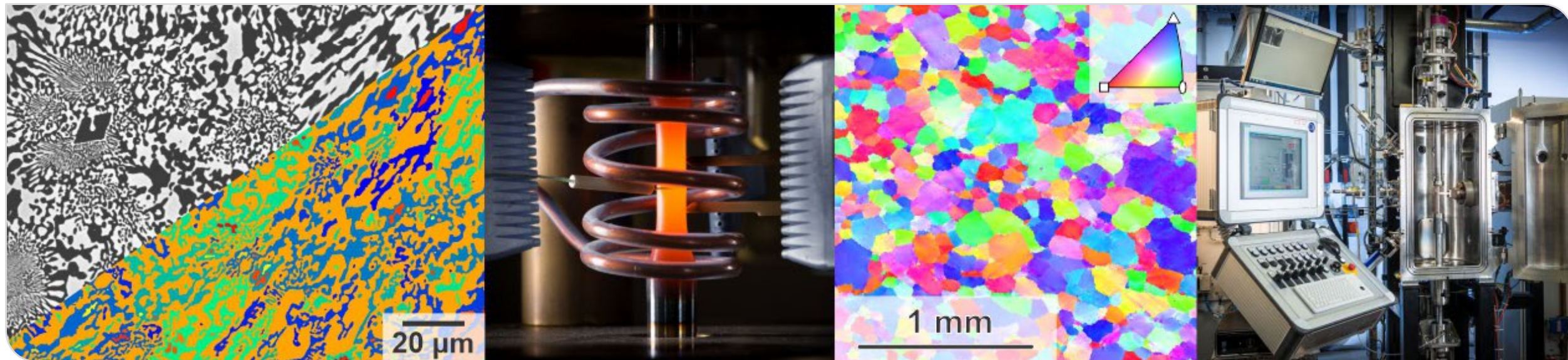


Phase Transformations in Materials

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

- Allotropic Transformations
 - Probability for Critical Nuclei, Impact of Diffusion
 - Growth, Impact of Rigidity

Nucleation

- A nucleation rate η might be considered that describes the number of newly activated nuclei in a certain time and within a certain volume, e.g. with $[\eta] = \frac{1}{\text{m}^3 \text{ s}}$.
- Since the nucleation process is determined by fluctuations, an Arrhenius type probability might be assumed (similar to what we have done for diffusion in Ch. 1b):

$$\eta \propto \exp - \frac{\Delta G^c}{k_B T}$$

- In contrast to other thermally activated processes, the activation barrier changes strongly with temperature in case of solidification since:

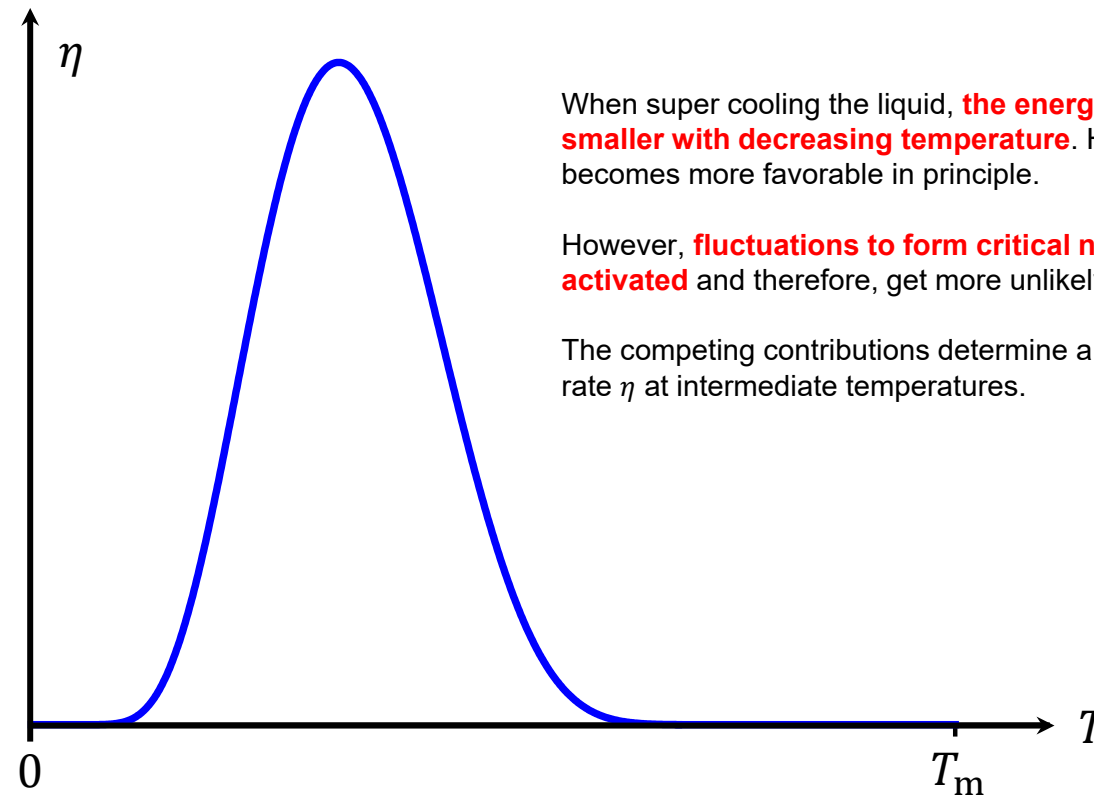
$$\Delta G^c \propto \frac{T_m}{\Delta T^2}$$

- Hence, we obtain:

$$\eta \propto \exp - \frac{T_m}{\Delta T^2 T} = \exp - \frac{T_m}{(T_m - T)^2 T}$$

Revision of Ch. 3b

Nucleation



When super cooling the liquid, **the energy barrier ΔG^c gets smaller with decreasing temperature**. Hence, nucleation becomes more favorable in principle.

However, **fluctuations to form critical nuclei are thermally activated** and therefore, get more unlikely at low temperatures.

The competing contributions determine a maximum nucleation rate η at intermediate temperatures.

