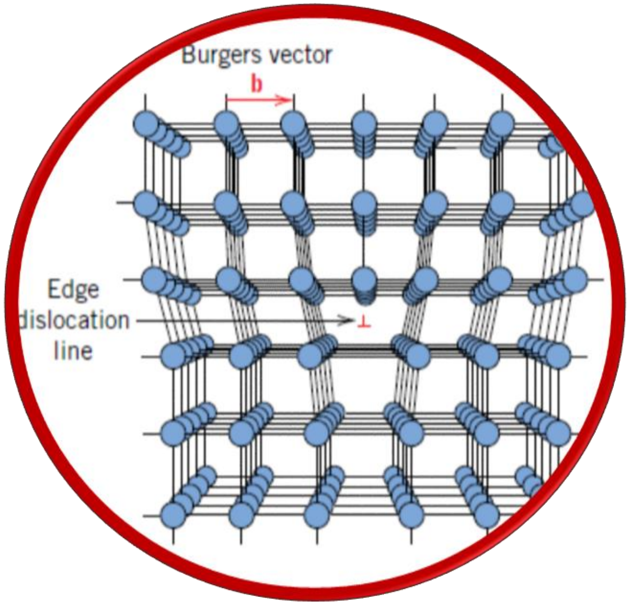
Review of basic concepts in materials science

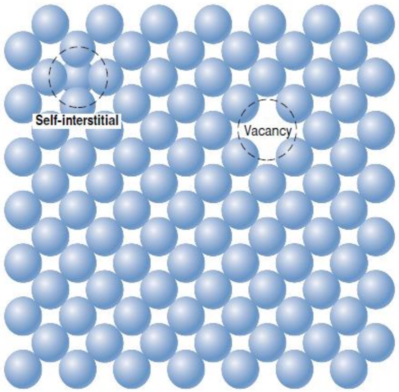


content

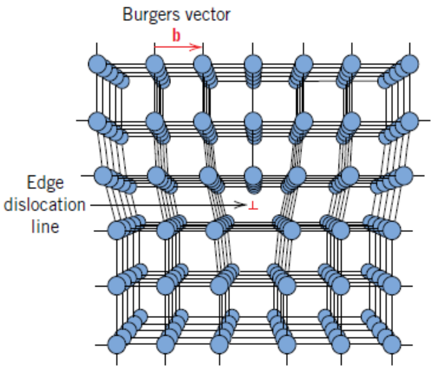
- Mechanical properties of Materials
- Thermodynamics
- Diffusion & nucleation

Defects in solids

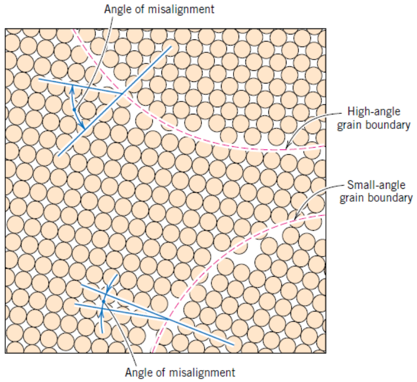
Vacancies



dislocations



grain boundaries



In thin crystalline films the presence of defects not only serves to disrupt the geometric regularity of the lattice on a microscopic level,

but significantly influences many film properties such as **chemical reactivity**, **electrical conduction**, and **mechanical behavior**.

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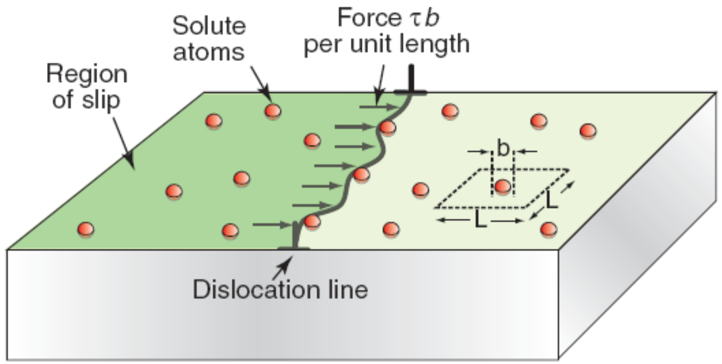
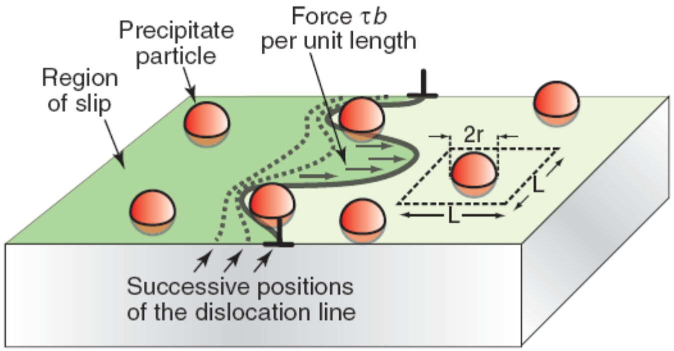
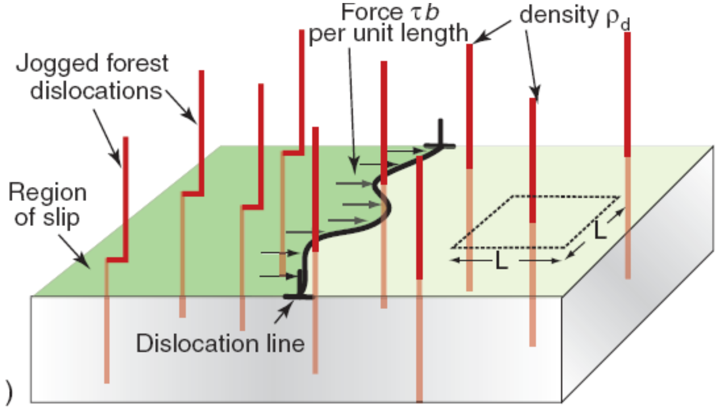
Strengthening by mechanisms



