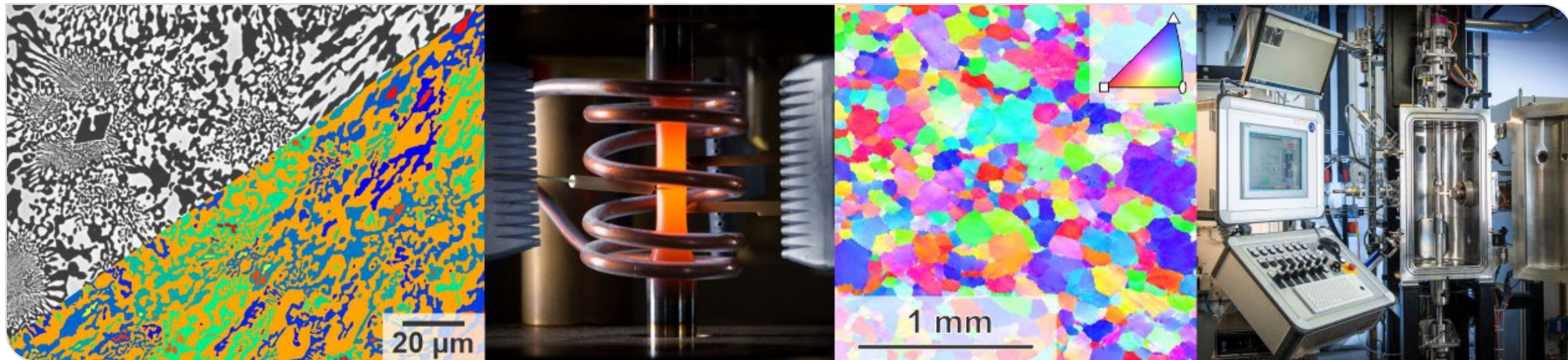


Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
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Topics

- Kinetic fundamentals
 - General Considerations
 - Diffusion
 - Phenomenological Description
 - Fick's Laws
 - Generalization
 - Simple Solutions of Fick's 2nd Law
 - Microscopic Considerations

General Considerations

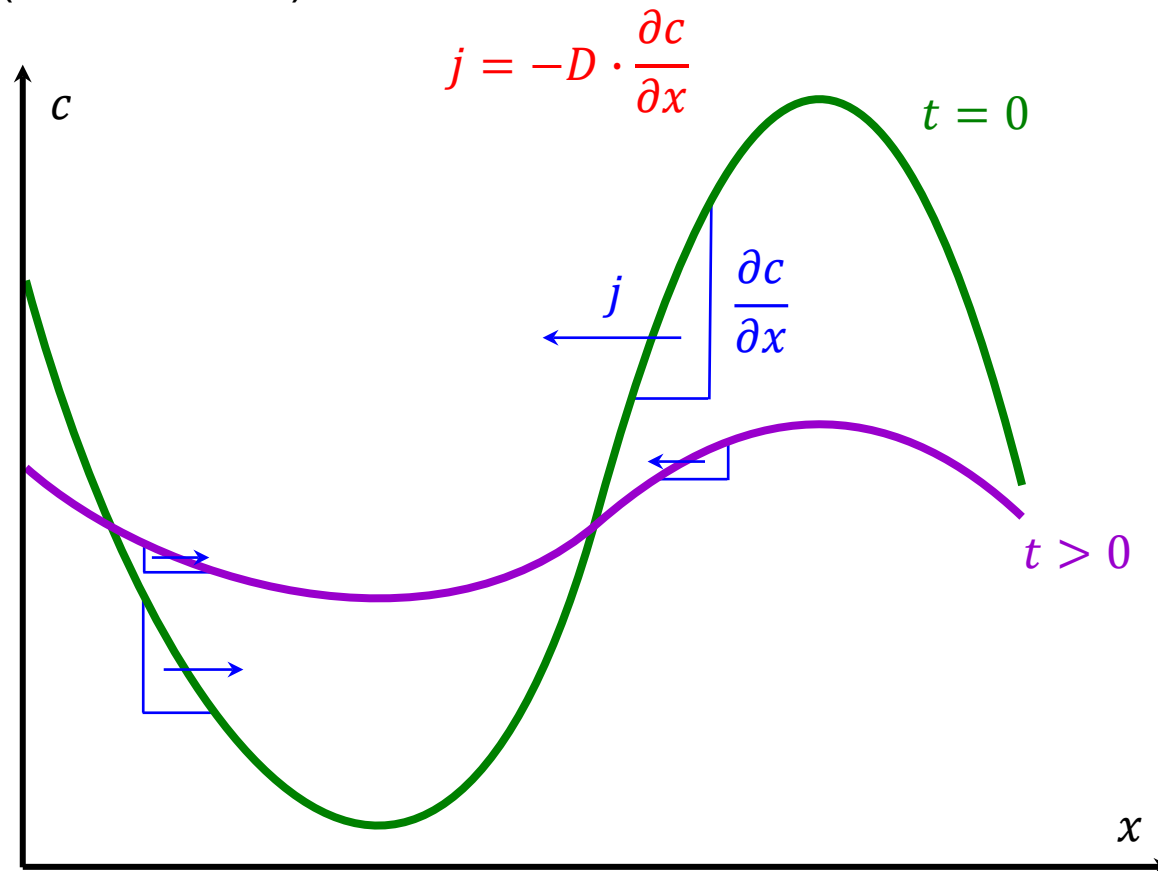
- Apart from the thermodynamic driving force of a process to occur, the **process evolution as a function of time** is needed to be investigated.
- In some cases, the changes driven by the driving force might occur
 - *instantaneous*, e.g. electric and magnetic changes
 - *quasi-instantaneous*, e.g. elastic and plastic deformation (due to mediation by lattice deformations/phonons somehow at a speed similar to the speeds of sound in solids)
 - *rather slow*, when transport of mass is associated with the change, e.g. diffusion and convection (different from some treatment in the anglo-saxonian where both is sometimes considered the same)
- For the first two cases, the thermodynamic driving forces might be sufficient to describe phase transformations. For the latter case, **transport phenomena** are **rate controlling** and need to be investigated to see whether a transformation can occur at all and how it occurs.

Diffusion

- Diffusion is the process of *usually* complete mixing without any external force caused by thermally induced Brown motion of atoms and molecules.
- Similar to the treatment of thermodynamics in Ch. 1a,
 - (i) a **phenomenological treatment** of the subject but
 - (ii) also a **statistical treatment** of the particle motionexist. Since the following considerations are seen as tools for the assessment of phase transformations, the use will be application-oriented and strict differentiation is not of interest.
- For the present lecture, **diffusion in liquids and solids** are of particular interest. Both **significantly depend on temperature** and **are progressing rather slow**.

Phenomenological: Fick's 1st Law

- The simplest approximation of the process of mixing is that a flux exists that is in opposite direction to concentration gradients (Fick's 1st law):



Phenomenological: Fick's 1st law

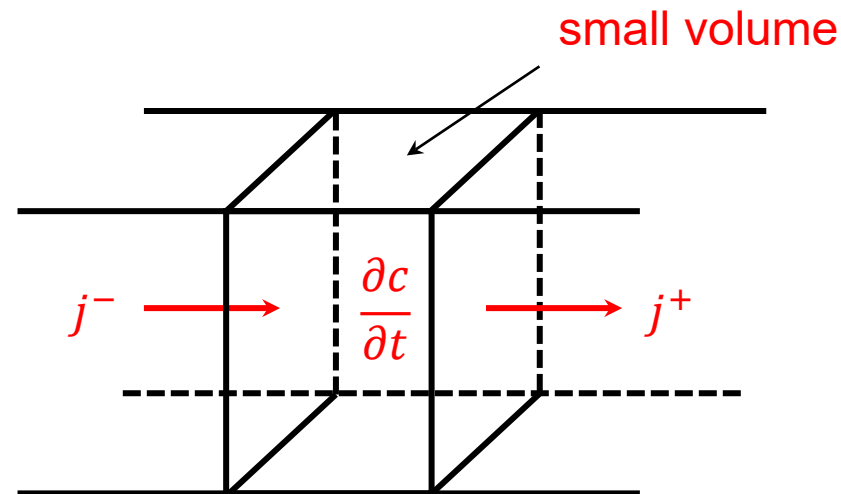
- As pointed out in Ch. 1a, concentrations are considered as *volumetric particle densities* $[c] = \frac{\text{mol}}{\text{m}^3}$ in this case. This is not necessarily the same as a composition description given by x_i , x_i^j , w_i and w_i^j !
- This allows for proper formulation of continuity in the second step. Hence, $\left[\frac{\partial c}{\partial x}\right] = \frac{\text{mol}}{\text{m}^4}$. The flux is given as an area-specific particle flux $[j] = \frac{\text{mol}}{\text{m}^2 \text{ s}}$.
- The proportionality is mediated by the **material's constant** D with $[D] = \frac{\text{m}^2}{\text{s}}$.
- The flux described by Fick's 1st law equilibrates concentration gradients and leads to mixing.

