Cemef

Centre de Mise en Forme des Matériaux

Dendrite growth kinetics in multicomponent system
-
Development of cross-diffusion model with thermodynamic coupling (PY \ KIND)

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4ème Atelier thermodynamique des verres - GDR TherMatHT – USTV
Marcoule – 11 Octobre 2019

PHYSALURGY

MODELS

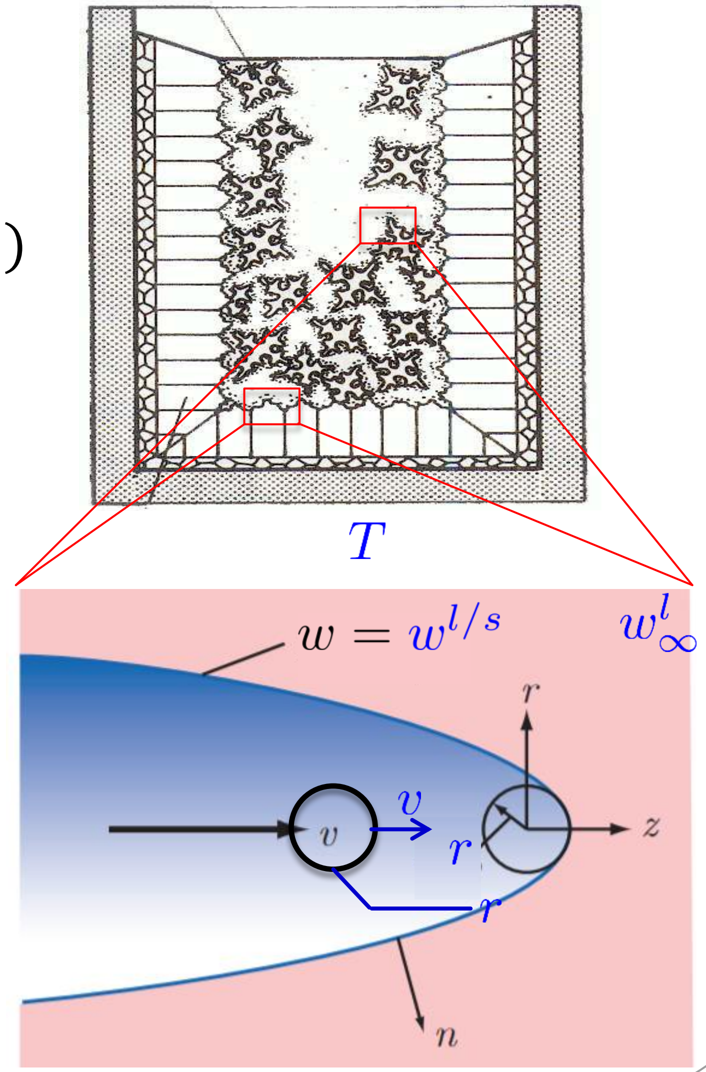
- PY\PATH: solidification PATH
  Solidification path (LR, GS, PE), tabulations for CIMLIB (CEMEF)library computations
- PY\KIND : KINetics Dendrites
  Dendrite growth kinetics (cross diffusion effect, curvature effect)
- PY\DIAN : DIffusion ANalytic
  Analytic growth kinetics in unsteady regime (semi-infinite domain, cross diffusion regime, Pl./Cyl./Sph.)
- PY\MIAN : MIcrostructure ANalytic
  Growth kinetics in unsteady regime (far-field approach, cross diffusion regime, Pl./Cyl./Sph.)
- PY\MIFT : MIcrostructure Front Tracking
  Growth kinetics – Numerical simulation (front-tracking simulation, cross diffusion regime, Pl./Cyl./Sph.)
- PY\MILD : MIcrosegregation Length Diffusion
  Microsegregation modelling based on diffusion length
- PY\PREC: PRECipitation
  Precipitation kinetics, precipitate size distribution
- PY\KINE : KINetics Eutectics
  Eutectic growth kinetics (curvature effect)

http://physalurgy.cemef.mines-paristech.fr

PY\KIND

DENDRITE GROWTH KINETICS

- Growth kinetics modelling: Kurz [Kur86]
  - Paraboloidal dendrite tip: Papapetrou [Pap35]
  - Thermodynamic equilibrium at s/l interface $w^{l/s} = f_0(T)$
  - Analytical solution: Ivantsov solution [Iva47] $r\ v = f_1(w^{l/s})$
  - Stability analysis: Mullins&Sekerka [Mul64]$\lambda^2\ v = f_2(w^{l/s})$
  - Marginal stability criterion: Langer [Lan78] $r \sim \lambda$
- Coupling with Thermo-Calc databases
  - Phase diagram properties
  - Interfacial energy influence
  - Cross-diffusion coefficient effect
- Advantages
  - Influence of local solidification processing with updated properties



[Dan09]