Revision of Ch. 3b

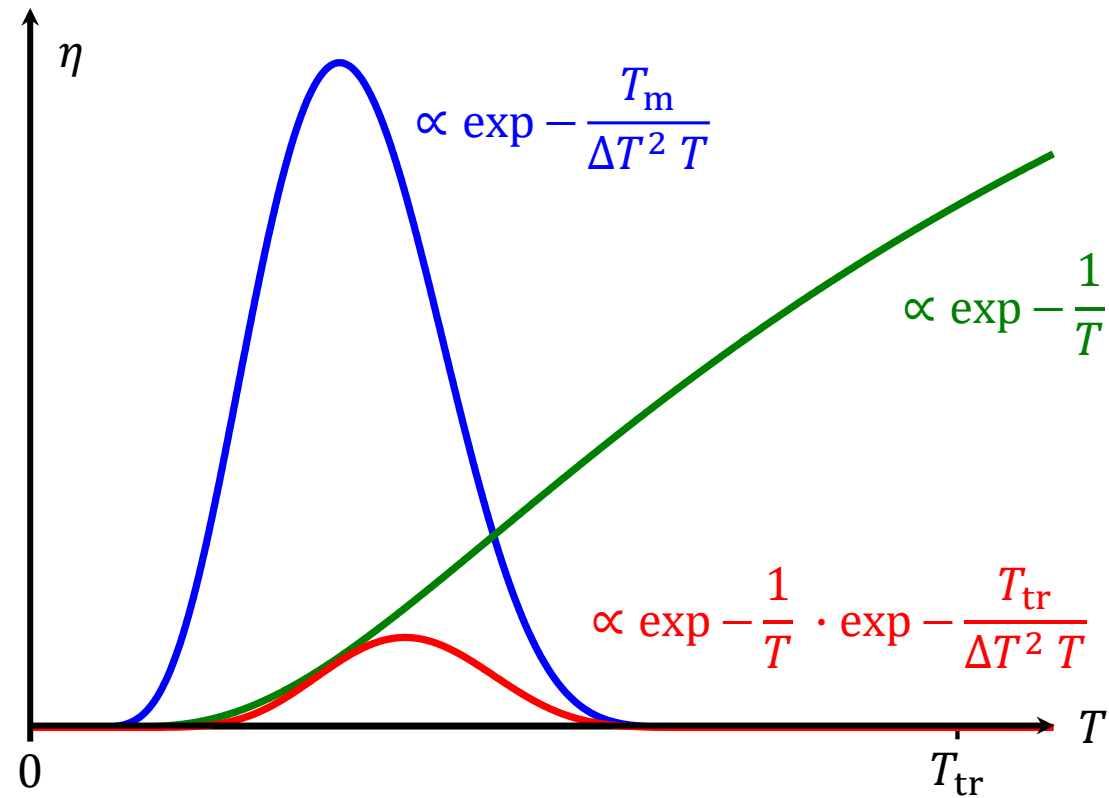
Nucleation

- In the liquid, the transport of atoms to the growing nuclei is easily achieved. In the solid, diffusion needs to take place in order to allow for the reconstructive phase transformation. The nucleation rate is altered by thermal activation of diffusion:

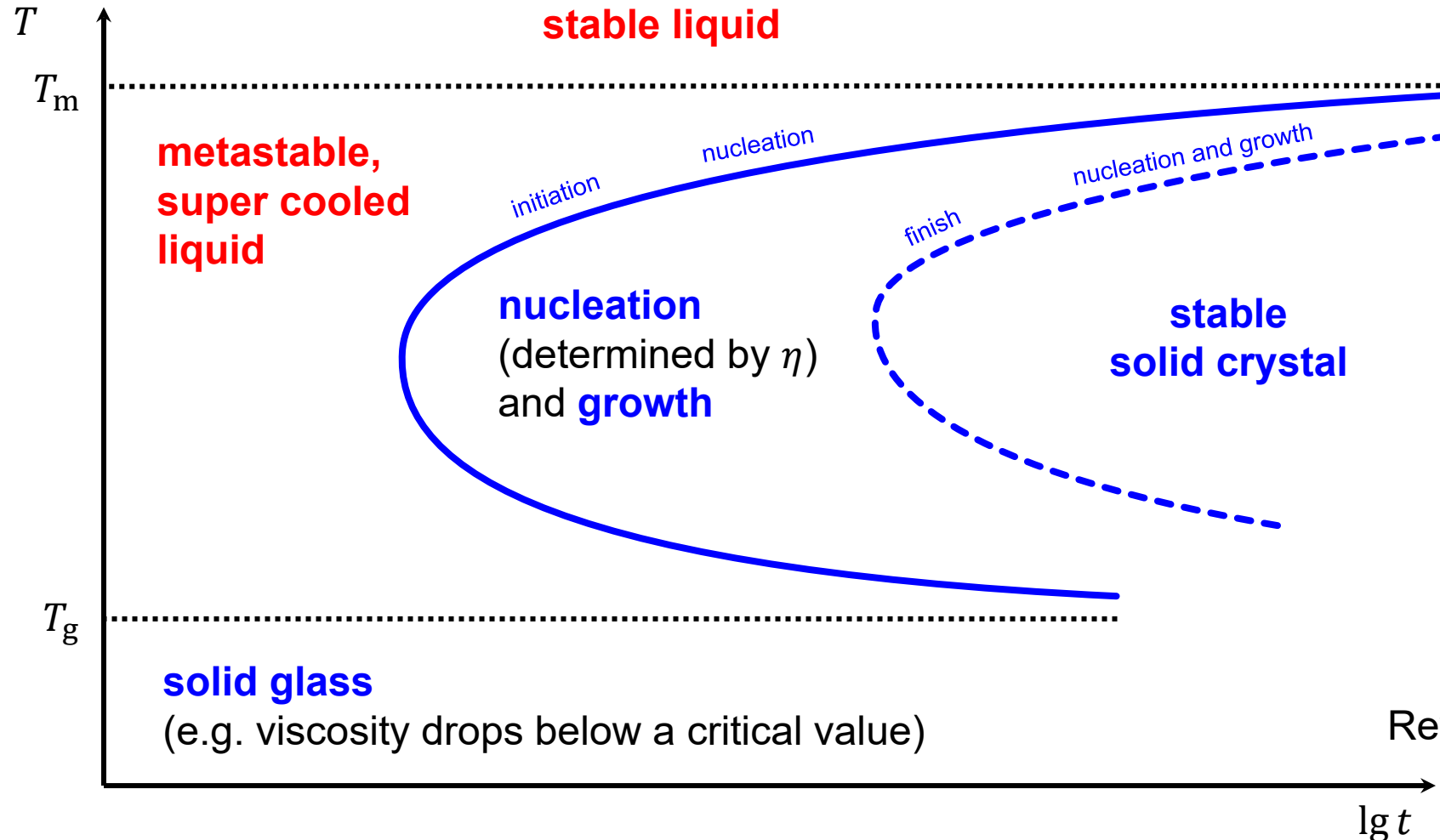
$$\eta \propto \exp \left(-\frac{\Delta G^{\text{diff}}}{k_B T} \right) \exp \left(-\frac{\Delta G^c(T)}{k_B T} \right)$$

- While the activation enthalpy of diffusion is rather constant with temperature, the nucleation barrier significantly depends on temperature $\Delta G^c(T) \propto \frac{T_{\text{tr}}}{\Delta T^2}$.