Phenomenological: Continuity

- In order to describe the temporal evolution, continuity of the process needs to be considered:

$$\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} = 0$$

- Continuity in this case means that the accumulation or loss rate of particles $\frac{\partial c}{\partial t}$ is balanced by the difference of incoming and outgoing fluxes to a small volume $\frac{\partial j}{\partial x}$. There are no sources or sinks of species nor reactions of species considered.



Phenomenological: Fick's 2nd Law

- A **linear, second-order partial differential equation** for the spatial and temporal evolution of $c(x, t)$ is obtained by combining both, Fick's 1st law and the continuity equation (Fick's 2nd law):

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

Phenomenological: Generalization

- The problem can be generalized to more complex cases:

multidimensional:

$$\mathbf{j} = -D \cdot \nabla c$$
$$j_k = -D \cdot \frac{\partial c}{\partial x_k}$$

The flux becomes a direction-dependent vector quantity determined by the vector gradient.

$$\frac{\partial c}{\partial t} = D \cdot \Delta c$$
$$\frac{\partial c}{\partial t} = D \cdot \sum_k \frac{\partial^2 c}{\partial x_k^2}$$

Phenomenological: Generalization

- The problem can be generalized to more complex cases:

multidimensional:

$$\frac{\partial c}{\partial t} = D \cdot \Delta c$$

reads:

$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$

for Cartesian coordinates x, y, z

$$\frac{\partial c}{\partial t} = \frac{D}{r} \cdot \left(\frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial c}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(r \frac{\partial c}{\partial z} \right) \right)$$

for cylindrical coordinates r, θ, z

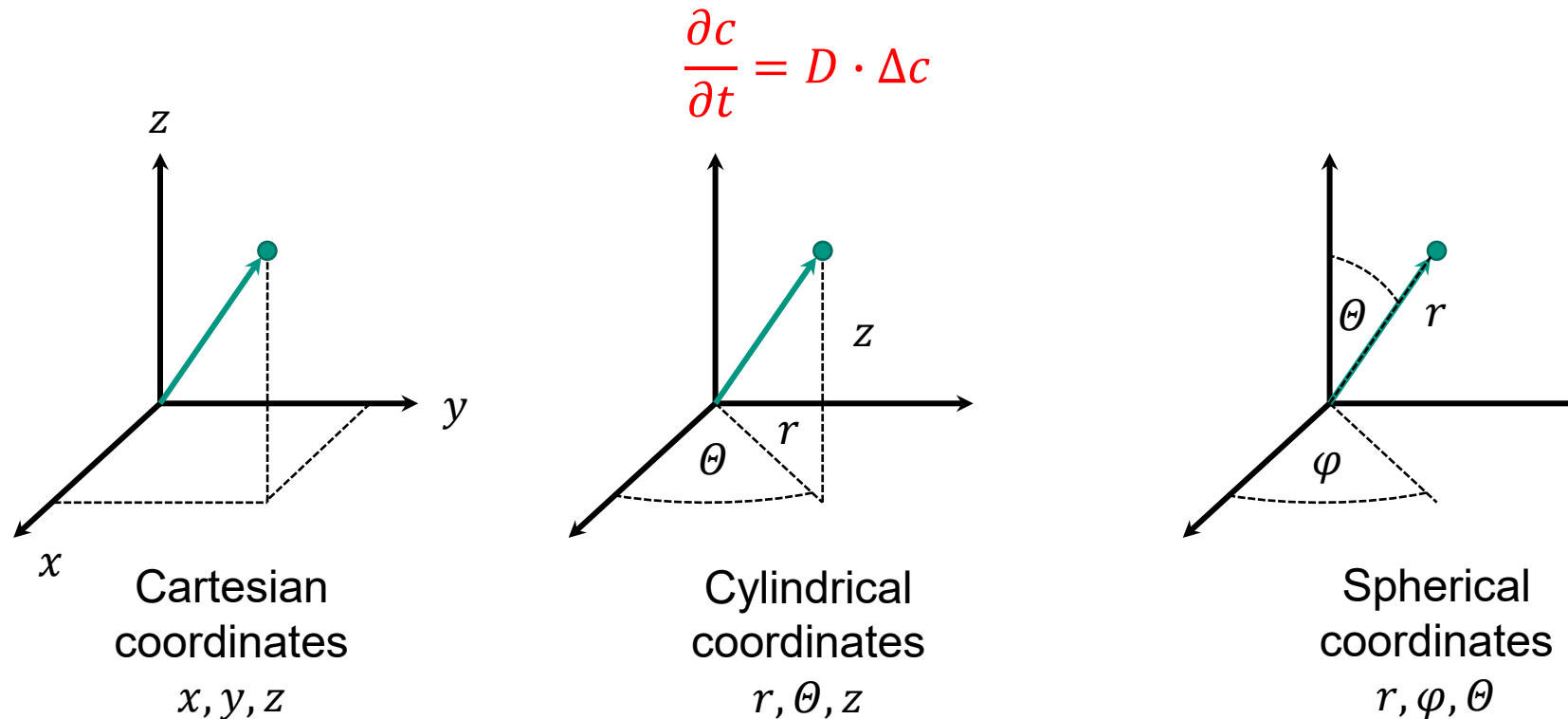
$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 c}{\partial \varphi^2} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} + \frac{\cot \theta}{r^2} \frac{\partial c}{\partial \theta} \right)$$

for spherical coordinates r, φ, θ

Phenomenological: Generalization

- The problem can be generalized to more complex cases:

multidimensional:



Phenomenological: Generalization

- The problem can be generalized to more complex treatment:

multidimensional, anisotropic:

$$\mathbf{j} = -\mathbf{D} \cdot \nabla c$$

$$j_k = -D_{kl} \cdot \frac{\partial c}{\partial x_l}$$

$$\frac{\partial c}{\partial t} = \mathbf{D} \cdot \Delta c$$

$$\frac{\partial c}{\partial t} = D_{kl} \cdot \frac{\partial^2 c}{\partial x_k \partial x_l}$$

In case of anisotropic diffusion, the diffusion coefficient becomes a tensor of rank two connecting the two vector quantities \mathbf{j} and ∇c .

Phenomenological: Generalization

- The problem can be generalized to more complex treatment:

non-linear:

$$\mathbf{j} = -D(c) \cdot \nabla c$$
$$j_k = -D(c) \cdot \frac{\partial c}{\partial x_k}$$

In most cases, the diffusion coefficient is depending on concentration, making the equations non-linear.

$$\frac{\partial c}{\partial t} = \nabla D(c) \cdot \nabla c$$
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_k} D(c) \cdot \frac{\partial c}{\partial x_k}$$

Phenomenological: Generalization

- The problem can be generalized to more complex treatment:

non-linear:

$$\mathbf{j} = -D(\mathbf{x}) \cdot \nabla c$$
$$j_k = -D(\mathbf{x}) \cdot \frac{\partial c}{\partial x_k}$$

Similarly, heterogeneous materials will have position-dependent diffusion-coefficients.

$$\frac{\partial c}{\partial t} = \nabla D(\mathbf{x}) \cdot \nabla c$$
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_k} D(\mathbf{x}) \cdot \frac{\partial c}{\partial x_k}$$

Phenomenological: Generalization

- Some notes on the equations:
 - Multi-component systems require a treatment of all the species in the system.
 - The concept of flux and continuity is very general and can be applied in many different disciplines, e.g. heat conduction, fluid dynamics, drift (diffusion) currents in semi-conductors, etc. Hence, the equations and/or their solutions are of general interest in engineering or science.
 - In some cases, mixing might lead to an increase of the thermodynamic potential (Gibbs free energy G) when preferred interactions of species are present. “Up-hill” instead of “down-hill” diffusion might occur in these cases and specific types of concentration gradients can build up and grow, for example during spinodal decomposition. Slight modifications to the diffusion equations can account for this. Nevertheless, most diffusion-controlled phase transformations are rate-controlled by “down-hill” diffusion even though decomposition of the material occurs! It’s just a matter of representation and identification of the respective gradients.