$$\tau_{ss} = \alpha E c^{1/2}$$

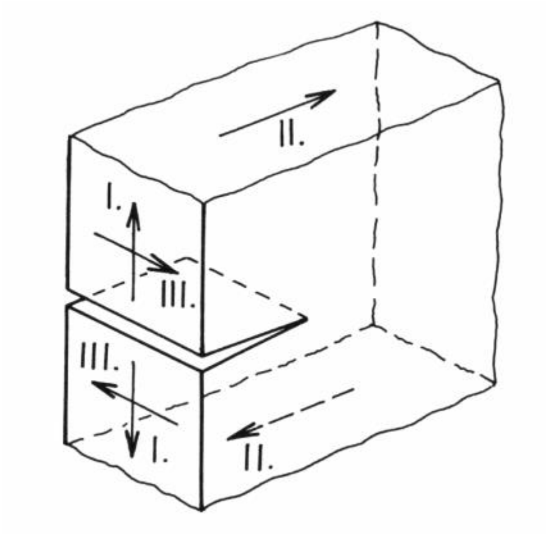


$$\tau_{ppt} = \frac{Eb}{L}$$

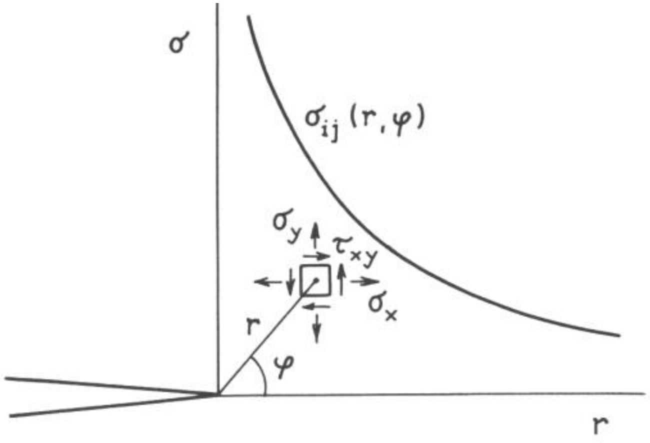


$$\tau_{wh} \approx \frac{Eb}{2}\sqrt{\rho_d}$$

Fracture modes and crack tip stress distribution



Fracture modes
I,II,III



Sneddon equation

$$\sigma_{n,ij}(r,\varphi) = \frac{K_n}{\sqrt{2\pi r}} f_{n,ij}(\varphi)$$

Stress intensity factors

Stress intensity factors – general form:

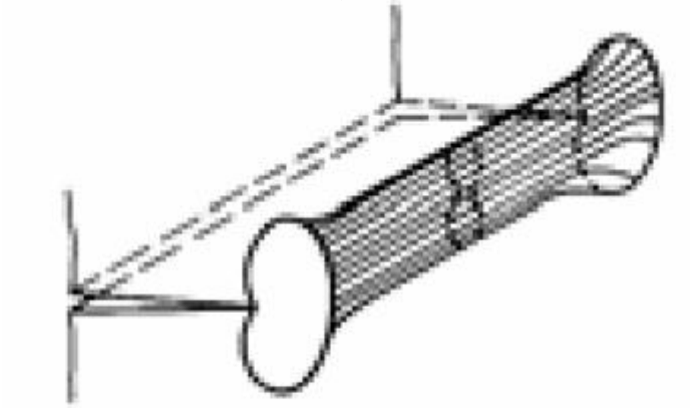
$K_n = \sigma Y \sqrt{a}$ mit

Y geometry factor
a crack length
σ stress

K_n depends on

- Shape and size of both crack and device/part
- Load distribution

Ductile materials: plastic zone around crack tip



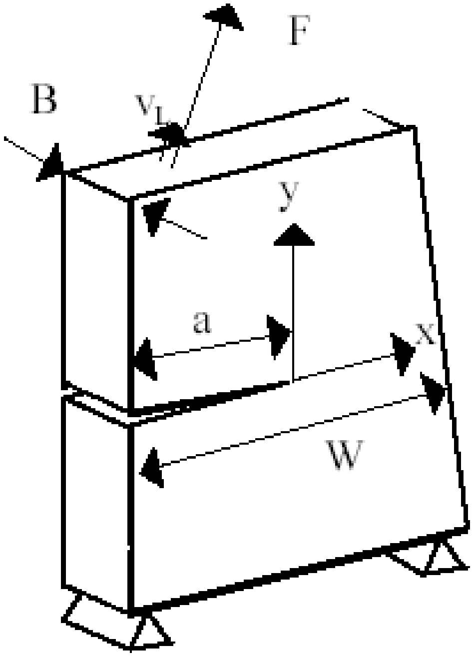
critical energy release rate

Energy release rate for mode I cracks:

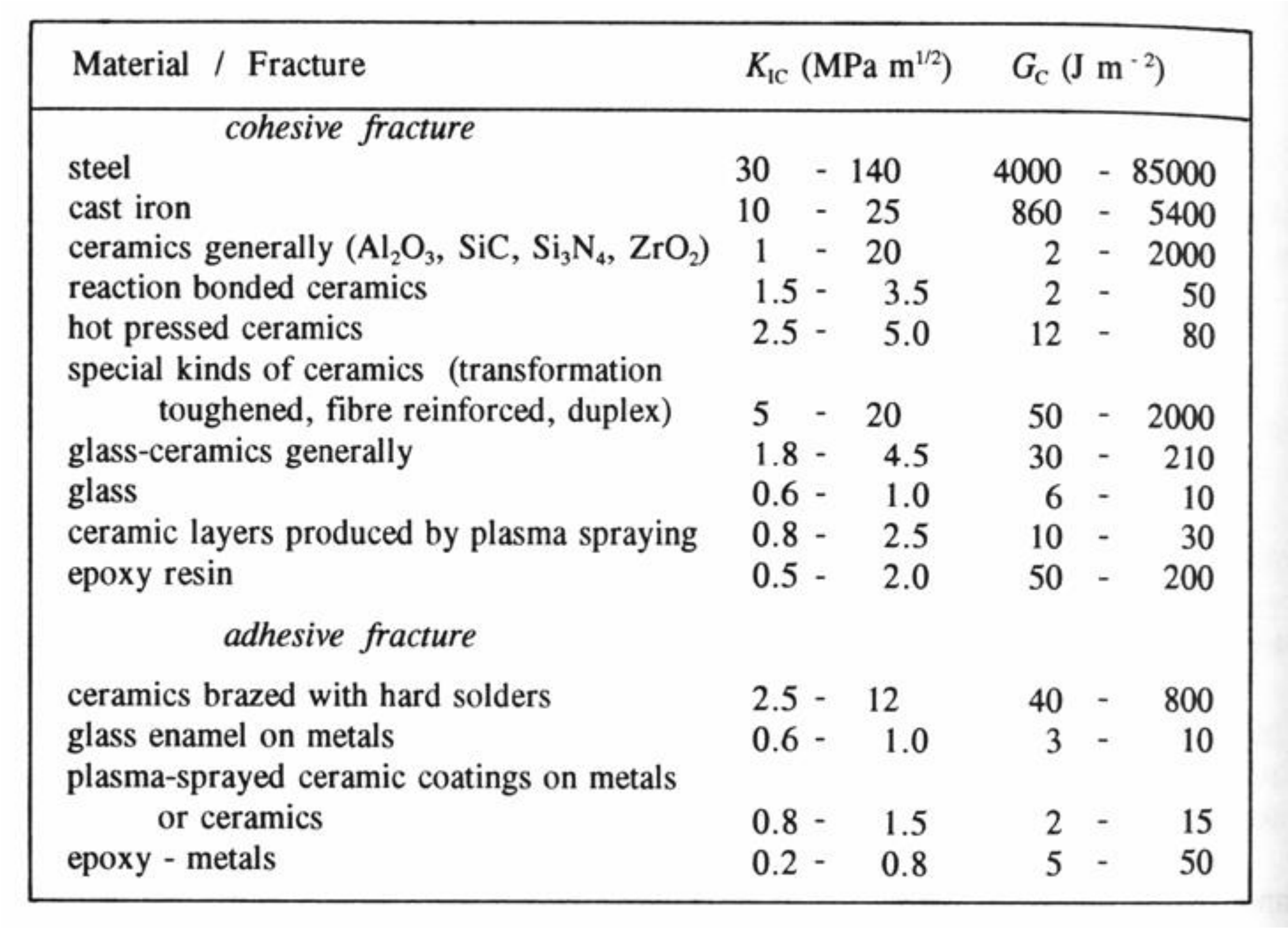
$$G = -\frac{1}{B}\frac{dW_{el}}{da}$$

Critical energy release rate:

$$G_C = 2(\gamma_s + \gamma_p)$$



typical fracture toughness values



Material / Fracture	K_{IC} (MPa m$^{1/2}$)	G_C (J m^{-2})
cohesive fracture		
steel	30 - 140	4000 - 85000
cast iron	10 - 25	860 - 5400
ceramics generally (Al_2O_3, SiC, Si_3N_4, ZrO_2)	1 - 20	2 - 2000
reaction bonded ceramics	1.5 - 3.5	2 - 50
hot pressed ceramics	2.5 - 5.0	12 - 80
special kinds of ceramics (transformation toughened, fibre reinforced, duplex)	5 - 20	50 - 2000
glass-ceramics generally	1.8 - 4.5	30 - 210
glass	0.6 - 1.0	6 - 10
ceramic layers produced by plasma spraying	0.8 - 2.5	10 - 30
epoxy resin	0.5 - 2.0	50 - 200
adhesive fracture		
ceramics brazed with hard solders	2.5 - 12	40 - 800
glass enamel on metals	0.6 - 1.0	3 - 10
plasma-sprayed ceramic coatings on metals or ceramics	0.8 - 1.5	2 - 15
epoxy - metals	0.2 - 0.8	5 - 50

thermodynamics

thermodynamics is **very definite** about those events that are **impossible** such as:

- gold films do not oxidize
- atoms do not normally diffuse up a concentration gradient.

thermodynamics is **noncommittal about permissible reactions and processes**. Thus, even though reactions are thermodynamically **favored, they may, in fact, not occur in practice**.

If a system changes from some initial (i) to final (f) state at constant temperature due to a chemical reaction or physical process, a free-energy change happens

$$\Delta G = \Delta H - T\Delta S$$

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thermodynamics

Spontaneous reactions occur at constant temperature and pressure when ΔG is negative.

The general chemical reaction involving three substances A, B, and C in equilibrium is

$$aA + bB \rightarrow cC.$$

$$\Delta G = cG_C - aG_A - bG_B$$

It is customary to denote the free energy of individual reactant or product atomic or molecular species by

$$G_i = G_i^0 + RT \ln a_i,$$

$$\Delta G^0 = cG_C^0 - aG_A^0 - bG_B^0.$$

where R is the gas constant and ΔG° is the free energy of the species in its so-called reference or standard state. For solids this is usually the stable pure material at one atmosphere and 298 K.

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thermodynamics

The activity a_i **may be viewed as an effective thermodynamic concentration** and reflects the change in free energy of the species when it is not in its standard state.

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c}{a_A^a a_B^b}$$

If we assume

$$0 = \Delta G^0 + RT \ln \left\{ \frac{a_{C(eq)}^c}{a_{A(eq)}^a a_{B(eq)}^b} \right\}$$

Then

$$-\Delta G^0 = RT \ln K,$$

where the equilibrium constant K is defined by the quantity in braces.

If there is a **supersaturation of reactants and a subsaturation of products** $\Delta G < 0$.

The reaction proceeds spontaneously as written from left to right with a driving force proportional to the magnitude of ΔG. For many practical cases a_i are close to unity and therefore we can approximate

$$\Delta G = \Delta G^0.$$

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thermodynamics

Quantitative information on the **feasibility of chemical reactions is thus provided by values of ΔG°**

ΔG° data for formation of metal oxides as a function of temperature is shown and known as an **Ellingham diagram**.

Example:
It is desired to deposit thin-film metal interconnections on a SiO_2 substrate and Al and Cu are possible candidates. Which one would be a better choice?

Assuming 400°C deposition temperature the relevant reactions are

$$Si + O_2 \rightarrow SiO_2 \qquad \Delta G^0_{SiO_2}\,(400°C) = -175\,\text{kcal}$$

$$4/3Al + O_2 \rightarrow (2/3)Al_2O_3 \qquad \Delta G^0_{Al_2O_3}\,(400°C) = -230\,\text{kcal}$$

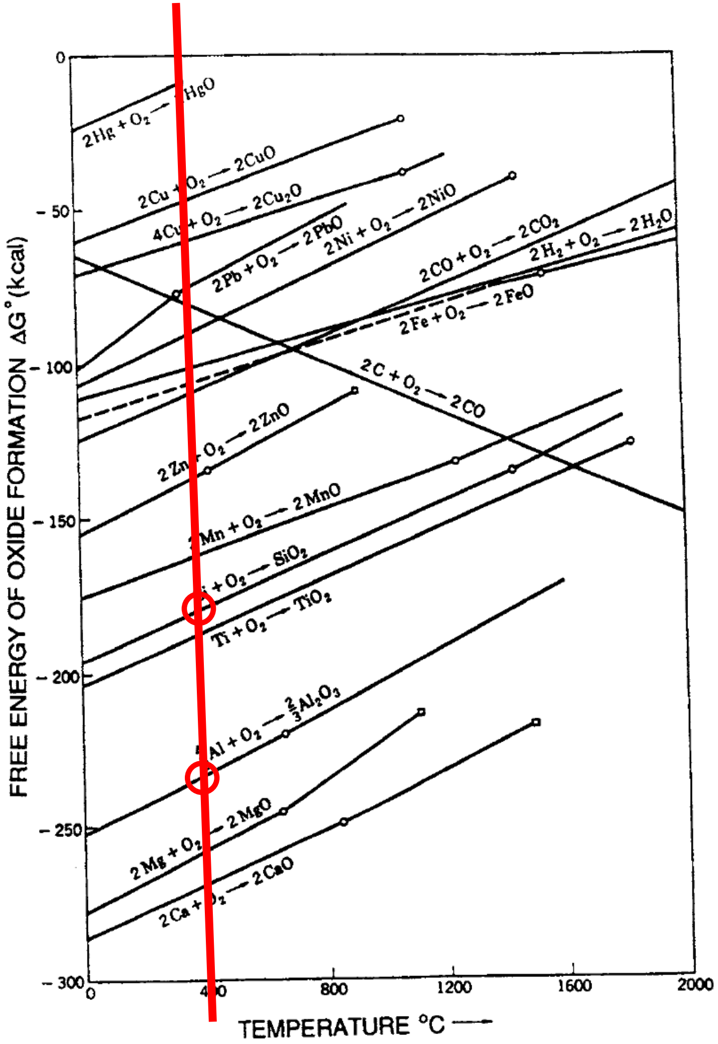
$$2Cu + O_2 \rightarrow 2CuO \qquad \Delta G^0_{CuO}\,(400°C) = -45\,\text{kcal.}$$

