Atomistic Simulation in the Model HEA: CuNiCoFe

D. Utt, A. Stukowski, K. Albe

TECHNISCHE UNIVERSITÄT DARMSTADT

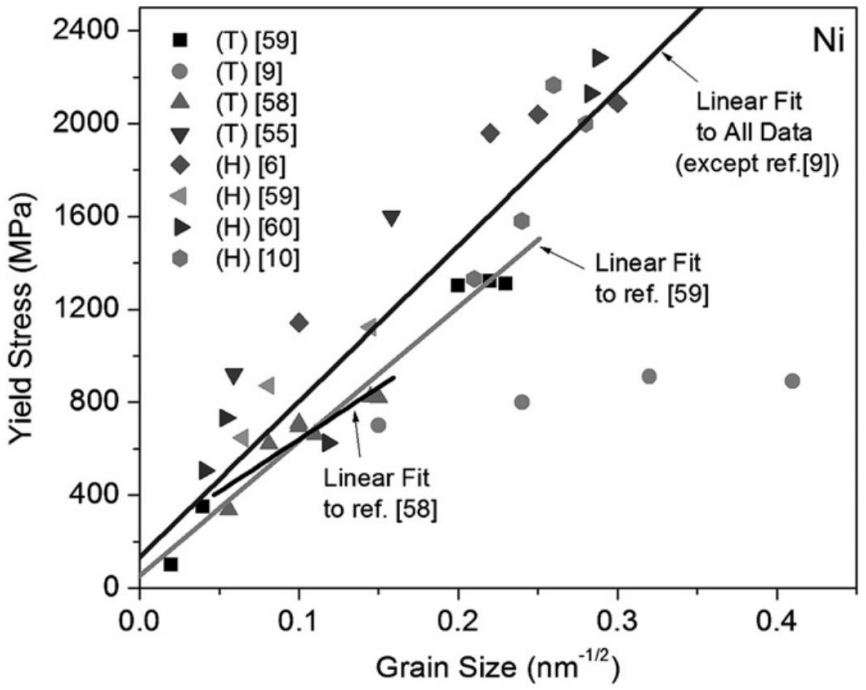
CCA HEA

DFG Deutsche Forschungsgemeinschaft

FACHGEBIET MATERIALMODELLIERUNG

Motivation

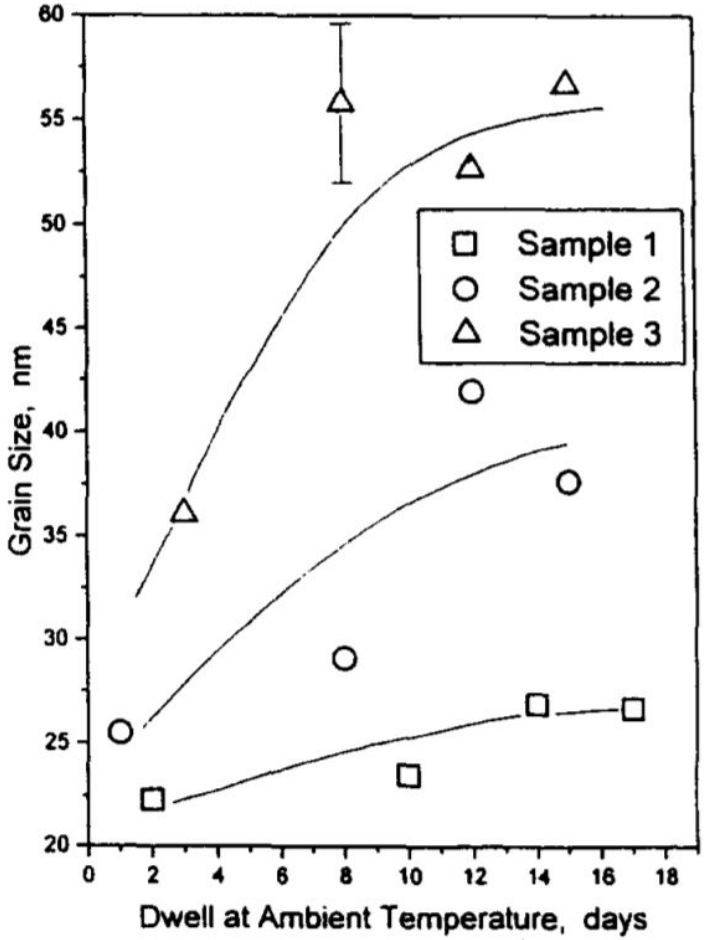
- Nanocrystalline metals show outstanding mechanical properties.



Carlton and Ferreira, Acta Materialia 55 (11), 2007

Motivation

- Nanocrystalline metals show outstanding mechanical properties.
- Small grain sizes are not stable in pure materials.



Gertsman and Birringer, Scripta Metallurgica et Materialia 30 (5), 1994

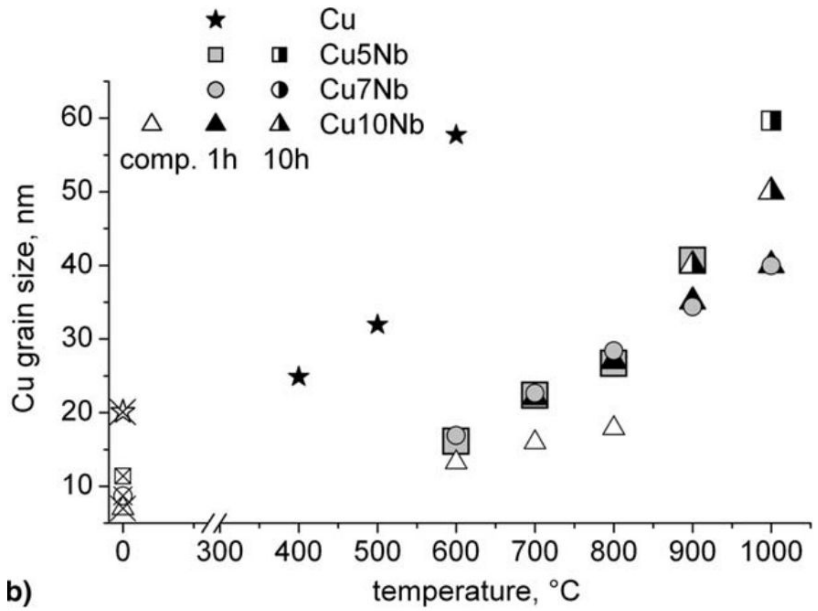
Motivation

- Secondary elements can be added to stabilize the microstructure.

Motivation

- Secondary elements can be added to stabilize the microstructure.

1. Kinetically:
   - Solute drag mechanism
   - Zener pinning

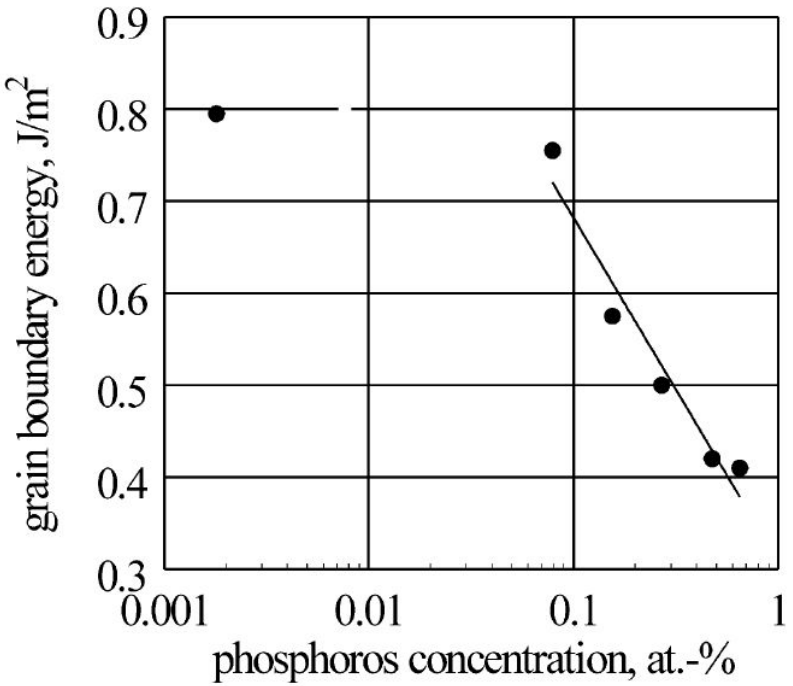


Cahn, Acta Metallurgica 10 (9), 1962
Nes et al., Acta Metallurgica 33 (1), 1985
Botcharova et al., Acta Materialia 51 (12), 2006

Motivation

- Secondary elements can be added to stabilize the microstructure.

1. Kinetically
2. Thermodynamically:
   - Segregation reduces GB energy to 0.
   - Removes driving force for grain growth.



Weissmüller, Nanostructured Materials, 3 (1-6), 1993
Kirchheim, Acta Materialia, 50 (2), 2002

Motivation

- Slower grain growth in HEAs?

Motivation

TECHNISCHE UNIVERSITÄT DARMSTADT

- Slower grain growth in HEAs?
  - Local disorder

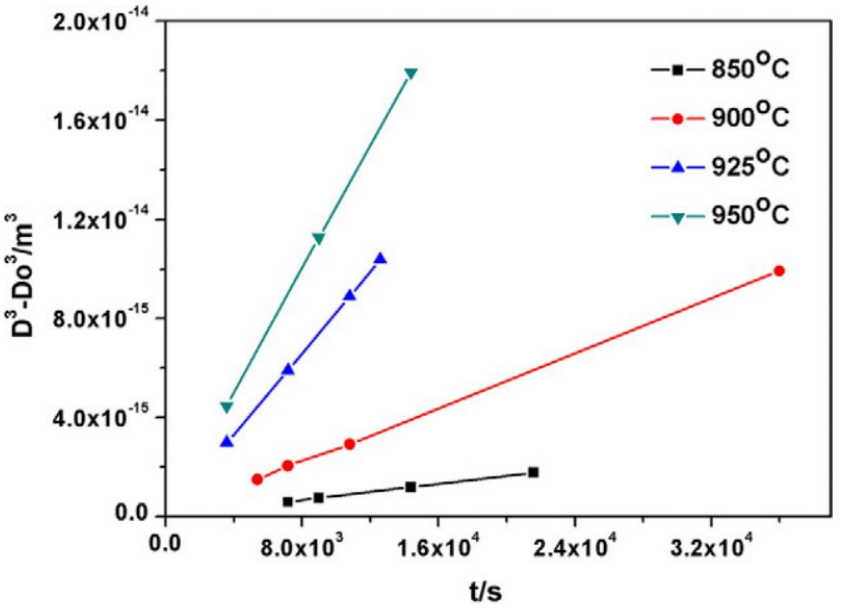
Motivation

TECHNISCHE UNIVERSITÄT DARMSTADT

- Slower grain growth in HEAs?
  - Local disorder
  - Segregation effects

Motivation

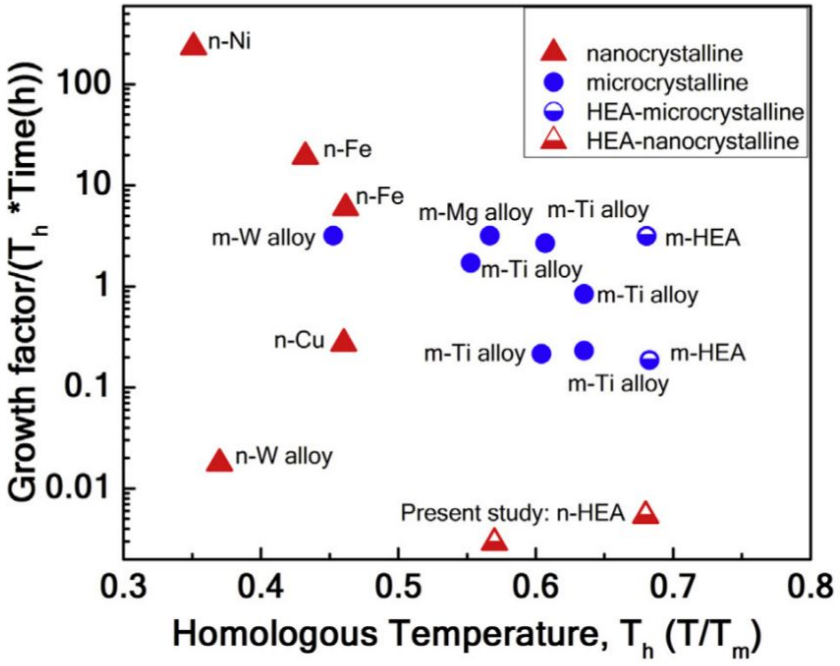
- Slower grain growth in HEAs?
  - Local disorder
  - Segregation effects
- Observed in microcrystalline FeCoNiCrMn
  - growth exponent = 3



Liu et al., Scripta Materialia 68 (7), 2013

Motivation

- Slower grain growth in HEAs?
  - Local disorder
  - Segregation effects
- Observed in microcrystalline FeCoNiCrMn
- Exceptional resistance against grain growth in CoCrFeNi
  - Zener pinning at precipitates



Praveen et al., Journal of Alloys and Compounds 662, 2016

Motivation

TECHNISCHE UNIVERSITÄT DARMSTADT

What is the origin of the reduced grain growth in HEAs?

Understanding kinetic and thermodynamic aspects.

Molecular Dynamics Study

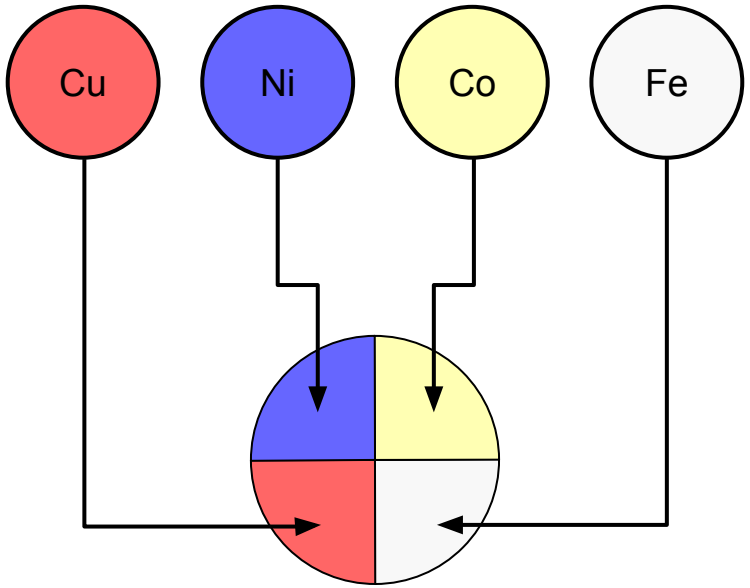
TECHNISCHE UNIVERSITÄT DARMSTADT

- Compare grain growth:
  - Cu
  - CuNiCoFe
  - Average atom

Molecular Dynamics Study

TECHNISCHE UNIVERSITÄT DARMSTADT

- Compare grain growth
- Average atom
  - Artificial element
  - Behaves like CuNiCoFe alloy
  - Leads to average matrix without local disorder
  - Selectively study effects of local disorder