Phenomenological: Some Selected Solutions

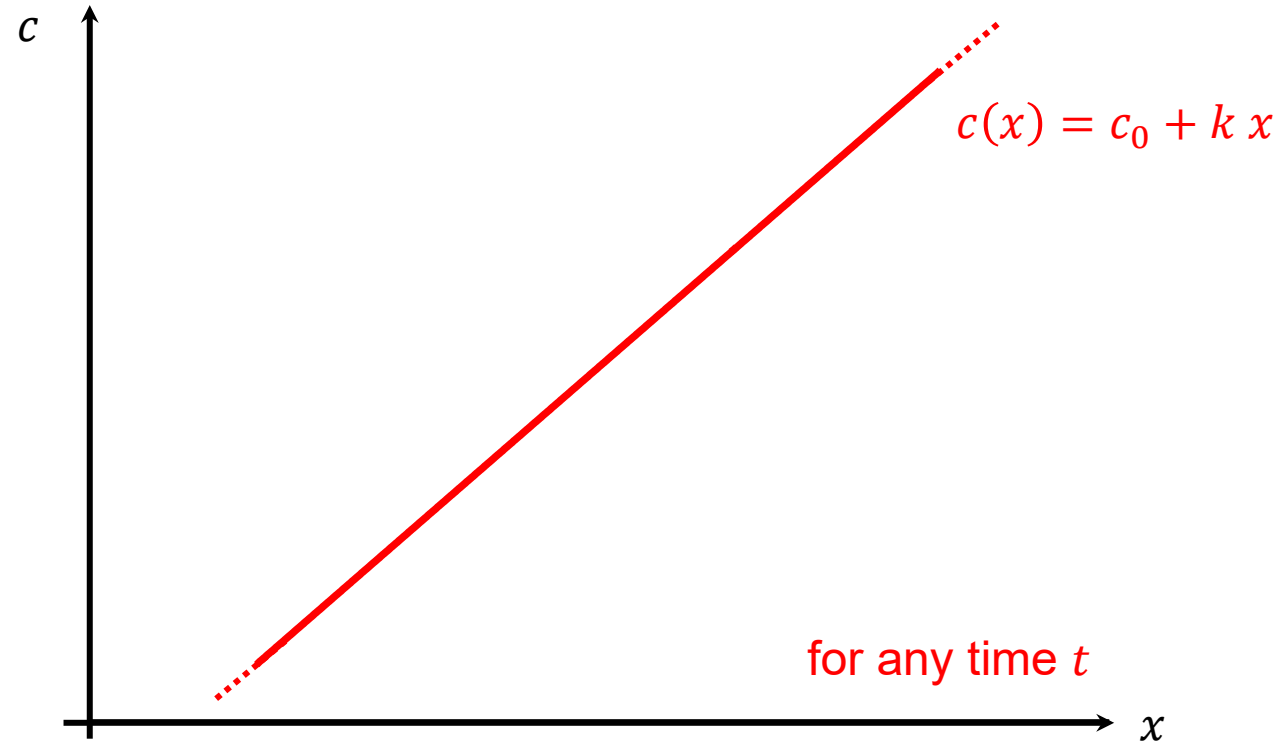
- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

Steady-state diffusion $\frac{\partial c}{\partial t} = 0$, linear one-dimensional:

$$\frac{\partial^2 c}{\partial x^2} = 0$$

$$c(x) = c_0 + k x$$

Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions

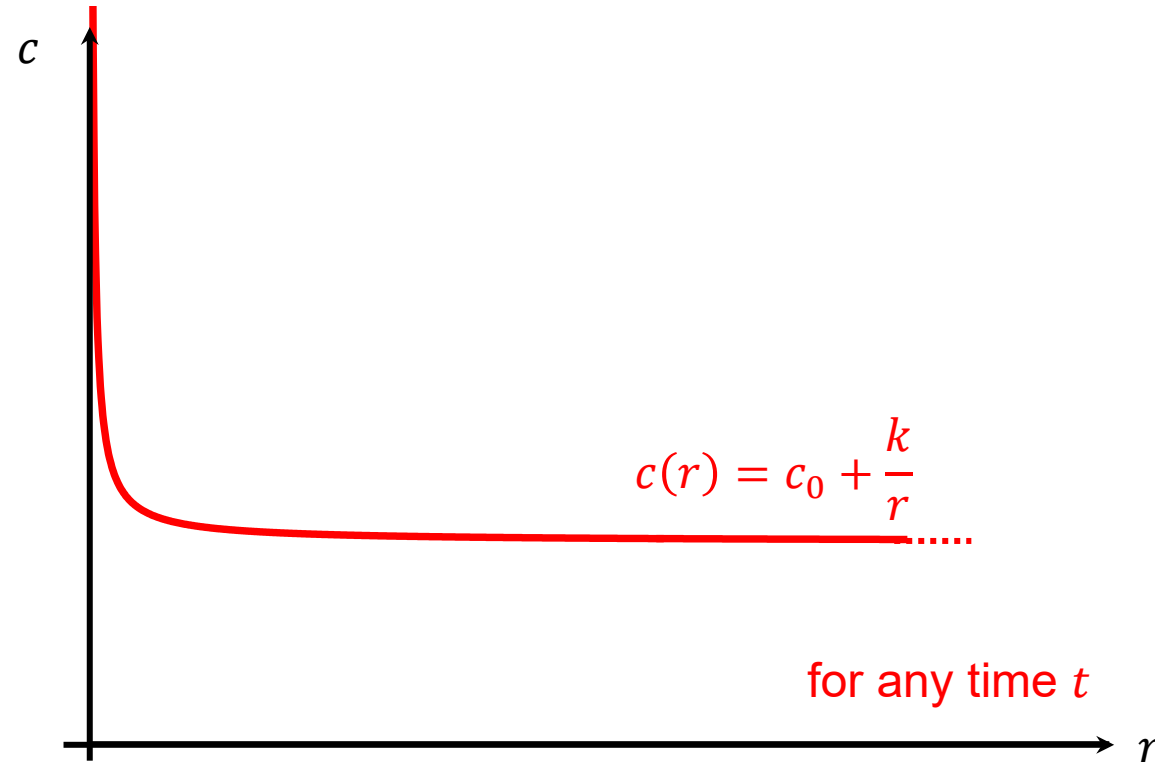
- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

Steady-state diffusion $\frac{\partial c}{\partial t} = 0$, spherical:

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) = 0$$

$$c(r) = c_0 + \frac{k}{r}$$

Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions

- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

Dissolution of a planar source:

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

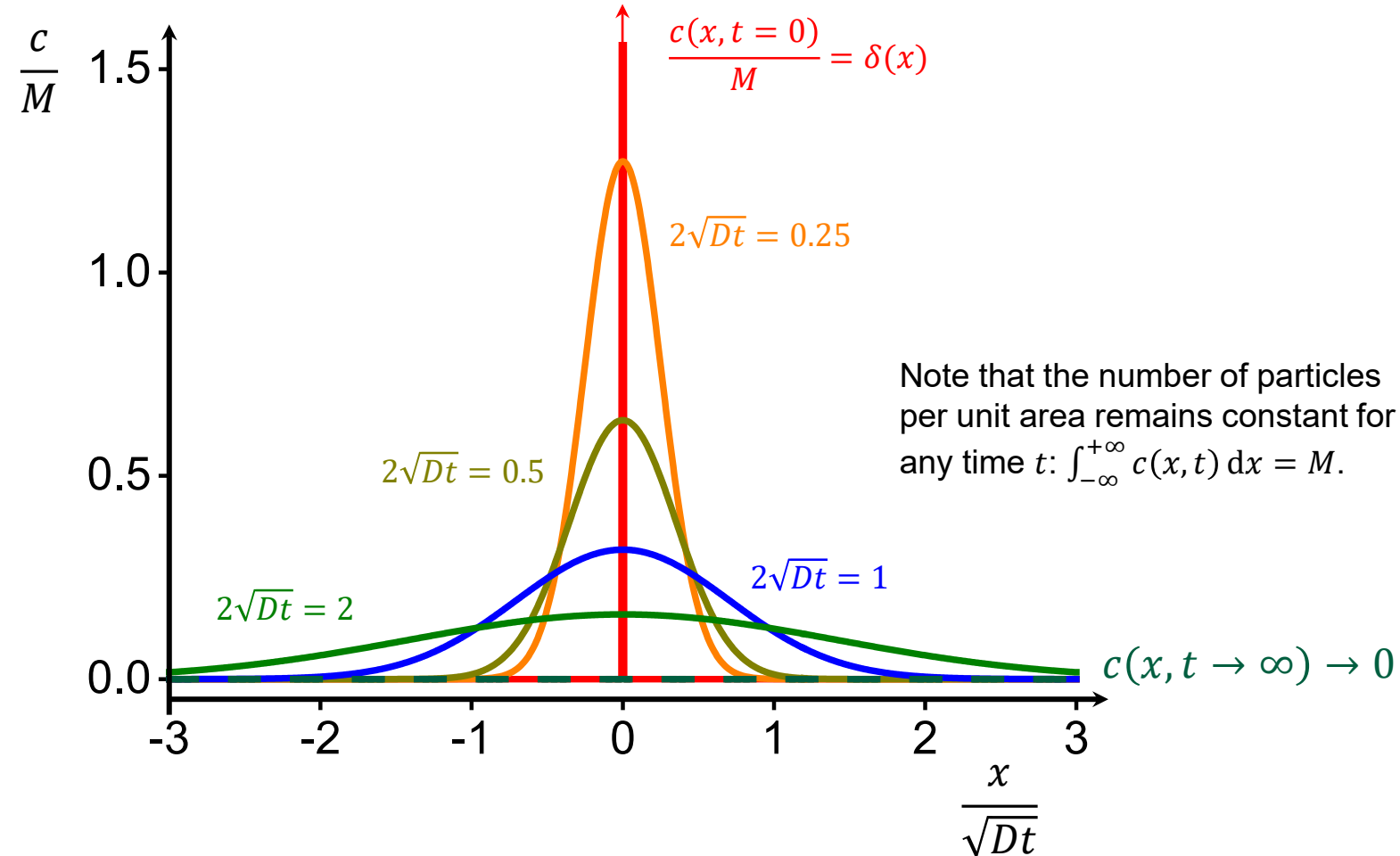
$$\text{with } c(x, t = 0) = M \delta(x)$$