After elimination of O_2 and algebraic addition of free energies the two reduction reactions are

$$(4/3)Al + SiO_2 \rightarrow (2/3)Al_2O_3 + Si \qquad \Delta G^0\,(400°C) = -55\,\text{kcal}$$

$$2Cu + SiO_2 \rightarrow 2CuO + Si \qquad \Delta G^0\,(400°C) = +130\,\text{kcal.}$$

Therefore, **Al films tend to reduce SiO_2 films**, leaving free Si behind. Cu is the better choice.



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Empa
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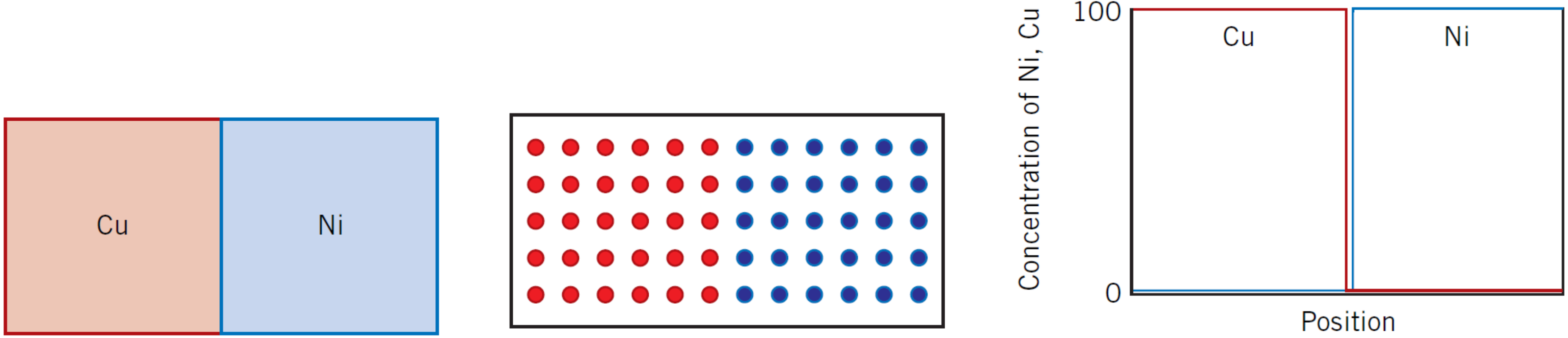
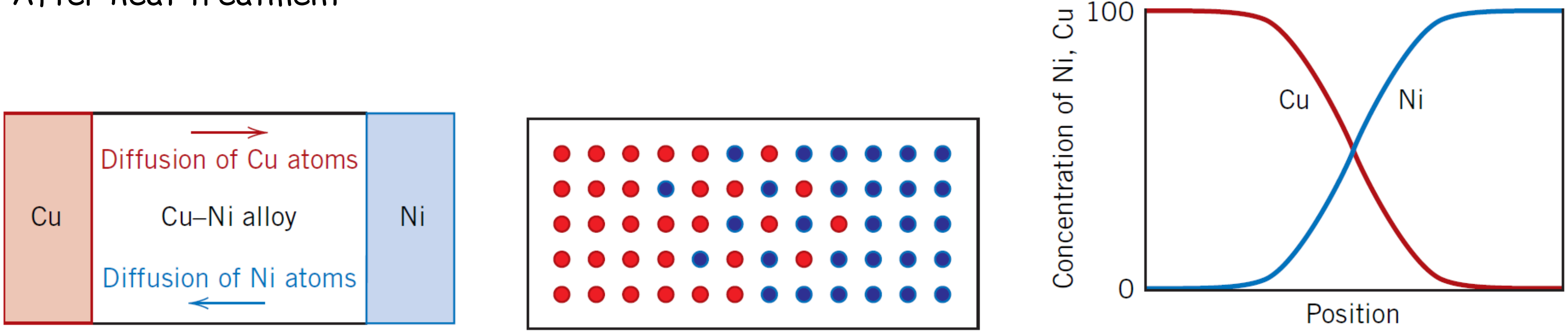
what is diffusion?

Before heat treatment



(a) (b) (c)

After heat treatment



(a) (b) (c)