PY\KIND – LINEARIZED SOLUTION

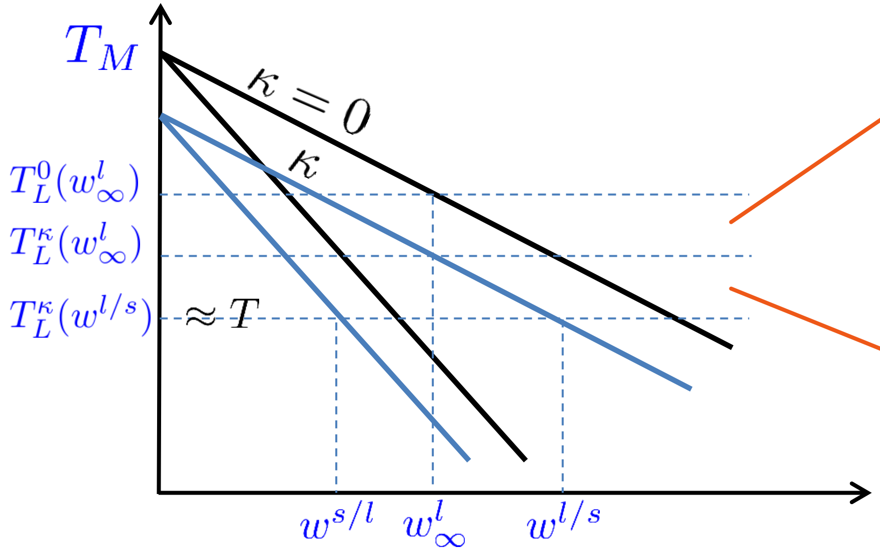
DENDRITE GROWTH KINETICS

- Undercooling expressions [Kur01]

Global undercooling

$$\Delta T = \Delta T_w + \Delta T_\kappa$$

$$\Delta T = T_L^0(w_\infty^l) - T$$



Curvature undercooling

$$\Delta T_\kappa = T_L^0(w_\infty^l) - T_L^\kappa(w_\infty^l) = \kappa\ \Gamma \approx \frac{2\ \Gamma}{r}$$

Solutal undercooling

$$\Delta T_w = T_L^\kappa(w_\infty^l) - T_L^\kappa(w^{l/s}) \approx m\left(w_\infty^l - w^{l/s}\right)$$

- Chemical diffusion
  Ivantsov relation [Iva47]

$$\Omega = \mathrm{Iv}(Pe) \qquad \begin{cases} \Omega = \dfrac{w^{l/s} - w_\infty^l}{w^{l/s} - w^{s/l}} \\ Pe = \dfrac{r\ v}{2\ D^l} \end{cases}$$

où $\mathrm{Iv}(x) = x\ \mathrm{e}^x\ \mathrm{E}_1(\mathrm{x})$

- Marginal stability criterion /
  Langer-Müller Krumbhaar [Lan78]

$$r^2\ v = \frac{D^l\ \Gamma}{\sigma^* m\left(w^{s/l} - w^{l/s}\right)}$$

Mullins Sekerka, 1964 [Mul64]

=> Computation of the r, v values for the provided coefficients : $m, k, w^{l/s}, D^l, \Gamma, \Omega$

PY\KIND – THERMODYNAMIC COUPLING

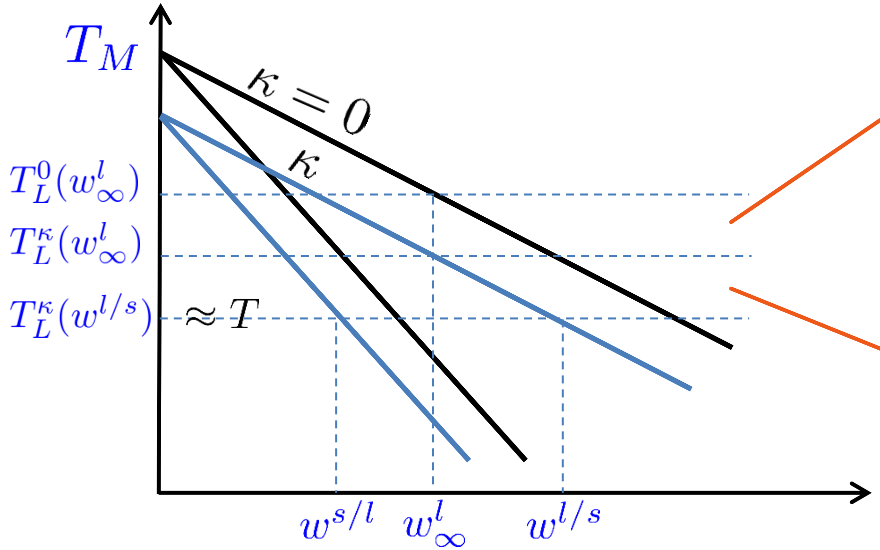
DENDRITE GROWTH KINETICS

❑ Undercooling expressions

Global undercooling

$$\Delta T = \Delta T_w + \Delta T_\kappa$$

$$\Delta T = T_L^0(w_\infty^l) - T$$



Curvature undercooling

$$\Delta T_\kappa = T_L^0(w_\infty^l) - T_L^\kappa(w_\infty^l) = \kappa\ \Gamma$$

~~$\approx \frac{2\Gamma}{r}$~~

Solutal undercooling

$$\Delta T_w = T_L^\kappa(w_\infty^l) - T_L^\kappa(w^{l/s})$$

~~$\approx m\left(w_\infty^l - w^{l/s}\right)$~~

❑ Chemical diffusion
Ivantsov relation [Iva47]

$$\Omega = \mathrm{Iv}(Pe) \qquad \begin{cases} \Omega = \dfrac{w^{l/s} - w_\infty^l}{w^{l/s} - w^{s/l}} \\ Pe = \dfrac{r\ v}{2\ D^l} \end{cases}$$

❑ Marginal stability criterion /
Langer-Müller Krumbhaar [Lan78]

$$r^2\ v = \frac{D^l\ \Gamma}{\sigma^*\left(T_L^\kappa(w_\infty^l) - T_L^\kappa(w^{l/s})\right)}$$

=> Computation of the r, v values with properties from thermodynamic database.