Nucleation

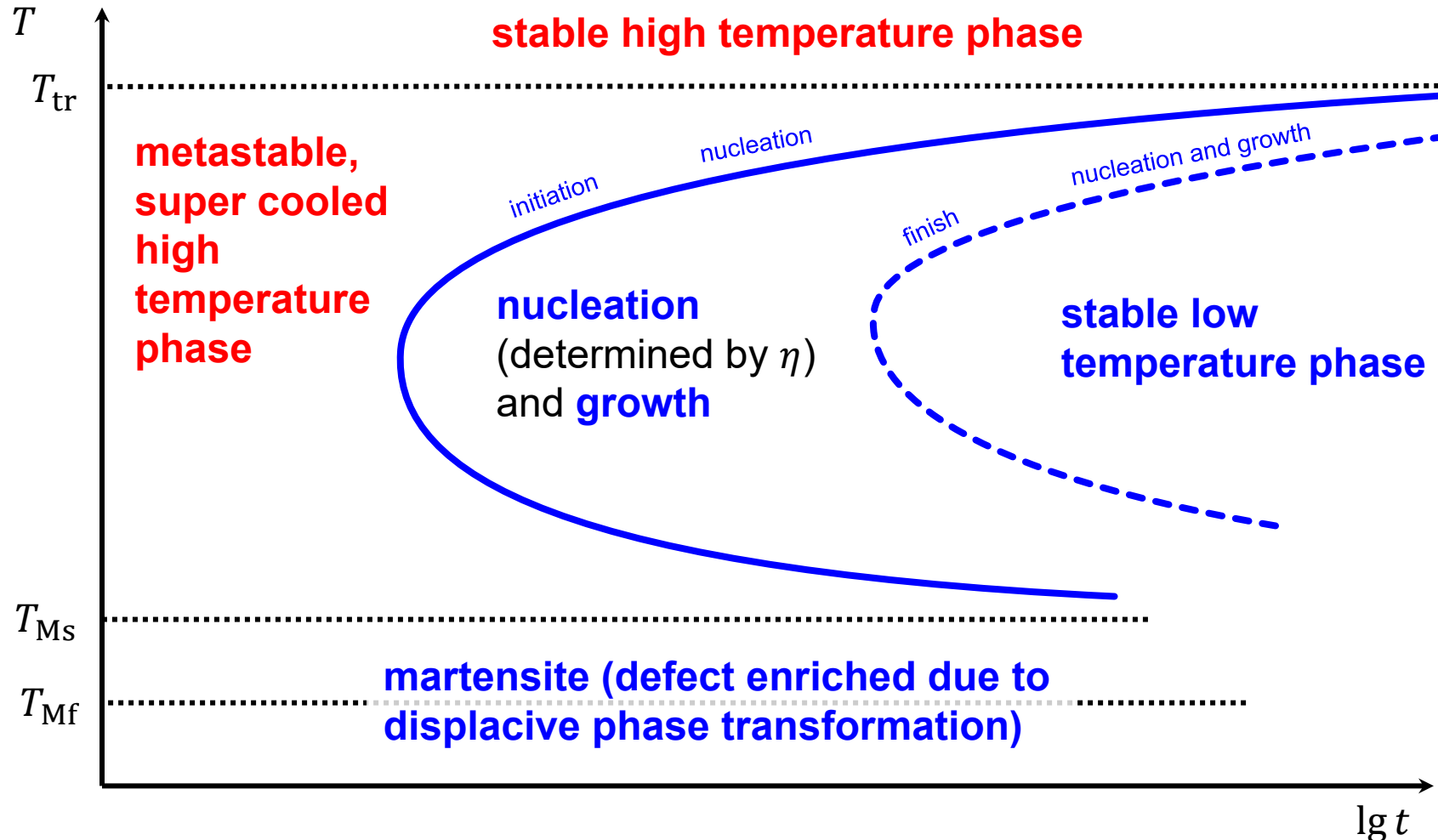


Time-Temperature-Transformation



Revision of Ch. 3b

Time-Temperature-Transformation



Displacive vs. Reconstructive

- The **reconstructive phase transformation can be suppressed** in case **diffusion processes cannot occur**, e.g. fast cooling/quenching at sufficiently high rate.
- As we have seen, the newly formed phase has a different volume than the high temperature phase. This corresponds to a blocked strain that causes **homogenous stresses within the super cooled high temperature phase**. If the stresses are large enough, the low temperature phase is formed by (more or less internal) deformation. Since no long-range atomic motion is involved, this type of transformation is distinguished as **displacive** (or **martensitic** or **diffusionless**) in nature.
- Note that the **deformation occurs instantaneously** (see Plasticity of Metals and Intermetallics on the rate of plastic strain release). Hence, the **time dependence of the martensitic transformation is not of interest**.
- However, the **amount of formed martensite** will be reached a maximum value for a distinct super cooling; **exactly to compensate the internal stress, not further**. Hence, its amount depends on super cooling. **Onset and finish temperatures** are observed.

Nucleation & Growth

- Simplified conditions of linear isothermal growth might be assumed in the following manner.
- **The growth occurs homogenous and isotropic at linear growth rate v with $[v] = \text{m/s}$.**
- **A nucleation rate η is considered constant.**
- In a short period of time $d\tau$:
 - The number of newly formed nuclei is $N = V \eta d\tau$.
 - The existing nuclei grow by $dR = v d\tau$ to a radius of $R = v (t - \tau)$ when nucleation took place at time τ .
 - The total volume is then:

$$\begin{aligned}
 V^{\text{tr},i} &= \int_0^t dV^{\text{tr},i} = \int_0^t \frac{4}{3} \pi v^3 (t - \tau)^3 V \eta d\tau = \frac{4}{3} \pi v^3 V \eta \int_0^t (t - \tau)^3 d\tau = \frac{4}{3} \pi v^3 V \eta \left[-\frac{1}{4} (t - \tau)^4 \right]_0^t \\
 &= \frac{\pi}{3} v^3 V \eta t^4
 \end{aligned}$$

