diffusing atom at the temperature T

DIFFUSION



Free energy profile in a 1D solid.
Periodic if the solid is crystalline!

We can assume *a* to be our unit of length

An **interstitial** (say, H in Si) is originally in the origin and a "jump" takes it either to +a (+1) or -a (-1) with **equal** probability. **No memory effects**: we will assume that every jump is independent from the previous. That is, jumps are described by a *stochastic variable x* :

$$x = \begin{cases} +1 & \text{prob} = 1/2 \\ -1 & \text{prob} = 1/2 \end{cases} \qquad \sigma^2 = \left\langle x^2 - \bar{x}^2 \right\rangle = \left\langle (x - \bar{x})^2 \right\rangle = \frac{1}{2}\left(1^2\right) + \frac{1}{2}\left(-1^2\right) = 1$$

so $\begin{cases} \bar{x} = 0 \\ \sigma^2 = 1 \end{cases}$ for one jump.

Let's try the new stochastic variable $y = x_1 + x_2$ (position after 2 jumps in units of *a*)

$$\bar{y} = \left\langle x_1 + x_2 \right\rangle = \bar{x}_1 + \bar{x}_2 = 0$$

$$\boxed{= 2\bar{x}_1\bar{x}_2 = 0}$$

$$\sigma^2 = \left\langle y^2 - \bar{y}^2 \right\rangle = \left\langle (x_1 + x_2)^2 \right\rangle = \sigma_1^{\,2} + \sigma_2^{\,2} + 2\left\langle x_1 x_2 \right\rangle = 2$$

DIFFUSION

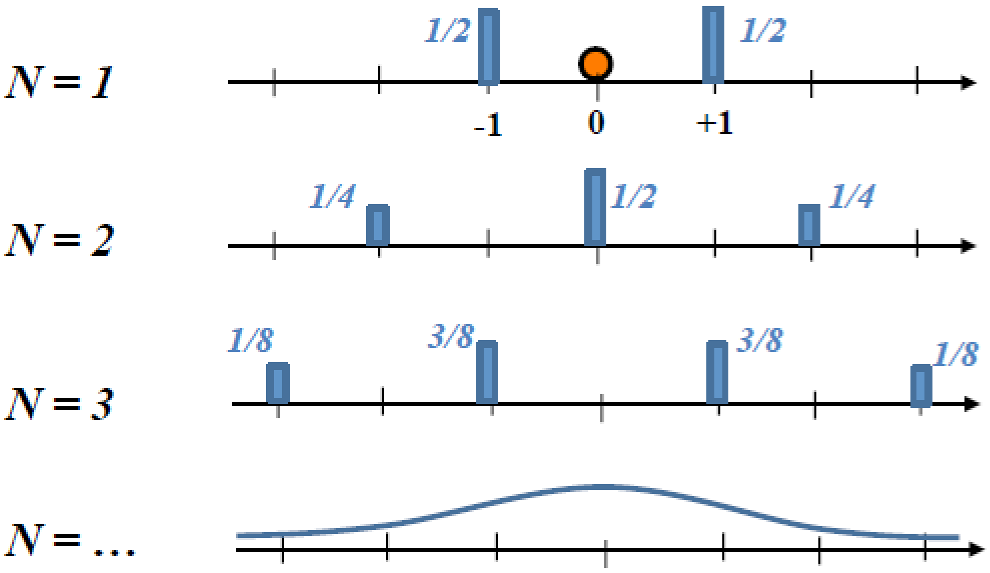
So, for $y = \sum_{i=1}^{N} x_i$ (position after N jumps) we get: $\boxed{\begin{cases} \bar{y} = 0 \\ \sigma_y^{\ 2} = N\sigma_i^{\ 2} = N \end{cases}}$

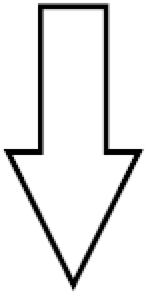
of course in a^2 units, really.

So the net motion is 0 on average, but the *square* of the distance from the starting point is proportional (infact equal, in a^2 units) to the number of jumps N

- But how many jumps does it make per unit of time?
- And how does the distribution looks for increasing N?

We answer the second question first -check the following scheme:





Clearly, it spreads with N!

THE CENTRAL LIMIT THEOREM

Basically $y = \sum_{i=1}^{N} x_i$ for large N will have a **Gaussian** distribution

Exercise: Let's try with x uniformly distributed between 0 and 1

$$\bar{y} = N/2 \qquad \sigma_y^{\,2} = N\int_{-1/2}^{1/2} x^2 dx = N\cdot\left[\frac{x^3}{3}\right]_{-1/2}^{1/2} = \frac{N}{12}$$

So the distribution (~Gaussian) will have average N/2 and standard deviation $\sigma = \sqrt{N/12}$

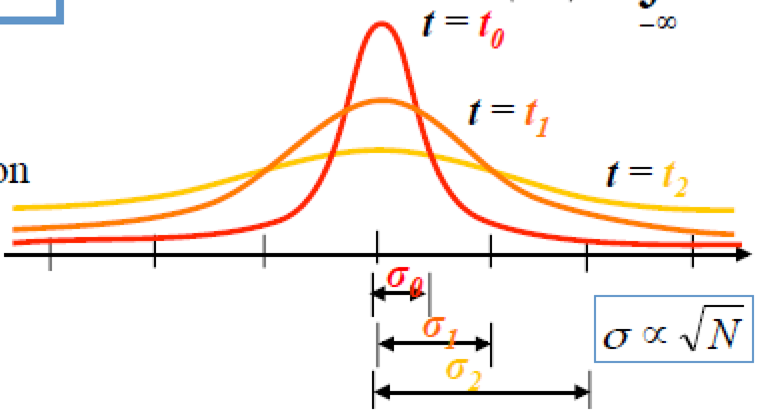
Q: will it ever be an *exact* Gaussian? ⇨ **A:** No -a Gaussian centred in N/2 would have a non-zero value for negative y. But it will be an excellent approximation.

$$\boxed{g(y,\sigma) = \frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{y^2}{2\sigma^2}}}$$

Gaussian with mean 0 and variance σ^2.

You can check that $\langle y^2\rangle = \int_{-\infty}^{+\infty} g(y,\sigma^2)y^2 dy = \sigma^2$

So, with time, a population of "walkers"/interstitials will **spread:**



$\sigma \propto \sqrt{N}$

Example:

$a \cong 10^{-10} m$

$N = 10^{10}$ jumps

$\sigma = \sqrt{10^{10}}\cdot 10^{-10} = 10^{-5} m$

It moves **10 μm**, not a **metre**!! (and 0 on average…)

The central limit theorem in action

Take a random variable x distributed according to any simple distribution such as a uniform distribution between zero and one (top-left column in the figure) or a uniform distribution set to zero inside the interval $0.2 < x < 0.8$ (top-right column).

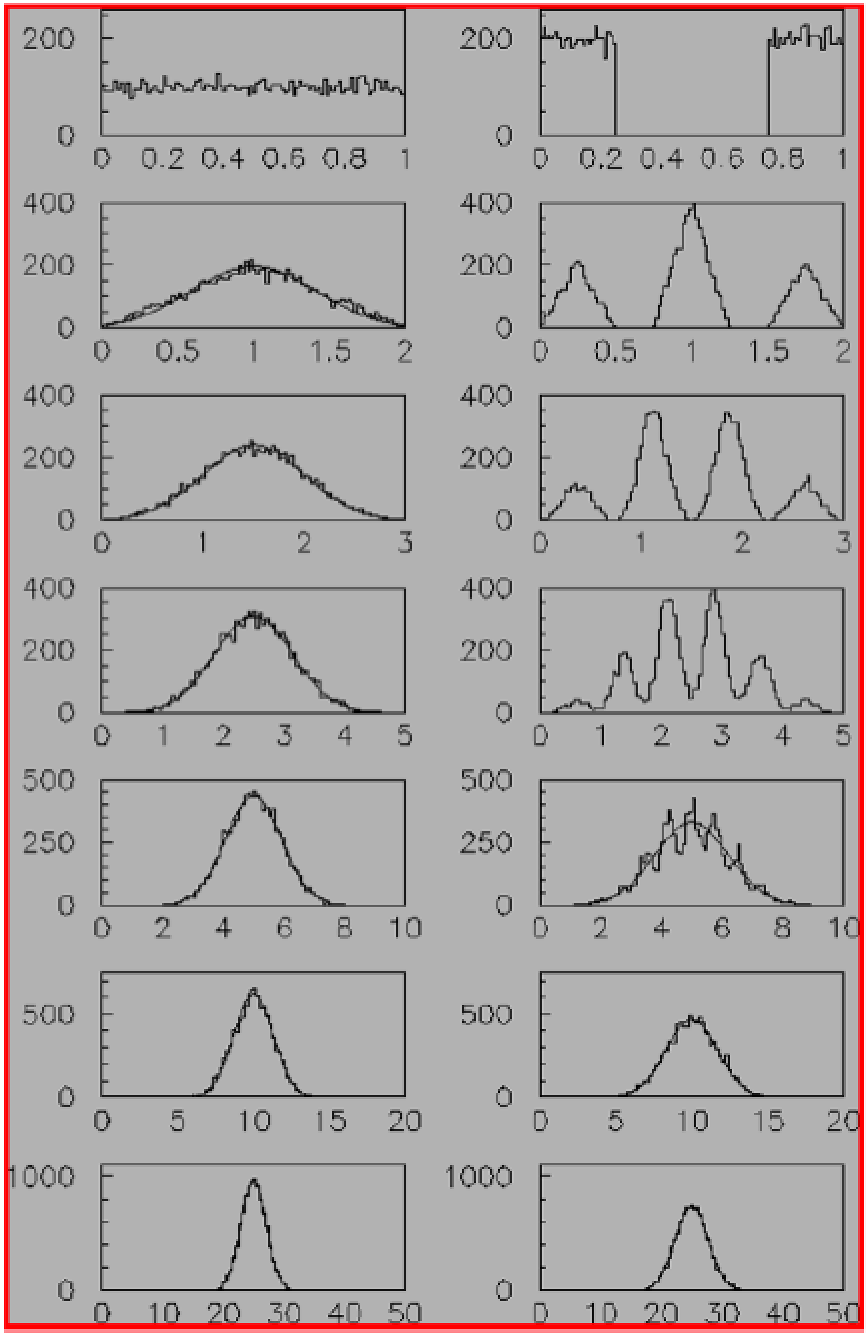
Now calculate a large number of times the sum of $N = 2, 3, 5, 10, 20$, or 50 independent values of x, and look at the way this sum is distributed →

The histograms you obtain look very soon like Gaussian distributions centered on $N/2$.