Dendrite growth kinetics / Fe-1% wt C – Datafile

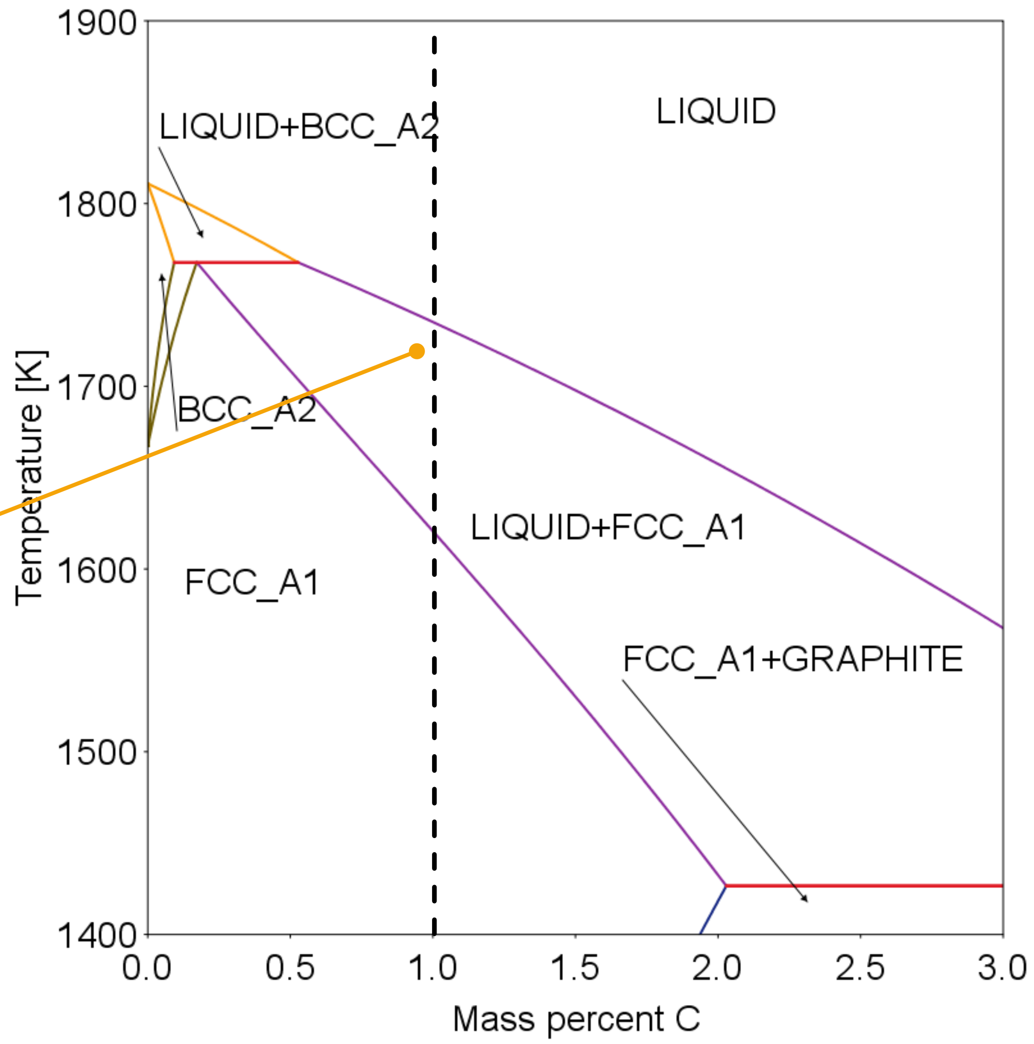
//	System of units
TEMPUNIT	K
COMPUNIT	W
//	Name of the database
DATABASE	FEGDR_TCFE6.GES5
//	Total number of elements
NUMBERELTS	2
//	Main element
MAINELT	FE
//	Element 1 symbol / min / max / nval
COMPINF	C 1 1 1
//	Velocity range
VELOCITY	1.E-10 1.E+2 201
//	Solid phase
PHASE	FCC_A1
//	Surface energy
ENERGINT	0.270
//	Sigma Star
SIGMASTAR	0.02533029591

......