Revision of Ch. 3b

Nucleation & Growth

- In contrast to the situation described in Ch. 3b, the transforming regions cannot rearrange when getting in contact. In the liquid, the nuclei can get in contact but are still able to grow further since the surrounding liquid won't resist. In the solid, the nucleation centers remain at their positions and the growing regions cannot rearrange.
- This needs to be considered during integration since already transformed material cannot undergo the transformation again.
- A simple Ansatz for the integration is that the increment in actually transformed volume becomes smaller and smaller with increasing volume fraction of already transformed material:

$$dV^{\text{tr}} = dV^{\text{tr},i} (1 - v^{\text{tr}})$$

$$dV^{\text{tr}} \left(1 - \frac{V^{\text{tr}}}{V}\right)^{-1} = dV^{\text{tr},i}$$

$$-V \ln \left(1 - \frac{V^{\text{tr}}}{V}\right) = -V^{\text{tr},i}$$

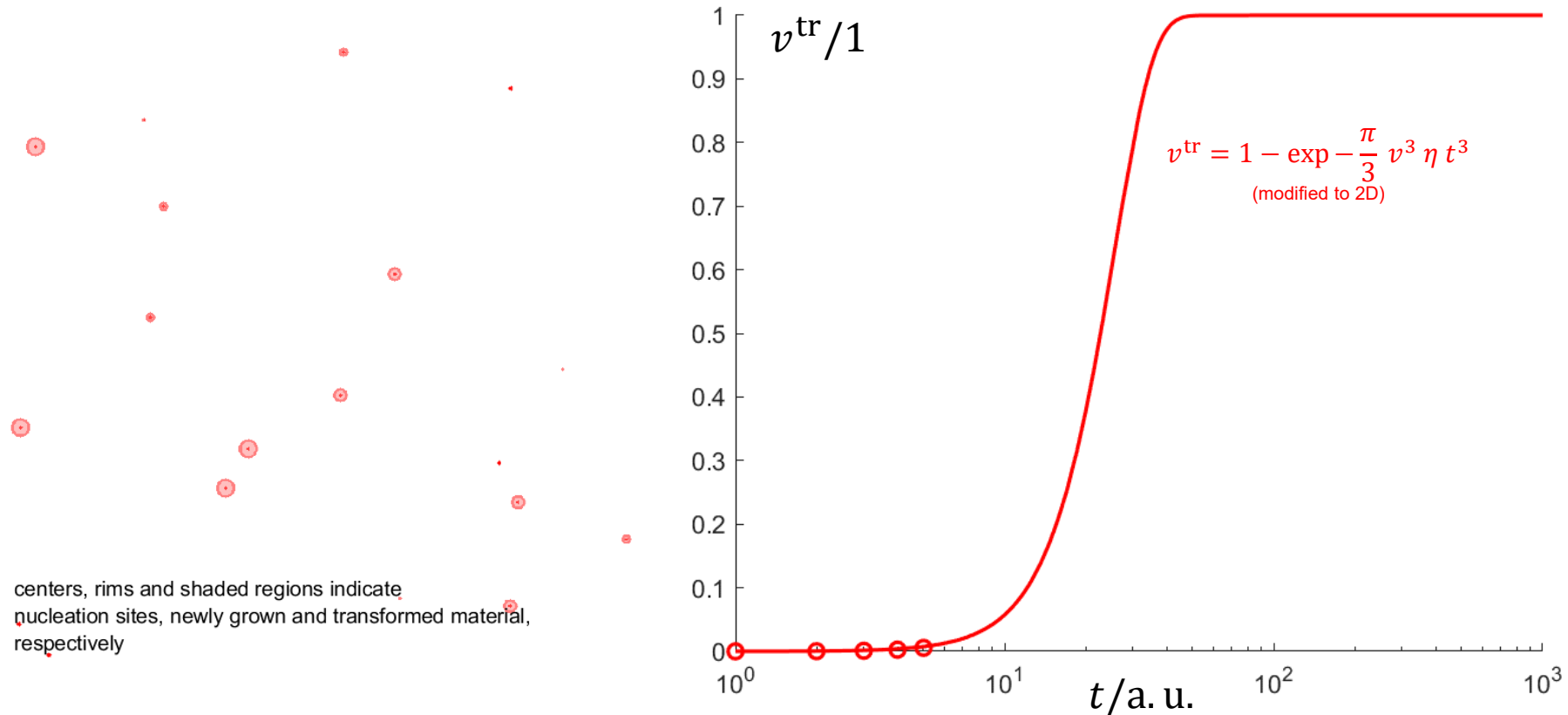
$$v^{\text{tr}} = \frac{V^{\text{tr}}}{V} = 1 - \exp - \frac{V^{\text{tr},i}}{V}$$

Nucleation & Growth

- Hence, the Johnson-Mehl-Avrami-Kolmogorow equation (in English literature, just Avrami equation) follows:

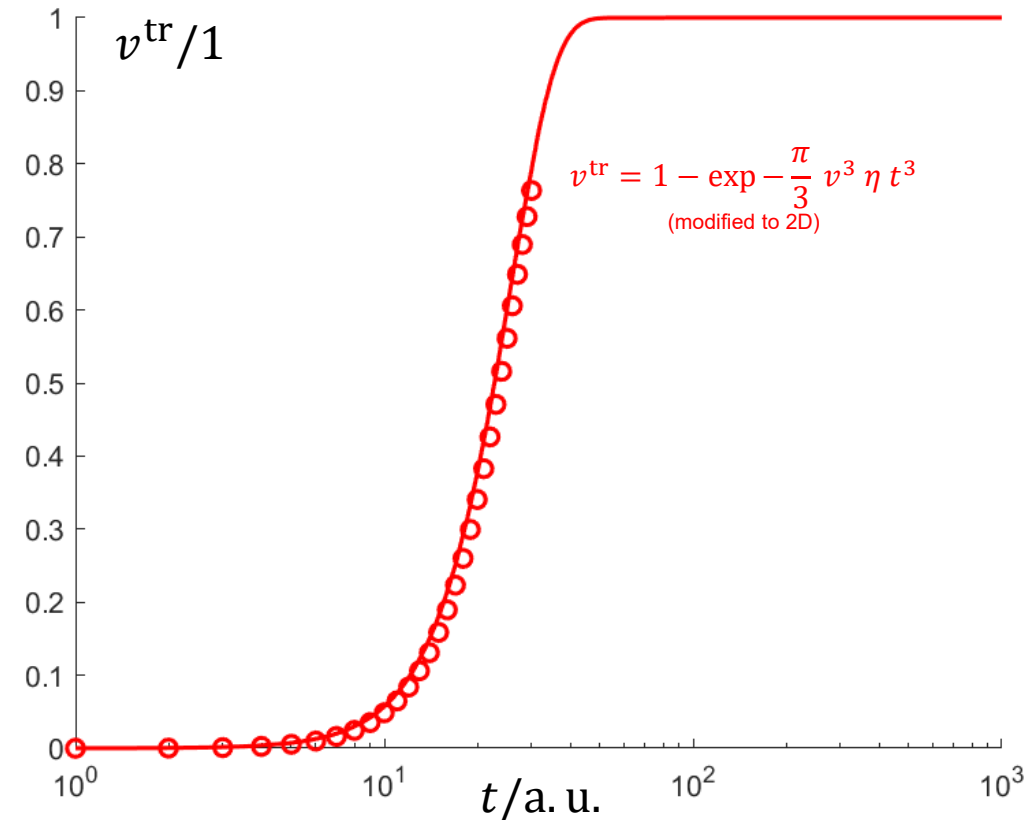
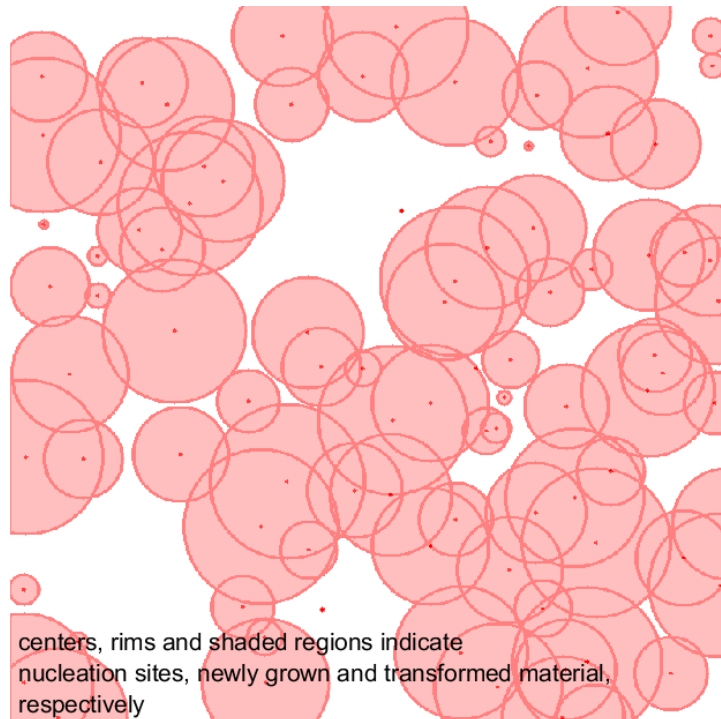
$$v^{\text{tr}} = \frac{V^{\text{tr}}}{V} = 1 - \exp - \frac{V^{\text{tr},i}}{V}$$
$$= 1 - \exp - \frac{\pi}{3} v^3 \eta t^4$$

Nucleation & Growth



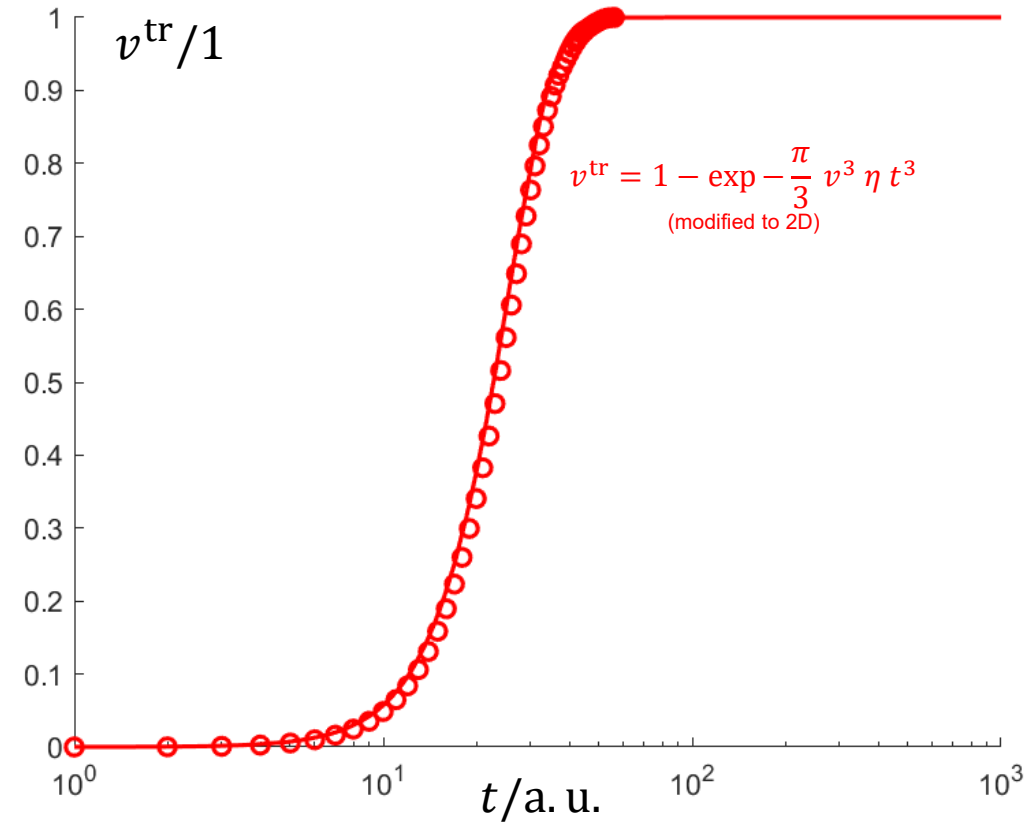
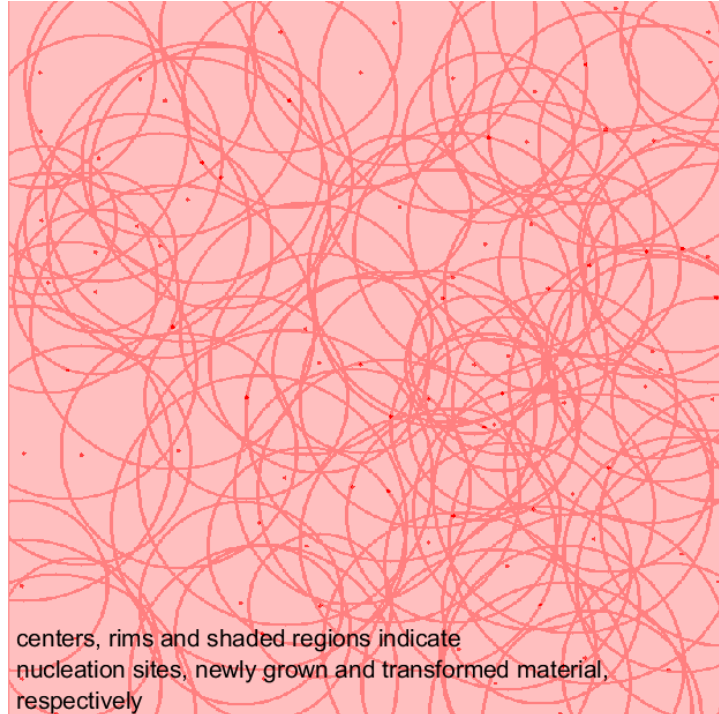
Initially, the transformed regions grow independently and free. The solution simplifies to: $v^{\text{tr}} \approx \frac{V^{\text{tr},i}}{V} = \frac{\pi}{3} v^3 \eta t^3$. ($1 - e^{-x} \approx x \forall x \ll 1$ or Ch. 3b)

