Thermodynamics and Correlation Effects on Diffusion in Al-Ni Melts

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Outline

- Motivation
- Darken‘s equation for liquids
- Experimental methods
  - Quasielastic Neutron Scattering (QNS)
  - Capillary techniques + X-ray Radiography (XRR)
  - Molecular Dynamic Simulation (MDS)
- Results in Al-Ni
- Conclusions

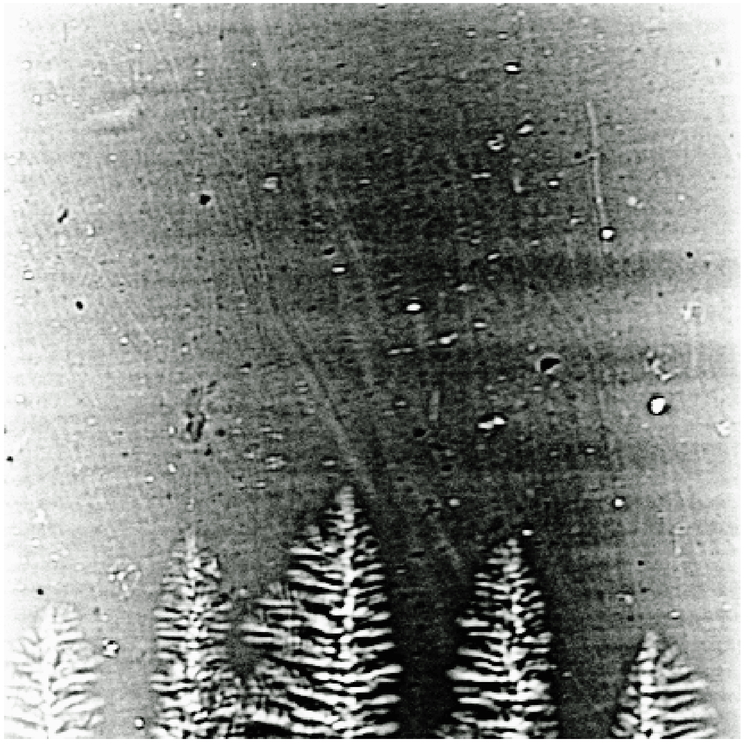
Motivation

- Materials Design from the Melt

⇒ Interplay of inter-diffusion and crystal growth

⇒ thermophysical properties

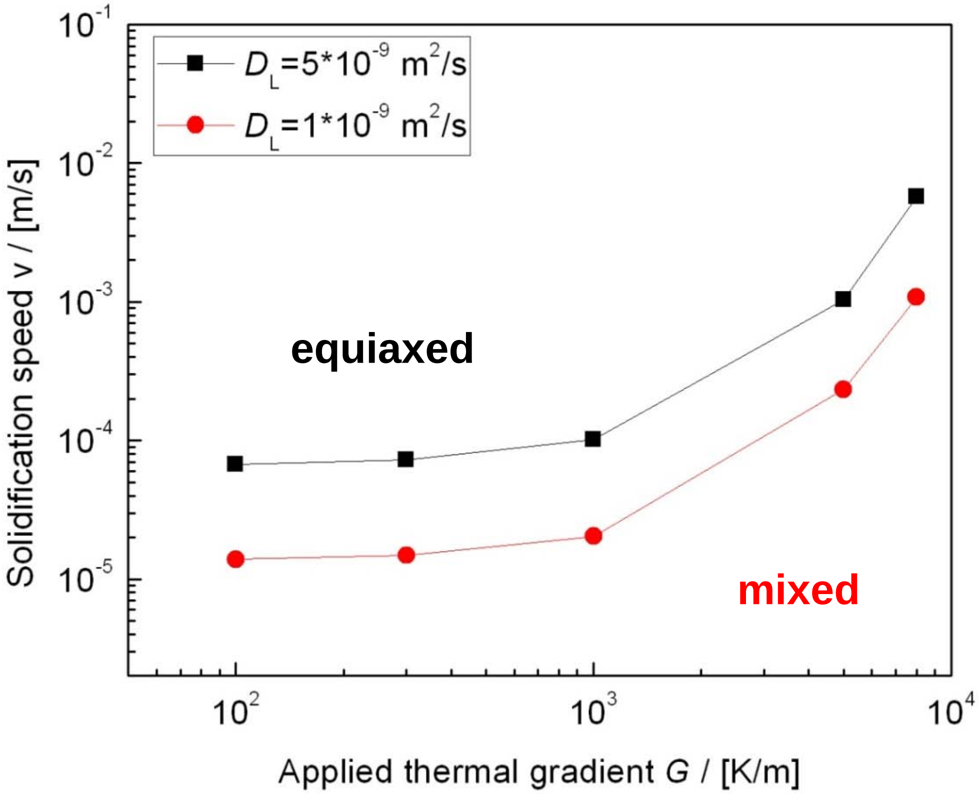
⇒ Influence of thermo-dynamics on diffusion



X-ray radiography: Al-Cu

L. Arnberg, R.H. Mathiessen, JOM 8 (2007) 20

Columnar to Equiaxed Transition (CET) in Al-Ti



analytical Hunt model parameters:

- $N_0 = 10^9\ m^{-3}$

- $\Delta T_N = 3.8\ K$

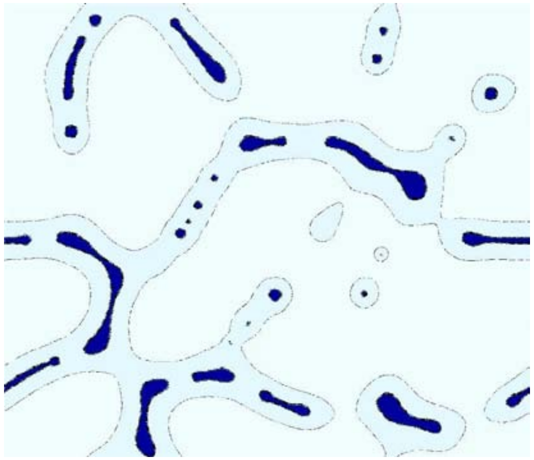
- $c_0 = 47\ at\%$

→ factor 8 difference

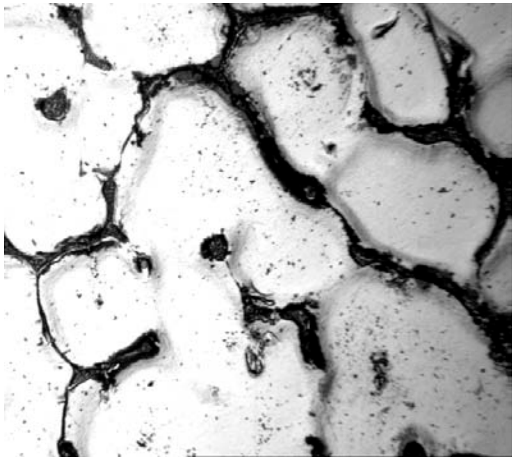
CET prediction depends sensitively on D_L(c,T)

Courtesy: Laszlo Sturz ACCESS

Pseudo Front Tracking Modelling of Solidification in Al-Cu4

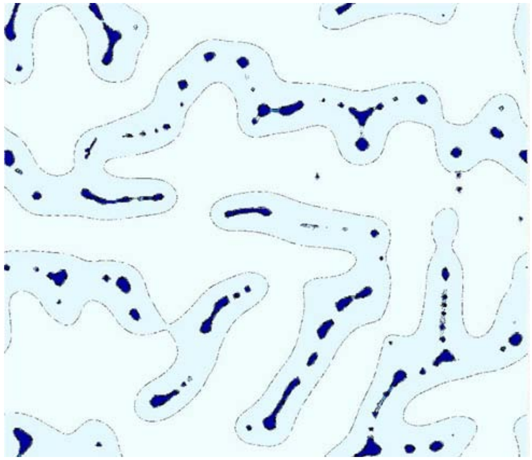


D_{AlCu} = 4.8 x 10^{-9} m²s^{-1}



500 x 430 µm²

micrograph section



D_{AlCu} = 1.0 x 10^{-9} m²s^{-1}

- **microstructure and phase distribution: best agreement for exp. D_{AlCu}**
- **model predictions require as input accurate liquid diffusion data**

Kasperovich, Meyer, Ratke, Int. Foundry Res. (2010)

Darken’s equation in Liquids?

- **solids:**

$D_{AB} = (D_B N_A + D_A N_B)\Phi S$

S as additional factor (“vacancy wind”)

- **liquids:**

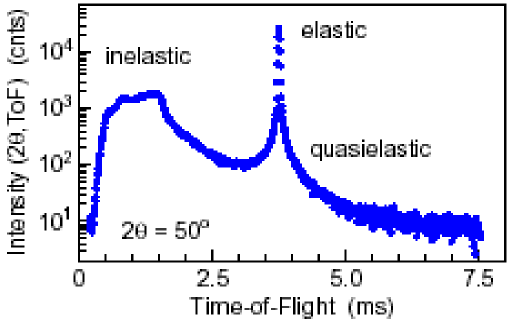
$D_{AB} = (D_B N_A + D_A N_B + D_{cross})\Phi = (D_B N_A + D_A N_B)\Phi S$

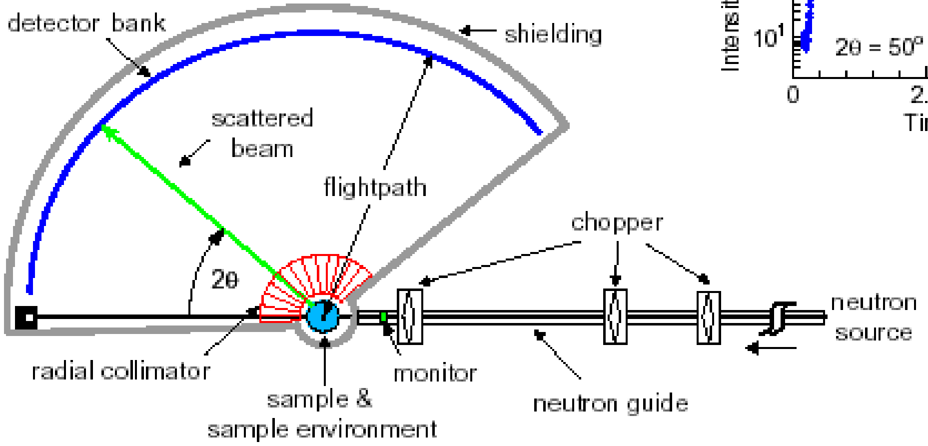
$$S = 1 + \frac{D_{cross}}{N_A D_B + N_B D_A}$$