The distribution widths also get larger and larger. They are proportional to the square root of N (it may not look that way in the figure because of the increasing scale).

Namely:

$$\sigma_N{}^2 = N\sigma^2 \rightarrow \sigma_N \propto \sqrt{N}$$



A MICROSCOPIC THEORY FOR $N(t)$

$$N(t) = \left(\frac{dN}{dt}\right)\cdot t$$

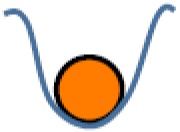
time passed from start

rate of jumping, that is how many jumps per unit time

$$\frac{dN}{dt} = \nu \cdot e^{-\frac{\Delta E}{k_b T}}$$

success rate = probability of having the energy to overcome the barrier

attempt rate = the vibration freq. of an atom in the potential wall



1D case

in reality, there are two barriers at each attempt/oscillation (and ΔE is really the ΔF associated with **each** of them).

$$\therefore \quad N(t) = 2\nu \cdot e^{-\frac{\Delta E}{k_b T}} \cdot t$$

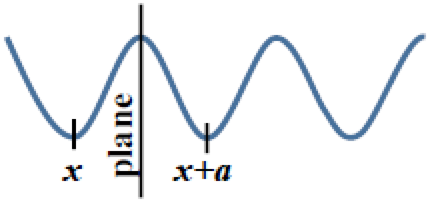
$$\boxed{\begin{cases} \sigma^2(t) = 2\nu \cdot e^{-\frac{\Delta E}{k_b T}} \cdot a^2 t \\ g(y,\sigma) = \dfrac{1}{\sqrt{2\pi\sigma}} e^{-\frac{y^2}{2\sigma^2(t)}} \end{cases}}$$

The variance of the interstitial position is measured in m^2

This is the solution for the distribution in the limit of large ***t*** !

DIRECT DERIVATION OF FICK'S LAW N°1

A direct derivation



We want the current J_{TOT} through a "plane" between $\boldsymbol{x}$ and $x+a$:

$$J_{dx} = \underbrace{n(x)\cdot a}_{\text{tot \# of walkers "at } x\text{"}} \cdot \underbrace{\nu e^{-\frac{\Delta E}{k_b T}}}_{\text{how many of these jump to the right (to } x+a\text{) per unit of time}} \qquad J_{sx} = -n(x+a)\cdot a\cdot \nu e^{-\frac{\Delta E}{k_b T}}$$

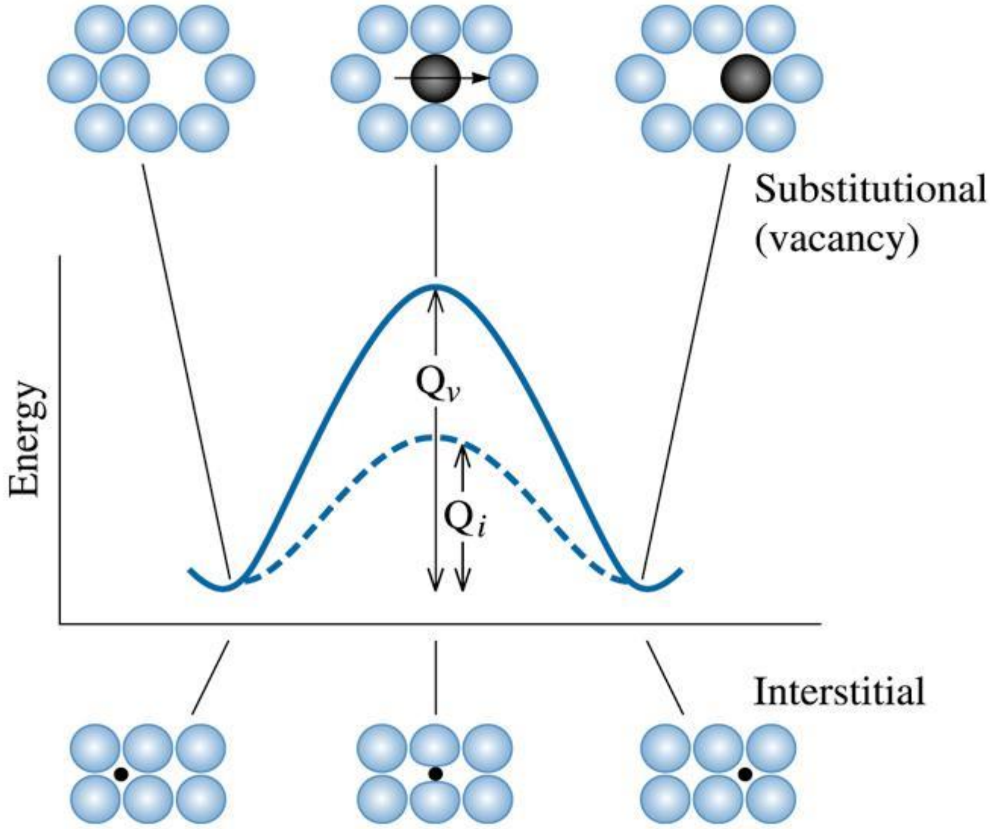
$$J_{TOT} = J_{dx} + J_{sx} = -\underbrace{\frac{[n(x+a)-n(x)]}{a}}_{\frac{\partial n}{\partial x}} \cdot \underbrace{a^2 \nu e^{-\frac{\Delta E}{k_b T}}}_{D} \Rightarrow \boxed{J_{TOT}(x,t) = -D\frac{\partial n}{\partial x}}$$

Fick's Law N° 1

plus sign here since the current to the left, J_{sx}, is negative in the expression above

Note:
it should be $J_{TOT} = -\dfrac{\partial}{\partial x}Dn$

La diffusione: un meccanismo termicamente attivato



Come tutti i meccanismi termicamente attivati, la diffusione dipende esponenzialmente dalla temperatura (legge di Arrhenius)

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

DIFFUSION COEFFICIENT

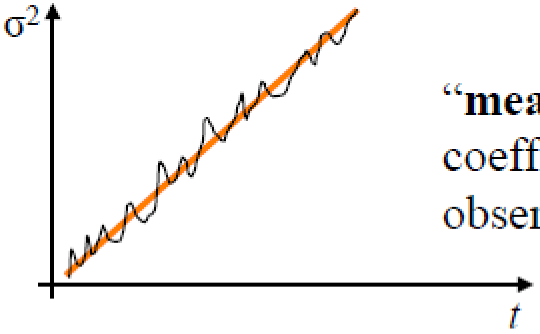
Note:

$$\begin{cases} \sigma^2(t) = 2D\,t \\ D = \nu \cdot e^{-\frac{\Delta E}{k_b T}} \cdot a^2 \end{cases}$$

This "**Diffusion Coefficient**" ***D*** depends on the material, temperature and impurity mass (through $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$). It's measured in $m^2/\sec$ (in fact, typically in $cm^2/\sec$).

$$D = \frac{\sigma^2}{2t}$$

(in 1D)



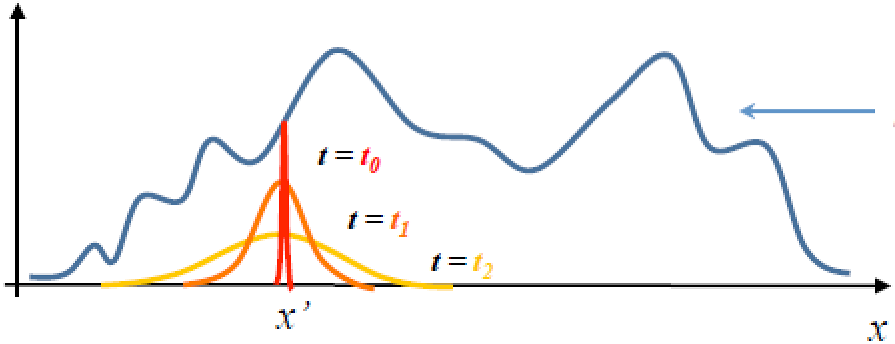
"**measuring**" the diffusion coefficient from the slope of the observed square displacement

$$\boxed{D = \frac{\sigma^2}{6t}}$$

In 3 dimensions, this is the result of Einstein's "**Brownian motion**" theory ~1905 (AA's "Annus Mirabilis").

EVOLUTION OF A DENSITY *n(x,t)*

We will stay in 1D and describe how a given $n(x,t)$ evolves with time.