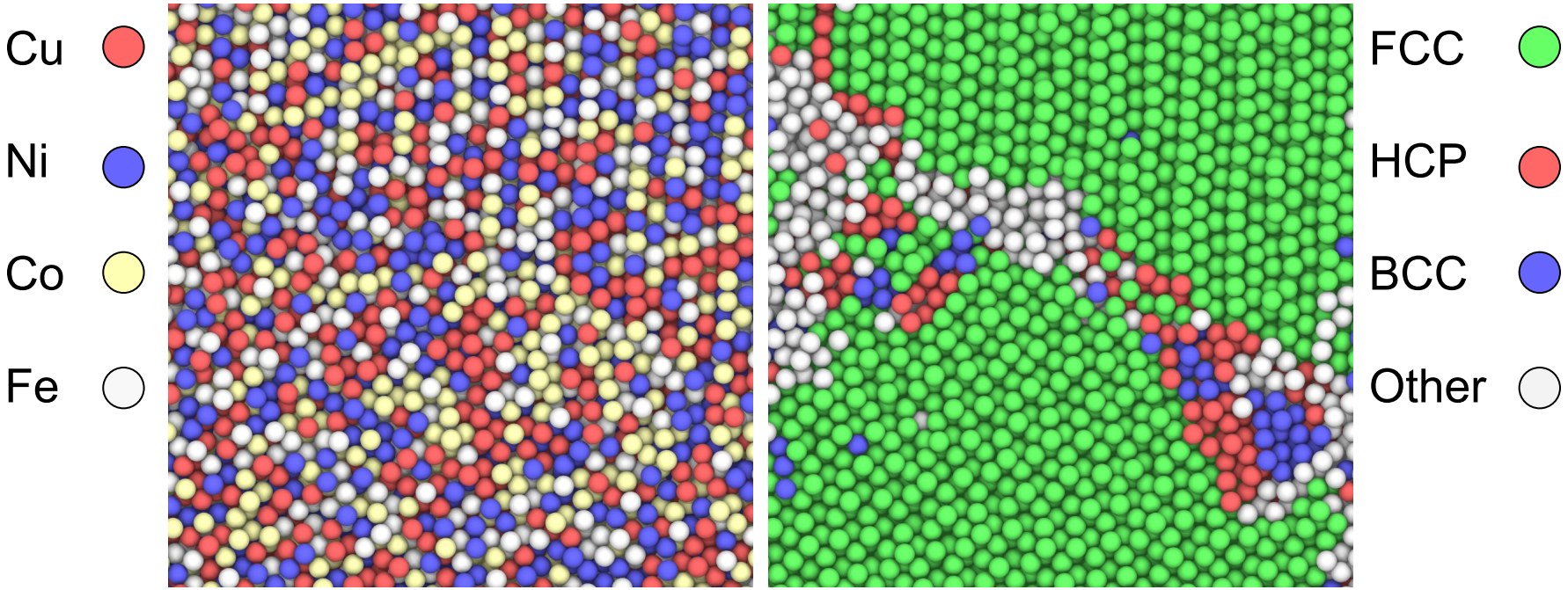
Average Atom

Varvenne et al., Physical Review B 93 (10), 2016

FACHGEBIET MATERIALMODELLIERUNG

Molecular Dynamics Study

- Compare grain growth
- Average atom
- Atoms will be color coded

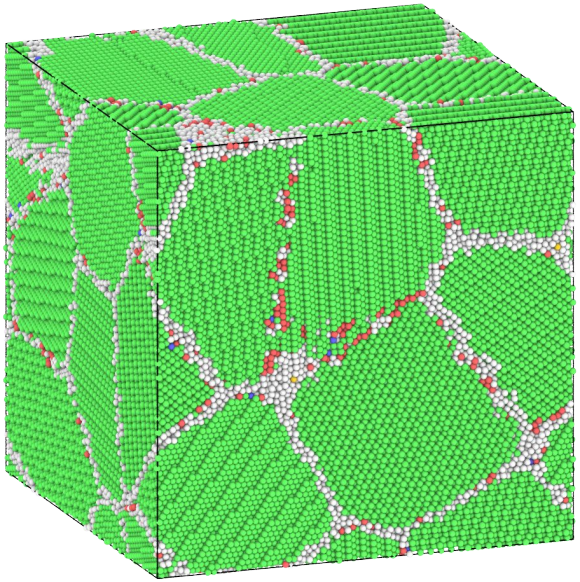


Stukowski, Modelling and Simulation in Materials Science and Engineering 18 (1) 2009

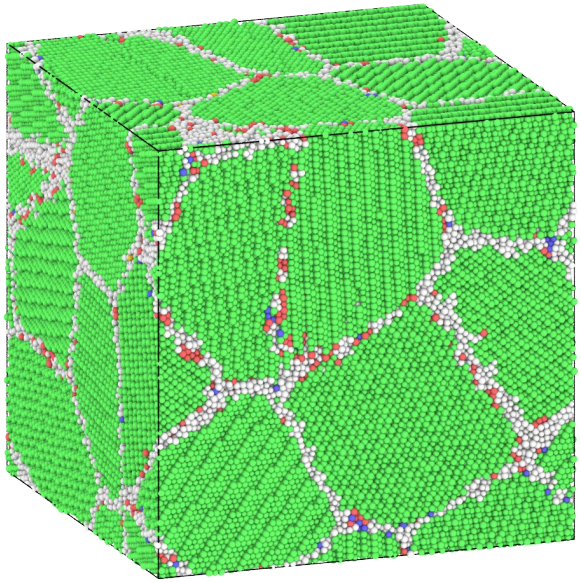
$t = t_{initial}$

TECHNISCHE UNIVERSITÄT DARMSTADT

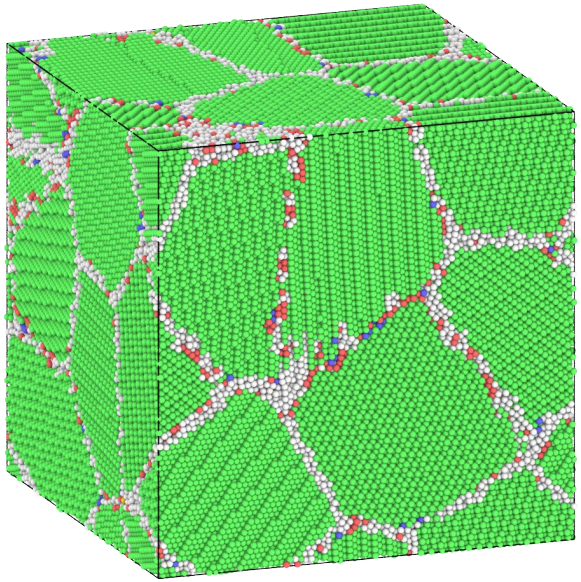
Cu



CuNiCoFe



Average Atom



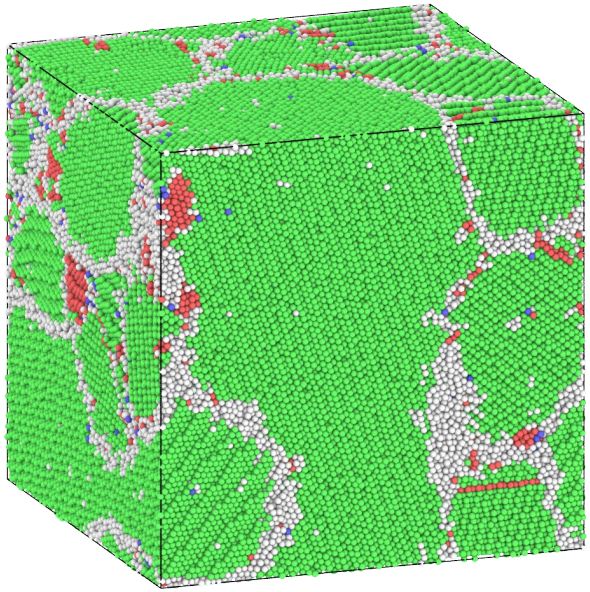
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

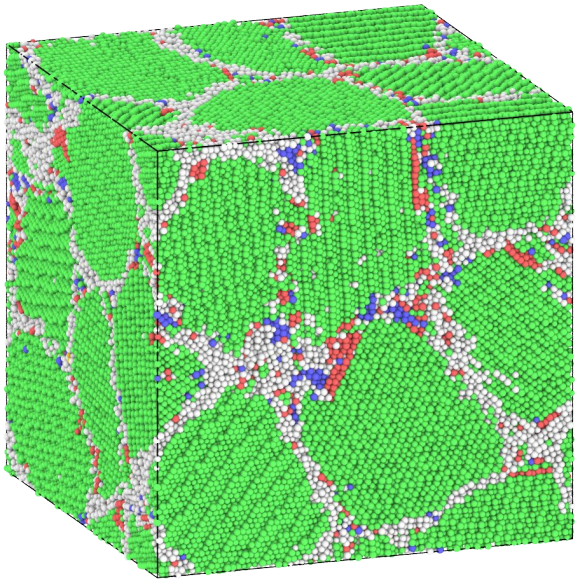
$t = 0.33\ t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

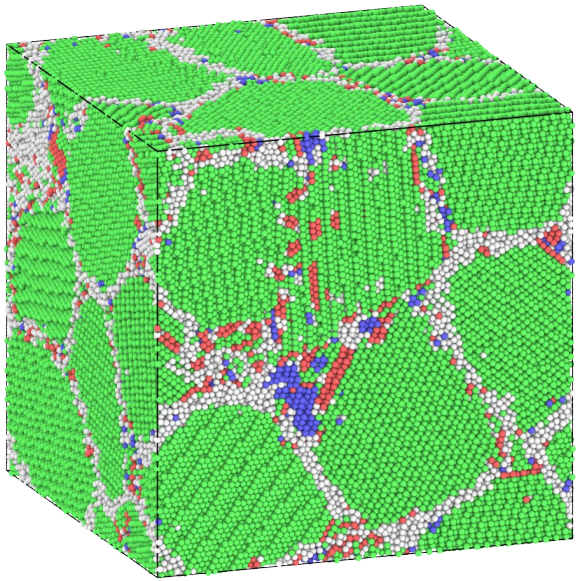
Cu



CuNiCoFe



Average Atom



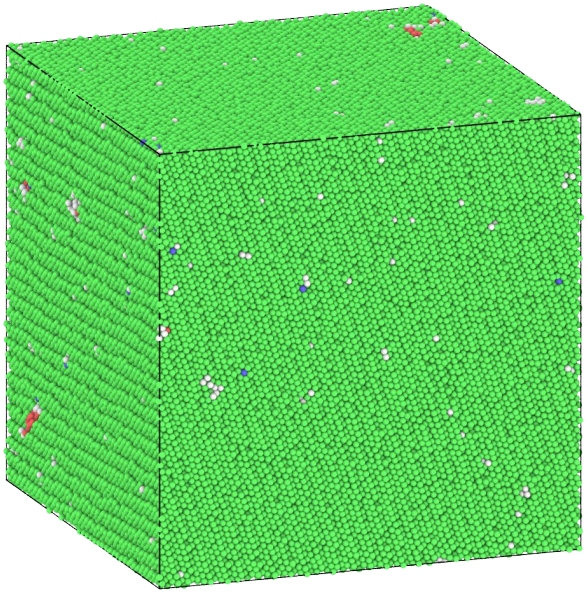
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

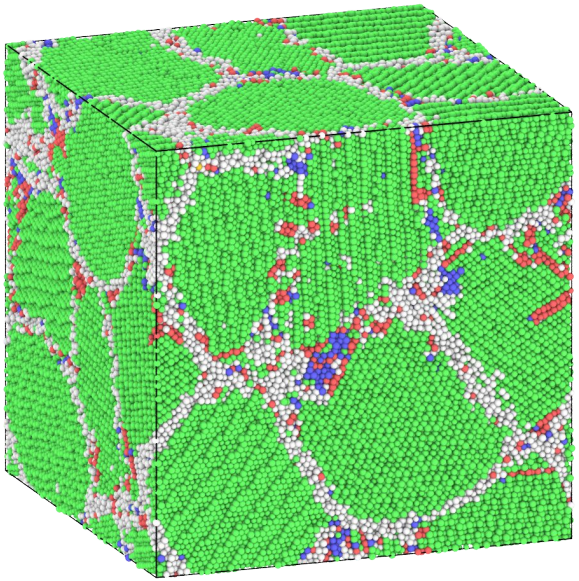
$t = t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

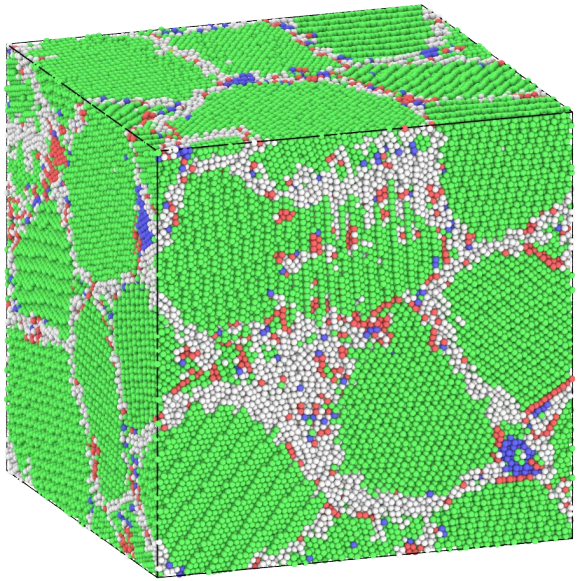
Cu



CuNiCoFe



Average Atom



FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

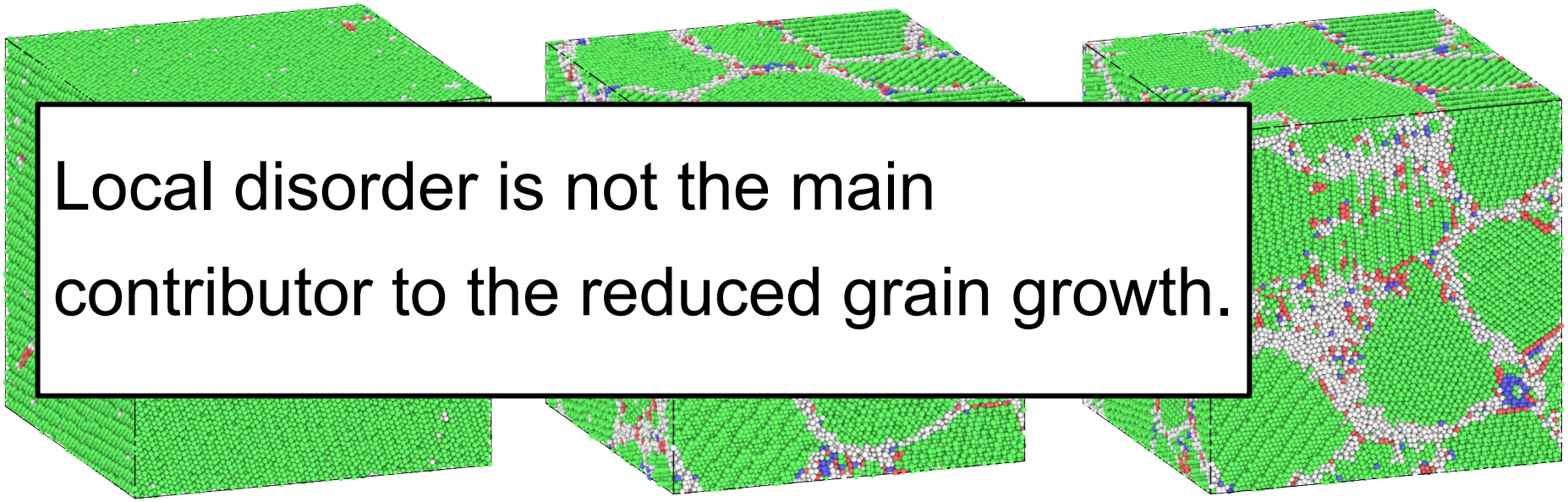
$t = t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

Cu

CuNiCoFe

Average Atom



Local disorder is not the main contributor to the reduced grain growth.

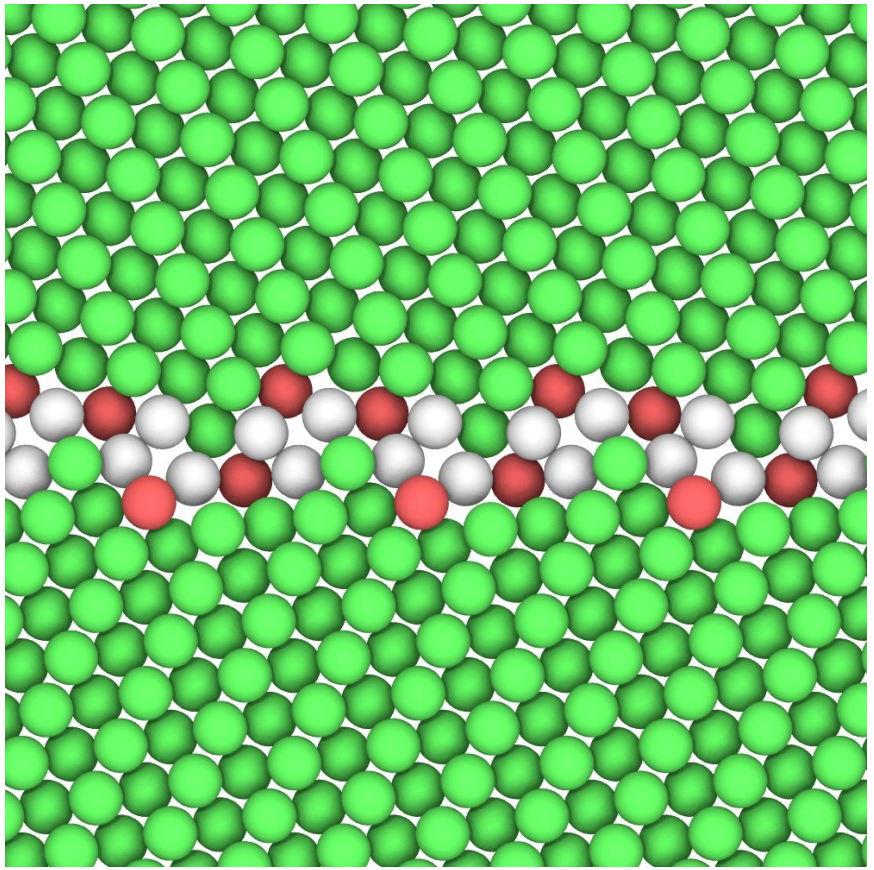
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