Darken, Trans. AIME (1948)
Manning, Phys. Rev. B (1961)
Kehr et al., Phys. Rev. B (1989)

Quasielastic Neutron Scattering (QNS)

- $\Delta D^*/D < 5\%$, incoherent scatterer only (Cu, Ni, Ti,…), convection free



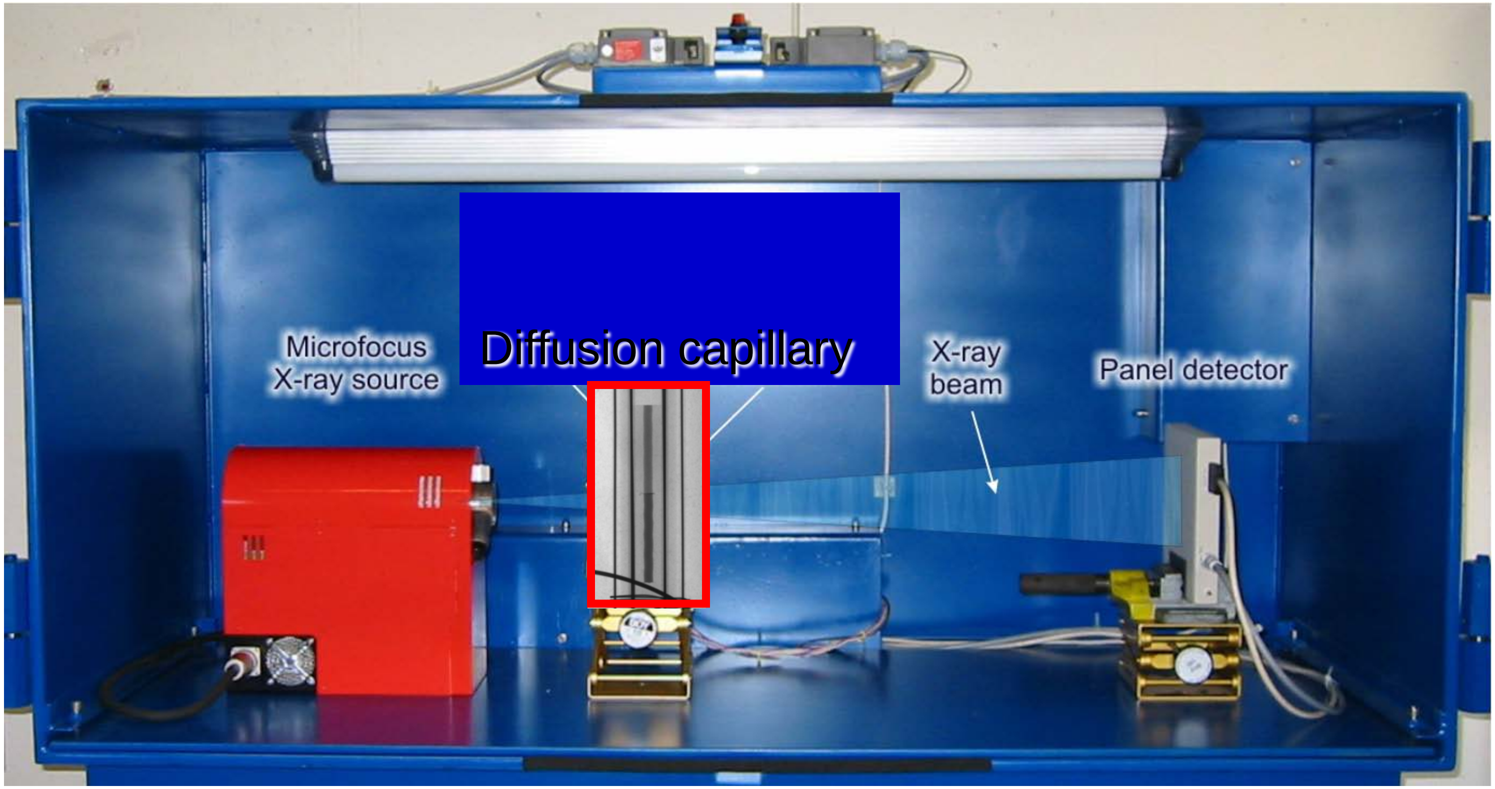


$$I(2\theta,\mathrm{ToF}) \rightarrow \Phi(q,t) = \frac{\langle \rho_q(t)^* \rho_q(0)\rangle}{\langle |\rho_q(0)|^2\rangle}$$

Meyer, Phys. Rev. B. (2010)