$n(x,0)$ = density of interstitials (or any other defect) at time $t = 0$

For every position x' the interstitials which started there will spread for $t_0 \rightarrow t_1 \rightarrow t_2$ like a broadening Gaussian centred in x', the evolution being :

$$\begin{cases} g(x-x',\sigma) = \dfrac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-x')^2}{2\sigma^2}} \\ \sigma^2(t) = 2Dt \end{cases}$$

the total density will be:

$$\begin{cases} n(x,t) = \displaystyle\int_{-\infty}^{+\infty} n(x',0)\, g(x-x',\sigma)\, dx' \\ \sigma^2(t) = 2Dt \end{cases}$$

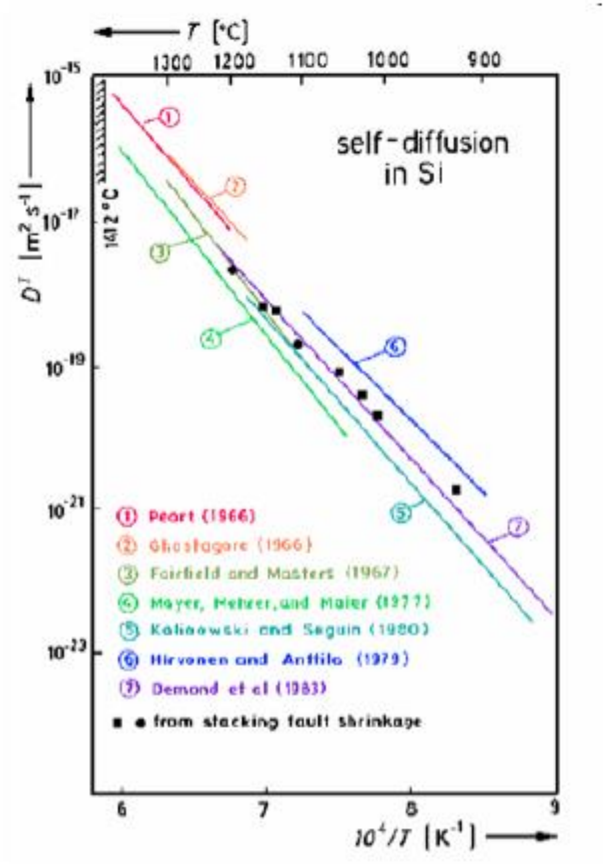
or, more explicitly:

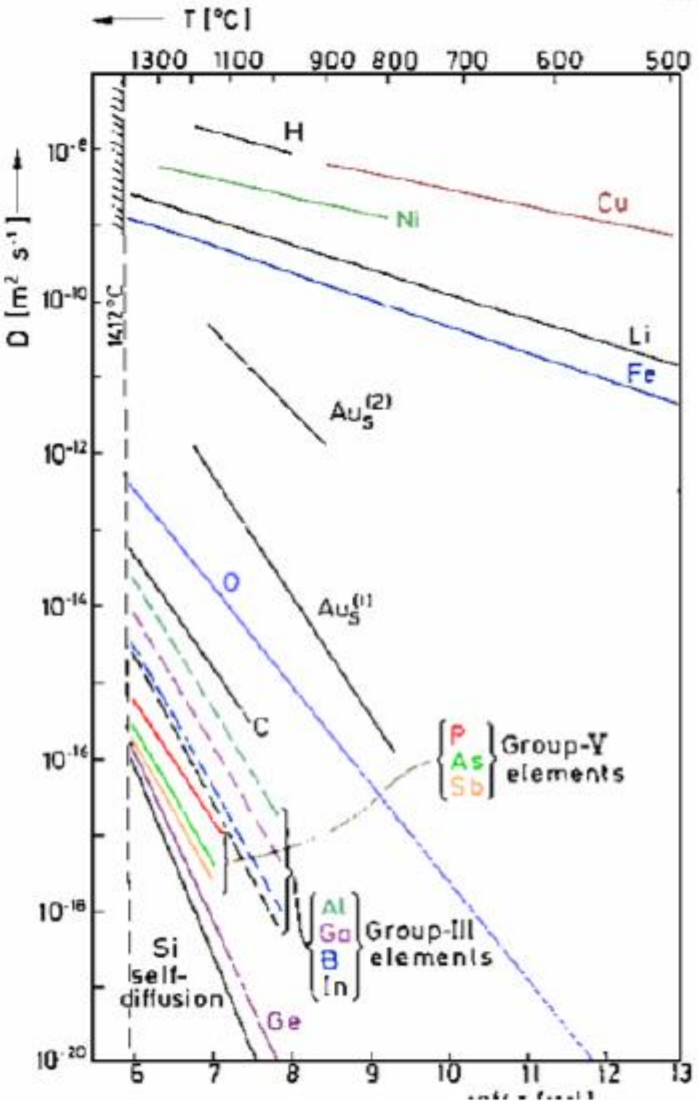
$$\boxed{n(x,t) = \int_{-\infty}^{+\infty} n(x',0) \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{(x-x')^2}{4Dt}} dx'}$$

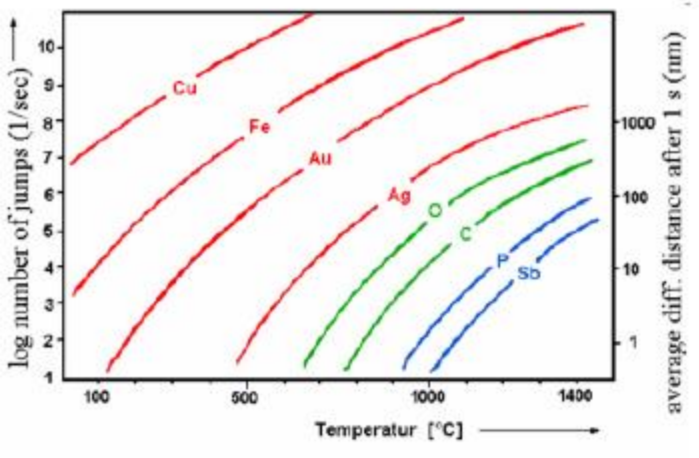
$n(x,t)$ solution, in integral form

to better appreciate this result, we will next look at Fick's Laws

Self diffu





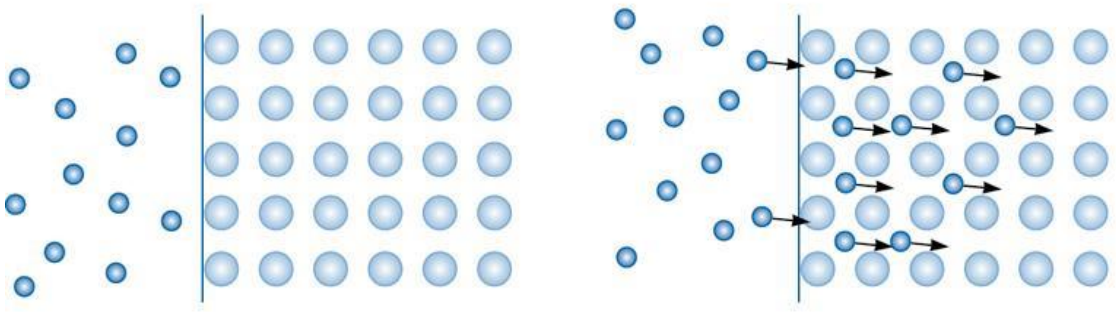


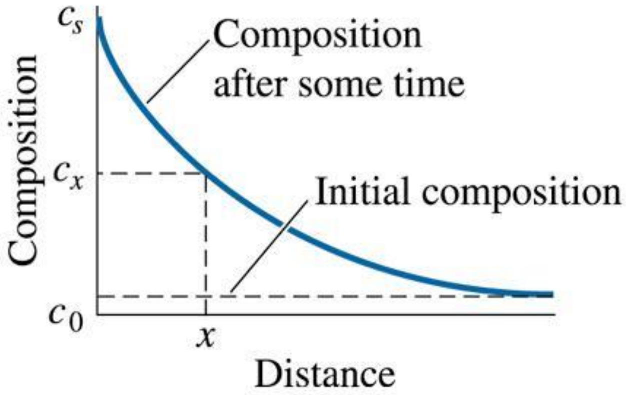
All images are taken from H.Föll' excellent website primer on materials defect http://www.tf.uni-kiel.de/matwis/amat/def_en/

La seconda legge di Fick

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

Consente di calcolare la concentrazione della specie che diffonde, in un punto arbitrario del sistema, dopo un certo tempo di diffusione ad una certa temperatura





FICK'S LAWS

Q: what equation(s) does *n(x,t)* obey?

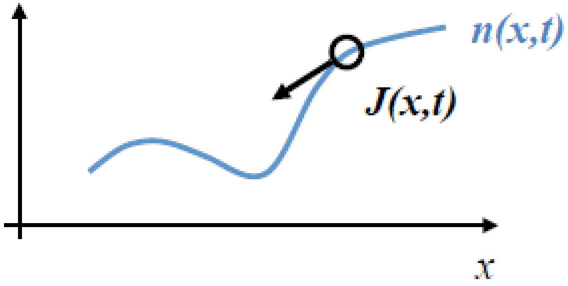
A: we cannot loose interstitial impurities, thus a continuity equation is obeyed. We can use the same conservation equation applying to electric charges:

$$\frac{\partial J}{\partial x} + \frac{\partial n}{\partial t} = 0 \quad \textbf{Continuity Equation}$$

where *J(x,t)* is now the current density of impurities in the material

Q: Any more equation linking *n* and *J* ?

A: Yes! We expect **Fick's Law N° 1** apply (a proof is provided further on)



$$\boxed{J(x,t) = -\widetilde{D}\,\frac{\partial n(x,t)}{\partial x}} \quad \textbf{Fick's Law N° 1}$$

where $\widetilde{D}$ is a "diffusion coefficient" in m^2/sec.