GB Mobility

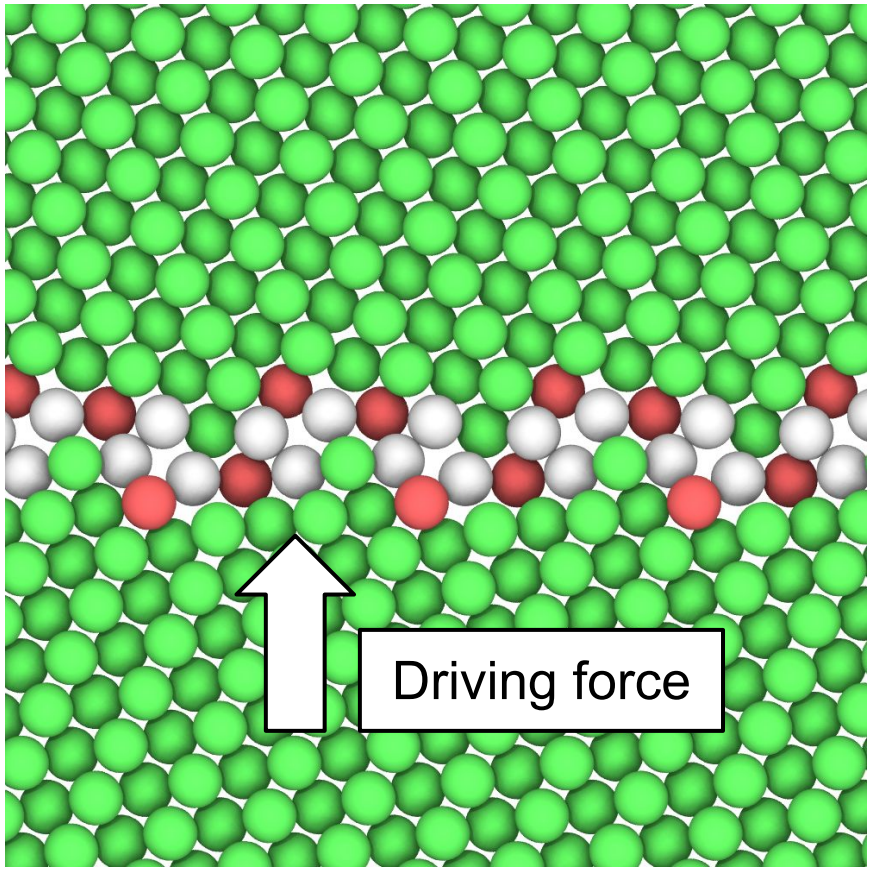
TECHNISCHE UNIVERSITÄT DARMSTADT

- Σ=11 (332) symmetrical tilt GB
- Bicrystalline simulation setup



GB Mobility

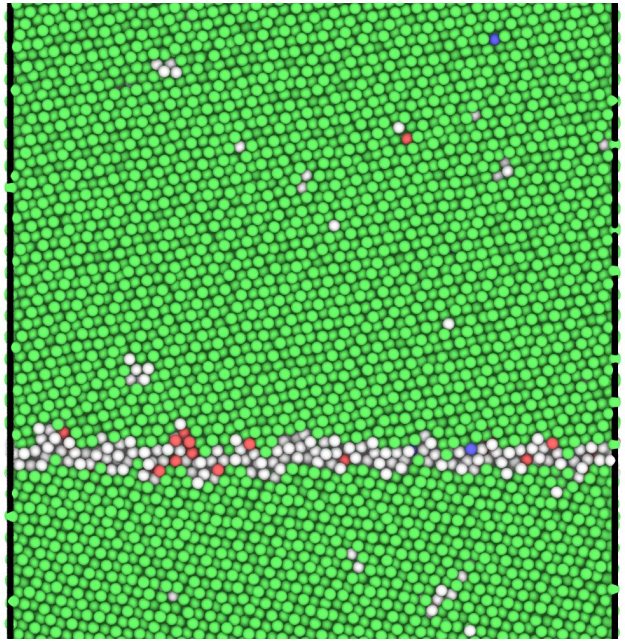
- Σ=11 (332) symmetrical tilt GB
- Bicrystalline simulation setup
- Apply artificial driving force to GB



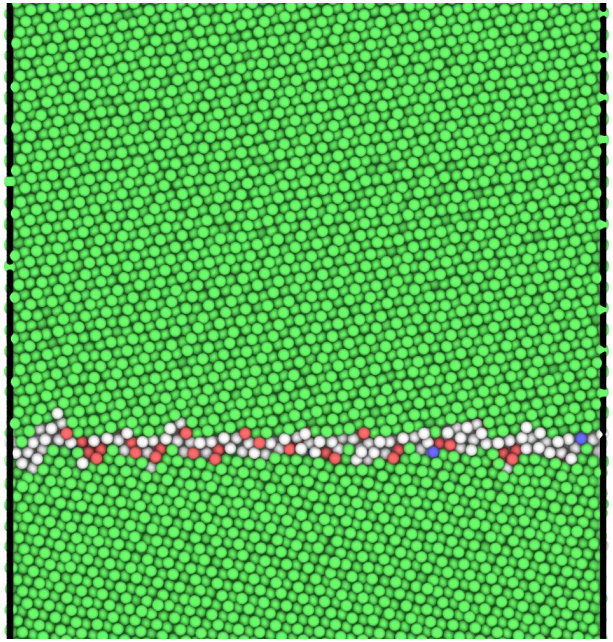
$t = t_{initial}$

TECHNISCHE UNIVERSITÄT DARMSTADT

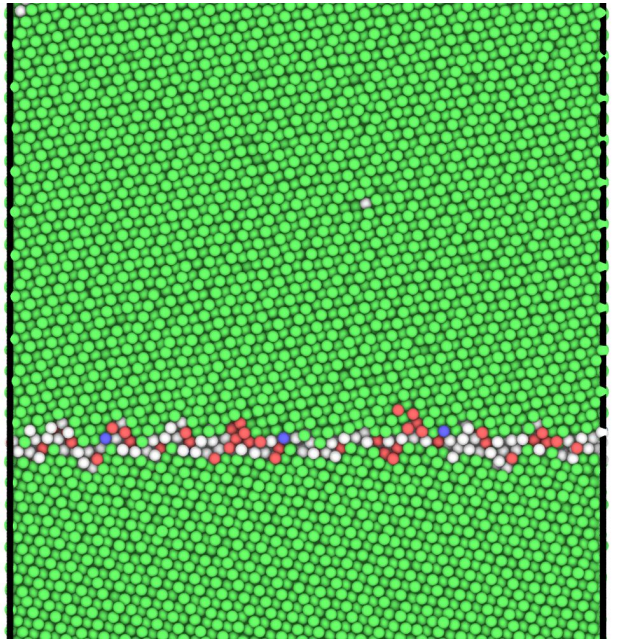
Cu



CuNiCoFe



Average Atom



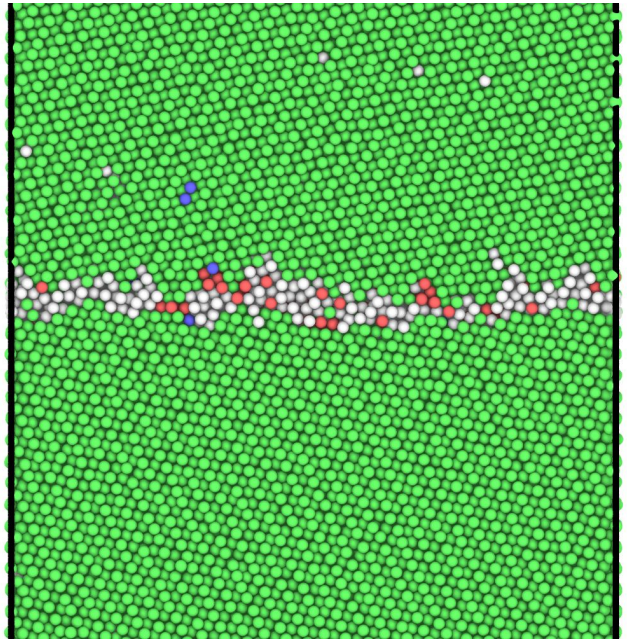
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

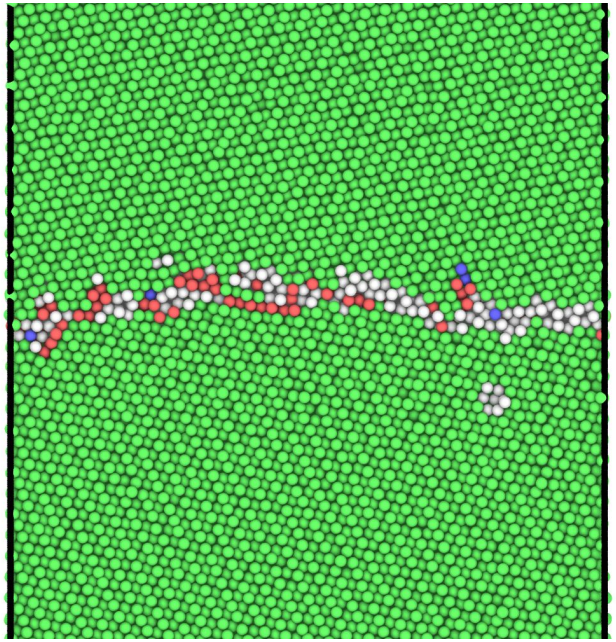
$t = 0.5\ t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

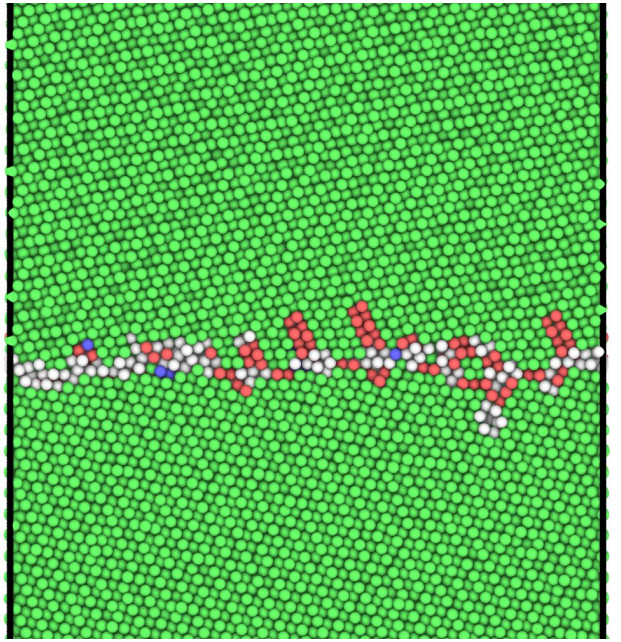
Cu



CuNiCoFe



Average Atom



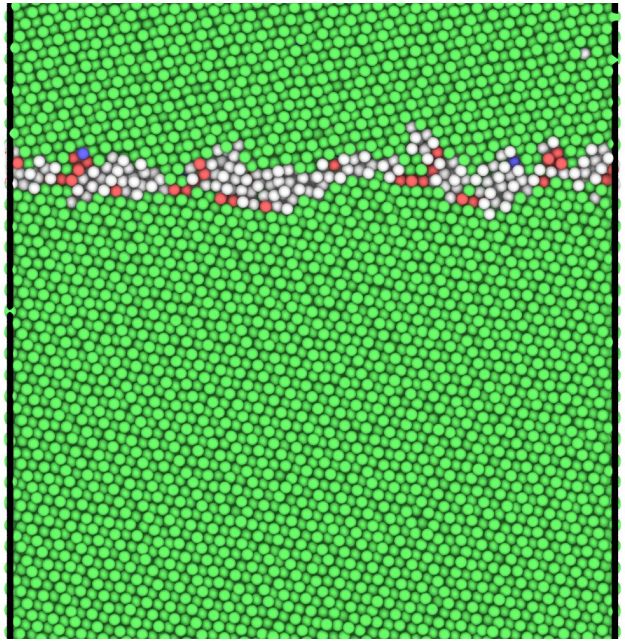
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

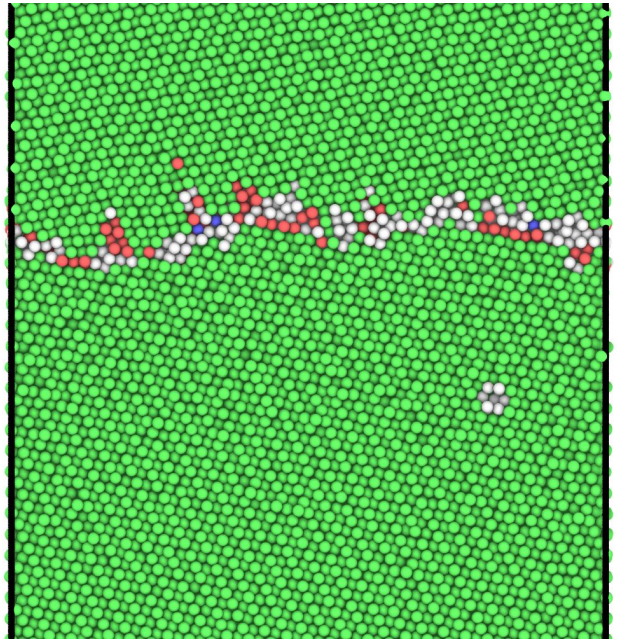
$t = t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

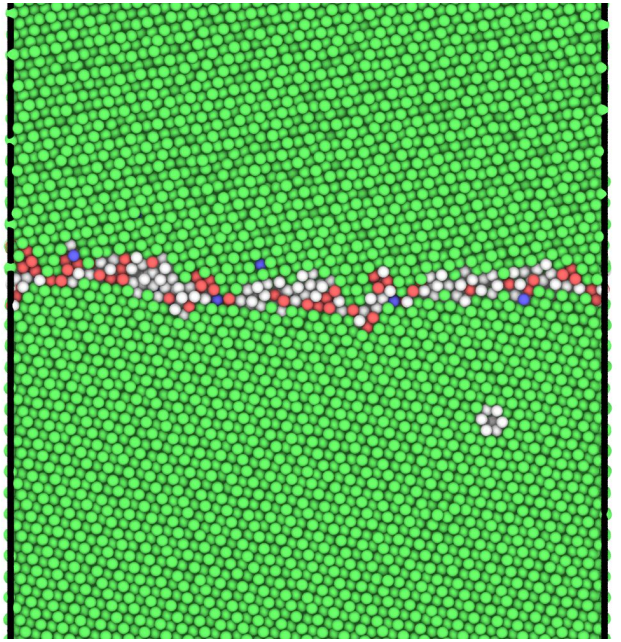
Cu



CuNiCoFe



Average Atom



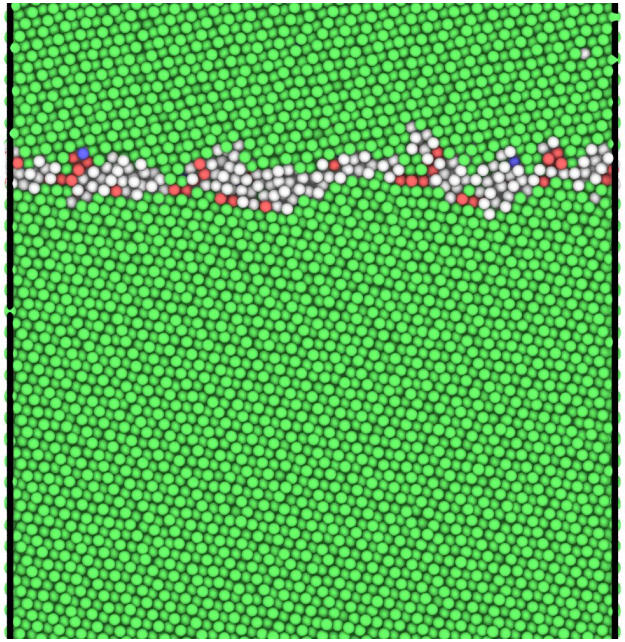
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

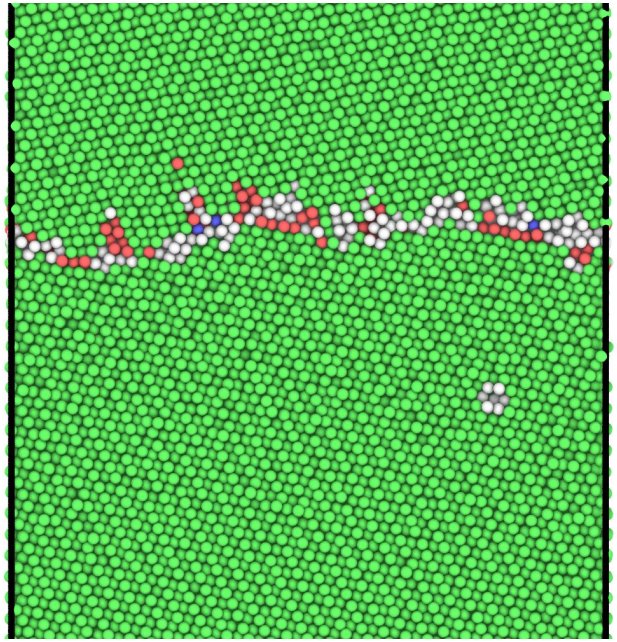
$t = t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