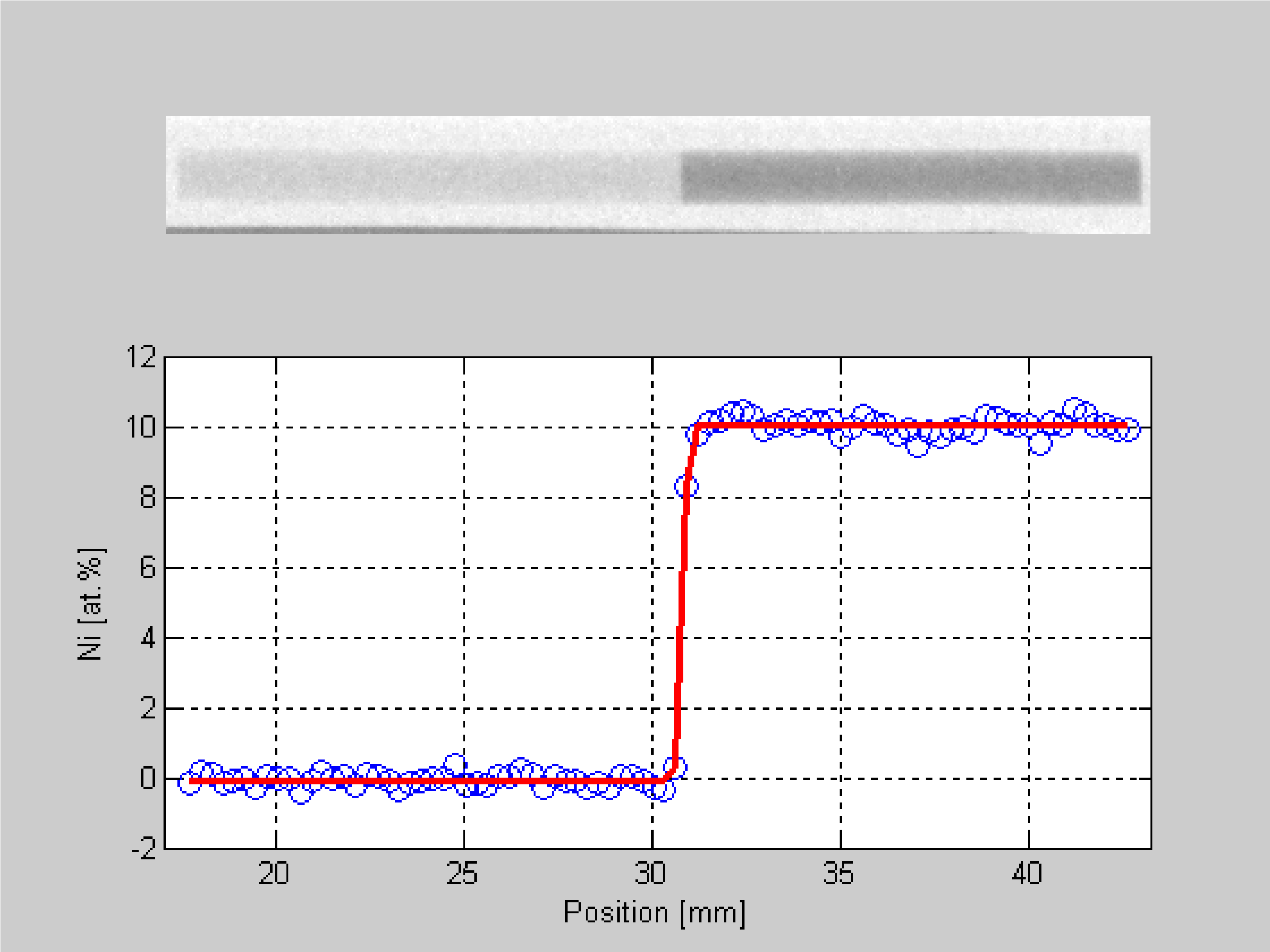
Capillary Techniques with X-ray Radiography

- $\Delta D_{AB}/D$ < 20%, contrast required



Griesche et al., Mat. Sci. For. (2010)

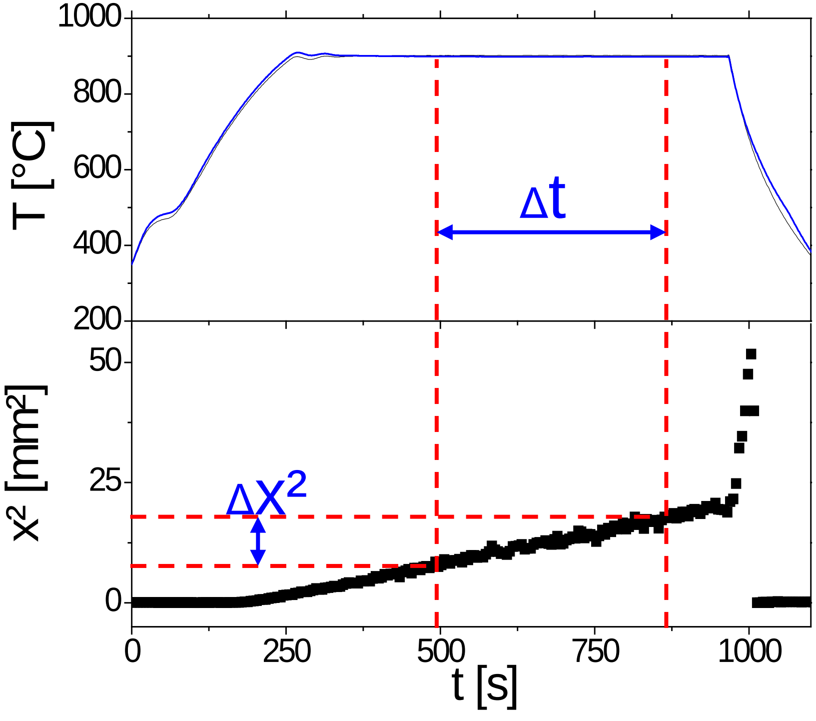
Al vs. $AlNi_{10}$ at.-%



Griesche et al., Rev. Sci. Instr. (2010)