// Diffusion matrix in liquid phase
DIFFUSION 5.221E-9

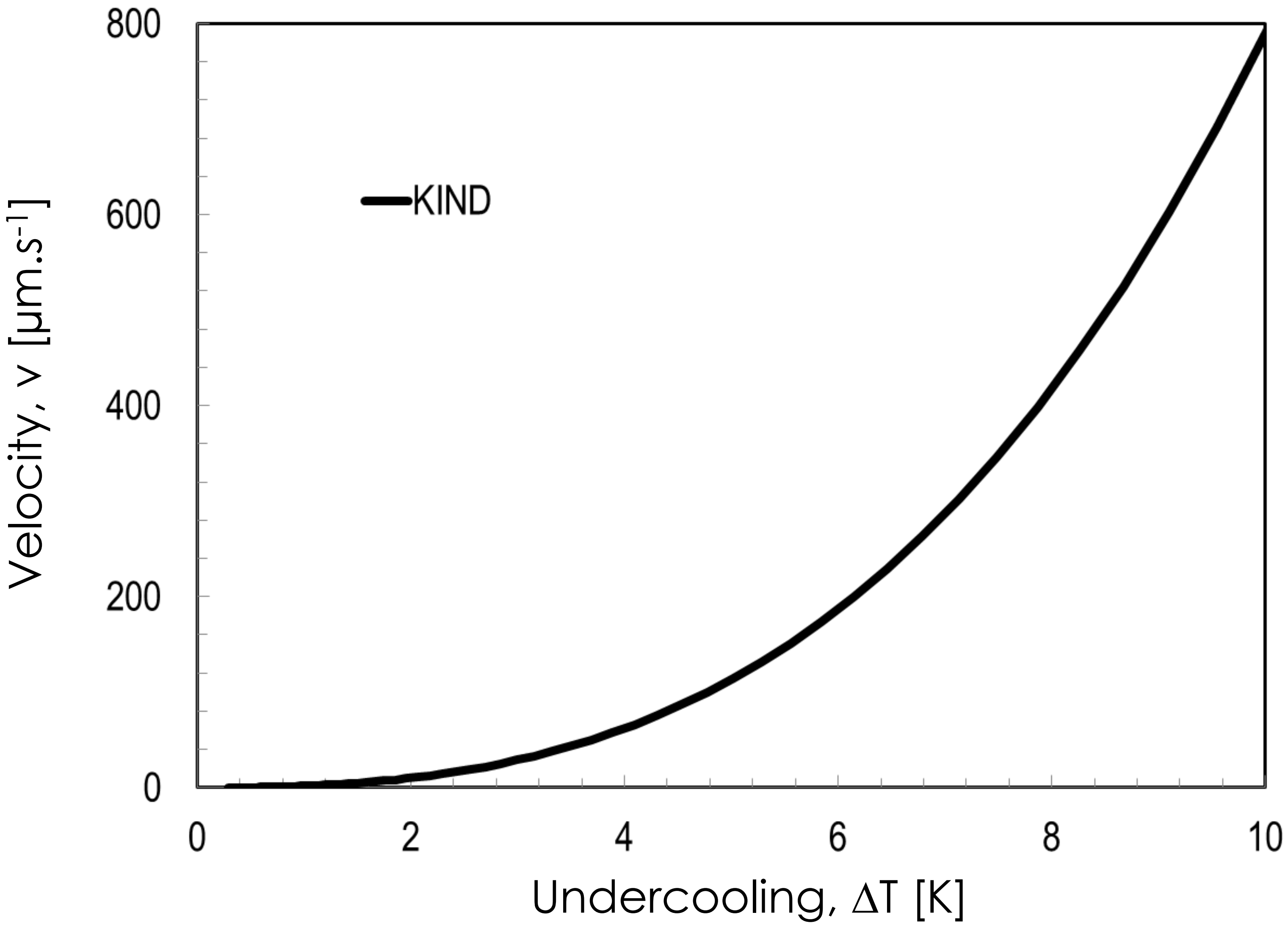
$$\Gamma = \frac{\sigma^{s/l}}{\Delta S_f}$$

MOBFE4 [The]