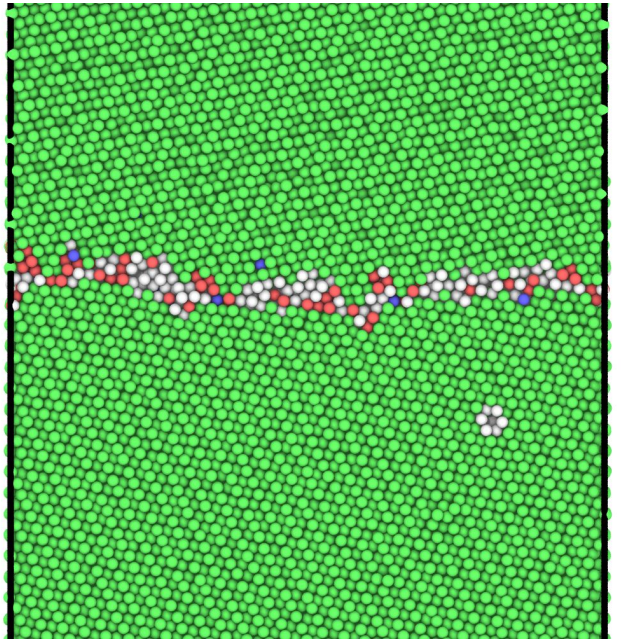
Cu



CuNiCoFe



Average Atom



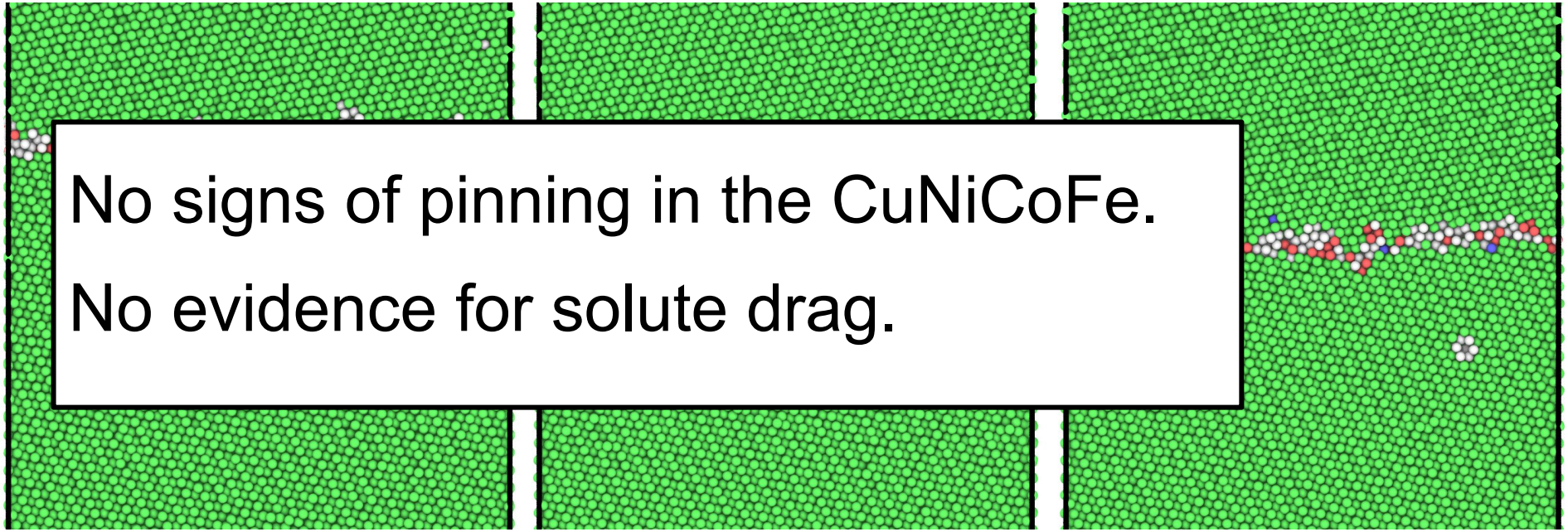
FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

$t = t_{final}$

TECHNISCHE UNIVERSITÄT DARMSTADT

Cu | CuNiCoFe | Average Atom



No signs of pinning in the CuNiCoFe.

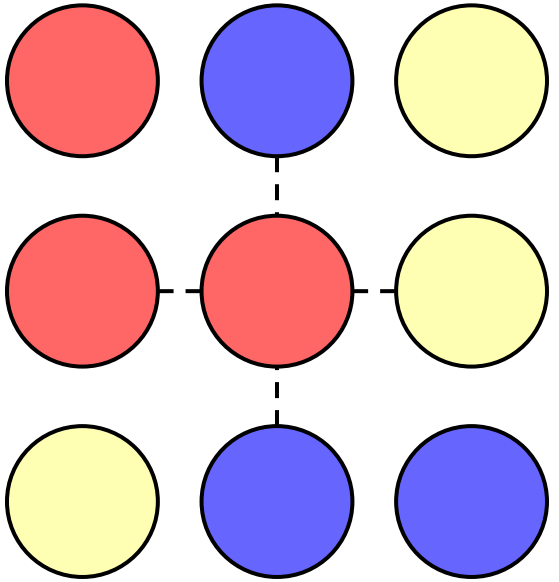
No evidence for solute drag.

FCC HCP BCC Other

FACHGEBIET MATERIALMODELLIERUNG

Simplified Lattice Monte-Carlo Model

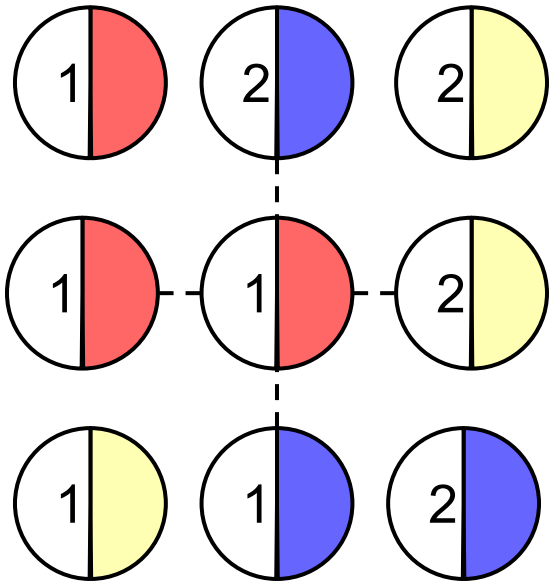
- Fixed FCC lattice considering only nearest neighbor interactions



Chookajorn and Schuh, Physical Review B 89 (6), 2014

Simplified Lattice Monte-Carlo Model

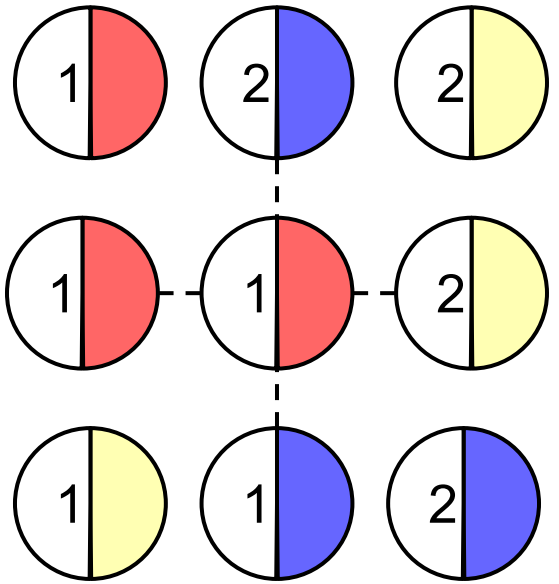
- Fixed FCC lattice considering only nearest neighbor interactions
- Every atom has two properties
  - Atom type (color)
  - Grain number (number)



Chookajorn and Schuh, Physical Review B 89 (6), 2014

Simplified Lattice Monte-Carlo Model

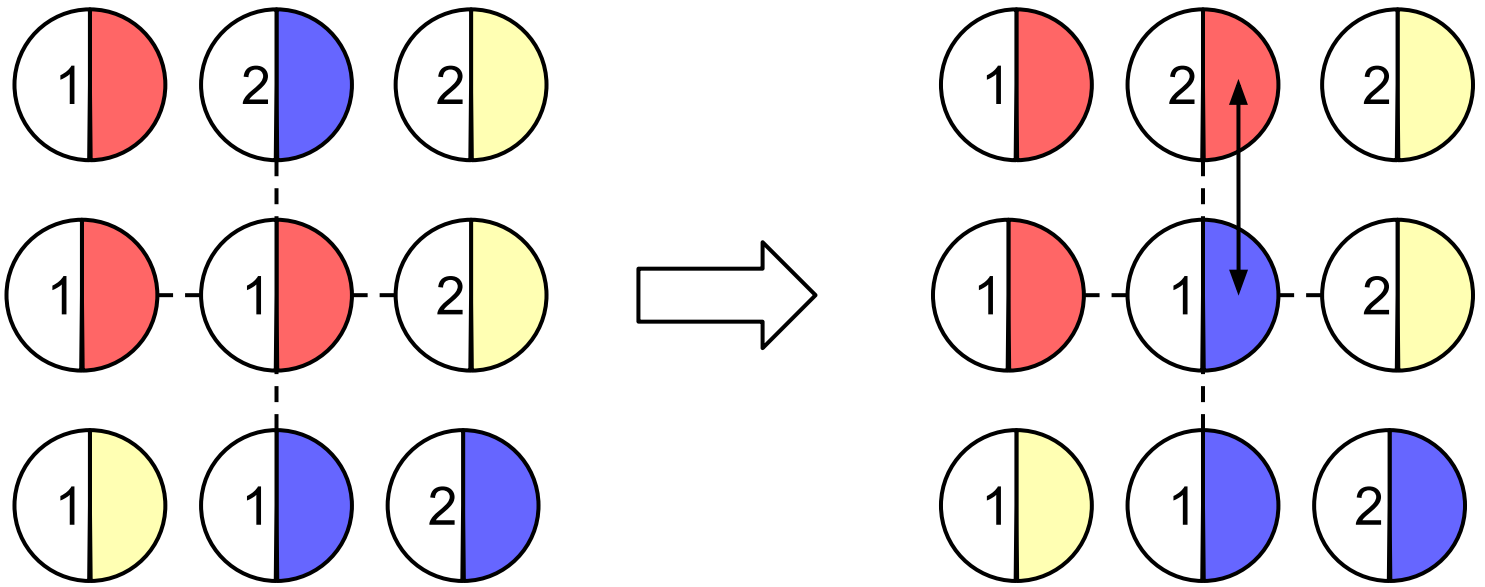
- Fixed FCC lattice considering only nearest neighbor interactions
- Every atom has two properties
  - Atom type (color)
  - Grain number (number)
- Periodic boundary conditions



Chookajorn and Schuh, Physical Review B 89 (6), 2014

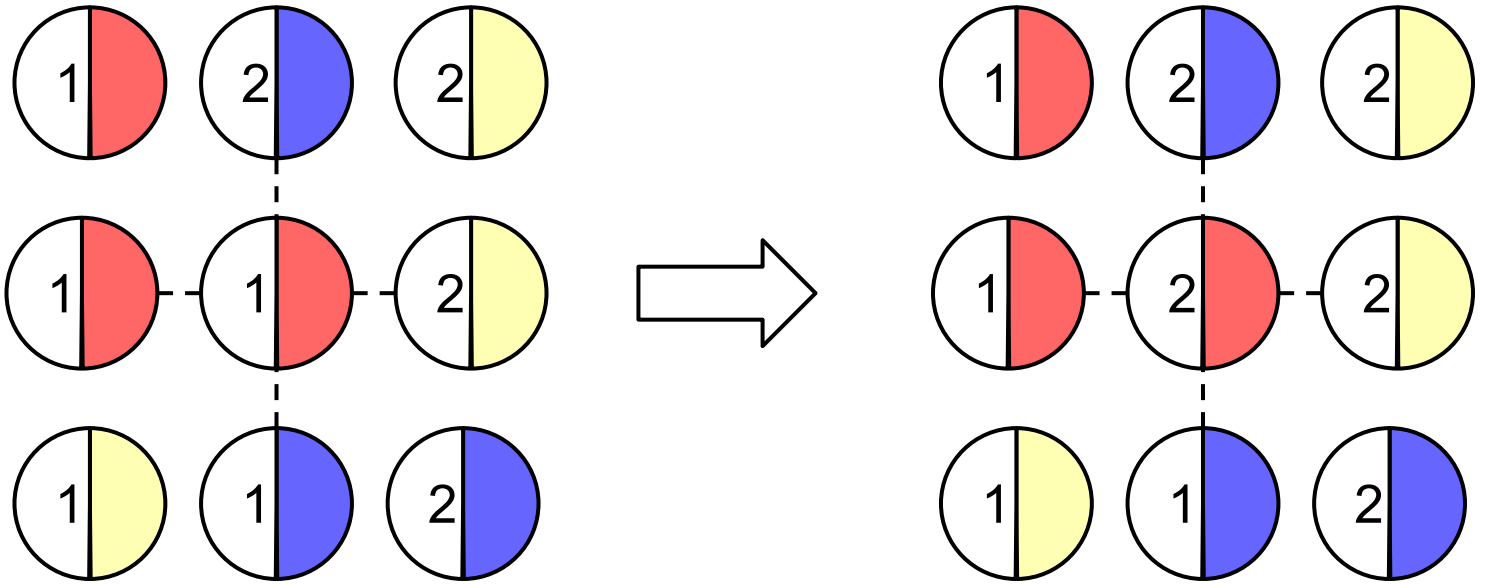
Simplified Lattice Monte-Carlo Model

- Each step an atom can swap:
  - Atom type



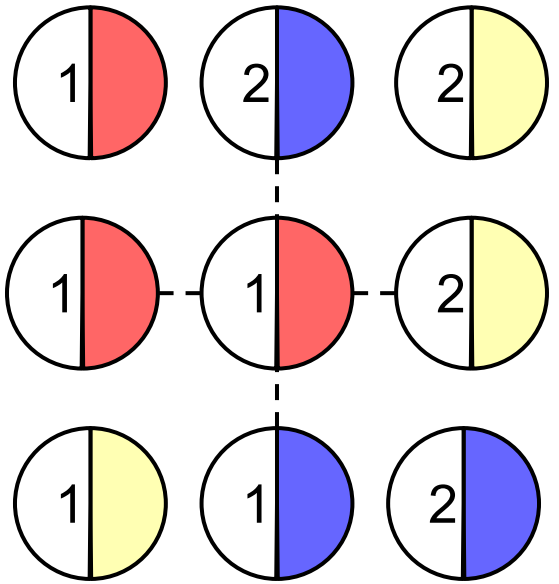
Simplified Lattice Monte-Carlo Model

- Each step an atom can swap:
  - Atom type
- Each step an atom change:
  - Grain number



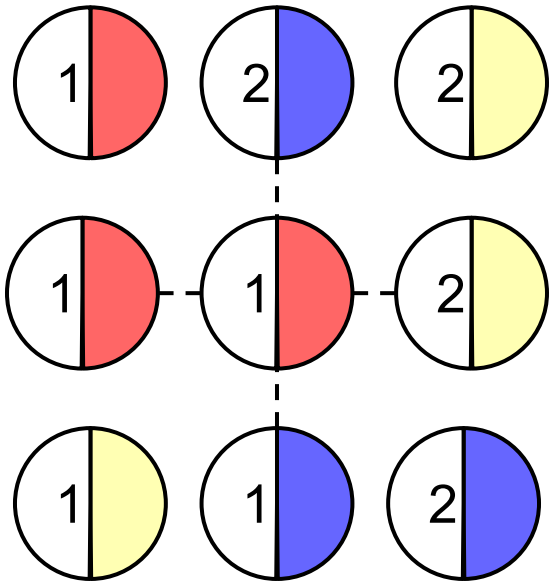
Simplified Lattice Monte-Carlo Model

- Site energy depends on direct neighbors.