Note: we do not know yet if this is the same as the D we just derived from stochastic theory

FICK'S LAWS

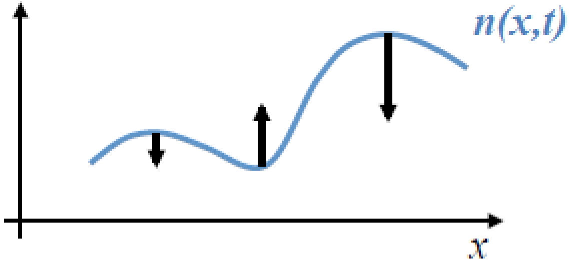
Note:
only if $\frac{\partial \tilde{D}}{\partial x} = 0$

To summarise, our empiric laws are:

$$\begin{cases} J(x,t) = -\tilde{D}\dfrac{\partial n(x,t)}{\partial x} \\ \dfrac{\partial J}{\partial x} + \dfrac{\partial n}{\partial t} = 0 \end{cases} \qquad \therefore \quad \frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} = -\frac{\partial}{\partial x}\left[-\tilde{D}\frac{\partial n}{\partial x}\right] = \tilde{D}\frac{\partial^2 n}{\partial x^2}$$

Fick's Law N° 2

$$\boxed{\frac{\partial n}{\partial t} = -\tilde{D}\frac{\partial^2 n}{\partial x^2}}$$



Clearly, n grows with time at minima, and decreases at maxima ($n(x,t) = const$ is, obviously, a solution for large t).

$$\left(\frac{\partial}{\partial t} - \tilde{D}\frac{\partial^2}{\partial x^2}\right)n(x,t) = 0$$

is another way to write the equation $n(x,t)$ satisfies empirically

FICK'S LAWS

We next justify this equation by proving from our microscopic theory, with $\widetilde{D} = D$:

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right) n(x,t) = \int_{-\infty}^{+\infty} n(x',0)\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right)\left[\frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x')^2}{4Dt}}\right] dx'$$

which is 0 if $$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right)\left[\frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x')^2}{4Dt}}\right] = 0$$

$$g(x,t) \propto \frac{1}{\sqrt{t}}\, e^{-\frac{x^2}{4Dt}} \; ;$$

$$\frac{\partial}{\partial x}[\ln f(x)] = \frac{f'(x)}{f(x)} \;\Rightarrow\; f'(x) = f(x)\frac{\partial}{\partial x}[\ln f(x)]$$

$$\Rightarrow \quad \frac{\partial g}{\partial t} = \frac{1}{\sqrt{t}}\, e^{-\frac{x^2}{4Dt}}\, \frac{\partial}{\partial t}\left[-\frac{1}{2}\ln t - \frac{x^2}{4Dt}\right] = g\left[-\frac{1}{2t} + \frac{x^2}{4Dt^2}\right]$$

$$\frac{\partial g}{\partial x} = g\, \frac{\partial}{\partial x}\left[-\frac{1}{2}\ln t - \frac{x^2}{4Dt}\right] = g\left[-\frac{x}{2Dt}\right] \; ; \qquad \frac{\partial^2 g}{\partial x^2} = g\,\frac{x^2}{4D^2t^2} + g\left(-\frac{1}{2Dt}\right)$$

$$\therefore \; \mathrm{D}\frac{\partial^2 g}{\partial x^2} = D\left[\frac{x^2}{4D^2t^2} - \frac{1}{2Dt}\right] g = g\left[-\frac{1}{2t} + \frac{x^2}{4Dt^2}\right]$$

The two terms are exactly Equal-QED

This proves Fick's Law No. 2, if the diffusion coefficient is $D = \nu \cdot e^{-\frac{\Delta E}{k_b T}} \cdot a^2$

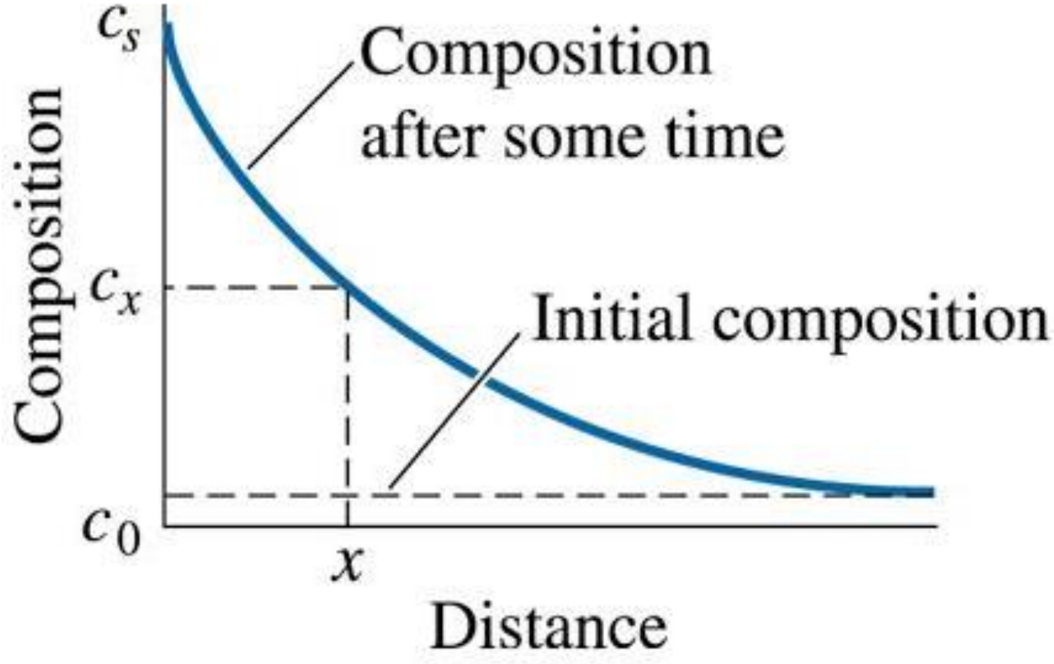
Una importante soluzione della seconda legge di Fick

Integrando la seconda legge di Fick con le condizioni al contorno:

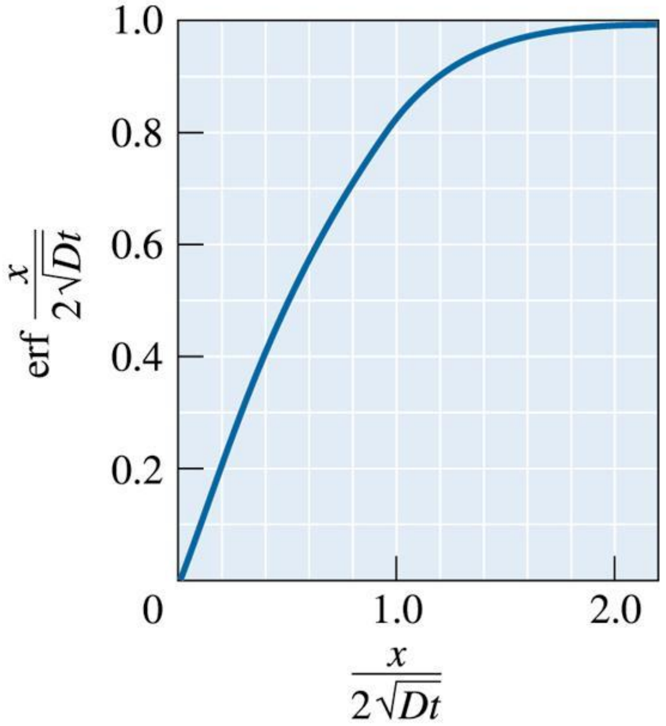
→ Concentrazione superficiale costante, c_s

→ Concentrazione iniziale c_0

$$\frac{c_s - c_x}{c_s - c_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



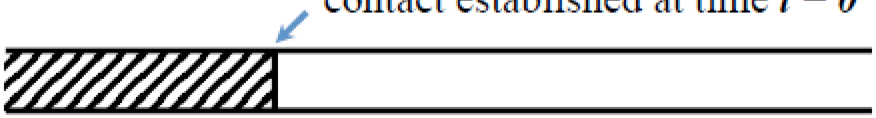
Valori della funzione errore per la valutazione dei profili di concentrazione con la soluzione della legge di Fick:



Argument of the error function $\frac{x}{2\sqrt{Dt}}$	**Value of the error function** $\mathrm{erf}\,\frac{x}{2\sqrt{Dt}}$
0	0
0.10	0.1125
0.20	0.2227
0.30	0.3286
0.40	0.4284
0.50	0.5205
0.60	0.6039
0.70	0.6778
0.80	0.7421
0.90	0.7970
1.00	0.8427
1.50	0.9661
2.00	0.9953

CARBURISATION OF IRON

Exercise: Carburisation of iron



contact established at time $t = 0$

a bar of steel with concentration of C

$n = c$

an infinite iron (pure) bar

$n = 0$

$$n(x,0) = \begin{cases} c & x < 0 \\ 0 & x \geq 0 \end{cases}$$

Problem: determine $n(x,t)$

$$n(x,t) = \int_{-\infty}^{+\infty} n(x',0)\, g(x - x', \sigma)\, dx' = \int_{-\infty}^{0} c \cdot \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{(x-x')^2}{4Dt}} dx'$$

$$= \frac{c}{\sqrt{2\pi}\sigma} \int_{-\infty}^{0} e^{-\frac{(x-x')^2}{2\sigma^2}} dx'$$

we change variable: $y = \frac{x' - x}{\sqrt{2}\sigma} \Rightarrow dy = \frac{dx'}{\sqrt{2}\sigma}$

$$= \frac{c}{\sqrt{2\pi}\sigma} \sqrt{2}\sigma \int_{-\infty}^{-\frac{x}{\sqrt{2}\sigma}} e^{-y^2} dy = c \int_{-\infty}^{-\beta} \frac{e^{-y^2}}{\sqrt{\pi}} dy$$

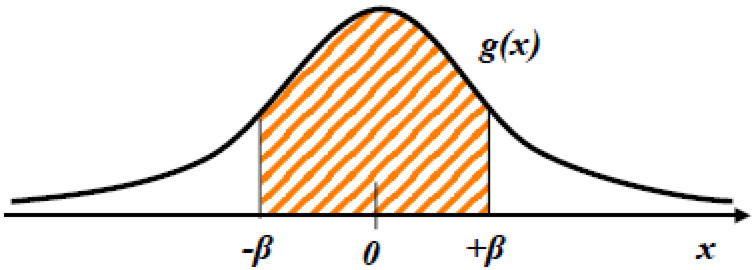
a *standard Gaussian* integral.

$$g(y,\sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{y^2}{2\sigma^2}}, \quad \text{if } \sigma^2 = \frac{1}{2} \rightarrow \sigma = \frac{1}{\sqrt{2}}, \quad \text{become} \quad g\left(y, \sigma = \frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{\pi}} e^{-y^2}$$

⇨ The **standard Gaussian**, which in the old times was tabulated..