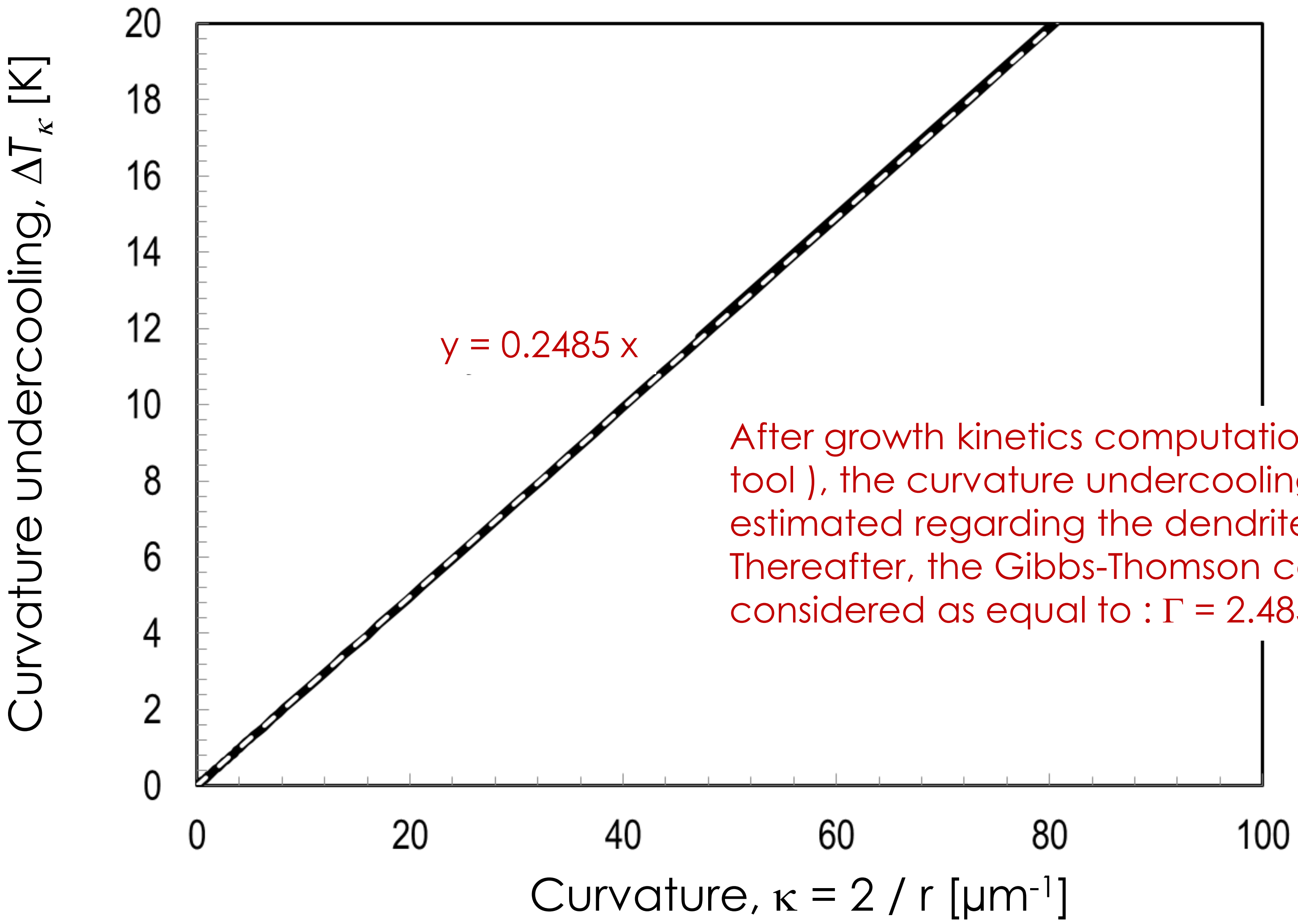
PY\KIND

DENDRITE GROWTH KINETICS / FE-1% WT C



PY\KIND

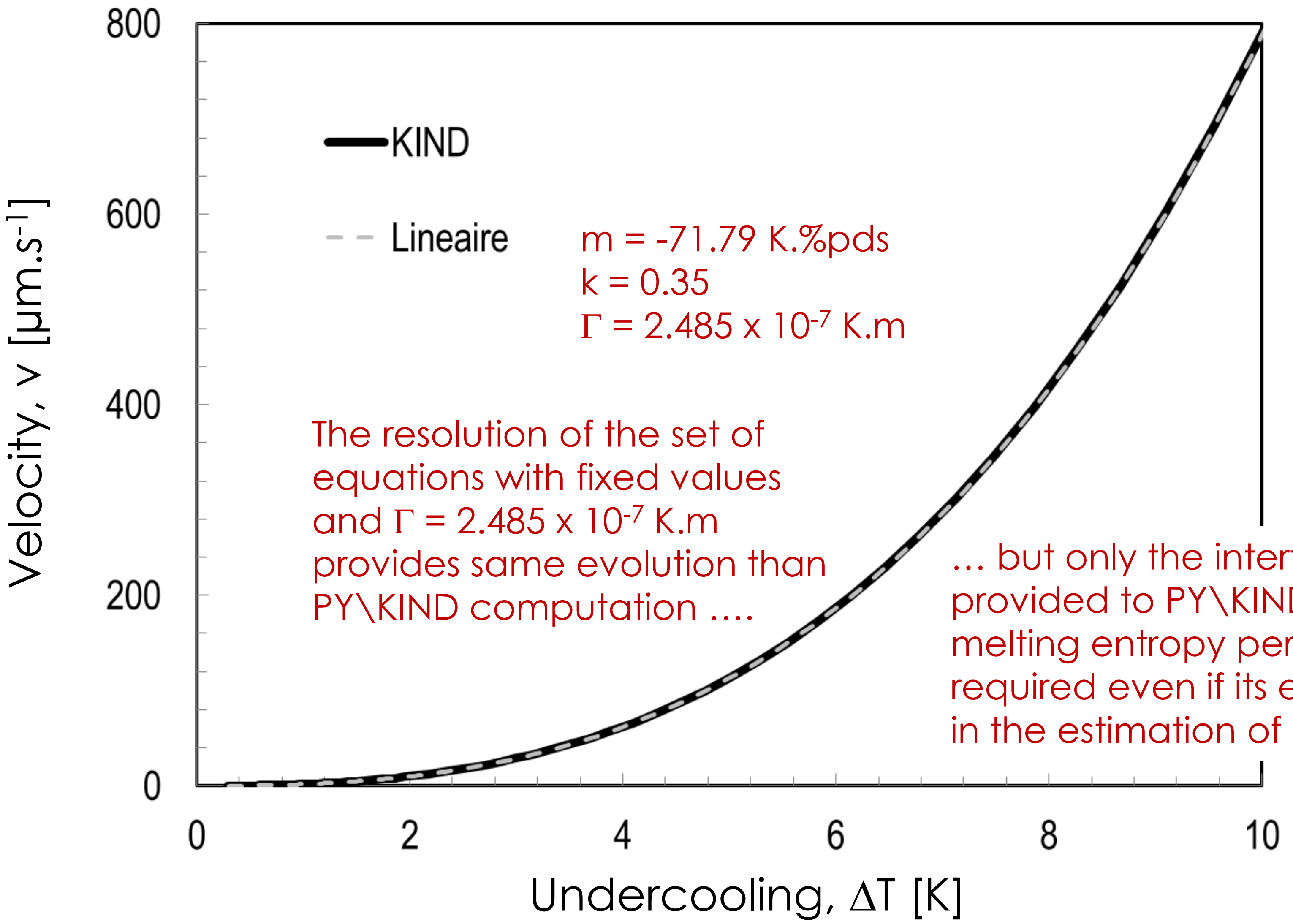
Dendrite growth kinetics / Fe-1% wt C



After growth kinetics computation (PY\KIND tool), the curvature undercooling can be estimated regarding the dendrite tip curvature. Thereafter, the Gibbs-Thomson coefficient is considered as equal to : $\Gamma = 2.485 \times 10^{-7}$ K.m

PY\KIND VS. LINEARIZED SOLUTION

DENDRITE GROWTH KINETICS / FE-1% WT C



m = -71.79 K.%pds
k = 0.35
Γ = 2.485 x 10^{-7} K.m

The resolution of the set of equations with fixed values and Γ = 2.485 x 10^{-7} K.m provides same evolution than PY\KIND computation ….

… but only the interfacial energy was provided to PY\KIND. In addition, the melting entropy per unit volume is not required even if its expression is involved in the estimation of the Γ coefficient

Dendrite growth kinetics in multicomponent alloy [Hun01]

Global undercooling

$$\Delta T = \Delta T_w + \Delta T_\kappa$$

$$\Delta T = T_L\left(\{w^l_{i,\infty}\}_{1\le i\le N}\right) - T$$

Curvature undercooling