Simplified Lattice Monte-Carlo Model

- Bond energy varies with direct neighbors.
- Parameters space:
  - Binary mixing enthalpies
  - Binary segregation enthalpies
  - Unary GB energies (γ_0)



Simplified Lattice Monte-Carlo Model

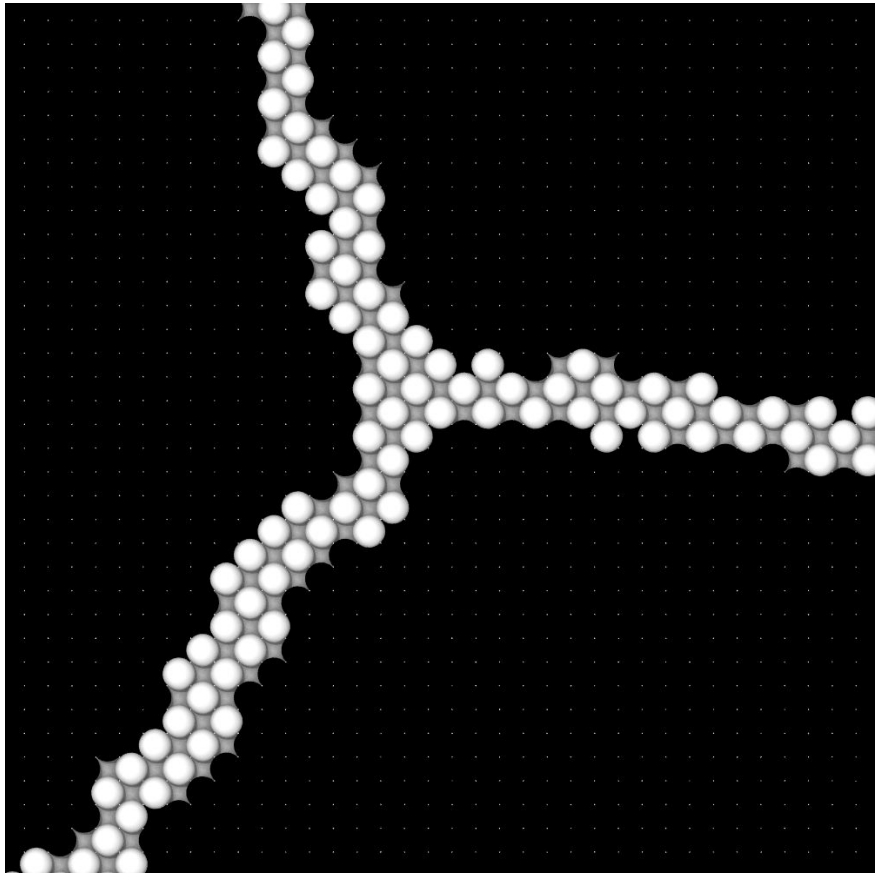
TECHNISCHE UNIVERSITÄT DARMSTADT

- Set all parameters
- Varied only GB energies (γ)
- Simulated annealing

Simplified Lattice Monte-Carlo Model

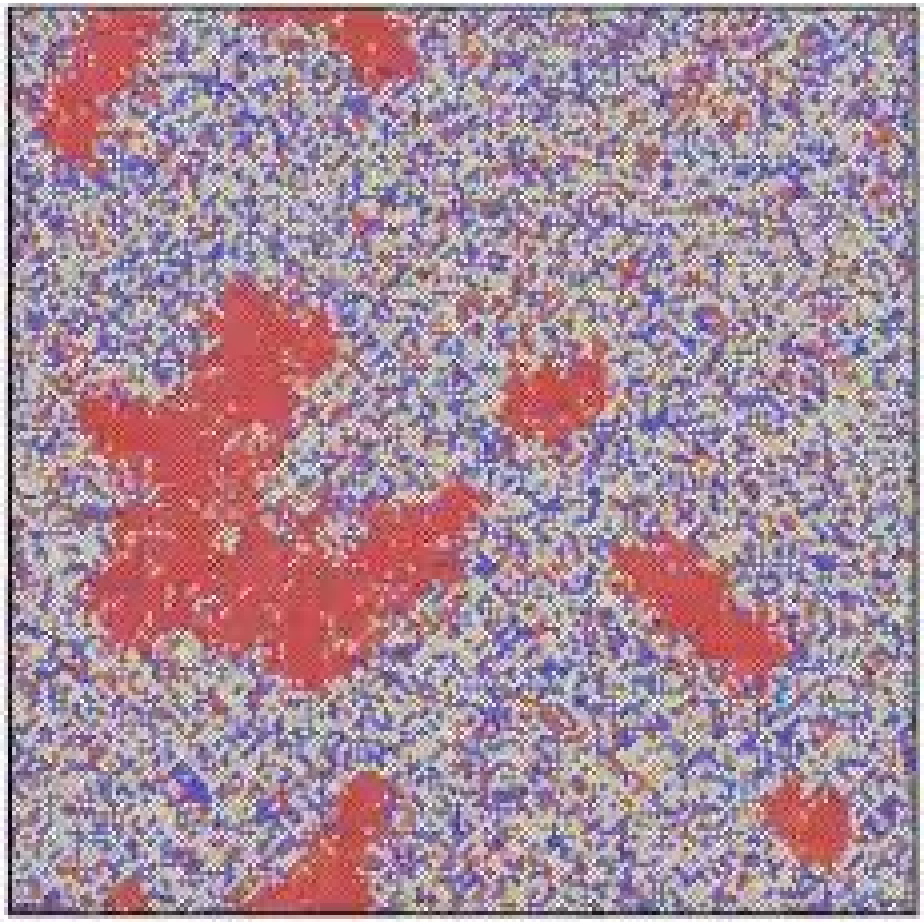
TECHNISCHE UNIVERSITÄT DARMSTADT

- Set all parameters
- Varied only GB energies (γ)
- Simulated annealing
- Atoms will be color coded
  - Type
  - Grain boundary
    - On boundary
    - Grain interieur

