Crystal growth rates in supercooled atomic liquid mixtures[1]

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ABSTRACT

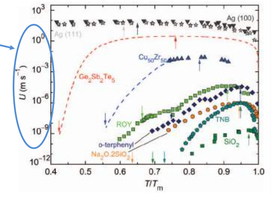
Crystallization is a fundamental process in materials science, providing the primary route for the realization of a wide range of new materials. Crystallization rates are also considered to be useful probes of glass-forming ability[2-3]. At the microscopic level, it is phenomenologically described by the classical crystal nucleation and growth theories[4]. Yet, solid formation is a far more complex process and markedly different crystal growth regimes in many binary liquid mixtures greatly challenge our understanding of crystallization[1-3,5,6]. Here[1], we study by experiments, theory and computer simulations the crystallization of supercooled mixtures of argon and krypton, showing that crystal growth rates in these systems can be reconciled with existing classical models only by explicitly accounting for non-ideal mixing effects. Our results highlight the importance of thermodynamic aspects in describing the crystal growth kinetics, providing a substantial step towards a more sophisticated theory of crystal growth.

CRYSTAL GROWTH

Crystallization rates in many systems[3] → maximum rate and huge variations

Technological goal: identification of *good glass-formers* (extreme crystal growth rate slowdown)

Locally Favoured Structures, diffusion, quantum effects, liquid pre-ordering, ...?

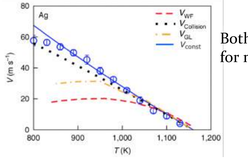


THE CLASSICAL MODEL

collision-limited (CL) $\nu_{\mathrm{CL}}(T) = \dfrac{\sqrt{3k_{\mathrm{B}}T/m}}{\Lambda(T)}$ — **ballistic** at short times, no activation barrier, weak T dependence

Wilson-Frenkel (WF) $\nu_{\mathrm{WF}}(T) = 6\dfrac{D(T)}{\Lambda^2(T)}$ — **diffusive** at longer times, activated process, strong T dependence

$$u(T) = f a(T) \nu(T) \exp\left(-\frac{\Delta S_{\mathrm{m}}}{R}\right)\left\{1 - \exp\left[-\frac{\Delta G(T)}{RT}\right]\right\}$$



Both models fail[2,6] (WF even at moderate supercooling) for many systems: metallic alloys, colloids, pure metals...

Unified picture of crystal growth mechanism?

THE EXPERIMENT

Experiments on Ar-Kr @ DESY and @ EU-XFEL

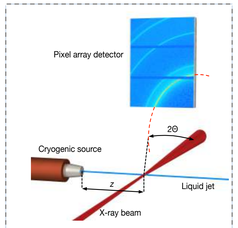
- Crystal growth rates ~ metallic alloys

- Miscible in the whole phase diagram (study several Kr fractions x)

- Many data for ΔG and ΔS_m are available → straightforward comparison with the model

- Lennard-Jones interactions: easy to simulate

v of the jet constant: distance from nozzle ↔ **time evolution** (t=z/v)



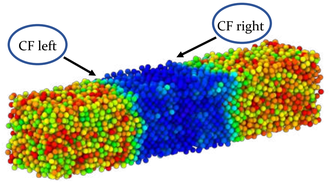
Liquid microjets technique[7]
Evaporative supercooling
X-ray diffraction

EXPERIMENTAL TECHNIQUE

SIMULATIONS

LAMMPS (www.lammps.sandia.gov)

Molecular Dynamics: seeded crystal growth, 10^4 atoms, PBC



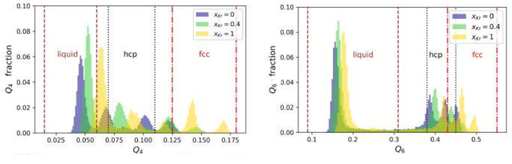
Track crystal front (CF) along time → **crystal growth rates**