CARBURISATION OF IRON

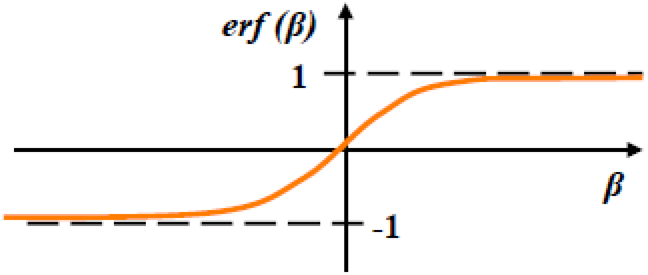
Error Function ***erf(β)*** :



$$\boxed{erf(\beta) = \int_{-\beta}^{+\beta} \frac{1}{\sqrt{\pi}} e^{-y^2} dy}$$

$$\boxed{\begin{cases} erf(\sigma) = 0.68 \\ erf(2\sigma) = 0.95 \\ erf(3\sigma) = 0.997 \end{cases}}$$

is the **error function**, defined in terms of the standard Gaussian.



$$\begin{cases} erf(0) = 0 \\ erf(+\infty) = 1 \\ erf(-\infty) = -1 \end{cases}$$

erf is odd: $\left(erf(-x) = -erf(x)\right)$, due the properties of integration:

$$\int_{-a}^{a} f(x)dx = -\int_{a}^{-a} f(x)dx$$

Coming back to our problem,

$$n(x,t) = c\int_{-\infty}^{-\beta} \frac{e^{-y^2}}{\sqrt{\pi}}dy = \frac{c}{2}\left[1 - erf(\beta)\right] \qquad \text{with} \qquad \begin{cases} \beta = \dfrac{x}{\sqrt{2}\sigma} \\ \sigma = 2Dt \end{cases}$$

thus:

$$\boxed{n(x,t) = \frac{c}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]}$$

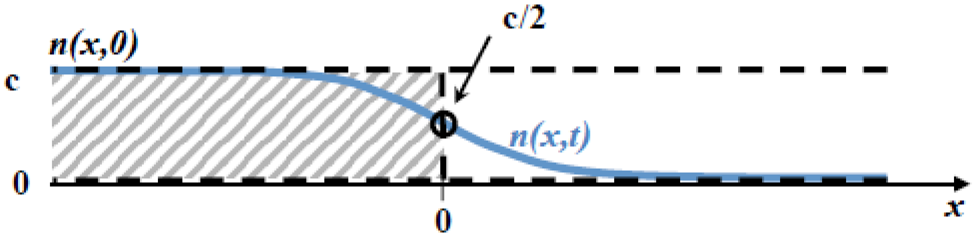
CARBURISATION OF IRON

Clearly, for $\begin{cases} t \to 0 \\ x > 0 \end{cases}$ $erf \to 1;\ n \to 0$. For $\begin{cases} t \to 0 \\ x < 0 \end{cases}$ $erf \to -1;\ n \to c$

For particular conditions, *n(x,t)* assumes the following values:

$n(0,t) = \frac{c}{2} \quad \forall t$ (just continuity) $\qquad \lim_{t\to\infty} n(x,t) = \frac{c}{2} \ \forall x$

For intermediate t :



ALSO NOTE:

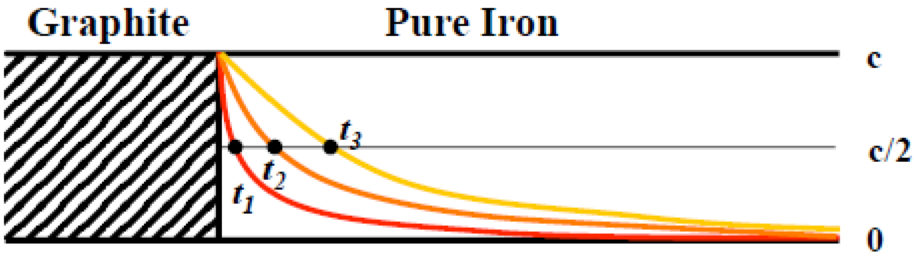
The fixed point $n(0,t) = {}^{c}\!/_{2} \ \forall t$ is a *boundary condition*: imposing it will automatically mean that the known solution applies for *x>0*, regardless the conditions (or even the *existence*) of the *x<0* region

… we can thus apply the x>0 solution to any problem where the density of defects at a boundary is fixed

CARBURISATION OF IRON

(1) constant concentration ***c*** for ***x=0***:

a good examples could be a system like this:

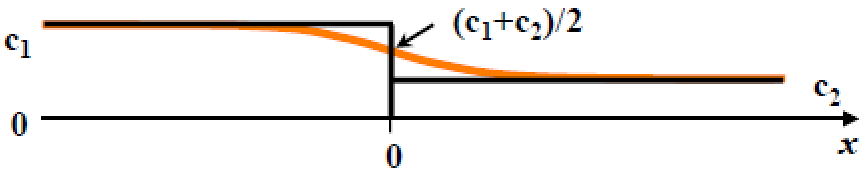


Behaviour for $t_1 < t_2 < t_3$

since *erf* (½) ≃ ½ , the position of the point where ½ of the boundary value is attained (front of carburisation entering the iron bar) is:

$x(t) = \sqrt{Dt}$ so, for: $D = 10^{-10}\, cm^2/s$; $t = 100 s$ ⇨ $x = \sqrt{10^{-8}} = 10^{-4}\, cm = 1 \mu m$ (not too much…)

(2) two different concentrations ***c_1*** and ***c_2***



Behaviour for $t > 0$

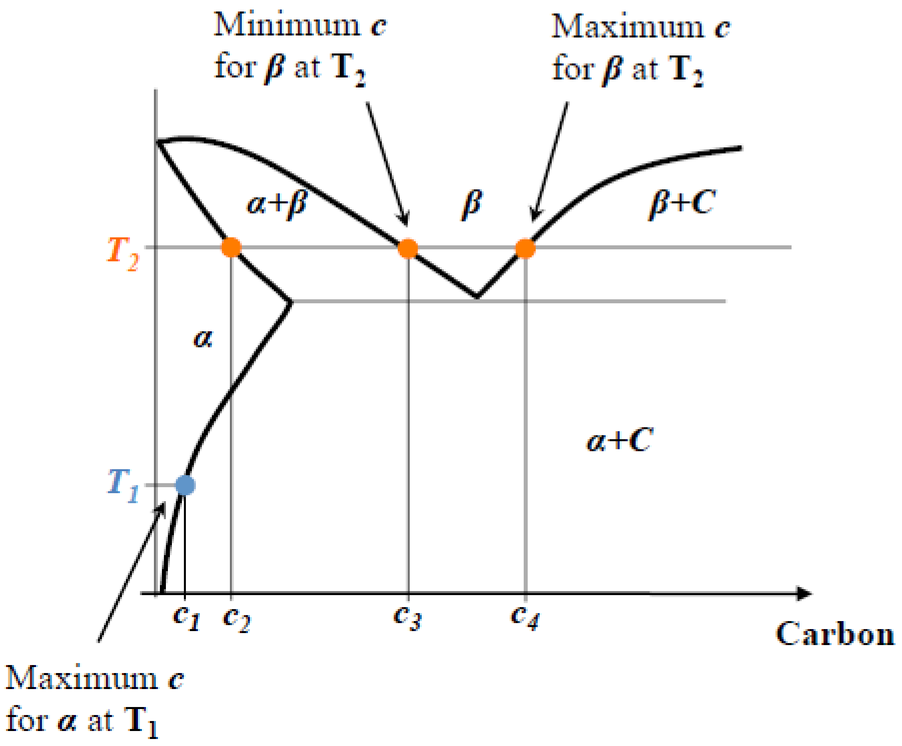
The solution will be a superposition (walkers ignore each other!).

$$n(x,t) = \frac{c_1}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] + \frac{c_2}{2}\left[1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] = \frac{c_1 + c_2}{2} - \frac{c_1 - c_2}{2}\, erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

so for $t \to \infty$: $n \to \dfrac{c_1 + c_2}{2}$

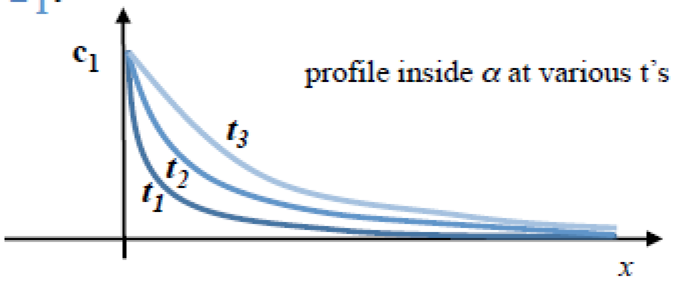
CARBURISATION

Example: concentration profiles for a typical phase diagram.

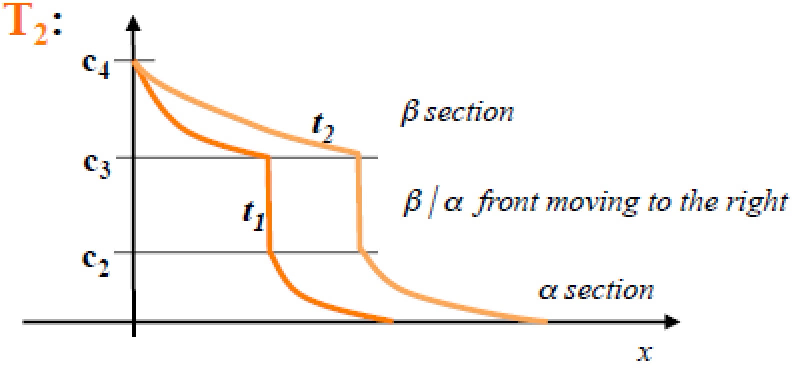


Time evolution of the *n(x,t)* profiles:

T = T$_1$:



T = T$_2$:



FICK'S LAW N°2 FOR VARYING *T*(*x*)

Finally, we can re-derive Fick's Law N°2 for a non uniform temperature

$$\begin{cases} J = -\dfrac{\partial Dn}{\partial x} = 0 \quad (*) \\ \dfrac{\partial J}{\partial x} + \dfrac{\partial n}{\partial t} = 0 \end{cases}$$

(and therefore, non uniform diffusion coefficient….)

$$T(x) \rightarrow D(x)$$

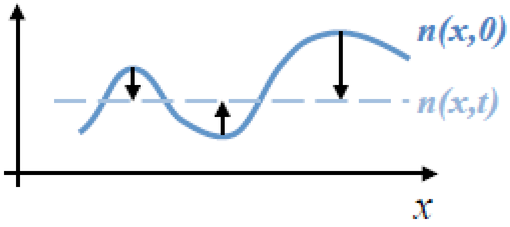
$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial^2}{\partial x^2}(Dn) = D\frac{\partial^2 n}{\partial x^2} + 2\frac{\partial D}{\partial x}\frac{\partial n}{\partial x} + n\frac{\partial^2 D}{\partial x^2}$$

Note: this goes beyond our "broadening Gaussians" model derivation which assumes ***D* = *const*** to prove the standard-form Fick's Law N°2. (*) Exercise: revise the argument in the last slide to show that this is the right form of FL #1 for *D*=*D*(*x*)

D really is a function of *x*, since could be $T(x) \neq \text{const}$ and ΔE is really $\Delta F(x)$ containing vibrational entropy components, usually lowering the barriers at higher temperatures. However, it must be a very smooth function, varying on macroscopic scales.