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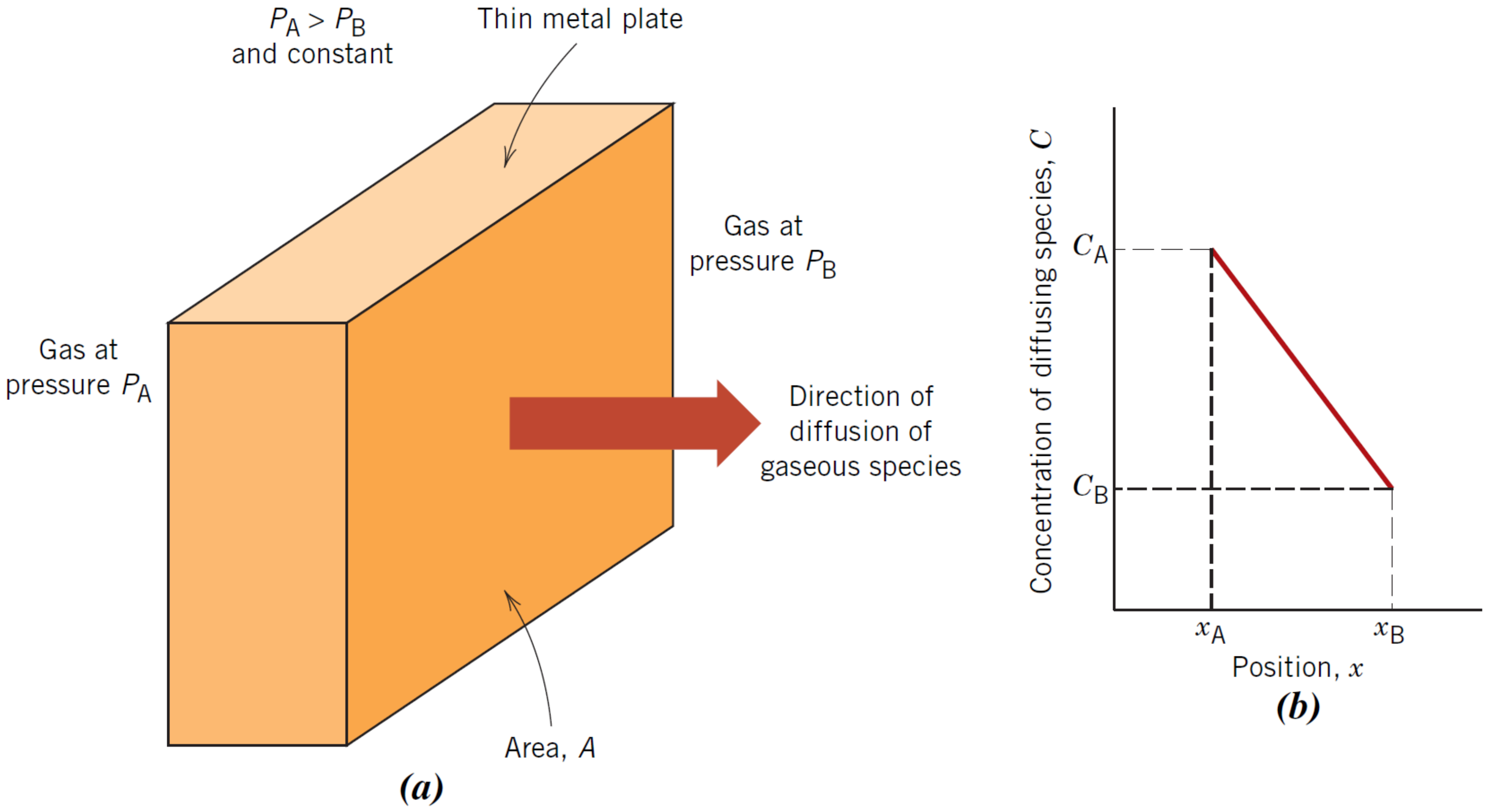
what is diffusion?



Steady-state diffusion across a thin plate leads to linear concentration profile

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Kinetics – mass transport - Fick's first law

In thin films phase transformations, recrystallization, compound growth and degradation phenomena are governed by diffusion.

Fick's law connects concentration gradients and the resultant diffusional transport:

$$J = -D\frac{dC}{dx}.$$

The units of C are typically atoms/cm^3, while the magnitude of the diffusion coefficient, D (cm^2/s). The units for J are atoms/m^{2}s).

D increases in exponential fashion with temperature according to a Maxwell-Boltzmann relation:

$$D = D_0 \exp -\frac{E_D}{k_B T}$$

where D_o is a constant and E_D is the activation energy for diffusion

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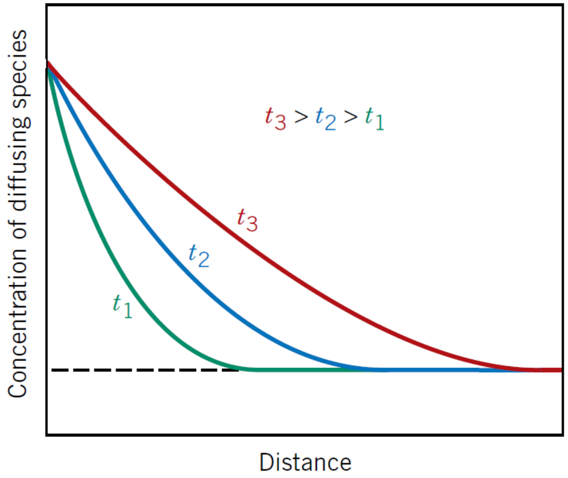
Kinetics – mass transport- Fick's second law

mass flow into and out of regions cause time-varying accumulations or depletions of atomic species governed, in one dimension, by the well-known equation

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

Most practical diffusion situations are nonsteady-state ones—that is, the diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting. This is illustrated in the following graph which shows concentration profiles at three different diffusion times



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Kinetics – mass transport- Fick’s second law

One practically important **solution is for a semi-infinite solid** in which the **surface concentration is held constant**. Frequently, the source of the diffusing species is a gas phase, the partial pressure of which is maintained at a constant value. Another case of practical relevance is the **case of a very thin film on a semi-infinite substrate**.

Consider an initially pure thick film (our semi-infinite solid) into which some solute diffuses from the surface. If the film thickness is very large or effectively infinite compared to the extent of diffusion, the situation can be physically modeled by the following initial and boundary conditions:

$$C(x,0) = 0 \quad \text{at } t = 0 \qquad \text{for } \infty > x > 0$$

$$C(\infty,t) = 0 \quad \text{at } x = \infty \qquad \text{for } t > 0.$$

A second boundary condition that must be specified concerns the nature of the diffusant distribution maintained at the film surface x = 0

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Kinetics – mass transport

In the first "erf" case, a thick layer of diffusant provides an essentially limitless supply of atoms maintaining a constant surface concentration C_o for all time.

$$C(0, t) = C_0 \qquad C(x, t) = C_0 \operatorname{erfc} \frac{x}{\sqrt{4Dt}} = C_0 \left(1 - \operatorname{erf} \frac{x}{\sqrt{4Dt}}\right);$$

In the second "gaussian" case, a very thin layer of diffusant provides an instantaneous source So of surface atoms per unit area. Here the surface concentration diminishes with time as atoms diffuse into the underlying substrate.

$$\int_0^\infty C(x, t)\, dx = S_0. \qquad C(x, t) = \frac{S_0}{\sqrt{\pi D t}} \exp -\left(\frac{x^2}{4Dt}\right).$$

These represent the simplest mathematical solutions to the diffusion equation and have been employed to determine doping profiles and junction depths in semiconductors.