$$\Delta T_\kappa = T^0_L\left(\{w^l_{i,\infty}\}_{1\le i\le N}\right) - T^\kappa_L\left(\{w^l_{i,\infty}\}_{1\le i\le N}\right) \approx \frac{2\,\Gamma}{r}$$

Solutal undercooling

$$\Delta T_w = T^\kappa_L\left(\{w^l_{i,\infty}\}_{1\le i\le N}\right) - T^\kappa_L\left(\{w^{l/s}_i\}_{1\le i\le N}\right)$$

Local equilibrium

$$\{w^{s/l}_i\}_{1\le i\le N} = F\left[\{w^{l/s}_i\}_{1\le i\le N}, T, r\right]$$

Ivantsov relation in multicomponent alloy

$\mathbf{U_i}$: Eigenvectors of $D^l\left[\{w^l_{i,\infty}\}_{1\le i\le N}, T\right]$

B_i: Eigenvalues of $D^l\left[\{w^l_{i,\infty}\}_{1\le i\le N}, T\right]$

$$\begin{cases} w^{l/s}_i - w^{s/l}_i = \sum_{k=1}^{N} C_k\, U_{ik}\, \frac{e^{-Pe_k}}{Pe_k} \\ w^{l/s}_i - w^l_{i,\infty} = \sum_{k=1}^{N} C_k\, U_{ik}\, E_1\left[Pe_k\right] \end{cases}$$

In a simplified presentation :

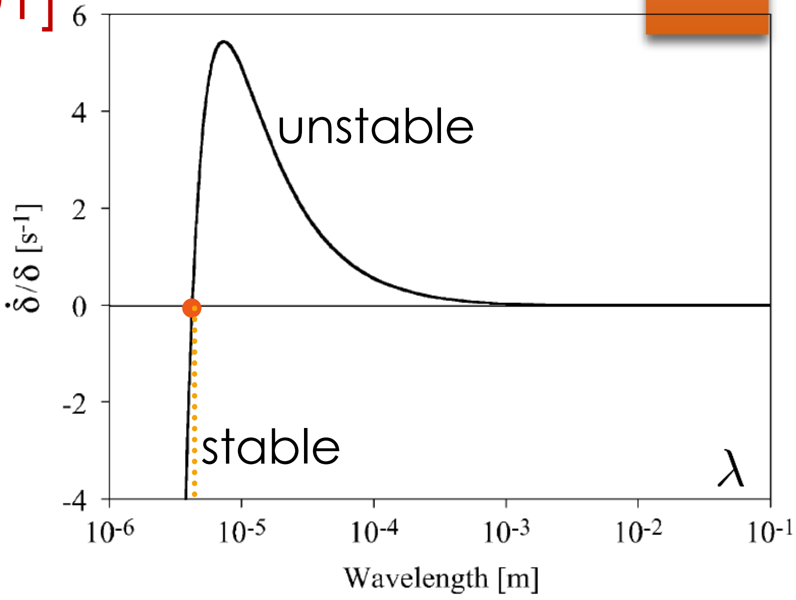
$$w^{l/s}_i - w^{s/l}_i = \sum_{j=1}^{N}\left(w^{l/s}_j - w^l_{j,\infty}\right)\sum_{k=1}^{N}\frac{U_{ik}\,U^{-1}_{kj}}{\mathrm{Iv}\left(Pe_k\right)}$$

where : $Pe_k = \frac{r\ v}{2\ B_k}$

Dendrite growth kinetics in multicomponent alloy [Hun01]