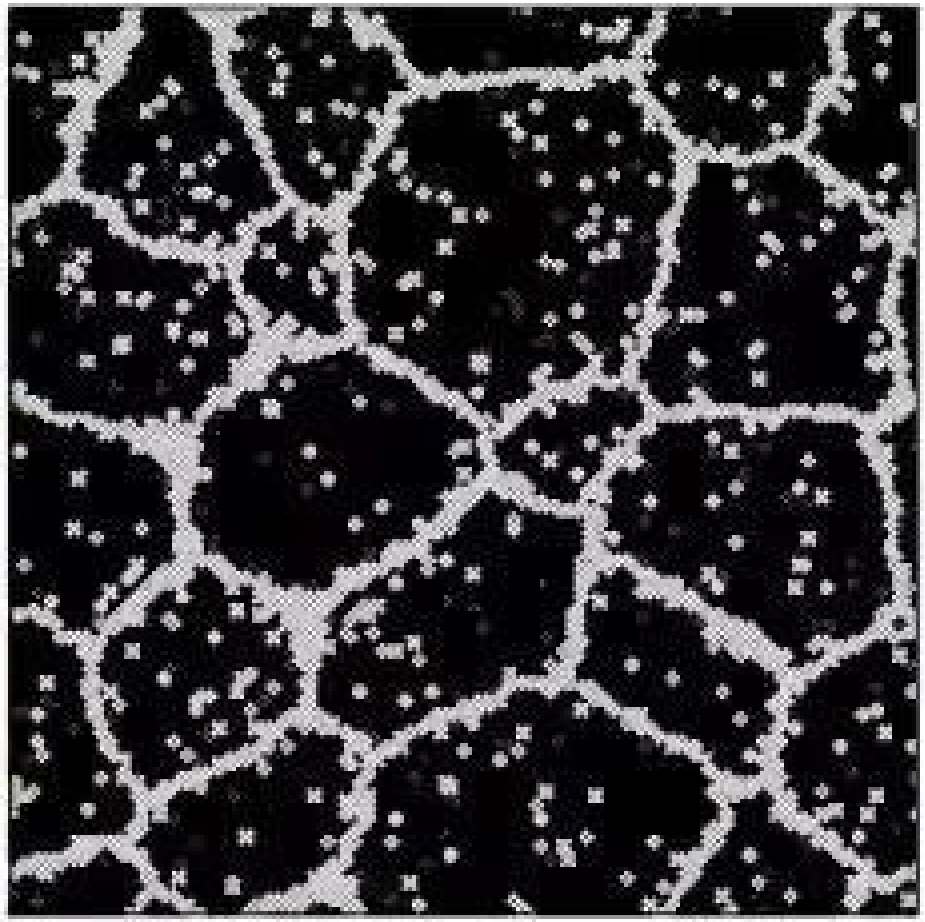


FACHGEBIET MATERIALMODELLIERUNG

$\gamma = 5.5\gamma_0$



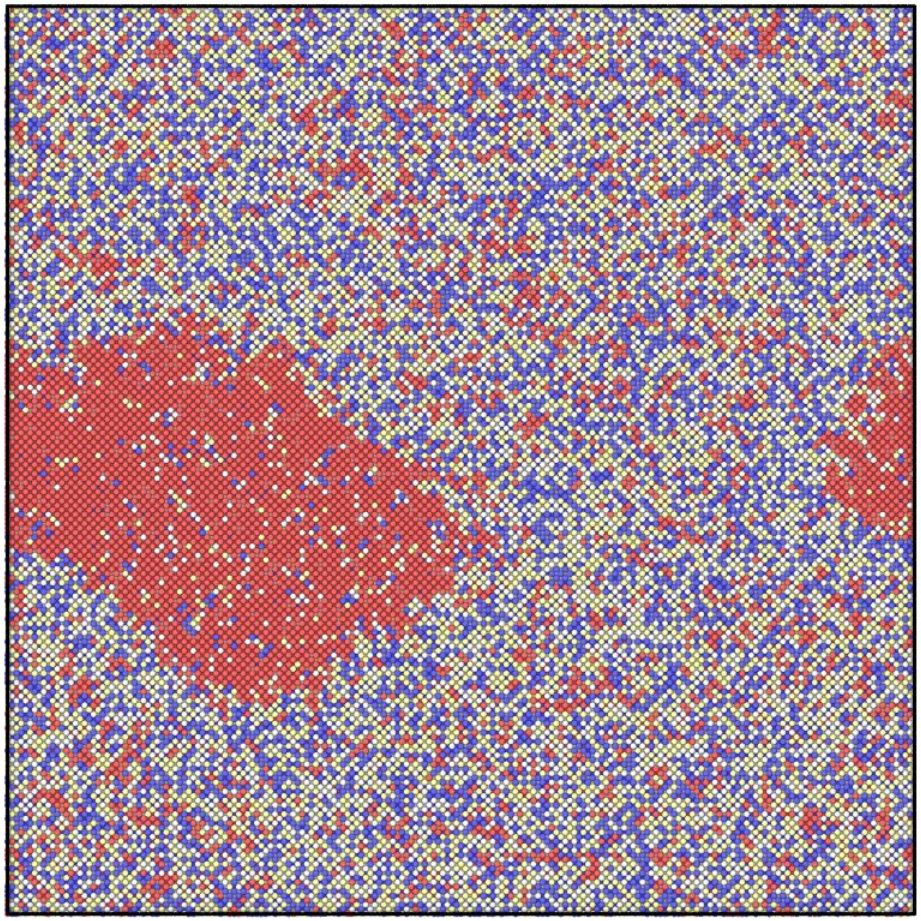
Atom Types

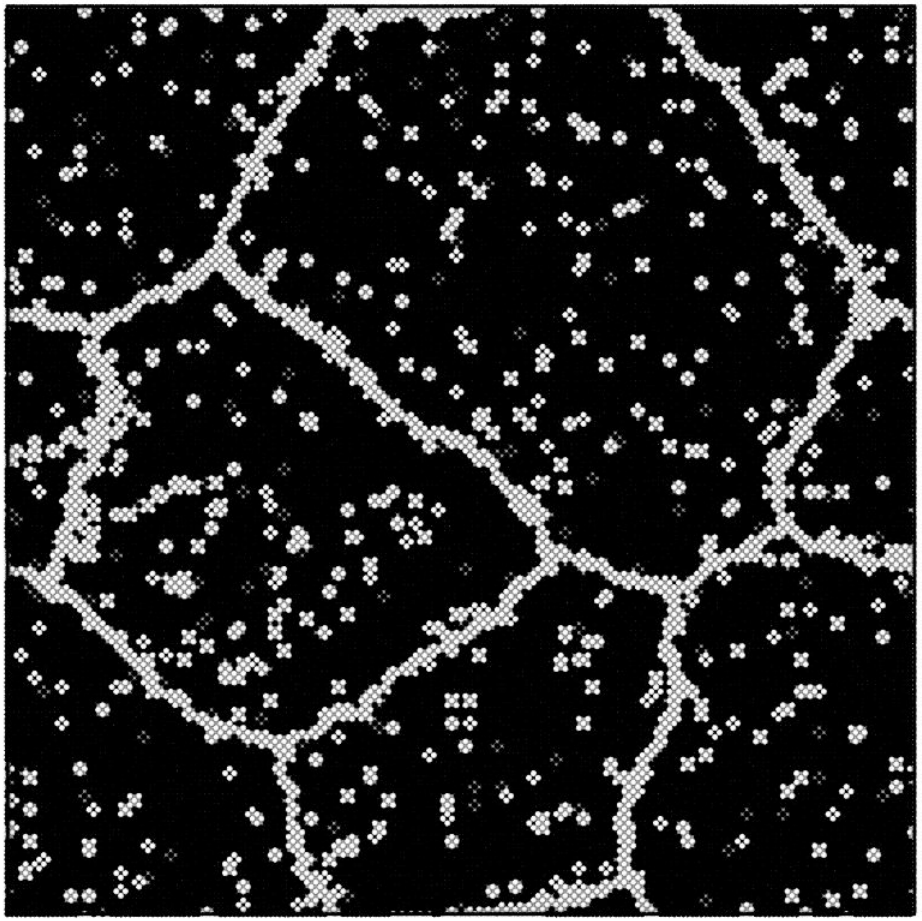


Grain Boundaries

$\gamma = 5.5\ \gamma_0$
Final Configuration

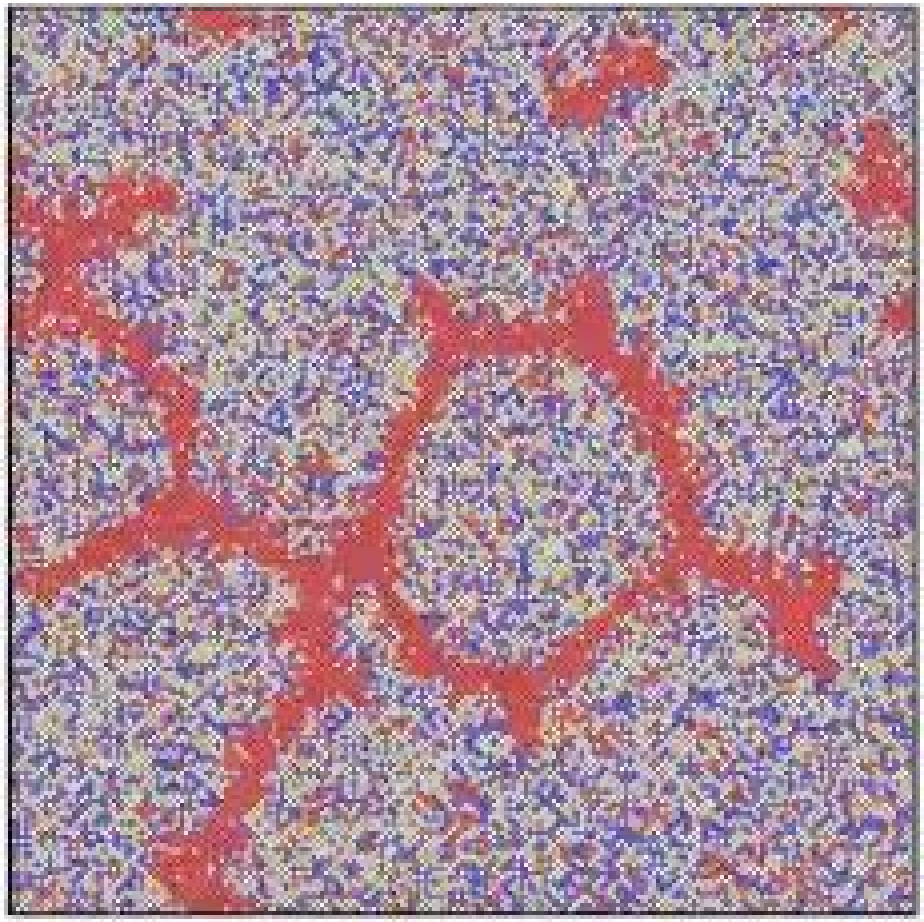
TECHNISCHE UNIVERSITÄT DARMSTADT



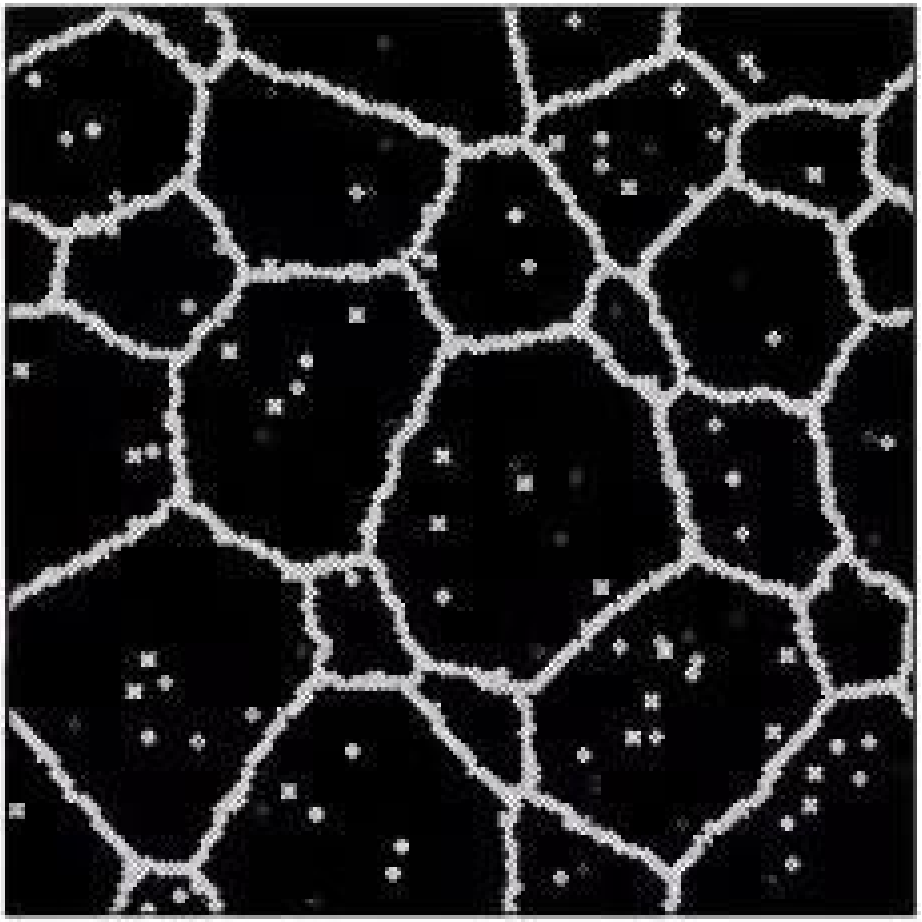


FACHGEBIET MATERIALMODELLIERUNG

$\gamma = 8\gamma_0$



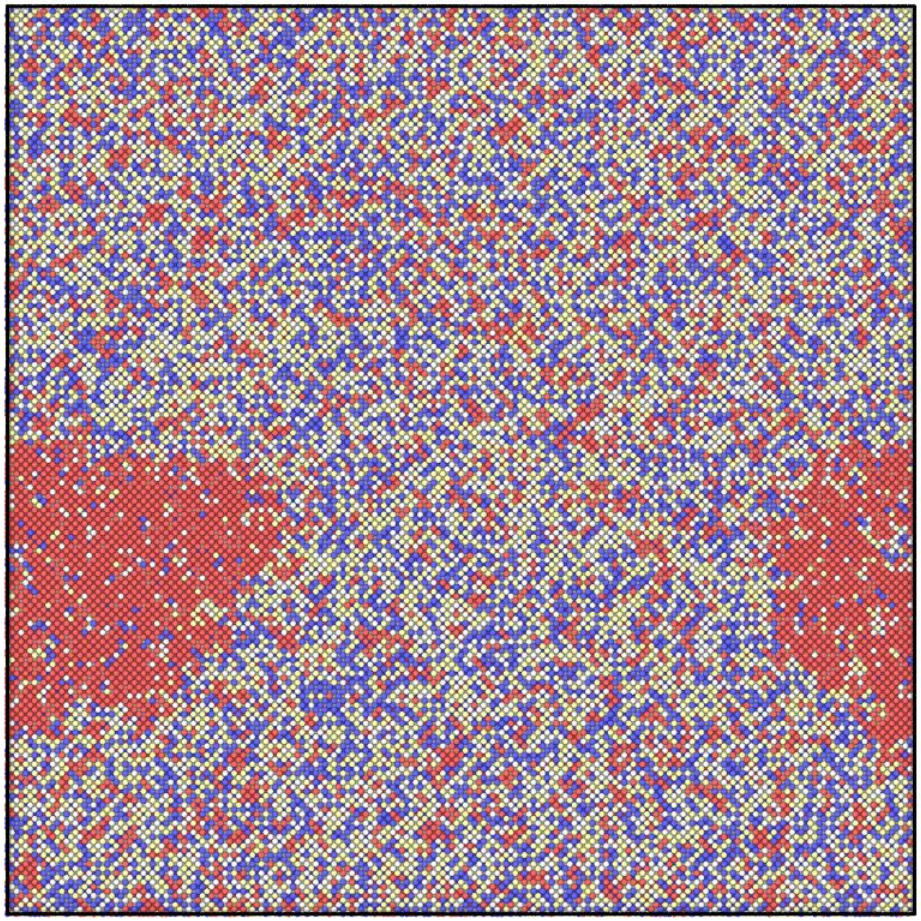
Atom Types

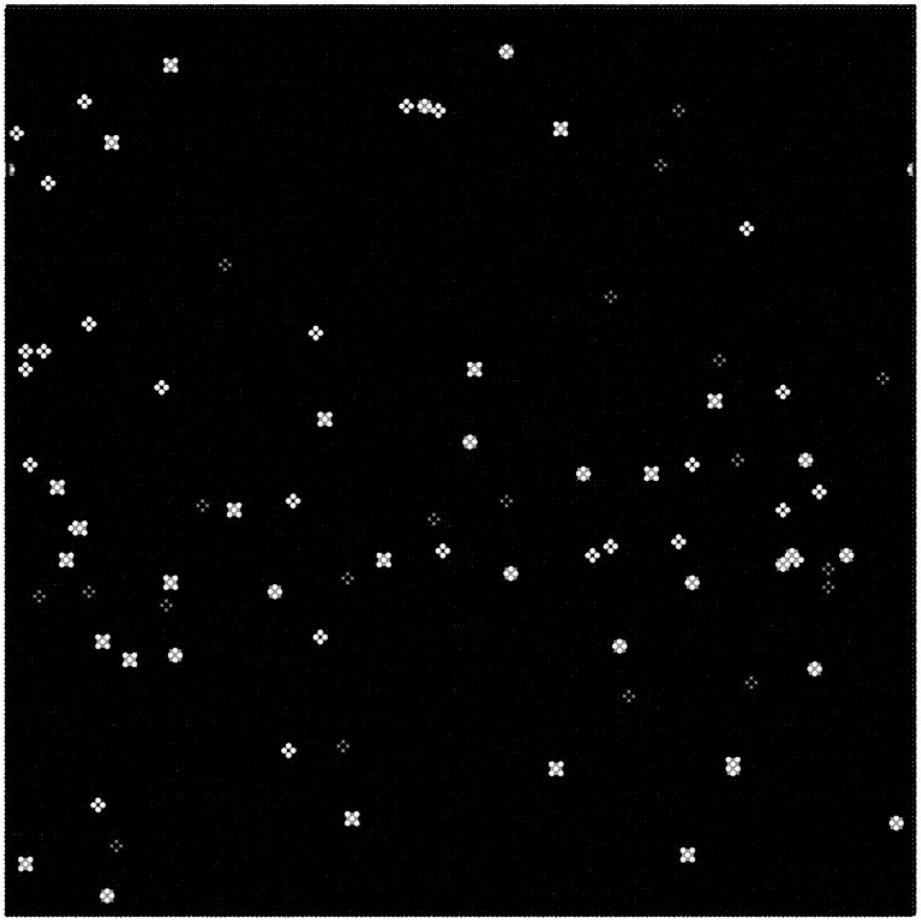


Grain Boundaries

$\gamma = 8\ \gamma_0$
Final Configuration

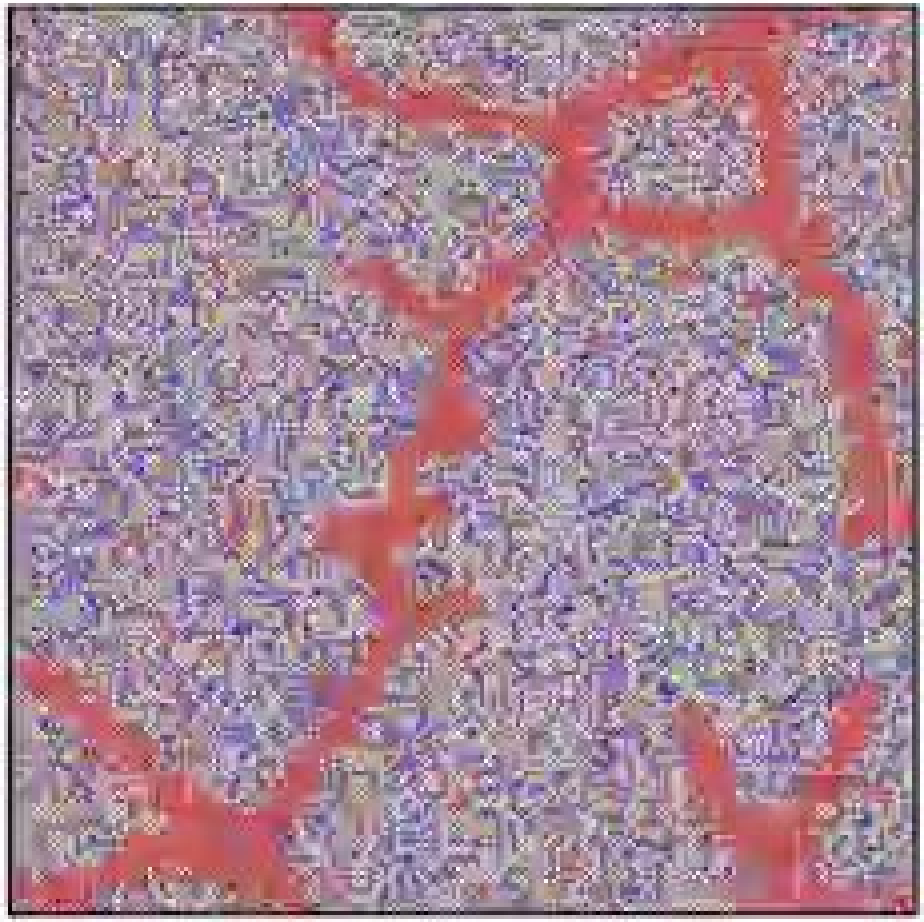
TECHNISCHE UNIVERSITÄT DARMSTADT



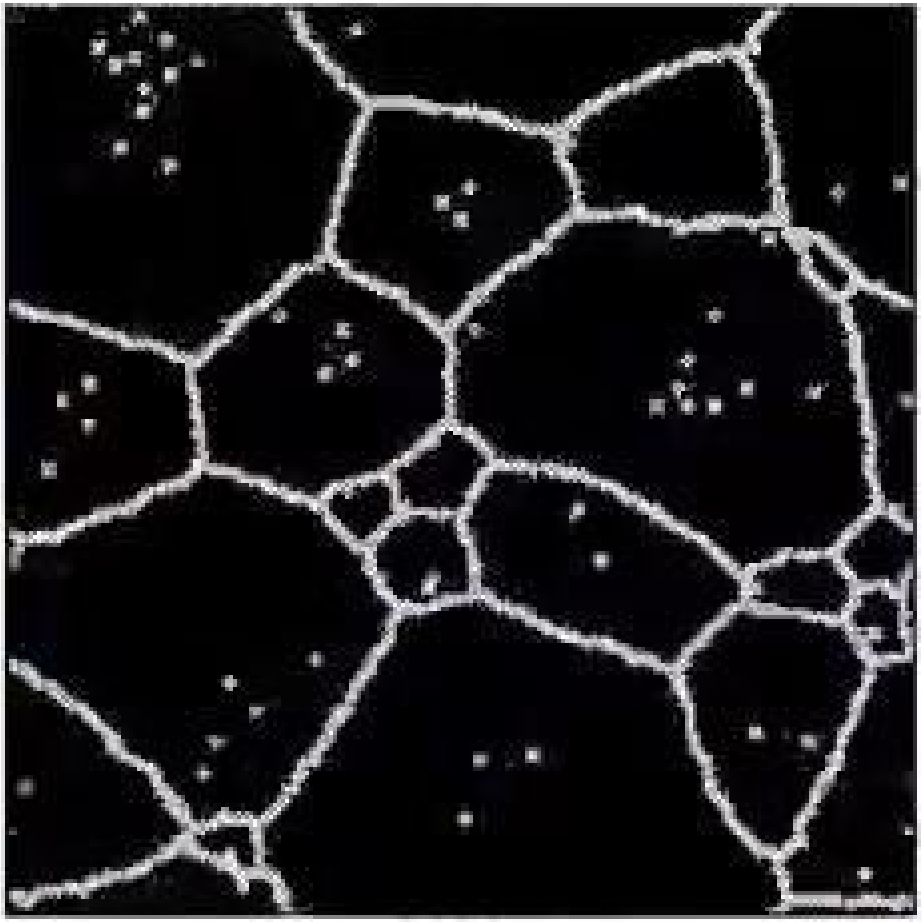


FACHGEBIET MATERIALMODELLIERUNG

$\gamma = 9.5\gamma_0$



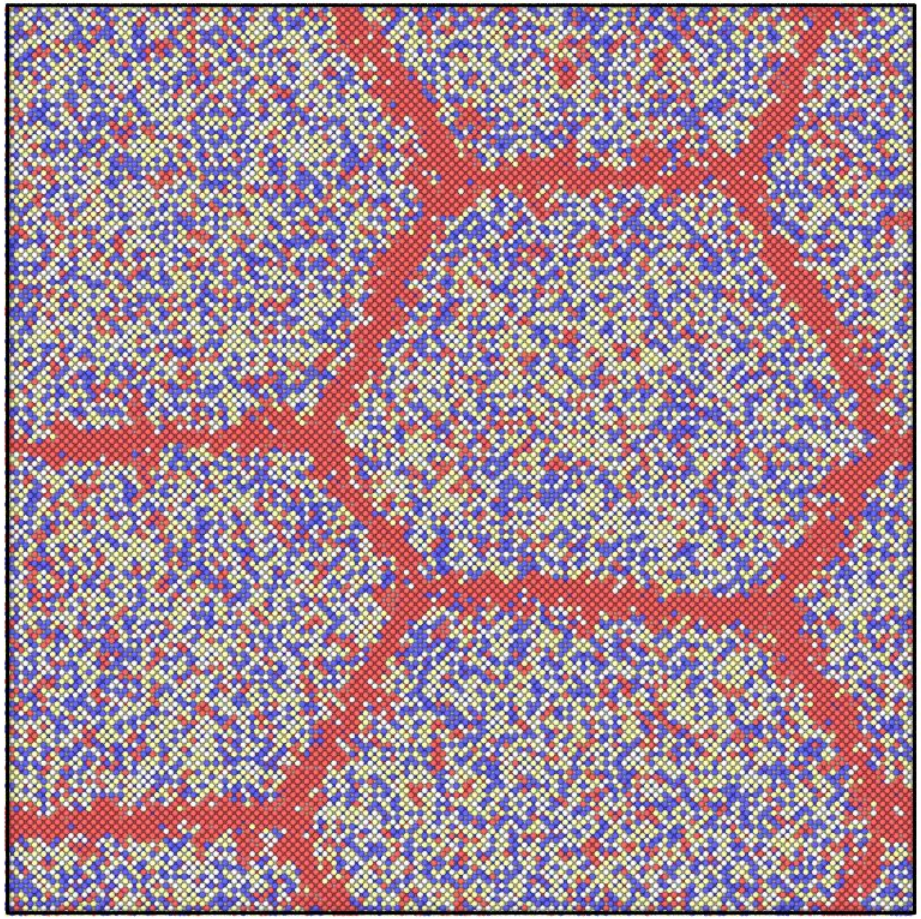
Atom Types

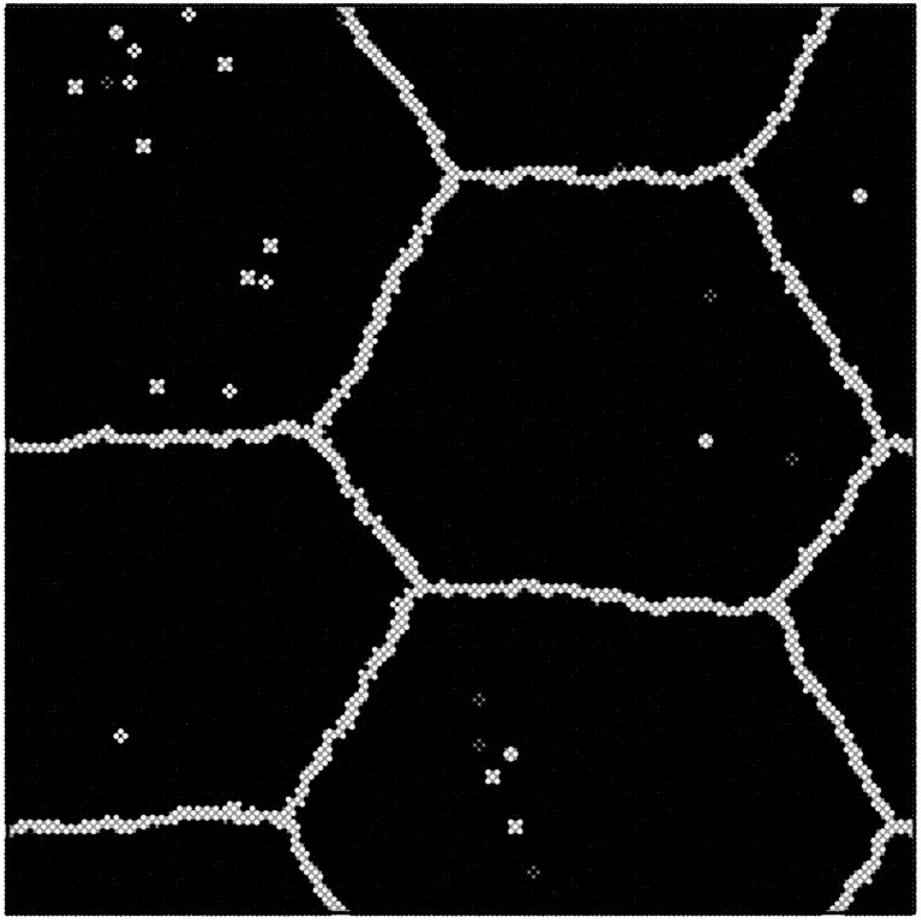


Grain Boundaries

$\gamma = 9.5\ \gamma_0$
Final Configuration

TECHNISCHE UNIVERSITÄT DARMSTADT

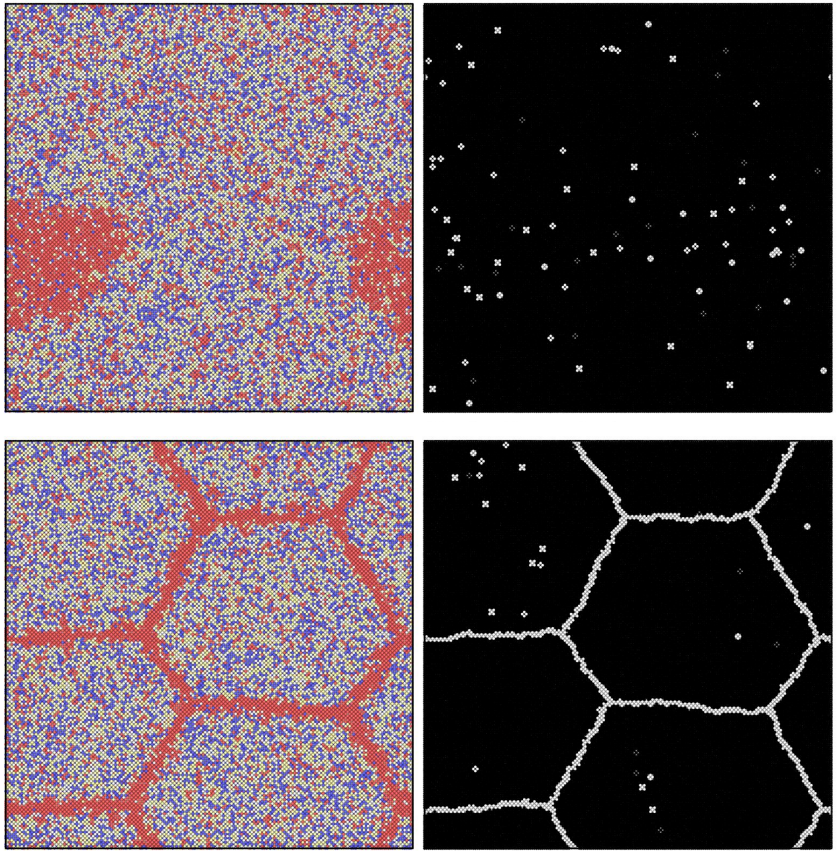




FACHGEBIET MATERIALMODELLIERUNG

Result

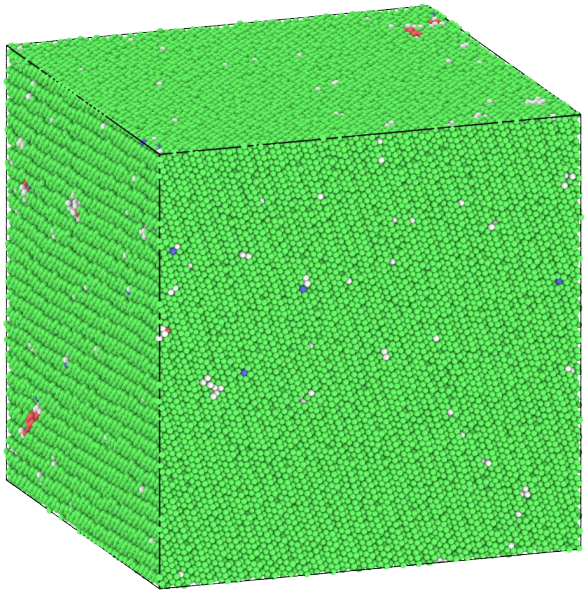
Segregation can strongly influence the final grain structure.



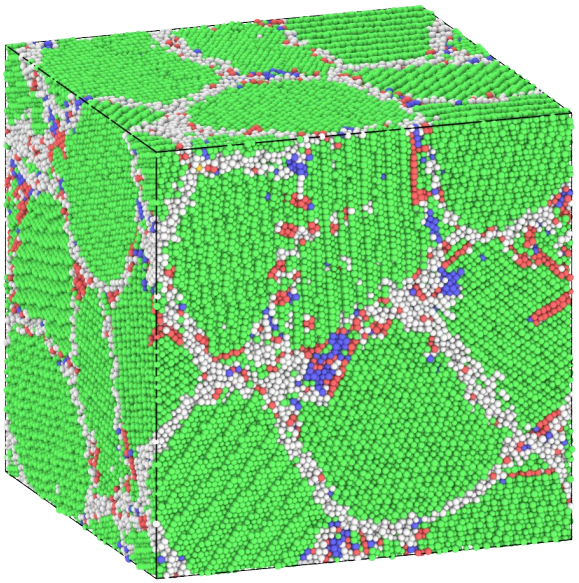
Conclusion

TECHNISCHE UNIVERSITÄT DARMSTADT

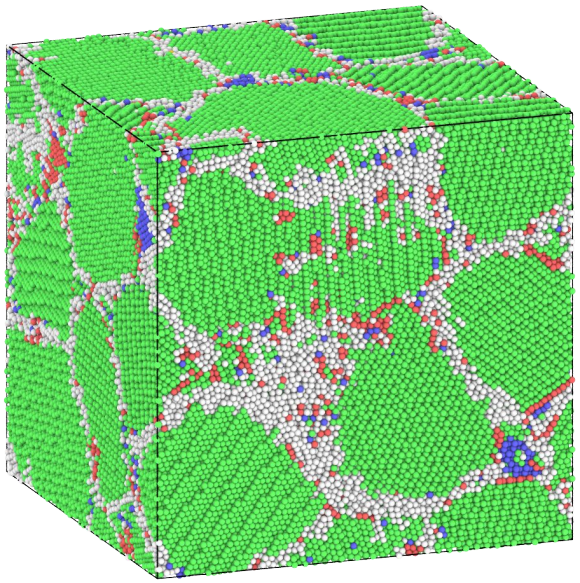
Cu



CuNiCoFe



Average Atom



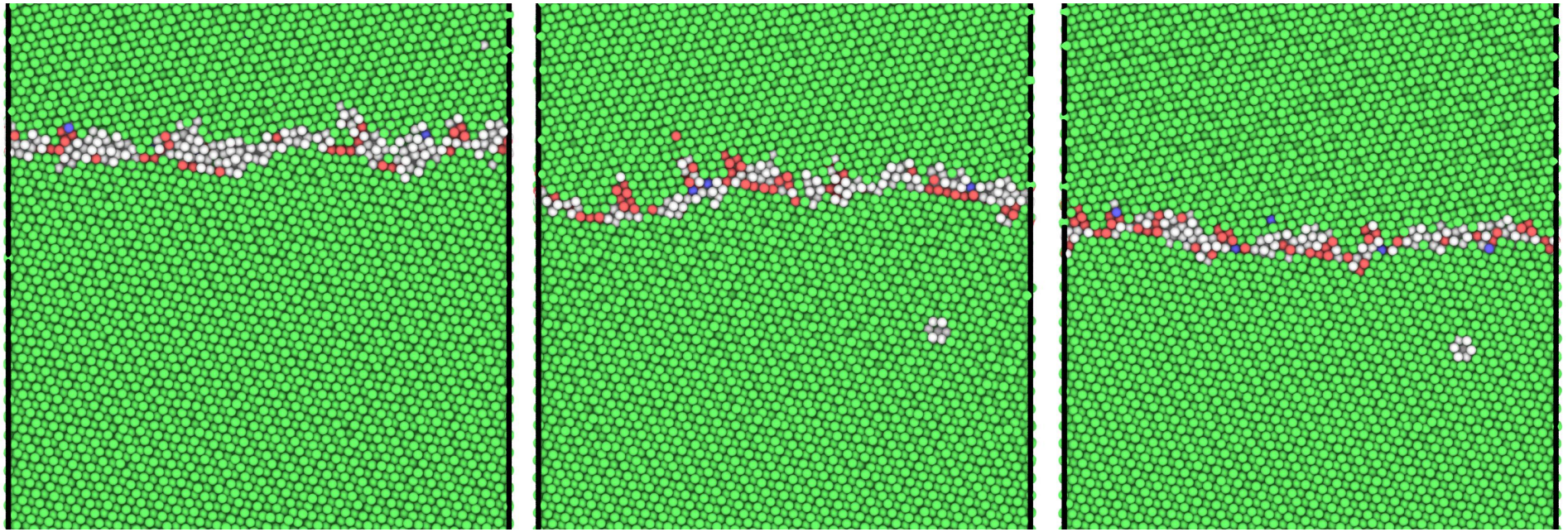
HEA shows strongly reduced grain growth.
It cannot be explained by local atomic disorder.

FACHGEBIET MATERIALMODELLIERUNG

Conclusion

TECHNISCHE UNIVERSITÄT DARMSTADT

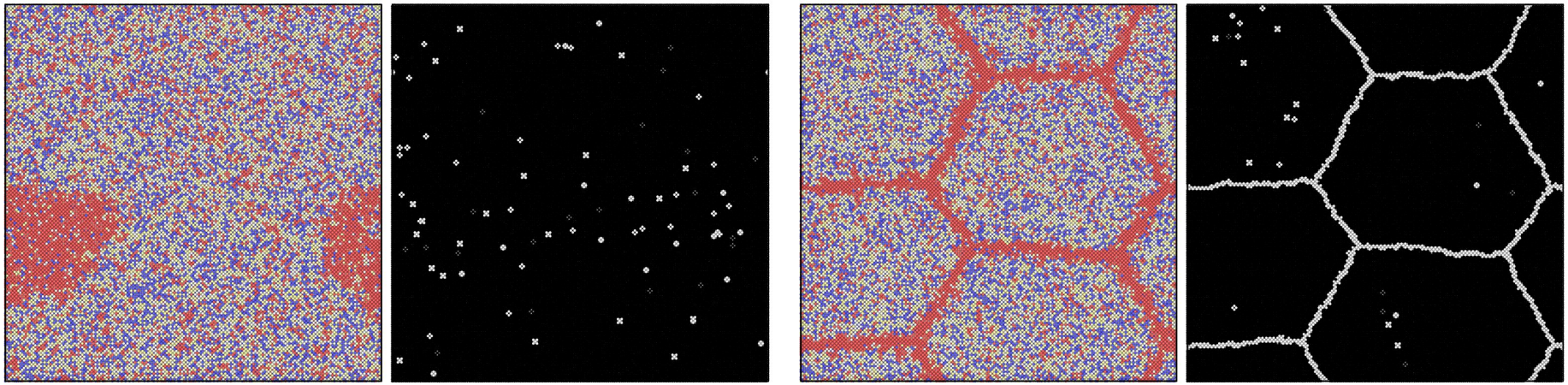
Cu | CuNiCoFe | Average Atom



HEA does not show significant signs of solute drag or Zener pinning.

FACHGEBIET MATERIALMODELLIERUNG

Conclusion



Segregation effects need to be explored further.

Acknowledgement

TECHNISCHE UNIVERSITÄT DARMSTADT

DFG Deutsche Forschungsgemeinschaft

SPP 2006: Legierungen mit komplexer Zusammensetzung - Hochentropielegierungen (CCA - HEA)

CCA HEA

TECHNISCHE UNIVERSITÄT DARMSTADT

Calculations for this research were conducted on the Lichtenberg high performance computer of the TU Darmstadt

FACHGEBIET MATERIAL MODELLIERUNG

Appendix Potentiale

TECHNISCHE UNIVERSITÄT DARMSTADT

$$\phi(r)=\frac{A\exp[-\alpha(r/r_e-1)]}{1+(r/r_e-\kappa)^{20}}-\frac{B\exp[-\beta(r/r_e-1)]}{1+(r/r_e-\lambda)^{20}}, \quad \text{(A3)}$$