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Kinetics – mass transport

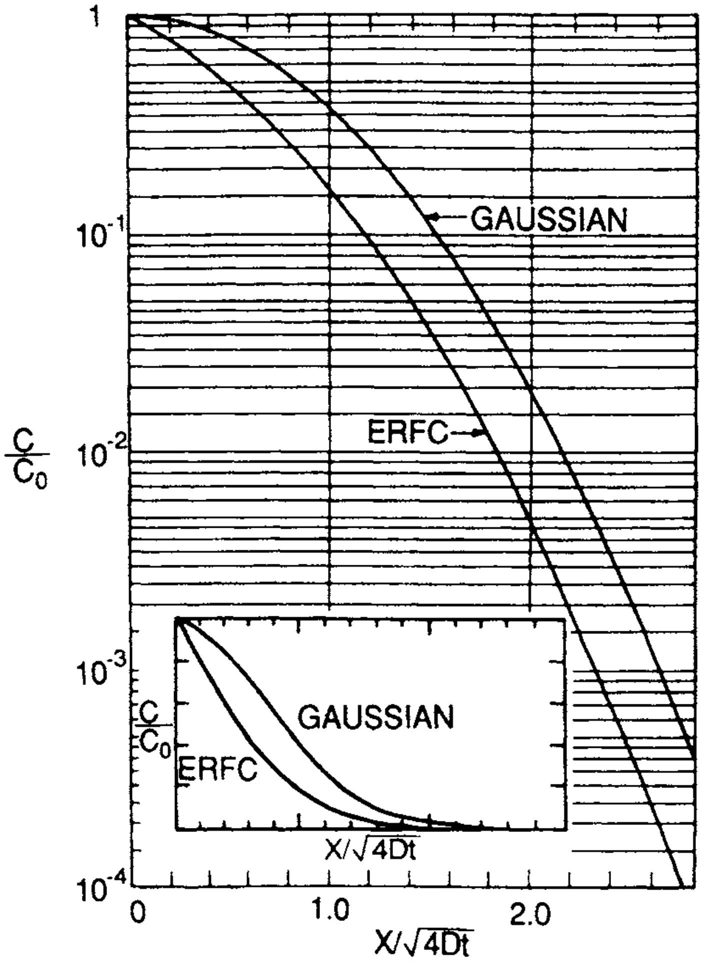
Normalized Gaussian and erfc curves of C/C_o vs $x/(4Dt)^{1/2}$. Both logarithmic and linear scales are shown.

Often it is of interest to calculate how the dimensions (x) of an atomic distribution spreads with time;

a measure of this is given by the random walk expression,

$x = 2(Dt)^{1/2}$

When $(Dt)^{1/2}$ becomes large compared to the film dimensions, the assumption of an infinite matrix is not valid and the solutions do not hold.



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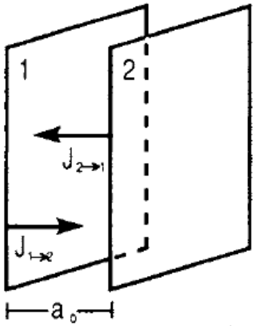
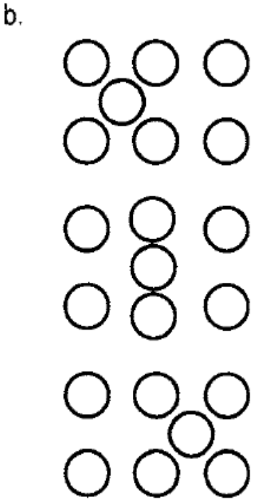
Atom movements

Each atom vibrates about its equilibrium position with
a characteristic lattice frequency, v, typically equal to 10^{13} s^{-1}.

Very few vibrational cycles have sufficient amplitude to cause the atom to actually jump into an adjoining occupied lattice site resulting in a direct atomic interchange and creating a flux J.

This depends on two energies – the energy to create a vacancy E_f and the energy to jump from one site to the next E_m. If we sum up partial fluxes:





$$J_N = -\frac{1}{6} a_0^2 v \exp - \frac{E_m}{k_B T} \exp - \frac{E_f}{k_B T} \left(\frac{dC}{dx}\right).$$

By comparison:

$$D_0 = \tfrac{1}{6} a_0^2 v \text{ and } E_D = [E_f + E_m].$$

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Atom movements

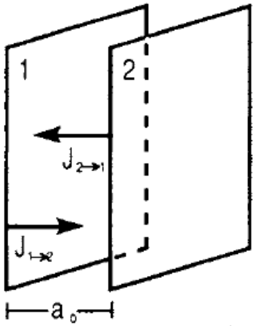
Although the above model is intended for atomistic diffusion in the bulk lattice, a similar expression for D would hold for transport through grain boundaries or along surfaces and interfaces of films.

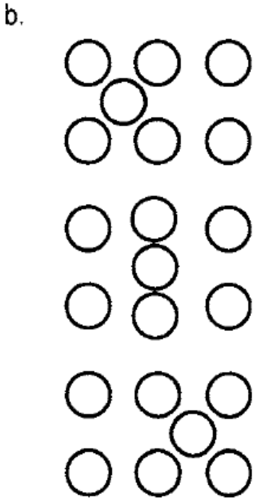
At such nonlattice sites, energies for defect formation and motion are expected to be lower, leading to high diffusivities.

Dominating microscopic mass transport is the Boltzmann factor exp $-E_D/k_BT$.

In such cases the kinetics can be described graphically by an Arrhenius plot in which the logarithm of the rate is plotted on the ordinate, and the reciprocal of the absolute temperature on the abscissa.

The slope of the resulting line is then equal to $-E_D/k_B$, from which the characteristic activation energy can be extracted.





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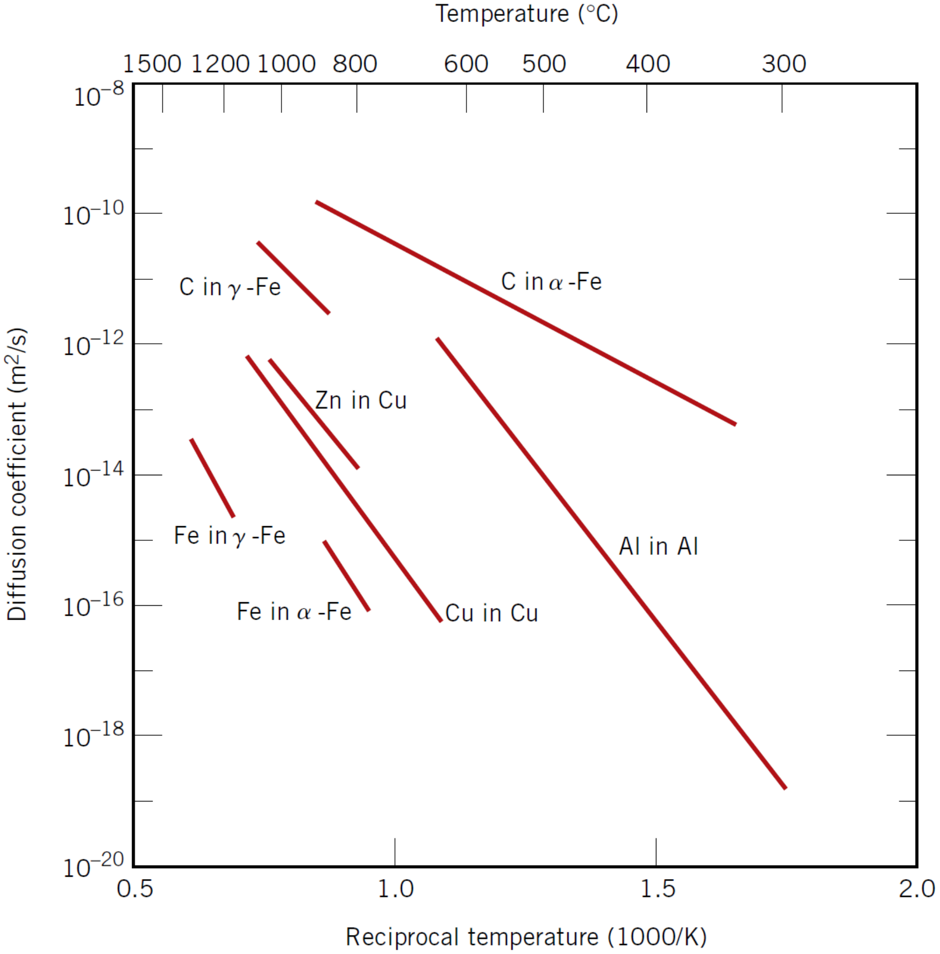
Diffusion coefficients