Image Analysis

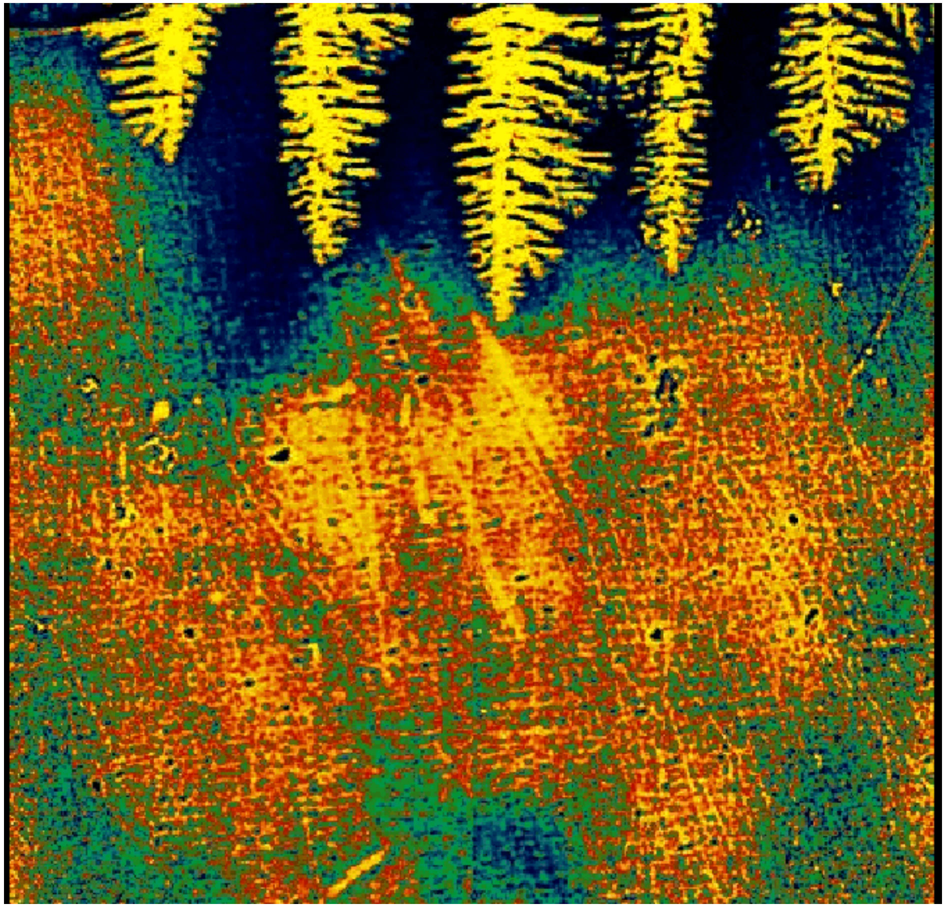
- $\Delta x^2 = 2D\Delta t$
- good statistics
- deviations from pure diffusion detectable (convection)
- no black box (better accuracy)
- *D*(T) measureable



Al-Cu

Zhang et al., Phys. Rev. Lett. (2010)

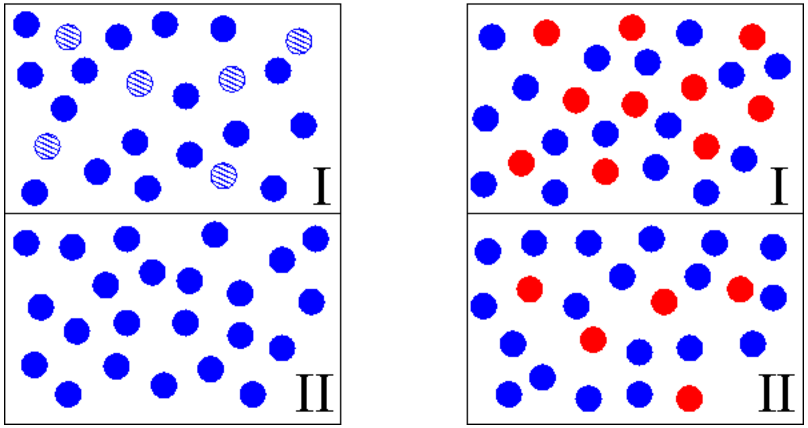
… more movies: $AlCu_{30}$ at.-%



Henri Nguyen-Thi, pers. comm.