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

when diffusion in positive and negative x direction is allowed.

The solution for diffusion in only one direction is the same but the factor 2 is missing.

Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions

- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

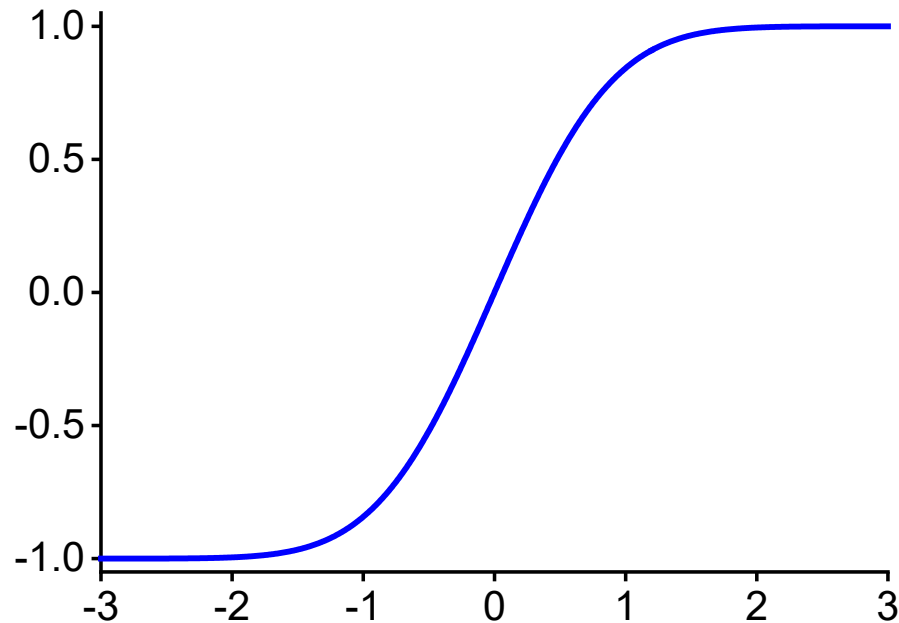
Diffusion couple:

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

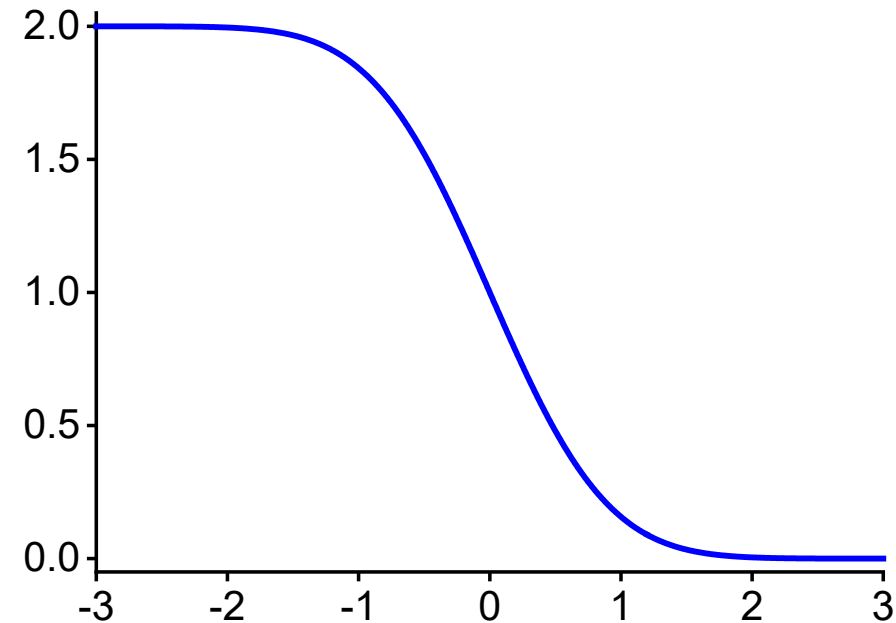
with $c(x < 0, t = 0) = c_1$ and $c(x > 0, t = 0) = c_2$

$$c(x, t) = c_1 + \frac{c_2 - c_1}{2} \operatorname{erfc}\left(-\frac{x}{2\sqrt{Dt}}\right)$$