where r_e is the equilibrium spacing between nearest neighbors, A, B, α, and β are four adjustable parameters, and κ and λ are two additional parameters for the cutoff. The electron density function is taken with the same form as the attractive term in the pair potential with the same values of β and λ, i.e.,

$$f(r)=\frac{f_e\exp[-\beta(r/r_e-1)]}{1+(r/r_e-\lambda)^{20}}. \quad \text{(A4)}$$

The pair potential between different species a and b is then constructed as

$$\phi^{ab}(r)=\frac{1}{2}\left[\frac{f^b(r)}{f^a(r)}\phi^{aa}(r)+\frac{f^a(r)}{f^b(r)}\phi^{bb}(r)\right]. \quad \text{(A5)}$$

Embedding energy functions that work well over a wide range of electron density require that three equations be used

144113-8

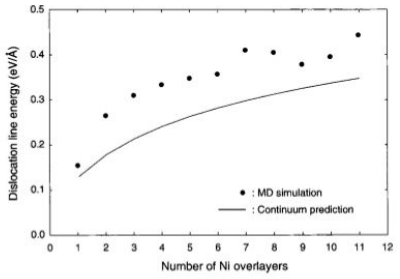
MISFIT-ENERGY-INCREASING DISLOCATIONS IN . . . PHYSICAL REVIEW B **69**, 144113 (2004)

to separately fit three different electron density ranges. For a smooth variation of the embedding energy, these equations are required to match values and slopes at their junctions. These equations are

$$F(\rho)=\sum_{i=0}^{3}F_{ni}\left(\frac{\rho}{\rho_n}-1\right)^i, \quad \rho<\rho_n, \quad \rho_n=0.85\rho_e, \quad \text{(A6)}$$

$$F(\rho)=\sum_{i=0}^{3}F_{i}\left(\frac{\rho}{\rho_e}-1\right)^i, \quad \rho_n\leqslant\rho<\rho_0, \quad \rho_0=1.15\rho_e, \quad \text{(A7)}$$

$$F(\rho)=F_e\left[1-\ln\left(\frac{\rho}{\rho_s}\right)^\eta\right]\left(\frac{\rho}{\rho_s}\right)^\eta, \quad \rho_0\leqslant\rho. \quad \text{(A8)}$$



$$\langle E_0\rangle=\sum_{i,X}c_X\langle F^X(\rho_i)\rangle+\frac{1}{2}\sum_{\substack{i,j\neq i\\X,Y}}V_{ij}^{XY}c_Xc_Y, \quad (3)$$

where $\langle s_i^X\rangle=c_X$. We then perform a Taylor expansion $\langle F^X(\rho_i)\rangle=\langle F^X(\bar{\rho}_i)\rangle+O(\rho_i-\bar{\rho}_i)^2$ around the average electron density $\bar{\rho}_i$, in which the first order term vanishes since $\langle(\rho_i-\bar{\rho}_i)\rangle=0$. Neglecting second and higher-order terms [34], which is the *only* approximation, the average energy is

$$\langle E_0\rangle=\sum_i F^A(\bar{\rho}_i)+\frac{1}{2}\sum_{i,j\neq i}V_{ij}^{AA}, \quad (4)$$

with $$F^A(\bar{\rho}_i)=\sum_X c_XF^X(\bar{\rho}_i),$$

$$V_{ij}^{AA}=\sum_{X,Y}c_Xc_YV_{ij}^{XY}, \quad \bar{\rho}_i=\sum_{j\neq i}\sum_X c_X\rho_{ij}^X, \quad (5)$$