Molecular Dynamic Simulation

- D_A, D_B, D_AB
- D_cross from velocity correlation functions
- $S = 1 + \dfrac{D_{cross}}{N_A D_\mathrm{B} + N_B D_\mathrm{A}}$
- $\Phi = \dfrac{N k_\mathrm{B} T x_\mathrm{A} x_\mathrm{B}}{S_\mathrm{cc}(q=0)}$
- $L = S\,(D_\mathrm{B} N_\mathrm{A} + D_\mathrm{A} N_\mathrm{B})$

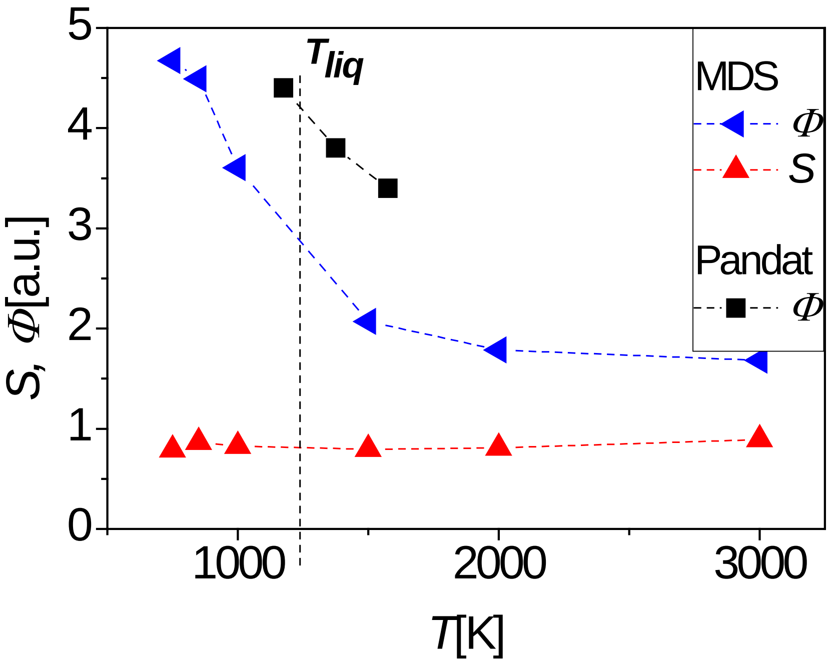


$$D = \lim_{t\to\infty} C \frac{\left\langle (\vec{r}(t) - \vec{r}(0))^2 \right\rangle}{6t}$$

Mishin et al., Phys. Rev. B (2002)

Results $Al_{80}Ni_{20}$

- Φ (Pandat) ~ Φ (MDS)
- strong temperature dependence of Φ in undercooled melt
- $S \approx 0,8$



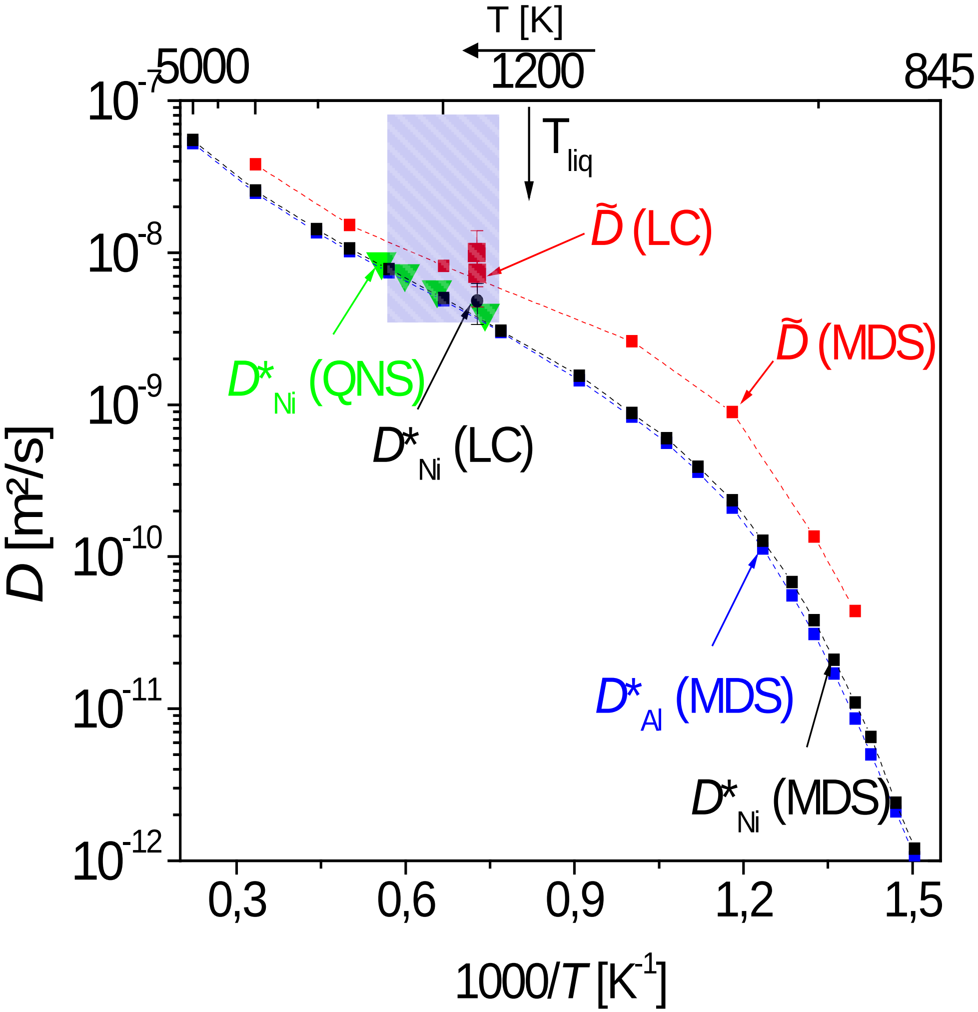
R. Schmid-Fetzer, Pandat calculations (2004)
Horbach et al., Phys. Rev. B (2007)