Phenomenological: Some Selected Solutions

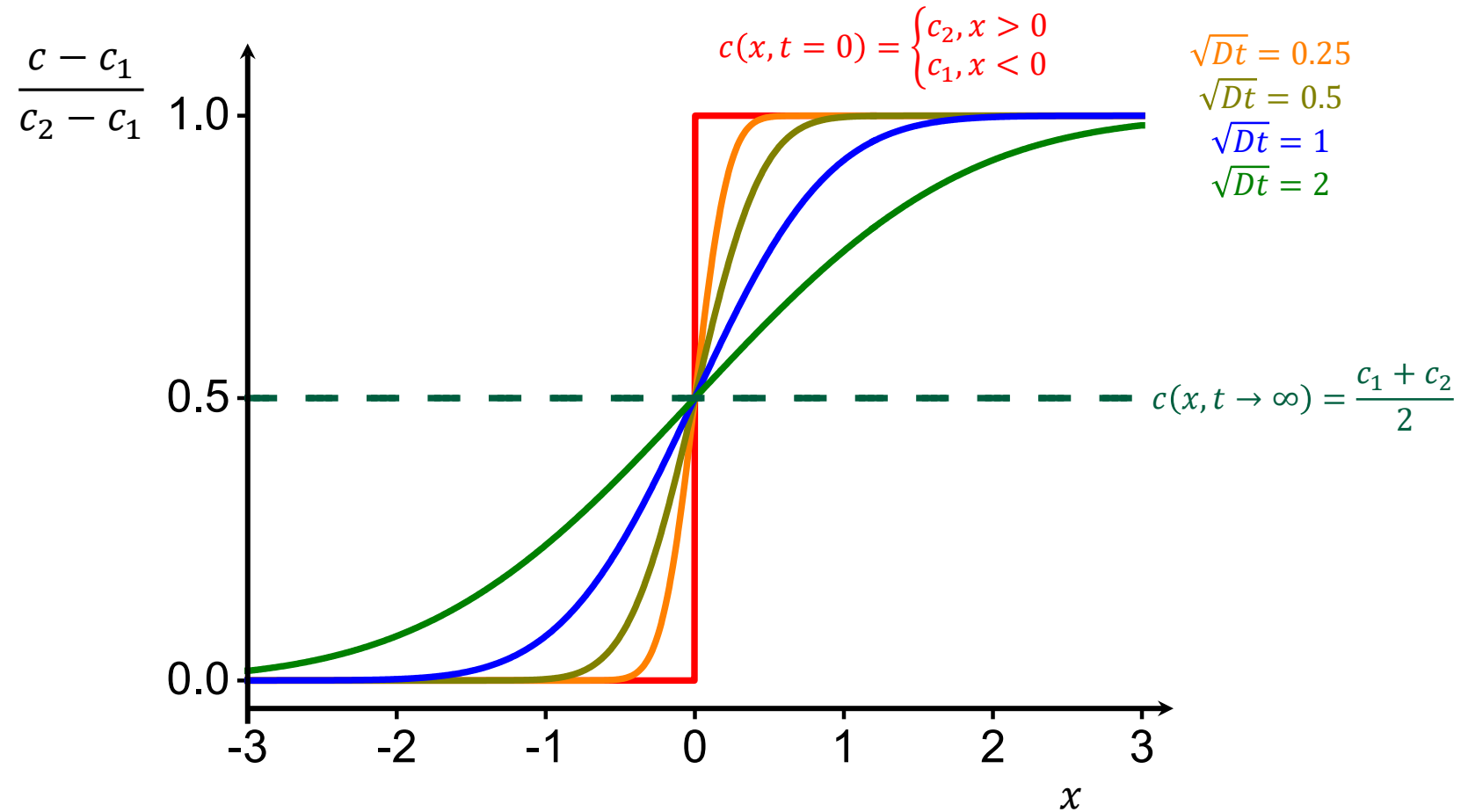


$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta$$

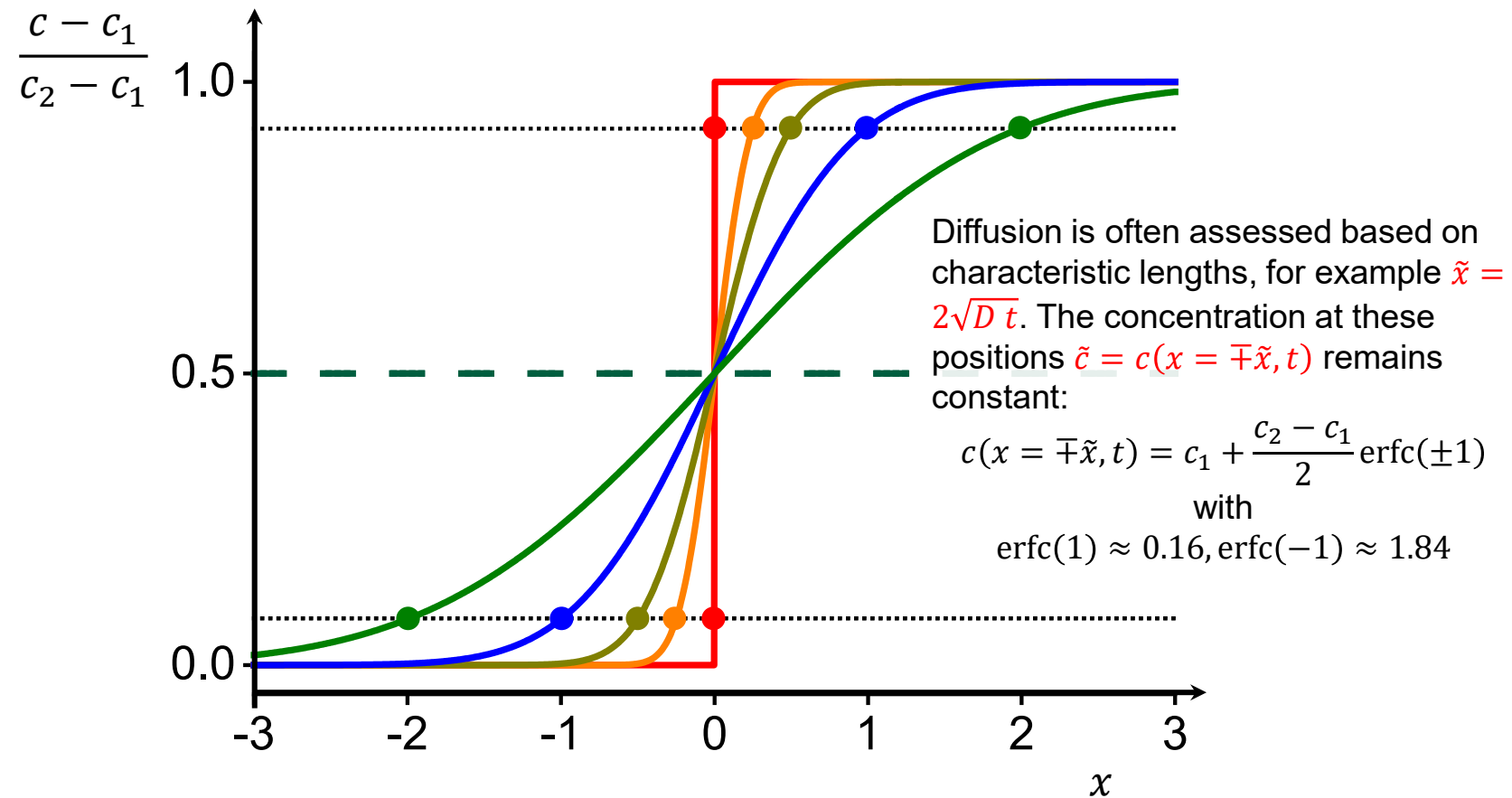


$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$$

Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions

- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

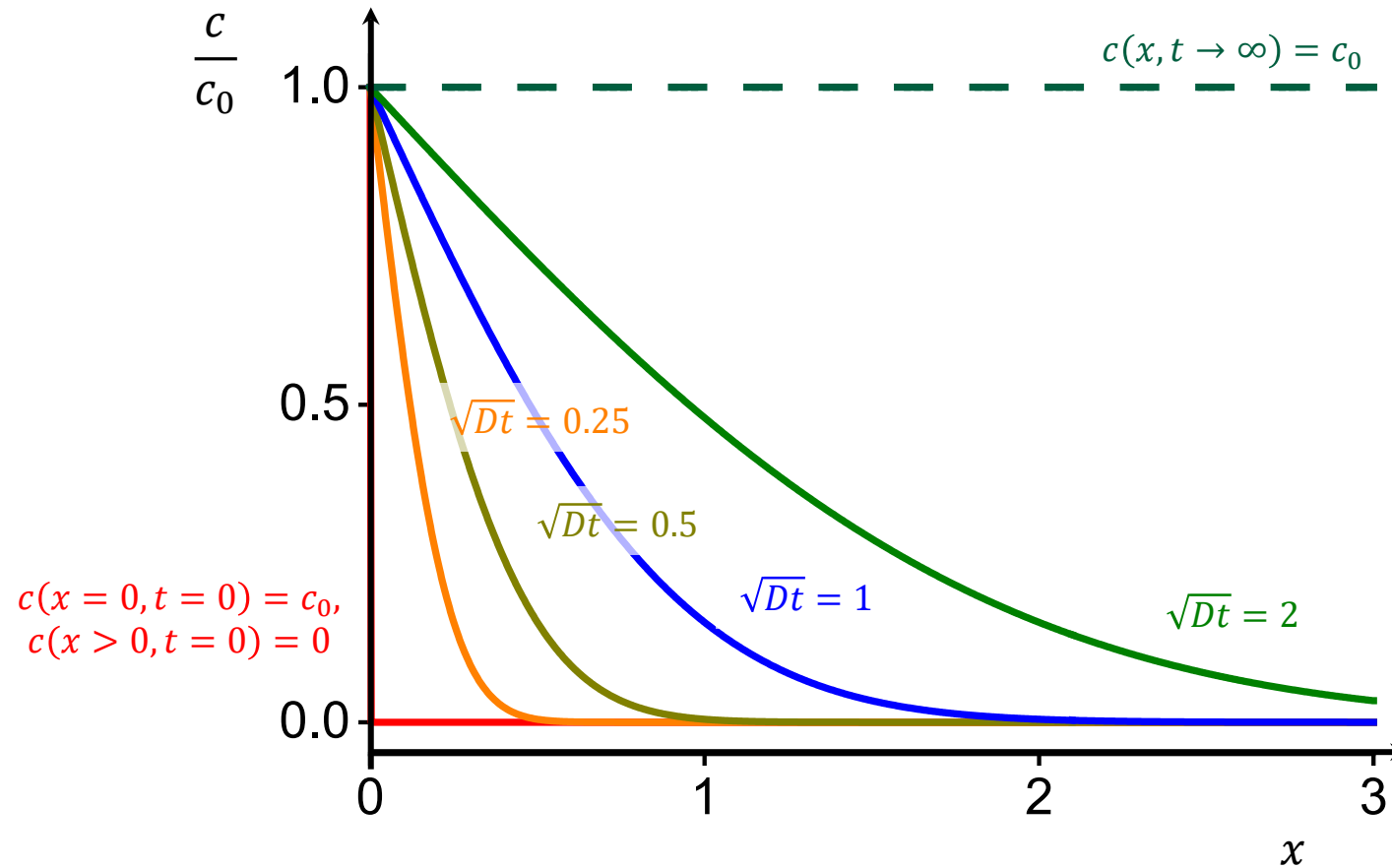
Constant supply on the surface:

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

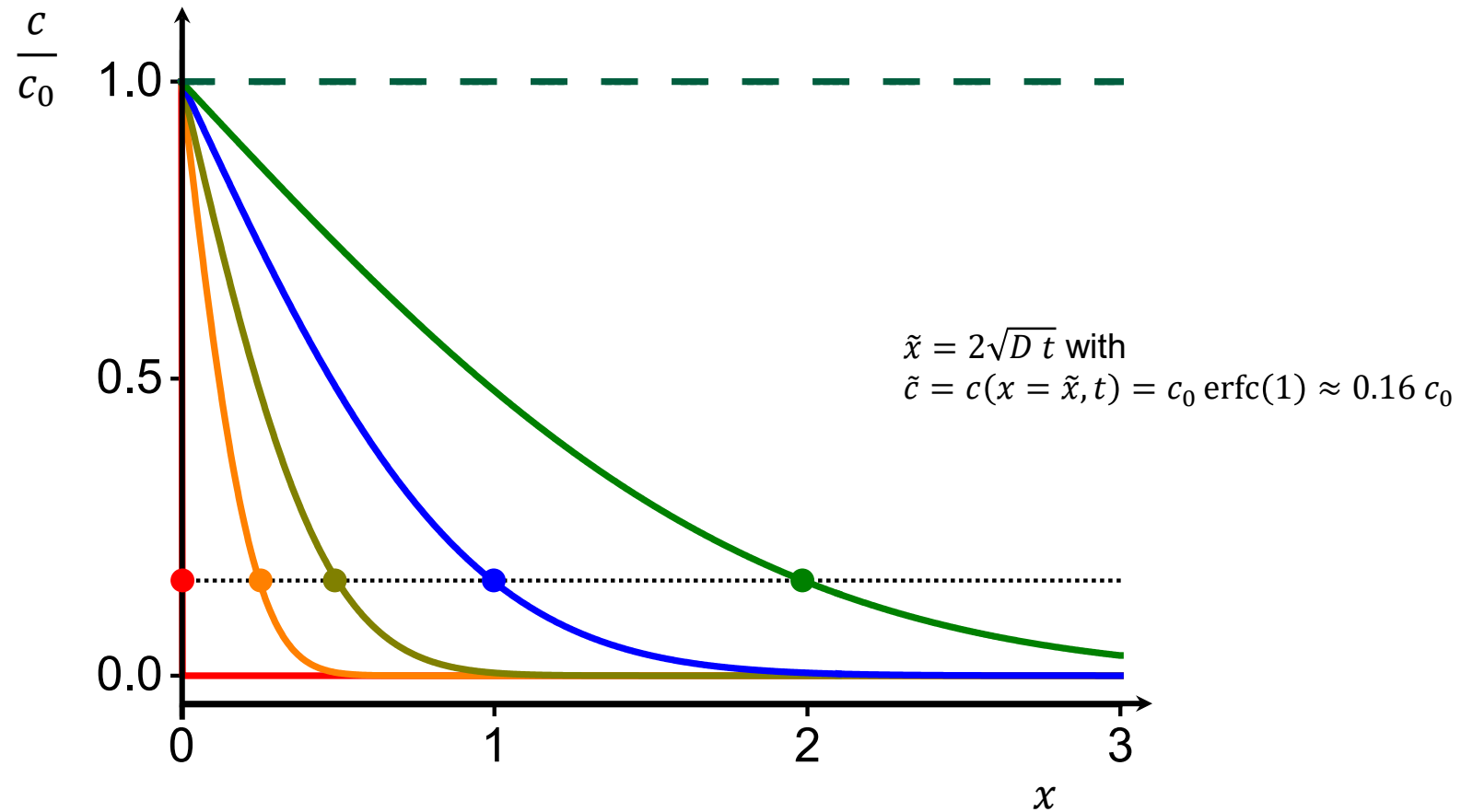
with $c(x = 0, t) = c_0$ und $c(x > 0, t = 0) = 0$

$$c(x, t) = c_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions



Phenomenological: Some Selected Solutions

- Under specific boundary and initial conditions, solutions of the diffusion equation can be obtained. Some simple solutions are useful to further assess more complex diffusion processes:

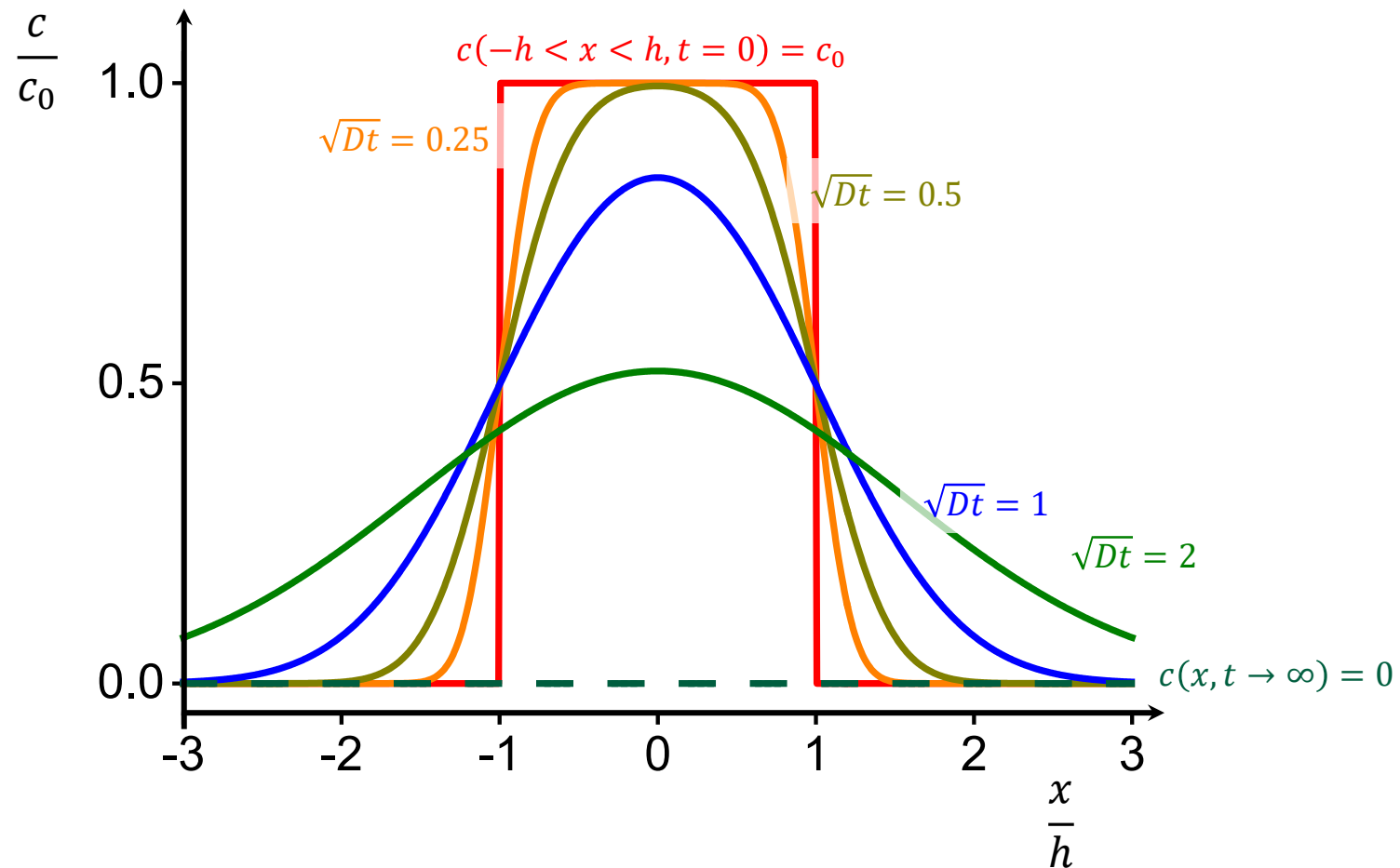
Slab dissolution:

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

with $c(-h < x < h, t = 0) = c_0$ und $c(x < -h \vee x > h, t = 0) = 0$

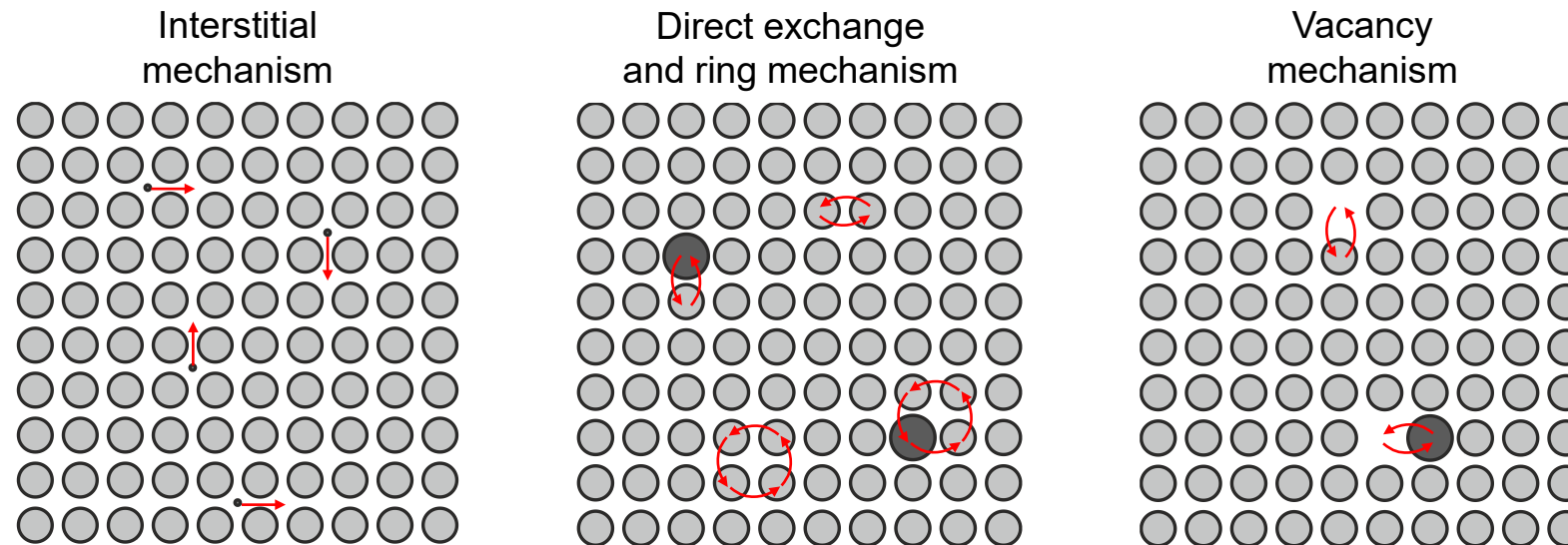
$$c(x, t) = \frac{c_0}{2} \left(\operatorname{erf} \left(\frac{x+h}{2\sqrt{Dt}} \right) - \operatorname{erf} \left(\frac{x-h}{2\sqrt{Dt}} \right) \right)$$

Phenomenological: Some Selected Solutions



Microscopic Considerations

- On microscopic scale, diffusion occurs with different mechanisms often associated with “diffusion vehicles”, namely **crystal defects mediating the motion of the atoms**.
- The **probability** of the different mechanisms is very different and strongly **depends on the conditions of diffusion**. Note that most of them do not correspond to a “free” random walk – the cancelation of the elementary mechanism back into the original situation is usually of higher probability.



= most important together with mechanisms involving agglomerates of point defects.

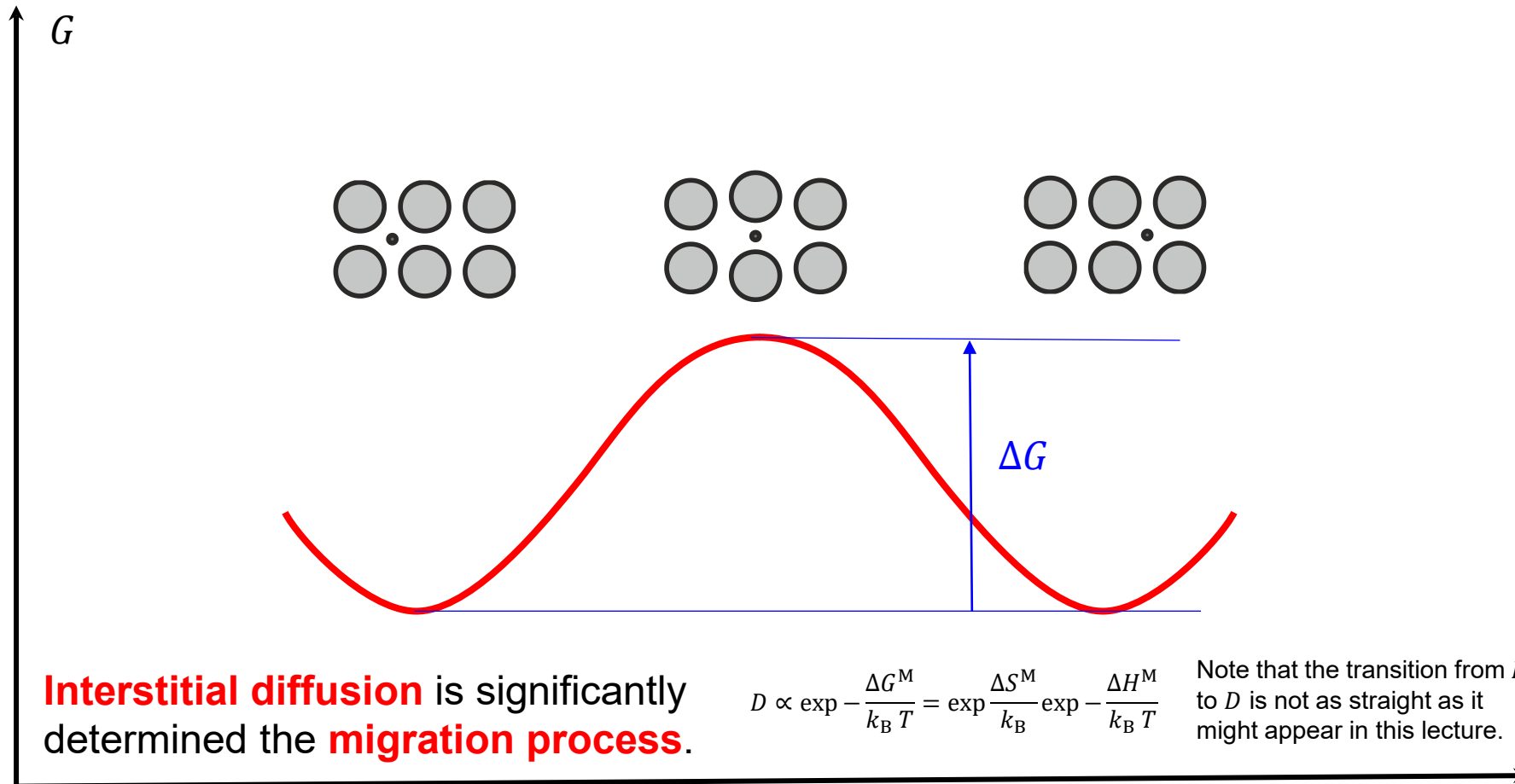
Microscopic Considerations

- An important feature of diffusion is that it is a **thermally activated process**. For the elementary mechanism to occur, a microscopic energy barrier needs to be overcome. The probability of which *can* be described by an Arrhenius type equation:

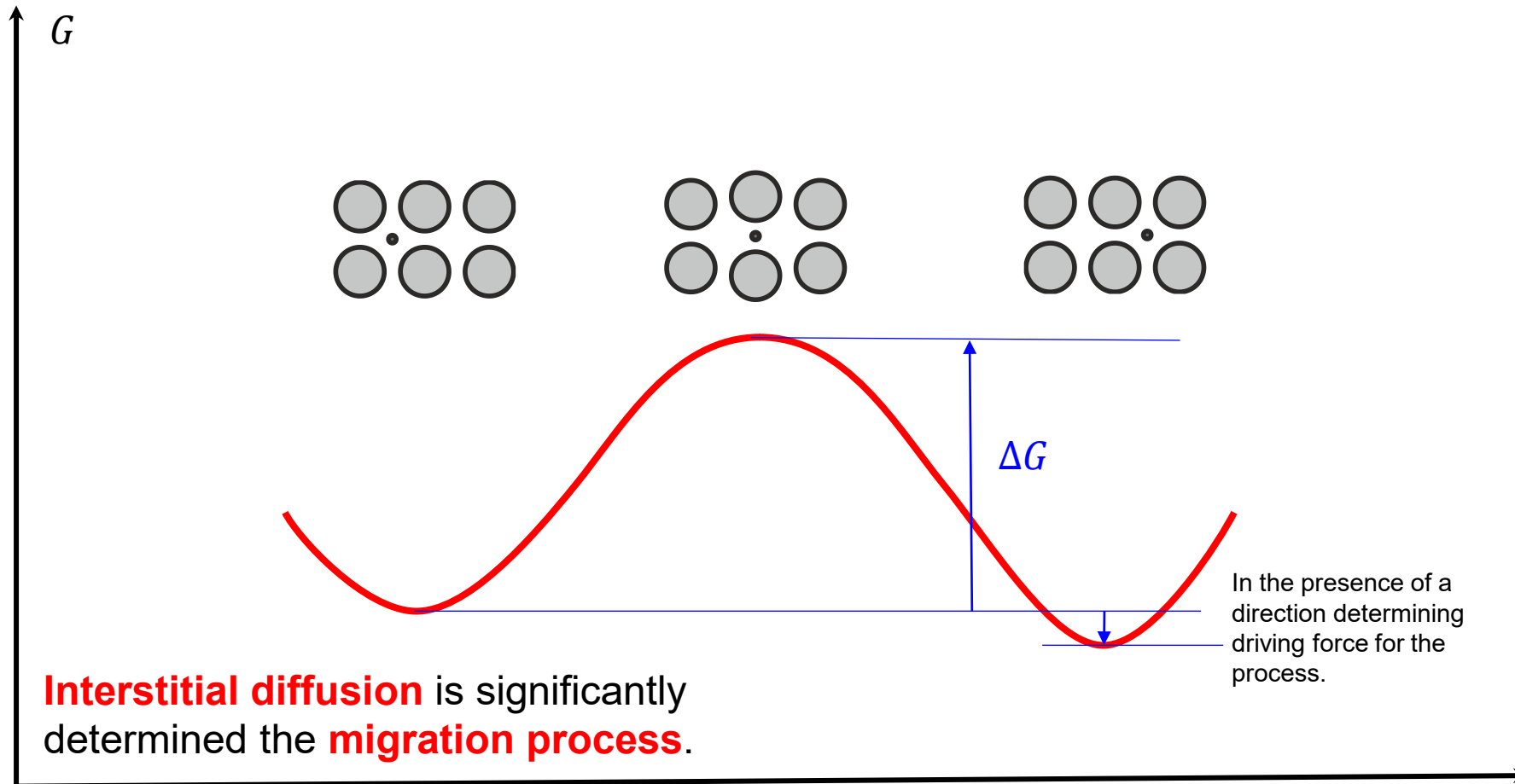
$$\Gamma = \nu \exp - \frac{\Delta G}{k_B T}$$

- Γ denotes the jump rate (probability to move from the position), an attempt rate ν (correlated to the frequency of vibration of the atoms, see Debye model in Ch. 1a) and the energy barrier ΔG to overcome.

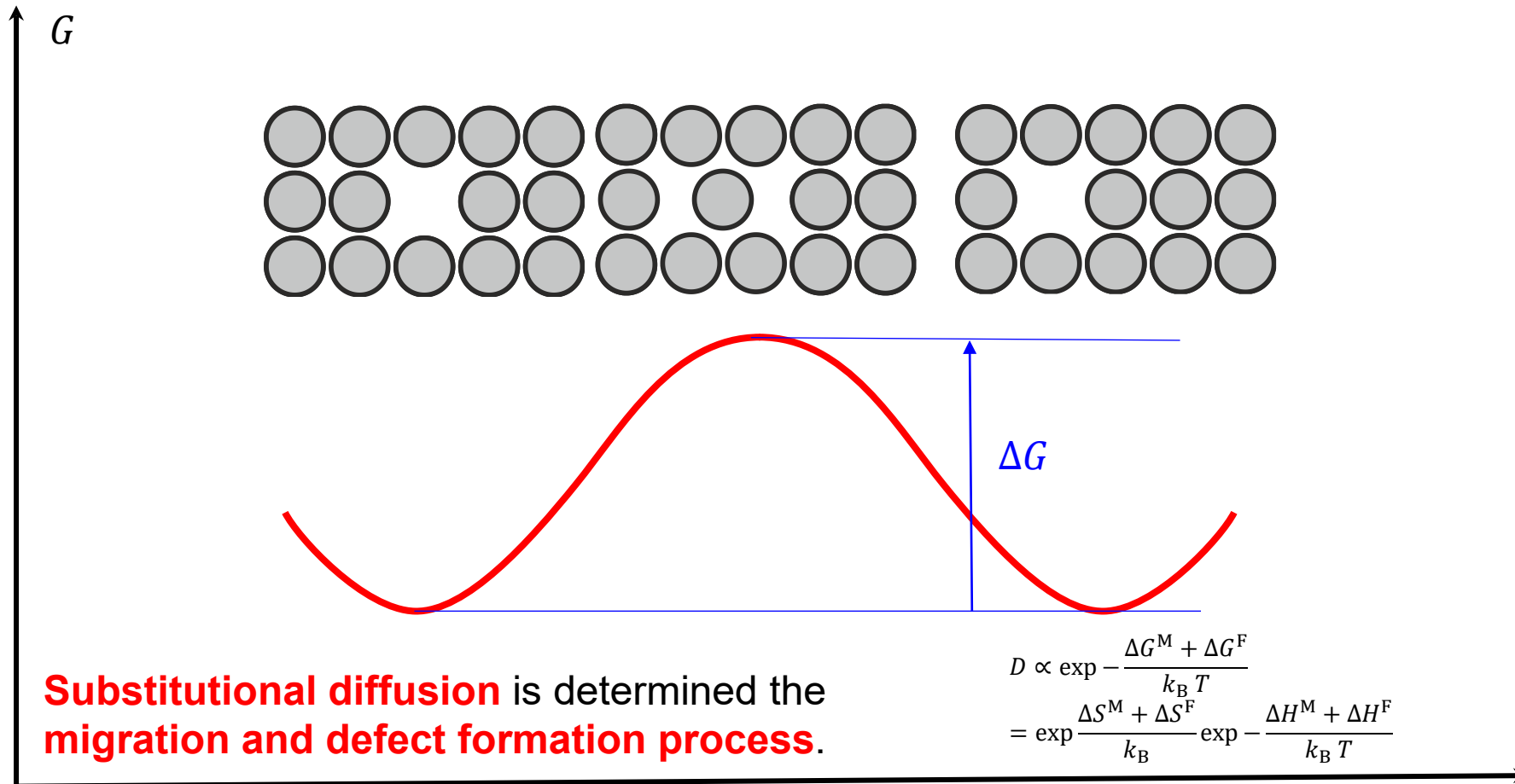
Driving Force



Driving Force



Driving Force



Diffusion

Matrix	Diffusant	$\Delta H/\text{eV}$	$D_0/\text{cm}^2\text{s}^{-1}$	$T/^\circ\text{C}$
$\gamma\text{-Fe}$	C	1.4	0.15	900 – 1050
	Fe	2.8	0.18	1060 – 1390
	Co	3.8	$3.0 \cdot 10^2$	1050 – 1250
	Cr	4.2	$1.8 \cdot 10^4$	1050 – 1250
	Cu	2.6	3	800 – 1200
	Ni	2.9	0.77	930 – 1050
	P	3.0	28.3	1280 – 1350
	S	2.1	1.35	1200 – 1350
	W	3.9	$1.0 \cdot 10^3$	1050 – 1250

H.K.D.H. Bhadeshia and R.W.K. Honeycombe: Steels - Microstructure and Properties, Amsterdam, Boston, etc.: Elsevier, Butterworth-Heinemann (2006)

Diffusion

Matrix	Diffusant	$\Delta H/\text{eV}$	$D_0/\text{cm}^2\text{s}^{-1}$	$T/^\circ\text{C}$
$\alpha\text{-Fe}$	C	0.8	$6.2 \cdot 10^{-3}$	
	N	0.8	$3.0 \cdot 10^{-3}$	
	Fe	2.5	0.5	700 – 750
	Co	2.3	0.2	700 – 790
	Cr	3.6	$3.0 \cdot 10^4$	
	Ni	3.7	9.7	700 – 900
	P	2.4	2.9	860 – 900
	W	3.0	$3.8 \cdot 10^2$	

H.K.D.H. Bhadeshia and R.W.K. Honeycombe: Steels - Microstructure and Properties, Amsterdam, Boston, etc.: Elsevier, Butterworth-Heinemann (2006)

Most Important Considerations

- From the slides before, following most important considerations need to be taken into account for the lecture:
 - Diffusion usually occurs “down-hill” in a way that concentration gradients become smaller. It slows down when the concentration gradient decreases. “Up-hill” diffusion can occur when the chemical potential increases during mixing.
 - Interstitial elements have very high diffusion coefficients even at rather low temperature due to movement on lattice voids which do not need to be formed.
 - Substitutional elements have low diffusion coefficients since vacancies need to be present in order to mediate the diffusion process of the atoms.
 - Free volume in the presence of defects facilitates diffusion (when trapping of elements is avoided!), e.g. diffusion is much faster at grain boundaries and dislocations in comparison to bulk diffusion.