⇨ $$D(x) = \nu \cdot e^{-\frac{\Delta F(x)}{k_b T(x)}} \cdot a^2$$

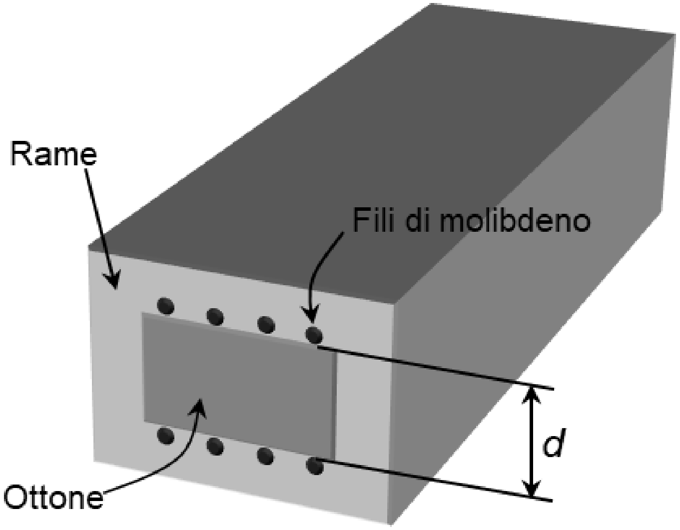
Local maxima still go down, and minima go up if we ignore second derivatives of *D*.



Diffusion coefficients in practice

- **Coefficient of Self-Diffusion**: diffusion of self-interstitials
- **Intrinsic Diffusion Coefficient**:
  Describes the diffusion of component A in B and viceversa: D_A^{in} and D_B^{in} (usually different")
- **Interdiffusion coefficient** (chemical coefficient, mutual diffusion coefficient): $\widetilde{D} = -\vec{J} \Big/ \frac{\partial c}{\partial x}$
  The overall coefficient that describes the overall diffusion between two parts of a solid in contact

Kirkendall's Experiments

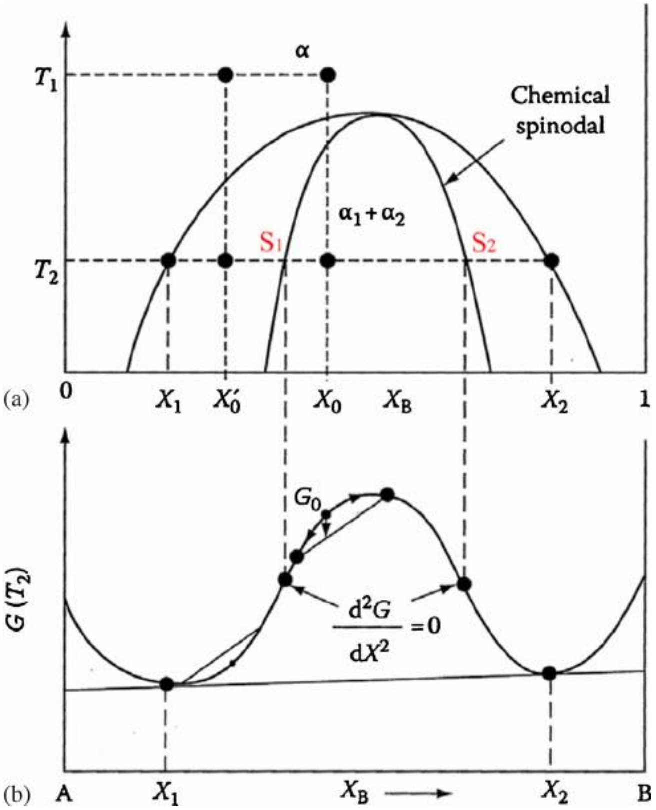


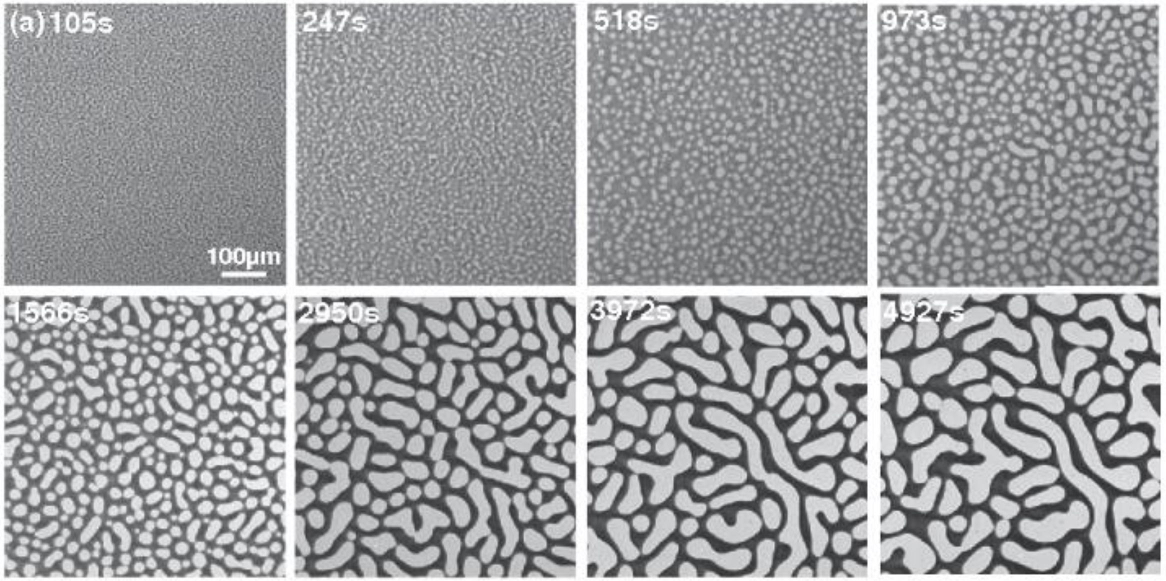
Darken's Equation

$$\widetilde{D} = N_B D_A^{in} + N_A D_B^{in}$$

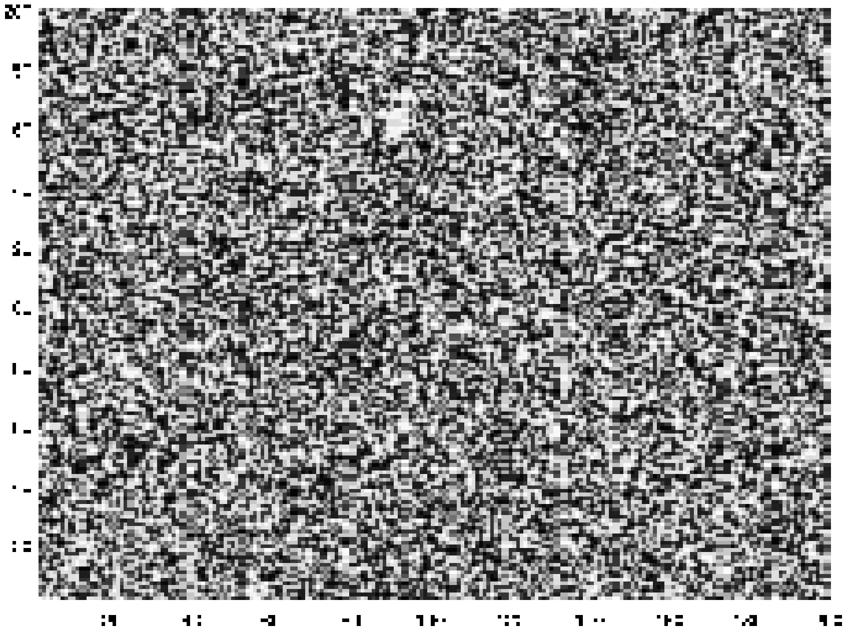
Spinodal decomposition

An “uphill” diffusion mechanism!