The magnitude of the diffusion coefficient D is indicative of the rate at which atoms diffuse.

The diffusing species and the host material influence the diffusion coefficient and it depends strongly on temperature.



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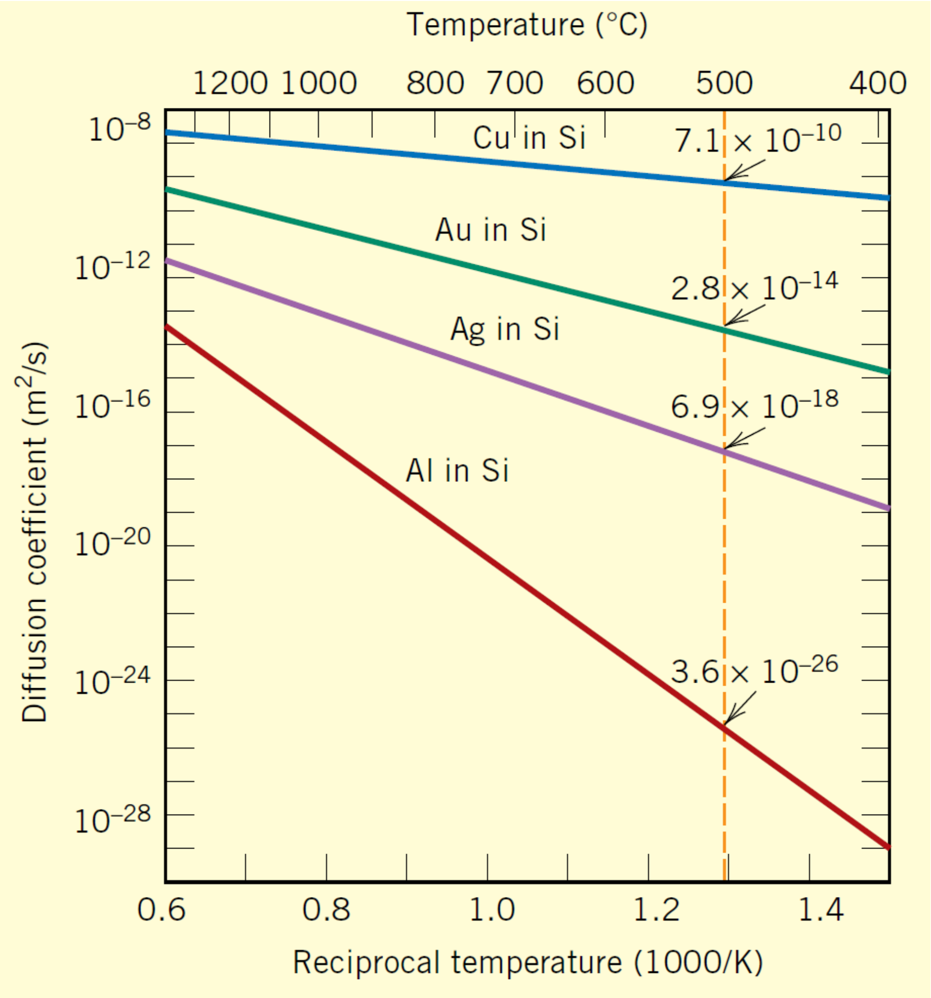
Diffusion coefficients

Diffusion coefficients vary up to 30 orders of magnitude



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Diffusion summary

Equation	***Solving For***
$J = \frac{M}{At}$	Diffusion flux
$J = -D\frac{dC}{dx}$	Fick's first law
$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$	Fick's second law
$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$	Solution to Fick's second law—for constant surface composition
$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$	Temperature dependence of diffusion coefficient

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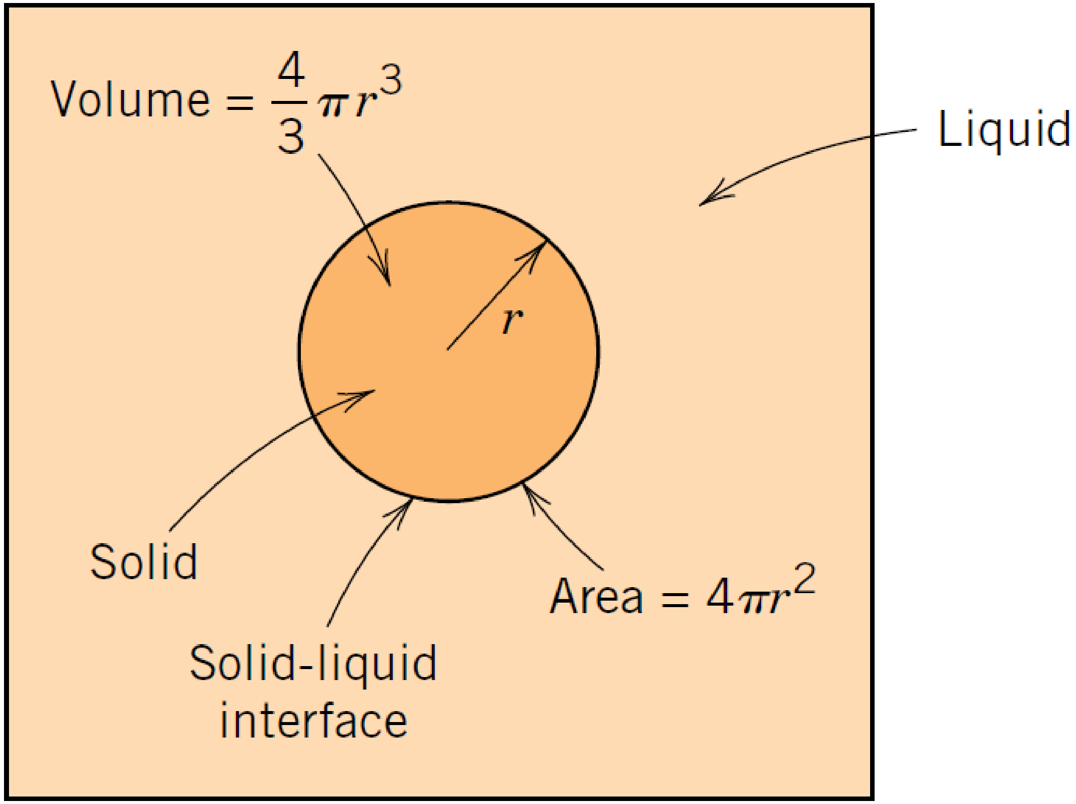
Nucleation