Instability wavelength

$$\frac{\dot{\delta}}{\delta} = \frac{v\ \omega\left(\kappa^s + \kappa^l\right)}{\kappa^s G^s - \kappa^l G^l}\left[\sum_{i=1}^{N}\left(m_i \sum_{j=1}^{N} F_j\ U_{ij}\right) - \Gamma\ \omega^2 - \frac{\kappa^s G^s + \kappa^l G^l}{\kappa^s + \kappa^l}\right]$$



F_j coefficients computations

$$\sum_{i=1}^{N}\left(m_i \sum_{j=1}^{N} F_j\ U_{ij}\right) - \Gamma\ \omega^2 - \frac{\kappa^s G^s + \kappa^l G^l}{\kappa^s + \kappa^l} = 0$$

where $\begin{cases} \omega = \dfrac{2\ \pi}{\lambda} \\ \lambda \approx r \end{cases}$

Langer-Müller Krumbhaar criterion

$$\mathbf{M} \cdot \mathbf{F} = \mathbf{N}$$

$$(M_{ij} F_j = N_i)$$

$$\begin{cases} M_{ij} = \dfrac{U_{ij}}{2}\left(1 + \sqrt{1 + \left(\dfrac{2\ \omega\ B_j}{v}\right)^2}\right) - \displaystyle\sum_{j=1}^{N} U_{ij} H_{ii} \\ N_i = -\displaystyle\sum_{k=1}^{N} \dfrac{v\ A_k U_{ik}}{2\ B_k}\left(-1 + \sqrt{1 + \left(\dfrac{2\ \omega\ B_k}{v}\right)^2}\right) \end{cases}$$

with:

$$w_i^{l/s} - w_i^{s/l} = \sum_{k=1}^{N} U_{ik}\ A_k$$

Dendrite growth kinetics in multicomponent alloy / Fe-1 wt% C-10wt% Cr

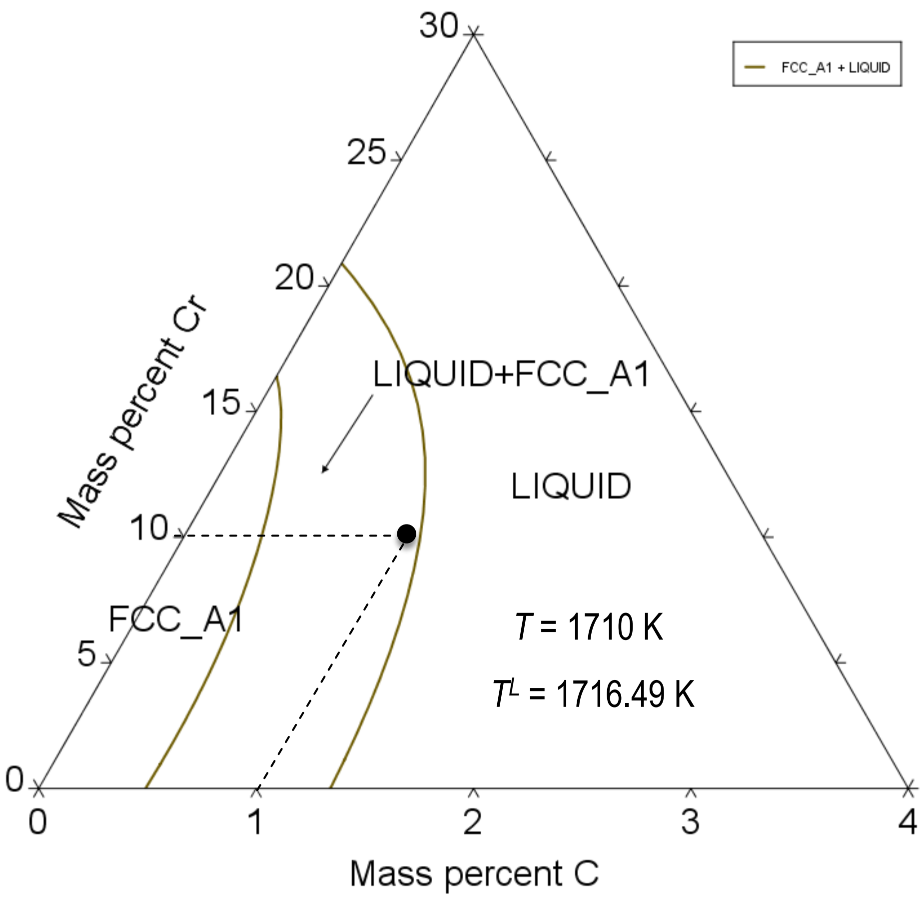
//	System of units			
TEMPUNIT	K			
COMPUNIT	W			
//	Name of the database			
DATABASE	FEGDR_TCFE6.GES5			
//	Total number of elements			
NUMBERELTS	3			
//	Main element			
MAINELT	FE			
//	Element 1 symbol / min / max / nval			
COMPINF	C	1	1	1
	Cr	10	10	1
//	Velocity range			
VELOCITY	1.E-10	1.E+2	201	
//	Solid phase			
PHASE	FCC_A1			
//	Surface energy			
ENERGINT	0.270			
//	Sigma Star			
SIGMASTAR	0.02533029591			

....