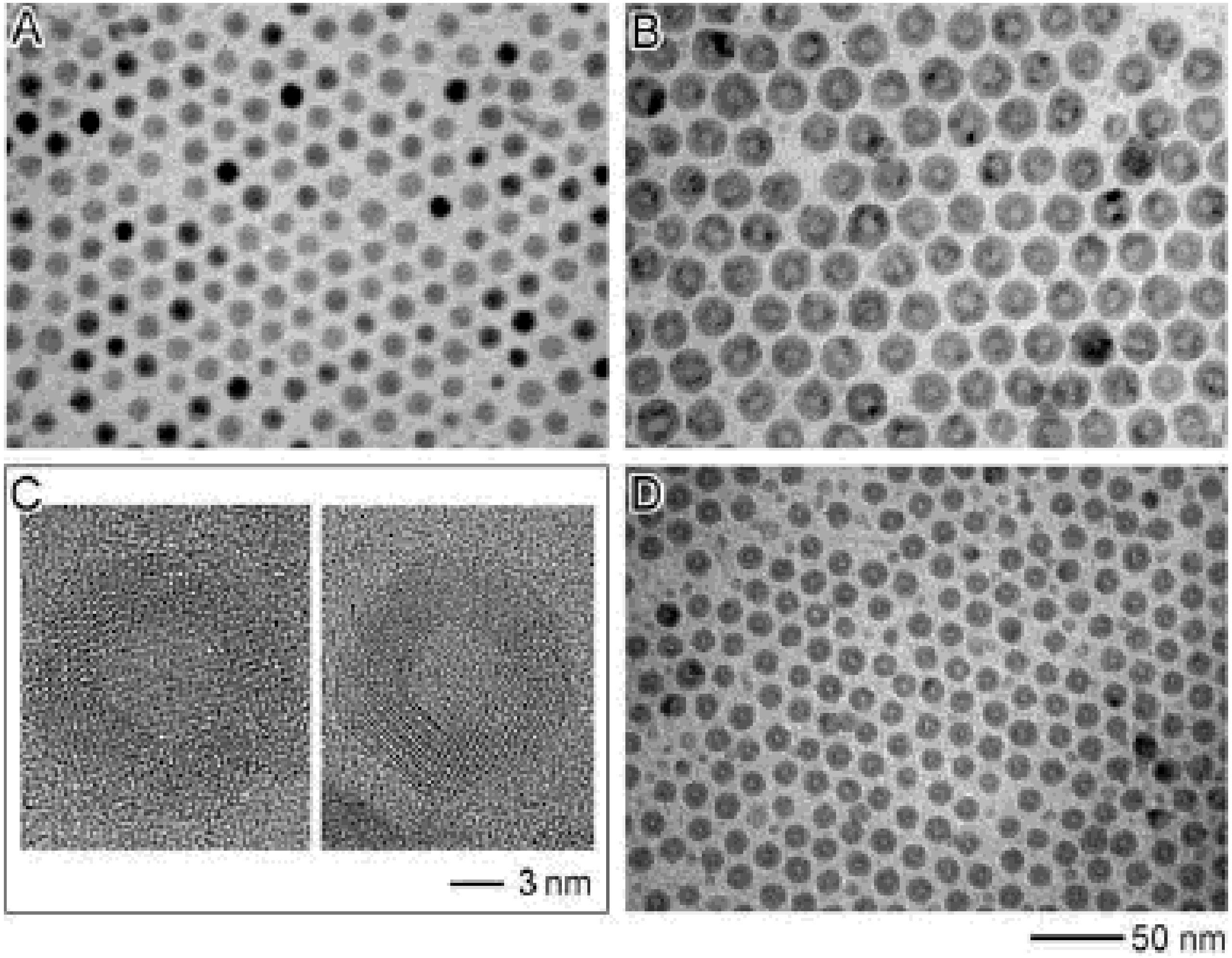
Spinodal decomposition



An interesting case:
Diffusion in Nanosystems

Diffusion in Nanosystems

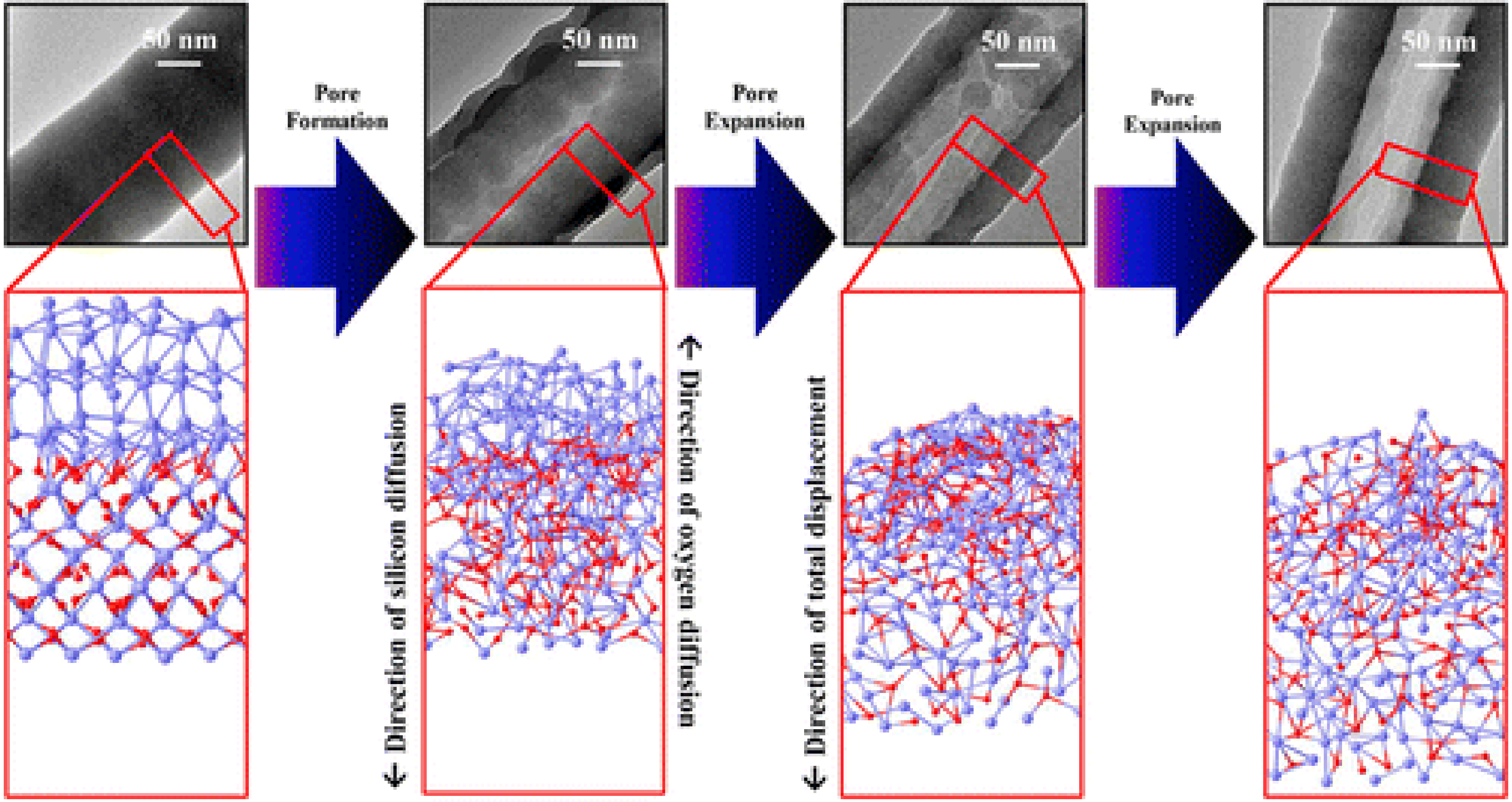
Creating hollow nanostructures via Kirkendall's effect



Yin et al., Science 304, 711 (2004)

Diffusion in Nanosystems

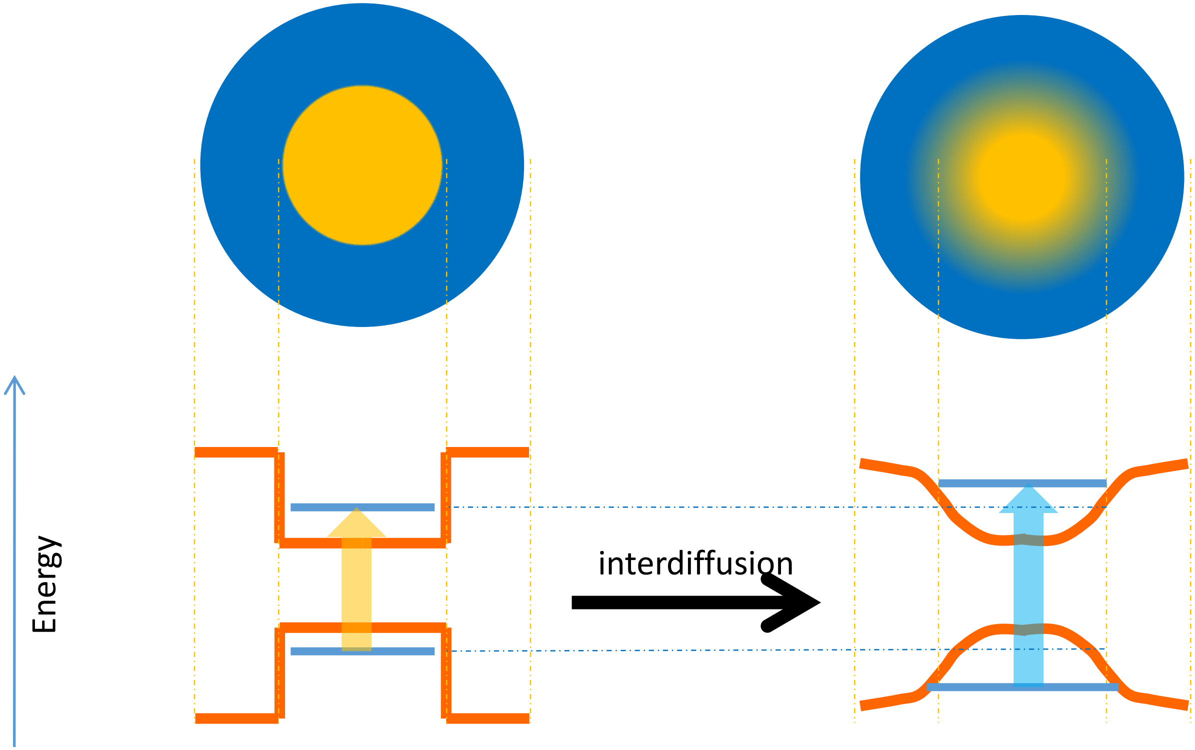
Creating hollow nanostructures via Kirkendall's effect