Nucleation & Growth



After certain amount of transformation the transformed regions impinge on one another. Reaction rate $\frac{dv^{\text{tr}}}{dt}$ decelerates.

Nucleation & Growth



Nucleation & Growth

- In order to evaluate the evolution of the transformation, we need to consider nucleation and growth:

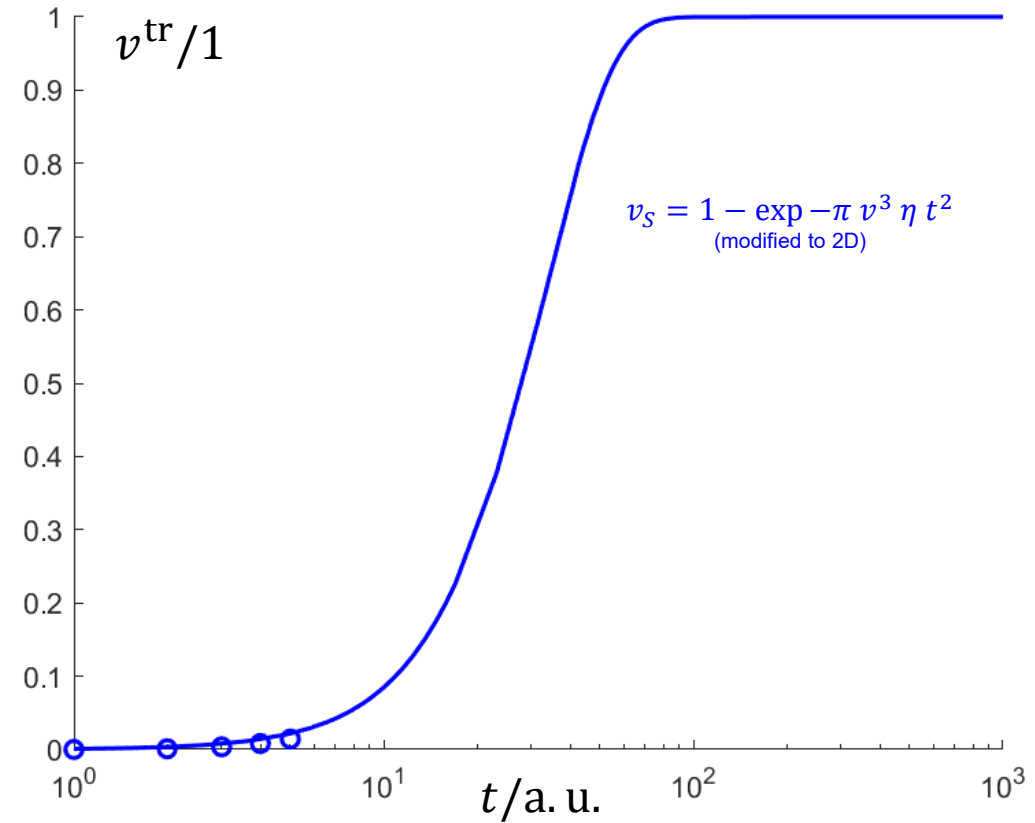
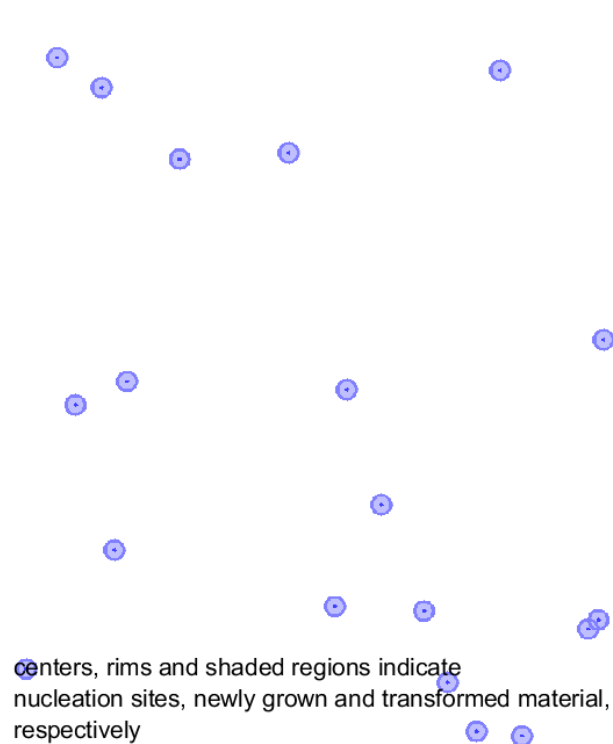
- In some cases (e.g. heterogeneous nucleation), all nucleation sites might be activated from the beginning and the number of nuclei is: $N = V \eta = \text{const.}$ This is called site saturation.