When the **critical boundaries separating stable phase fields one equilibrium phase diagrams are crossed, new phases appear.**

What is the energy needed of forming a single stable nucleus and how many stable nuclei form per unit volume per unit time?



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Nucleation

Consider the homogeneous nucleation of a spherical solid phase of radius r from a prior supersaturated vapor.

The gas-to-solid transformation results in a reduction of the chemical free energy of the system given by

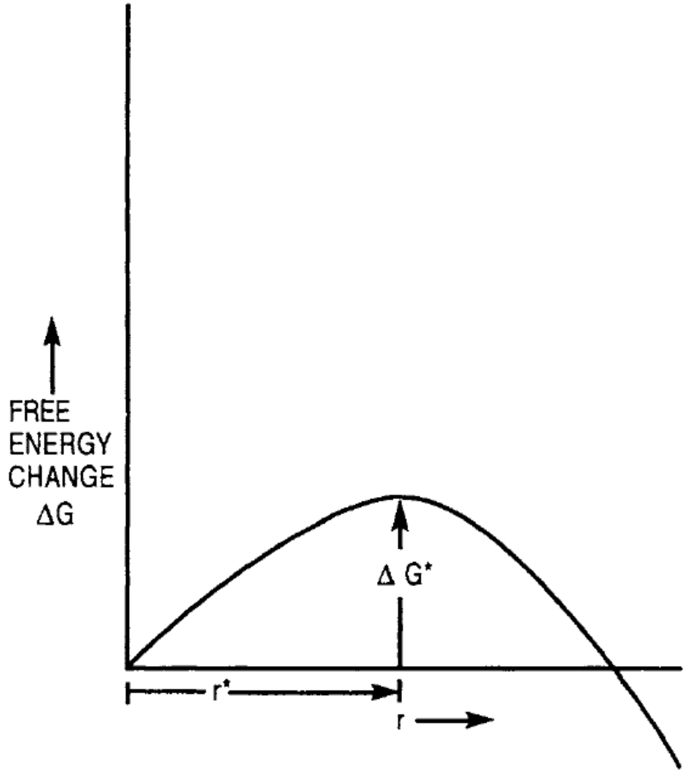
$$4/3\pi r^3 \Delta G_v$$

and an increase in the surface free-energy of the system given by

$$4\pi r^2 \gamma$$

where γ, is the solid-vapor interfacial energy per unit area and

$$\Delta G = \tfrac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma.$$



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Nucleation

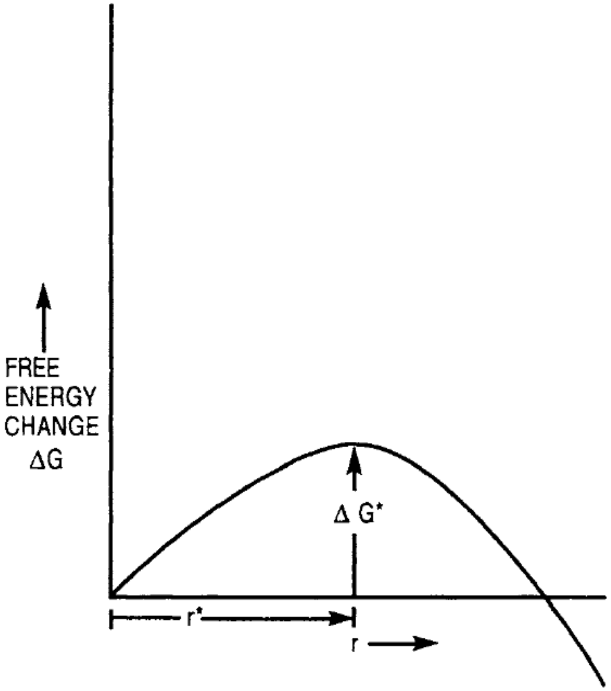
Minimization of ΔG with respect to r, or $d(\Delta G)/dr = 0$, yields the equilibrium size of r equal

$$r^* = -2\gamma/\Delta G_V$$

and $\Delta G^*(r^*)$

$$\Delta G^* = 16\pi\gamma^3/3(\Delta G_V)^2.$$

If a solid-like spherical cluster of atoms momentarily forms by some thermodynamic fluctuation, but with radius less than r*, the cluster is unstable and will shrink by losing atoms. Clusters larger than r* have surmounted the nucleation energy barrier and are stable



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Nucleation rate

The nucleation rate is essentially proportional to the product of three terms, namely,

$$\dot{N} = N^* A^* \omega \qquad (\text{nuclei/cm}^3\text{-s}).$$

N* is the equilibrium concentration (per cm^3) of stable nuclei and ω is the rate at which atoms impinge (per cm^2 s) onto the nuclei of critical area, A* (cm^2).

It is appropriate to take

$$N^* = n_s \exp - \Delta G^*/k_B T,$$

And it can be shown that

$$\dot{N} = n_s \left[\exp - \frac{\Delta G^*}{k_B T} \right] 4\pi r^2 \frac{\alpha (P_V - P_S) N_A}{\sqrt{2\pi \mathrm{MRT}}}.$$

Where M is the atomic weight, and α the sticking coefficient.

Nucleation rate

$$\dot{N} = n_s\left[\exp -\frac{\Delta G^*}{k_B T}\right]4\pi r^2 \frac{\alpha(P_V - P_S)N_A}{\sqrt{2\pi MRT}}.$$

The most influential term in this expression is the exponential factor. It contains ΔG^*. When the vapor supersaturation is sufficiently large, homogeneous nucleation in the gas is possible.

This phenomenon is a troublesome one in chemical vapor deposition processes since any solid particles that nucleate may settle on and be incorporated within growing films, thus destroying their integrity.

Heterogeneous nucleation of films is a more complicated subject in view of the added interactions between deposit and substrate and the nucleation at surface sites in this case are kinks, ledges, dislocations, etc.