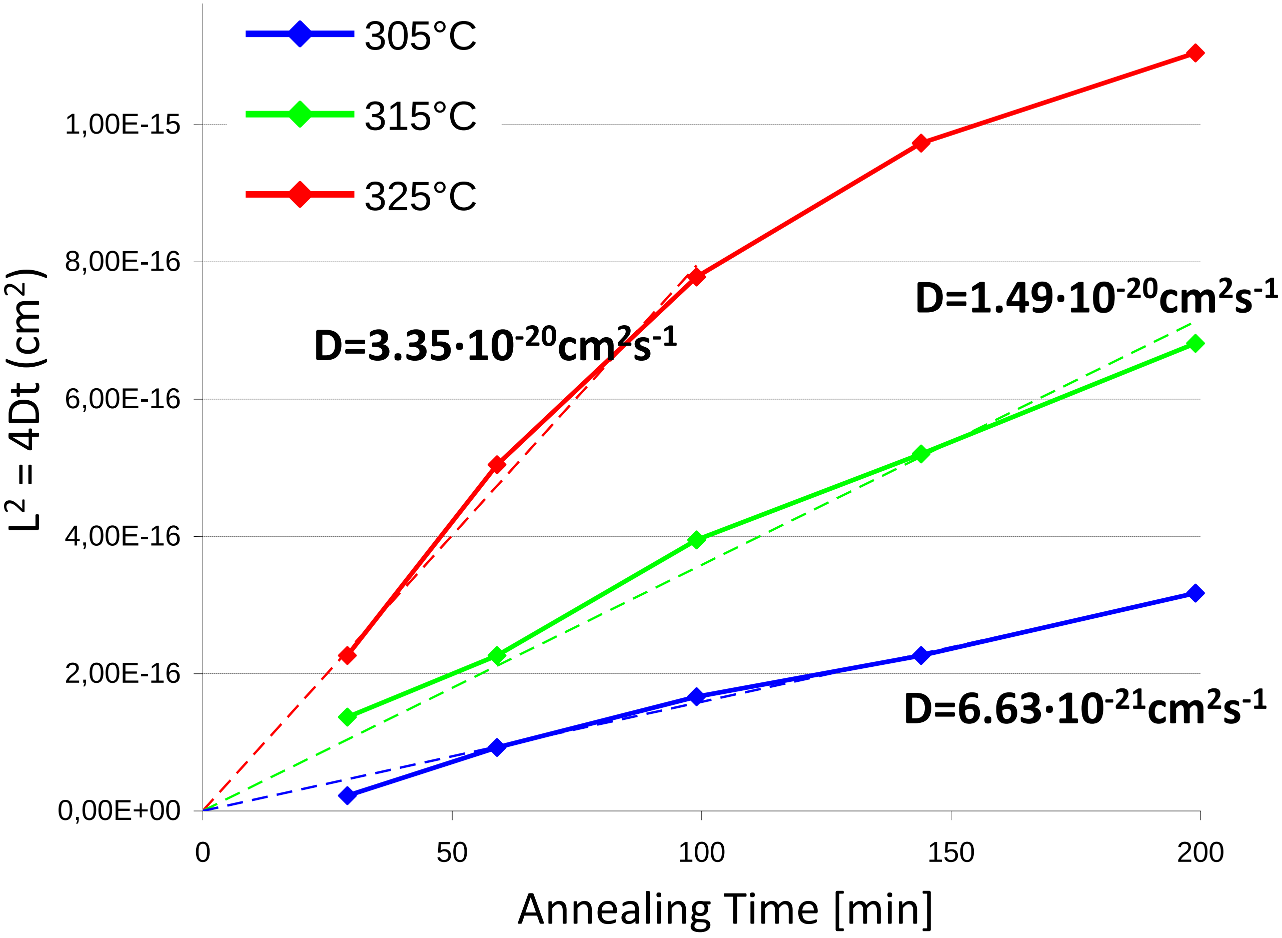
Son et al., Nano Lett. 15, 6914 (2015))

Diffusion in Nanosystems

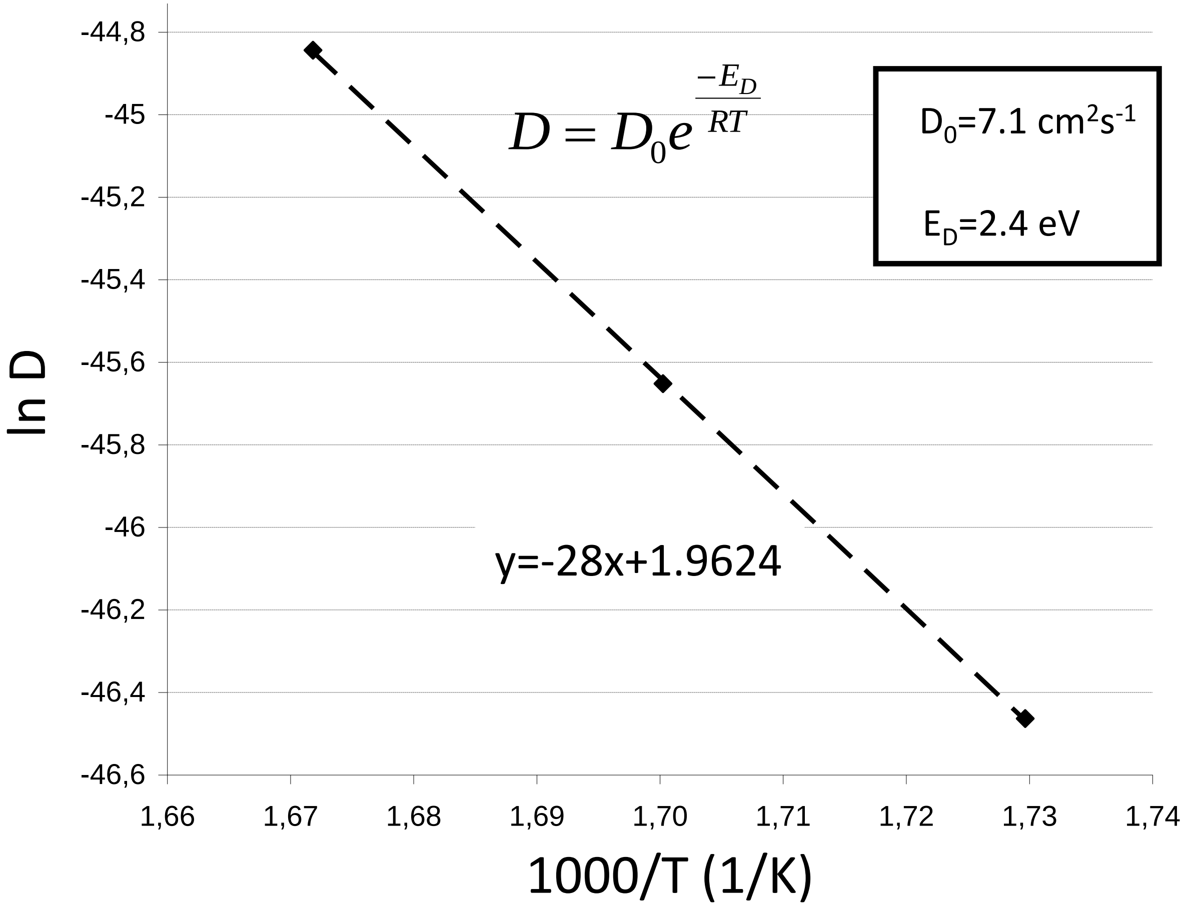
Some work from our labs: Diffusion in nanoheterostructures



Diffusion Length vs. Time



Arrhenius Plot and Diffusion coefficient for CdSe/CdS



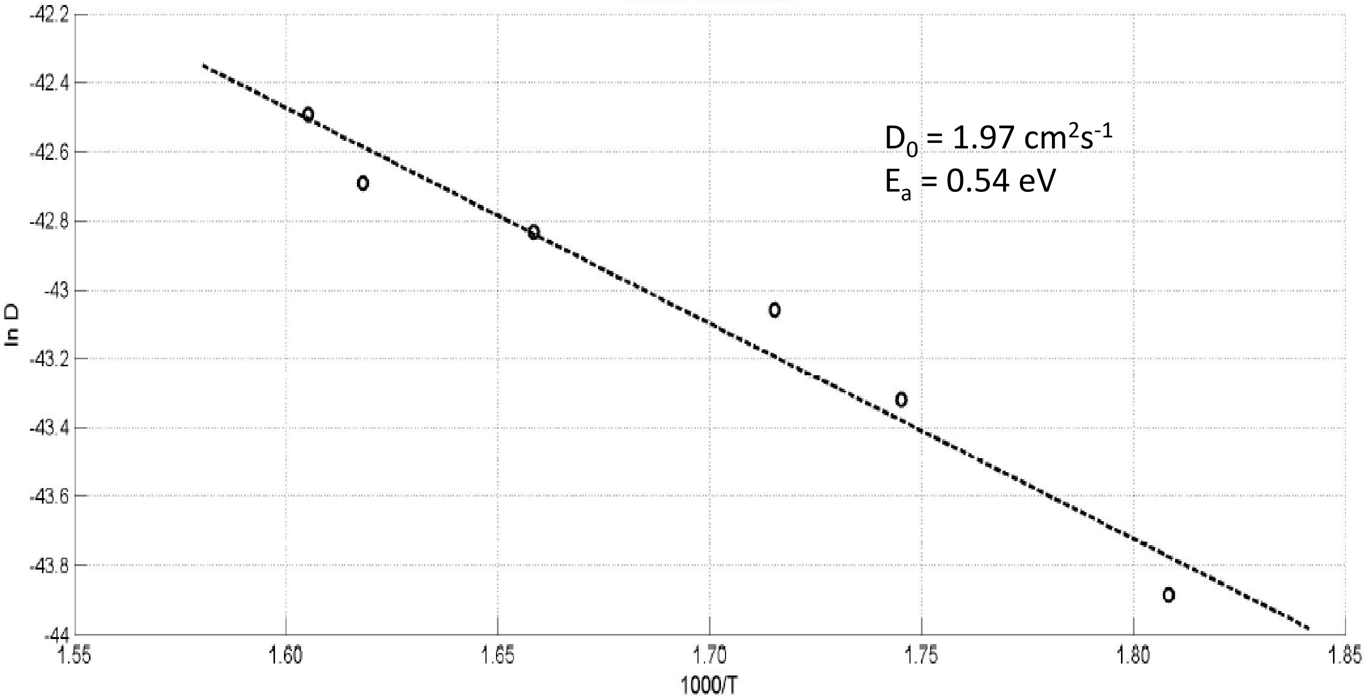
$$D = D_0 e^{\frac{-E_D}{RT}}$$

D_0=7.1 cm^{2}s^{-1}

E_D=2.4 eV

y=-28x+1.9624

Another System: CdSe/ZnSe



D_0 = 1.97 cm^2s^{-1}
E_a = 0.54 eV