- Hence, the integration is simply: $V^{\text{tr},i} = \frac{4\pi}{3} v^3 V \eta t^3.$

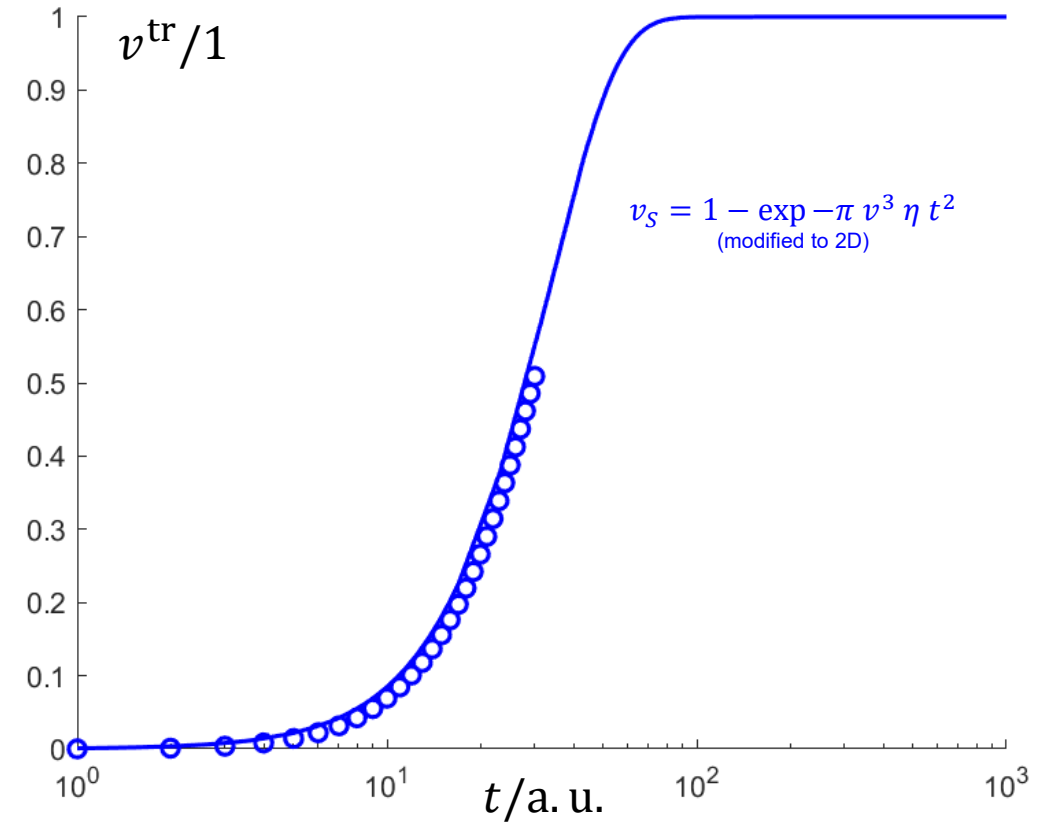
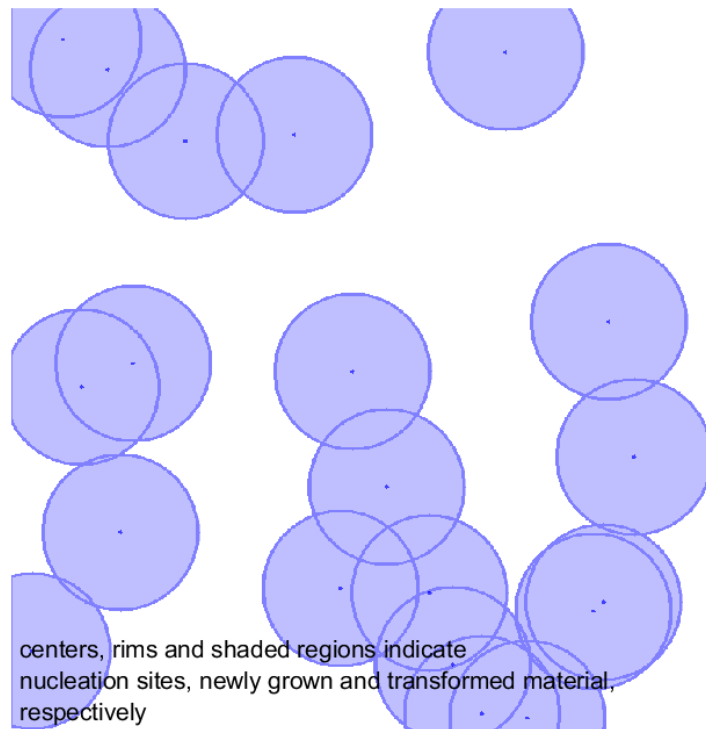
- Considering the confinement:
$$v^{\text{tr}} = \frac{V^{\text{tr}}}{V} = 1 - \exp - \frac{V^{\text{tr},i}}{V}$$

$$= 1 - \exp - \frac{4\pi}{3} v^3 \eta t^3$$

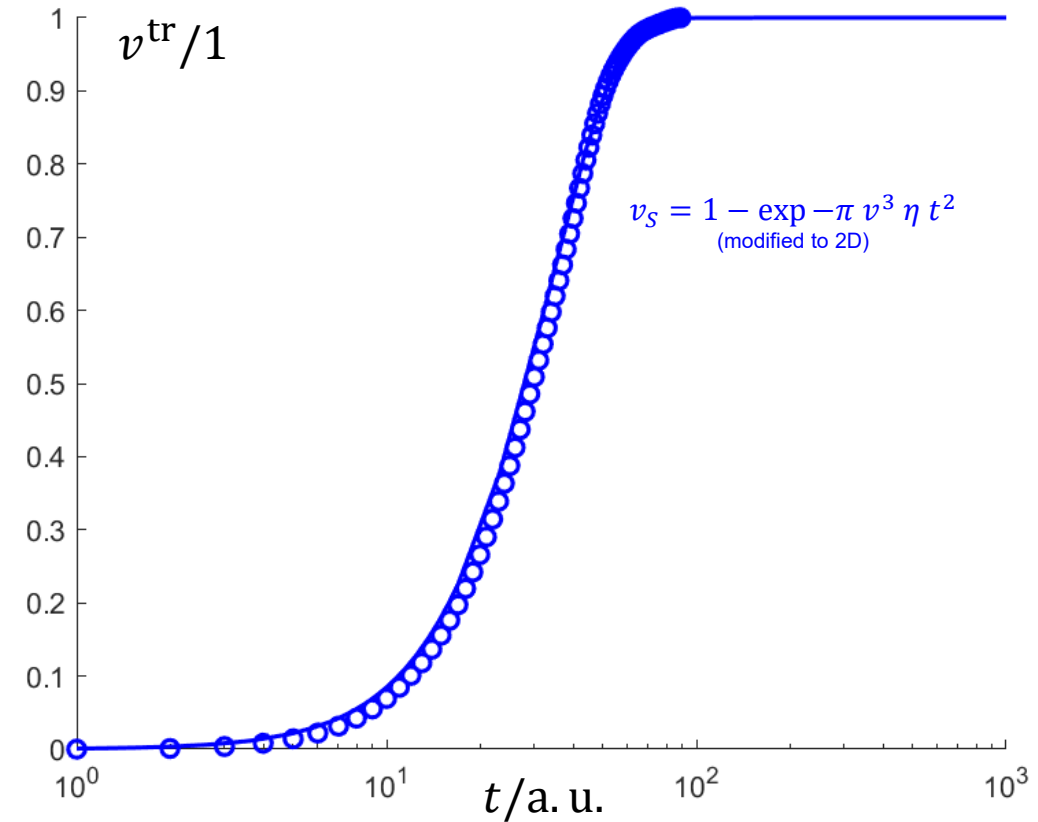
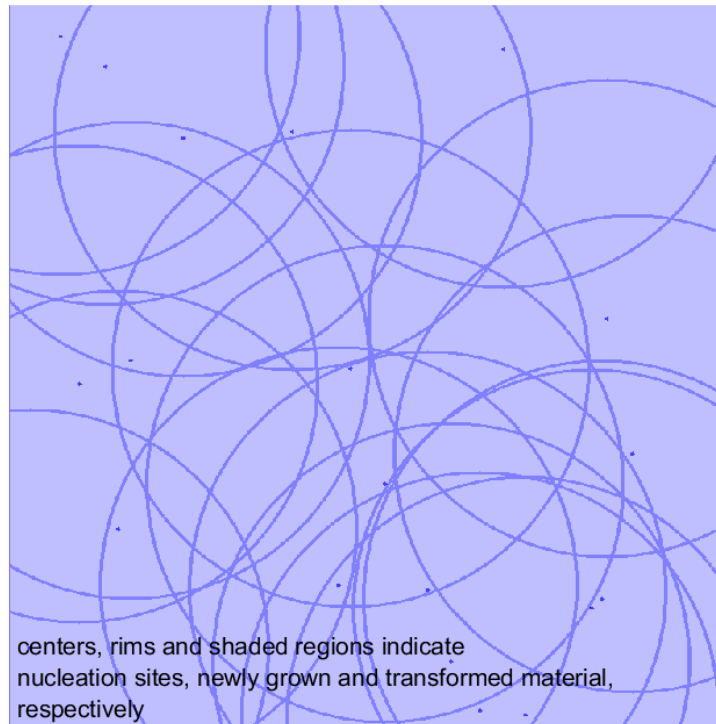
Nucleation & Growth