Structural order parameter

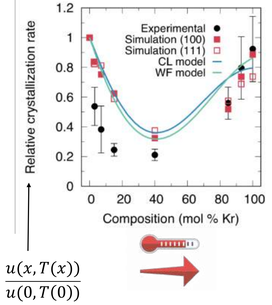
$$q_{lm}(i) = \frac{1}{N_b(i)}\sum_{j=1}^{N_b(i)} Y_{lm}(\theta(\mathbf{r}_{ij}),\phi(\mathbf{r}_{ij})) \qquad q_l(i) = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|q_{lm}(i)|^2}$$

$$S_i = \sum_{j=1}^{N_b(i)} \frac{\mathbf{q}_6(i)\cdot\mathbf{q}_6(i)}{|\mathbf{q}_6(i)|\,|\mathbf{q}_6(j)|}$$

Averaged Local Bond Order Parameters[8] → crystal structures detection



WHICH MODEL?



$\dfrac{u(x,T(x))}{u(0,T(0))}$

- Experimental data also include nucleation events (composition-dependent)

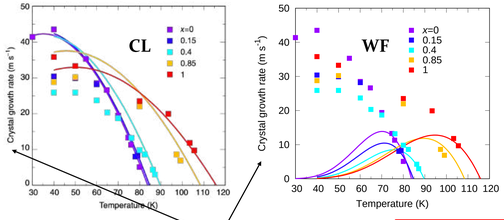
- Many crystallites in the microjet *vs* seeded (biased) growth

- Nontrivial temperature-dependent behavior

→ Remarkable *qualitative* agreement (experiment and simulations)

→ MD simulations capture relevant details!

Only simulations: fixed x, change T



$u(T(x)) = u(T)|_x$

Are both models wrong?

AN IMPROVED THERMODYNAMIC THEORY

Modified collision-limited model: non ideal mixing effects

New crystal addition rate $\tilde{\nu}_{\mathrm{CL}}(T) = \nu_{\mathrm{CL}}(T)\Phi$ where $\Phi = 1 + \dfrac{d\ln\gamma_\alpha^{\mathrm{L}}}{d\ln x_\alpha}$

(multiplicative correction to particle velocity)

In fact, the thermodynamic driving force: $\Delta G = G^{\mathrm{L}}(x_A,T) - G^{\mathrm{C}}(x_A,T)$

$$G^{\mathrm{L,C}}(x_A,T) = x_A g_{\mathrm{A}}^{\mathrm{L,C}}(T) + (1-x_A) g_{\mathrm{B}}^{\mathrm{L,C}}(T) + g_{\mathrm{mix}}(x_A,T) + g_{\mathrm{E}}^{\mathrm{L,C}}(x_A,T)$$

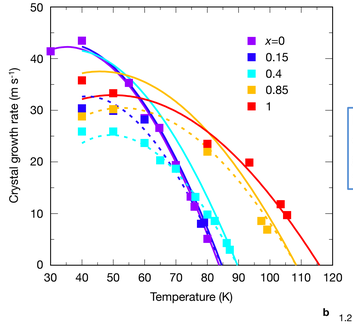
← **excess free energy** (usually neglected)

ideal A-B mixing

$$g_{\mathrm{E}}^{\mathrm{L,C}}(x_A,T) = \left[(1-x_A)\ln\gamma_{\mathrm{B}}^{\mathrm{L,C}} + x_A\ln\gamma_{\mathrm{A}}^{\mathrm{L,C}}\right]RT$$

activity coefficients

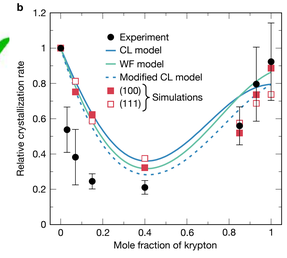
RESULTS & PERSPECTIVES



Dashed lines: **modified CL**
Full lines: original CL

Noticeable *quantitative* description of crystal growth rates even at ~ 60% supercooling degree

Modified CL also fits relative growth rates as a function of Kr fraction



WHAT'S NEXT?

Next steps:
→ other mixtures (metallic alloys)
→ study model systems (role of interaction parameters)
→ study of nucleation
(in collaboration with EU-Xfel)

REFERENCES

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