Results $Al_{80}Ni_{20}$

- sim. & exp. show excellent agreement

- $D^*_{Ni} \approx D^*_{Al}$
- $D_{AlNi} > D^*_{Ni}, D^*_{Al}$

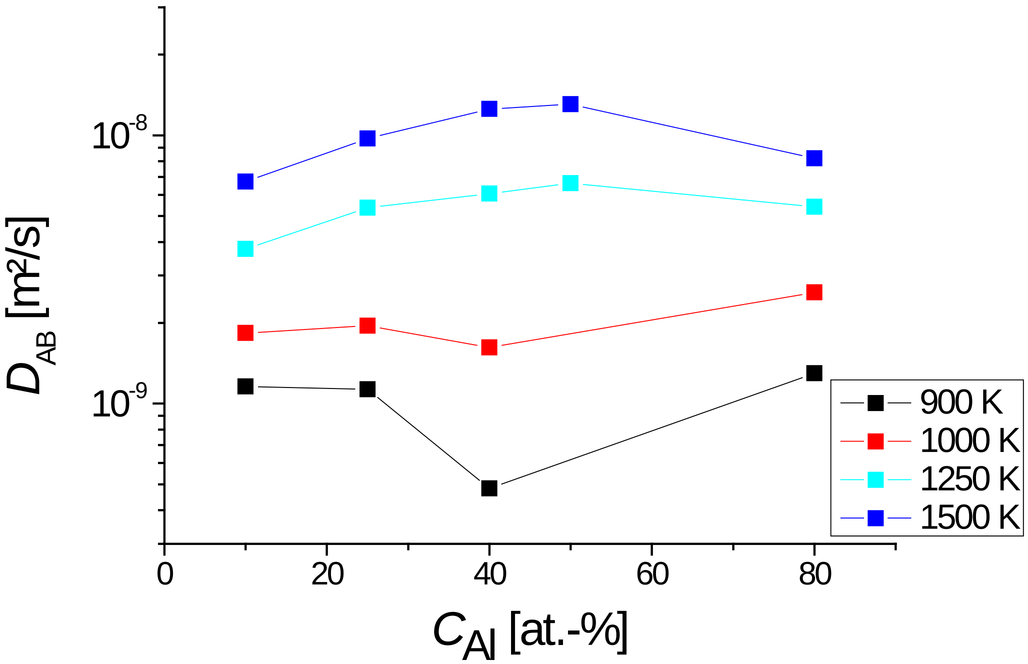
- slowing down of diffusivity in undercooled region (arresting of atoms)
- change in diffusion mechanism



Horbach et al., Phys. Rev. B (2007)

Al-Ni (MDS): D_{AB}

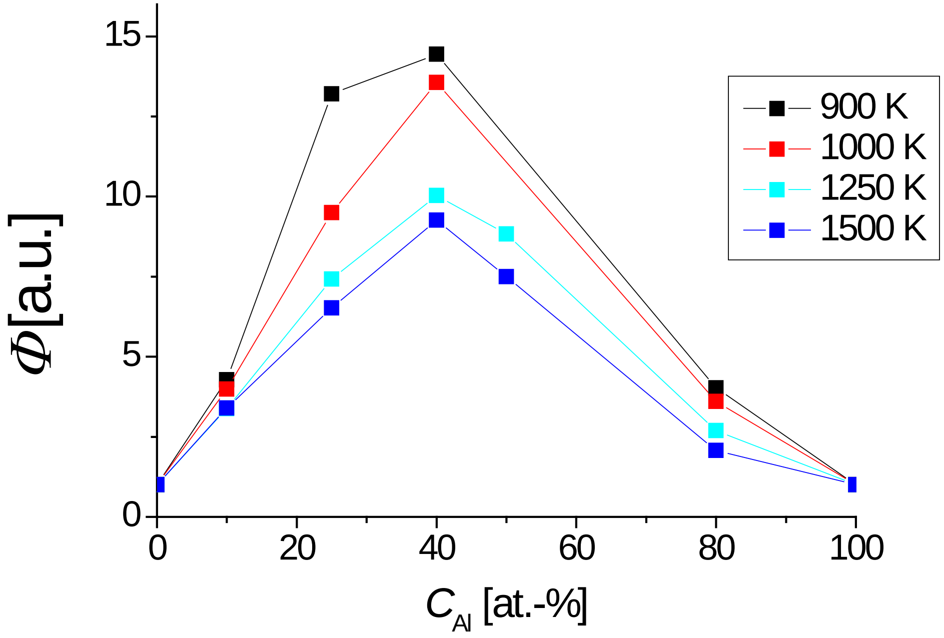
- D_{AB} increases with T
- Maximum of D_{AB} in equilibrium melt
- Minimum of D_{AB} in undercooled melt