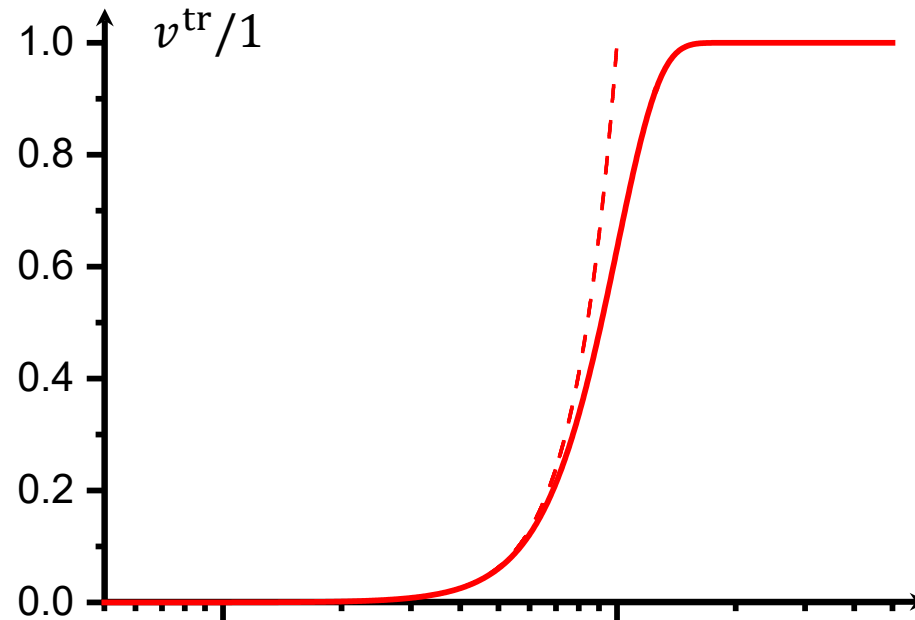
Nucleation & Growth



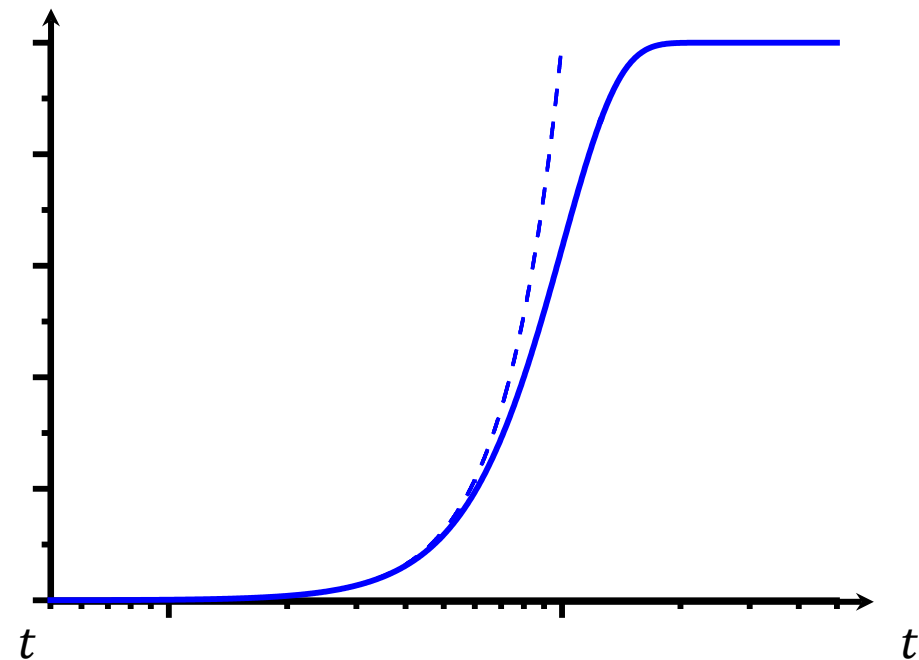
Nucleation & Growth



Nucleation & Growth



$$v^{\text{tr}} = 1 - \exp - \frac{\pi}{3} v^3 \eta t^4 \approx \frac{\pi}{3} v^3 \eta t^4$$



$$v^{\text{tr}} = 1 - \exp - \frac{4\pi}{3} v^3 \eta t^3 \approx \frac{4\pi}{3} v^3 \eta t^3$$