Zhou et al., Physical Review B, 69(144113), 2004

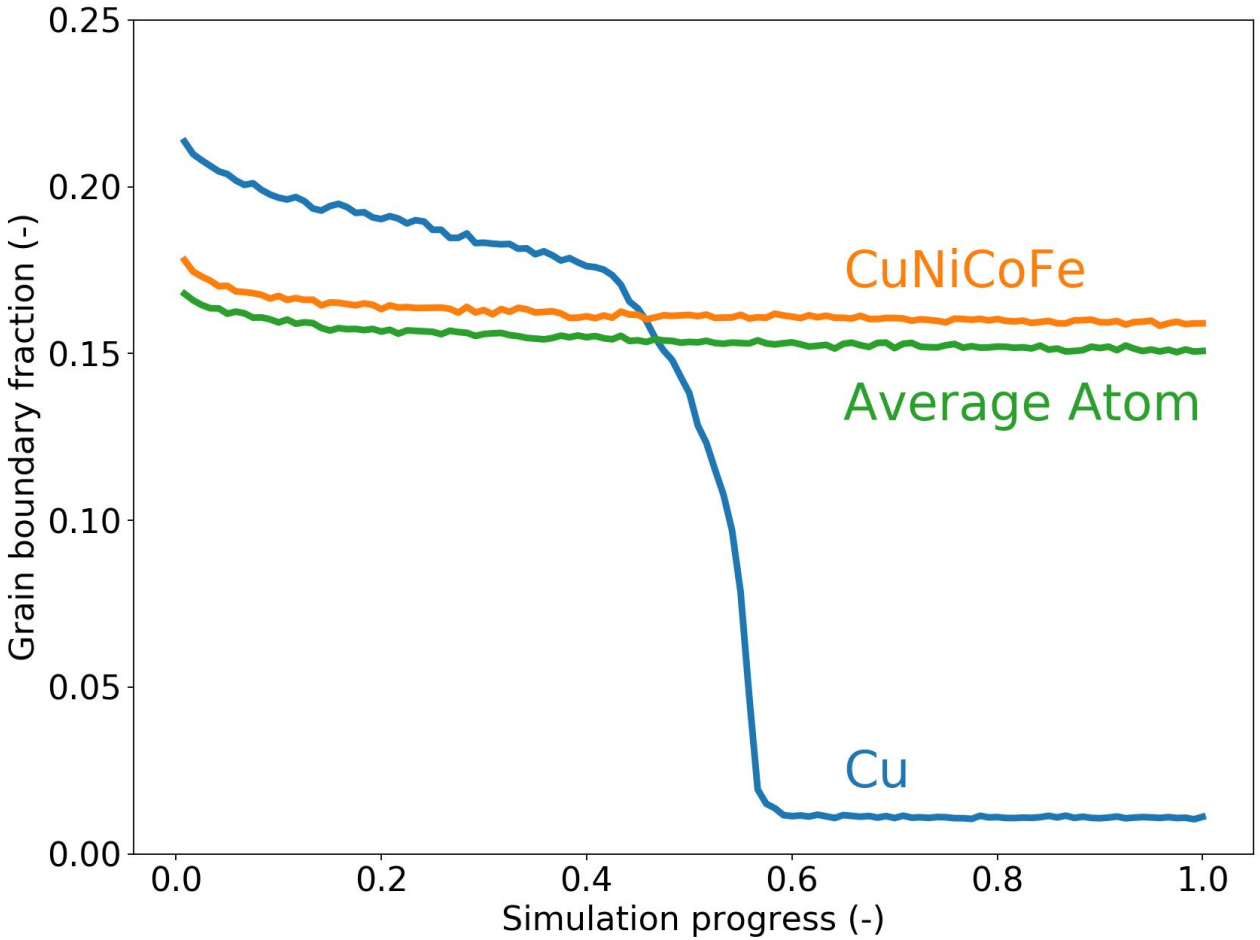
Varvenne et al., Physical Review B, 93(104201), 2016

Appendix Average Atom

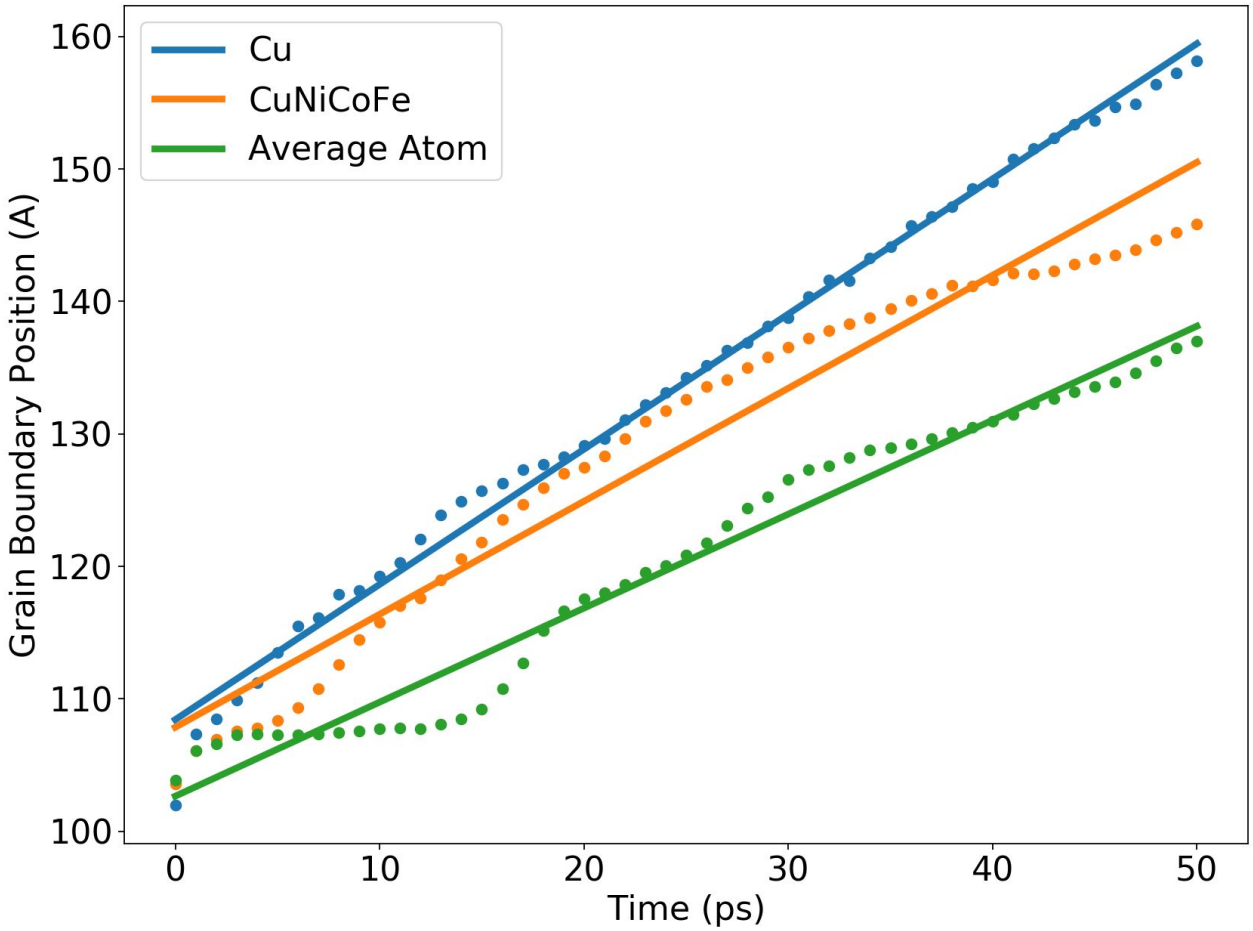
TECHNISCHE UNIVERSITÄT DARMSTADT

	CuNiCoFe	Average Atom
a_0 (A)	3.572	3.570
E_{Coh} (eV)	-4.141	-4.137
C_{11} (GPa)	172	170
C_{44} (GPa)	100	101
C_{12} (GPa)	124	120
γ_{SF} (mJ/m^2)	10.6	26.9
γ_{USF} (mJ/m^2)	44.8	129.4

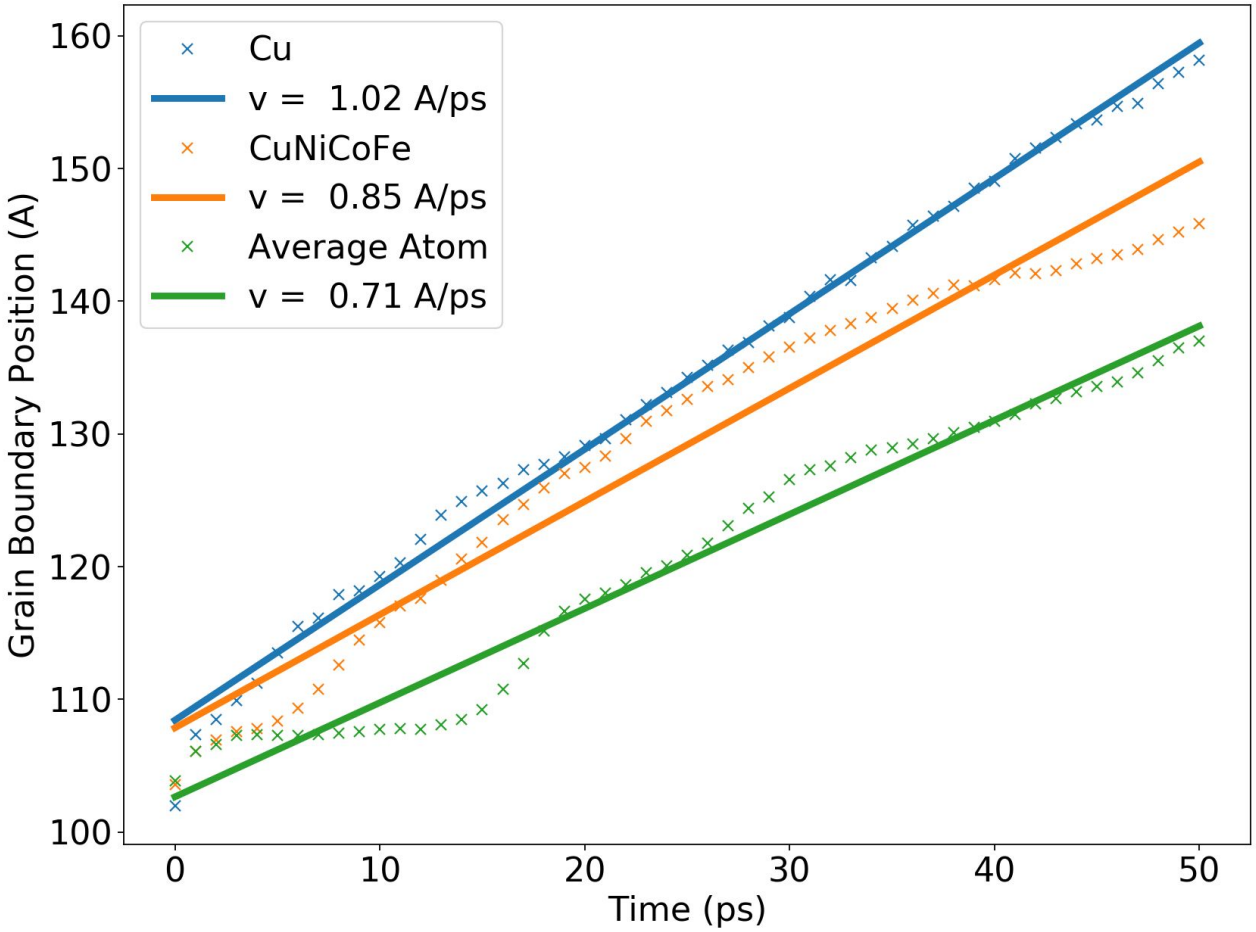
Appendix Nanocrystal



Results


Cu
CuNiCoFe
Average Atom
Grain Boundary Position (A)
Time (ps)
100
110
120
130
140
150
160
0
10
20
30
40
50

Appendix GB velocity



Appendix

Table 2.1: Bond energies in a polycrystalline binary alloy in full and simplified forms.

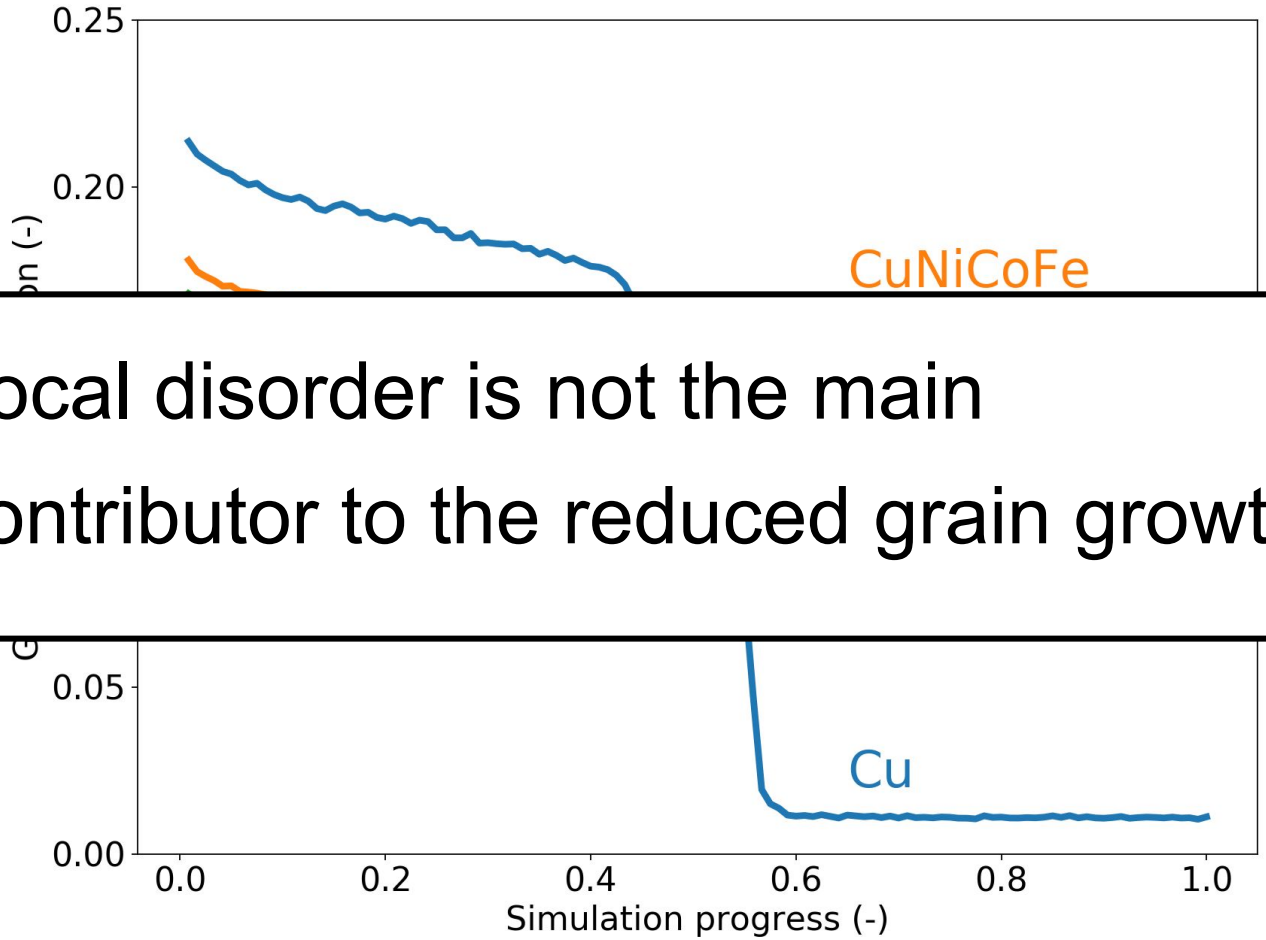
Bond energy	Full form	Simplified form
E_c^{AA}	E_c^{AA}	E_c^{AA}
E_c^{BB}	E_c^{BB}	E_c^{AA}
E_c^{AB}	$\left(\frac{E_c^{AA} + E_c^{BB}}{2}\right) + \omega_c$	$E_c^{AA} + \omega_c$
E_{gb}^{AA}	$E_c^{AA} + \frac{2\Omega^A \gamma_0^A}{zt}$	$E_c^{AA} + \frac{2\Omega^A \gamma_0^A}{zt}$
E_{gb}^{BB}	$E_c^{BB} + \frac{2\Omega^B \gamma_0^B}{zt}$	$E_c^{AA} + \frac{2\Omega^A \gamma_0^A}{zt}$
E_{gb}^{AB}	$\left(\frac{E_c^{AA} + E_c^{BB}}{2}\right) + \omega_{gb} + \frac{1}{zt}\left(\Omega^A \gamma_0^A + \Omega^B \gamma_0^B\right)$	$E_c^{AA} + \omega_{gb} + \frac{2\Omega^A \gamma_0^A}{zt}$

$$\Delta H^{mix} = z\omega_c X(1-X),$$

$$\Delta H^{seg} = z\left[\omega_c - \frac{\omega_{gb}}{2} - \frac{1}{2zt}\left(\Omega^B \gamma_0^B - \Omega^A \gamma_0^A\right)\right]$$

T. Chookajorn PhD Thesis, Massachusetts Institute of Technology, 2013

Results



Local disorder is not the main contributor to the reduced grain growth.