Al-Ni (MDS): *Φ*

- *Φ* decreases with *T*

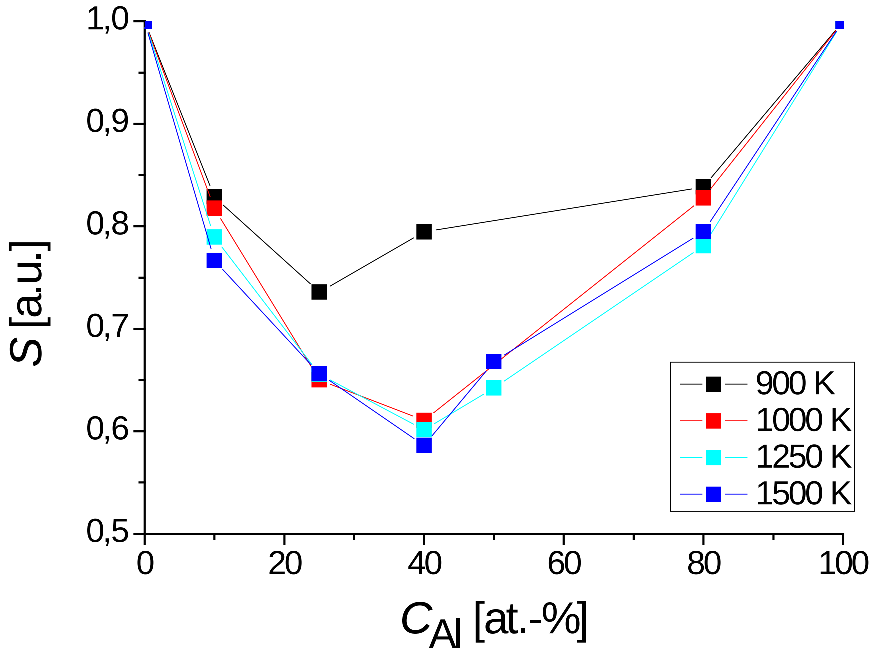
- always a maximum for concentrated solution
- Φ overcompensated by „cage effect “



Al-Ni (MDS): *S*

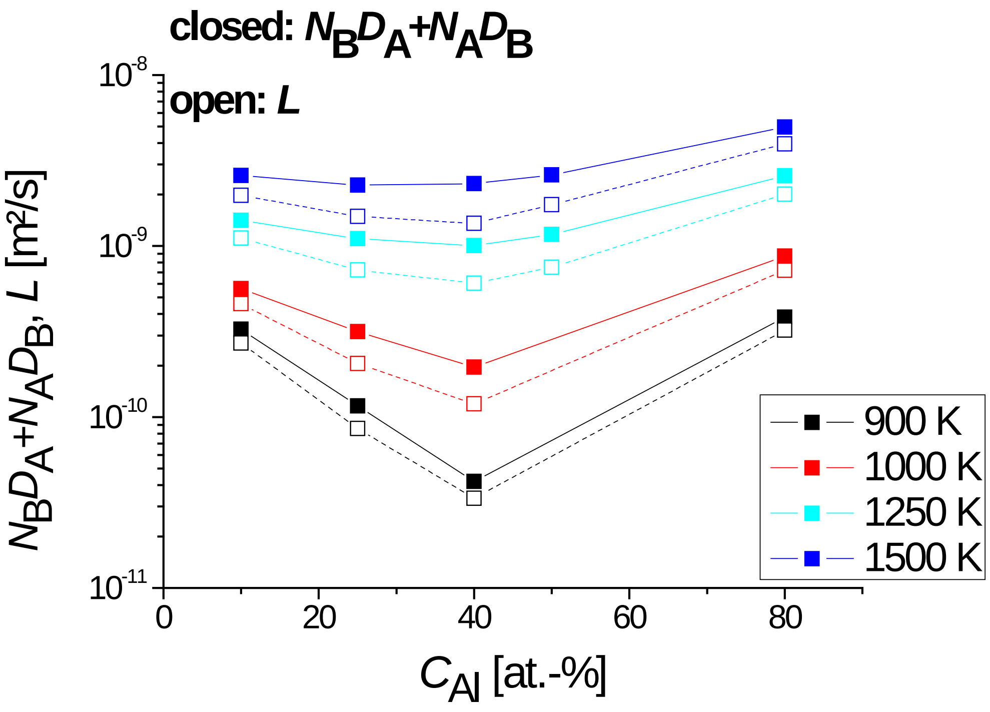
- increasing *S* with undercooling

$$S = 1 + \frac{D_{\mathrm{cross}}}{N_A D_{\mathrm{B}} + N_B D_{\mathrm{A}}}$$



Al-Ni (MDS): $(N_B D_A + N_A D_B)$, L

- $L = S\,(N_B D_A + N_A D_B)$
- slowing down due to cage effect



Conclusions

- coupling of experimental techniques (QNS, diffusion capillary techniques + *in situ* diagnostics) with simulation methods (MDS) helps revealing mechanisms

- slowing down of dynamics in undercooled melts due to collective effects (arresting of atoms)

- cross-correlation effects decrease with increasing undercooling

Thank you for your attention !