// Diffusion matrix in liquid phase

DIFFUSION	**5.221E-9**	**-0.684E-9**
	-1.208E-9	**2.975E-9**

MOBFE4 [The]



DENDRITE GROWTH KINETICS IN MULTICOMPONENT ALLOY / FE -[0.5-1.5] WT% C -[5-15] WT% CR

❑ Cross diffusion effect

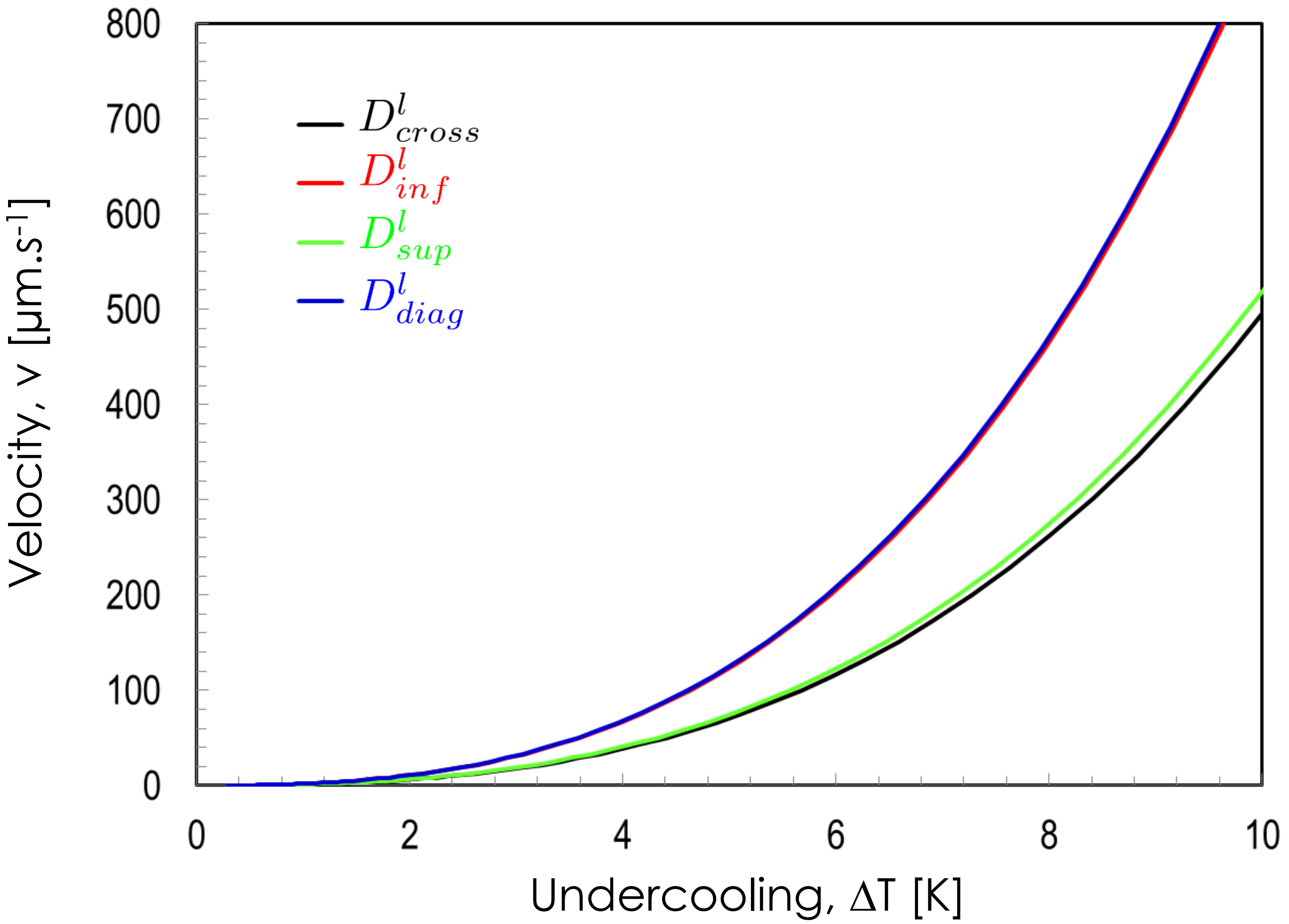
- LIQUID

		C	Cr	
D^l_{cross}	C	5.221	- 0.684	x 10^{-9} m^2 s^{-1}
	Cr	- 1.208	2.975	
D^l_{inf}	C	5.221	**0**	x 10^{-9} m^2 s^{-1}
	Cr	- 1.208	2.975	
D^l_{sup}	C	5.221	- 0.684	x 10^{-9} m^2 s^{-1}
	Cr	**0**	2.975	
D^l_{diag}	C	5.221	**0**	x 10^{-9} m^2 s^{-1}
	Cr	**0**	2.975	

❑ Alloy composition effect

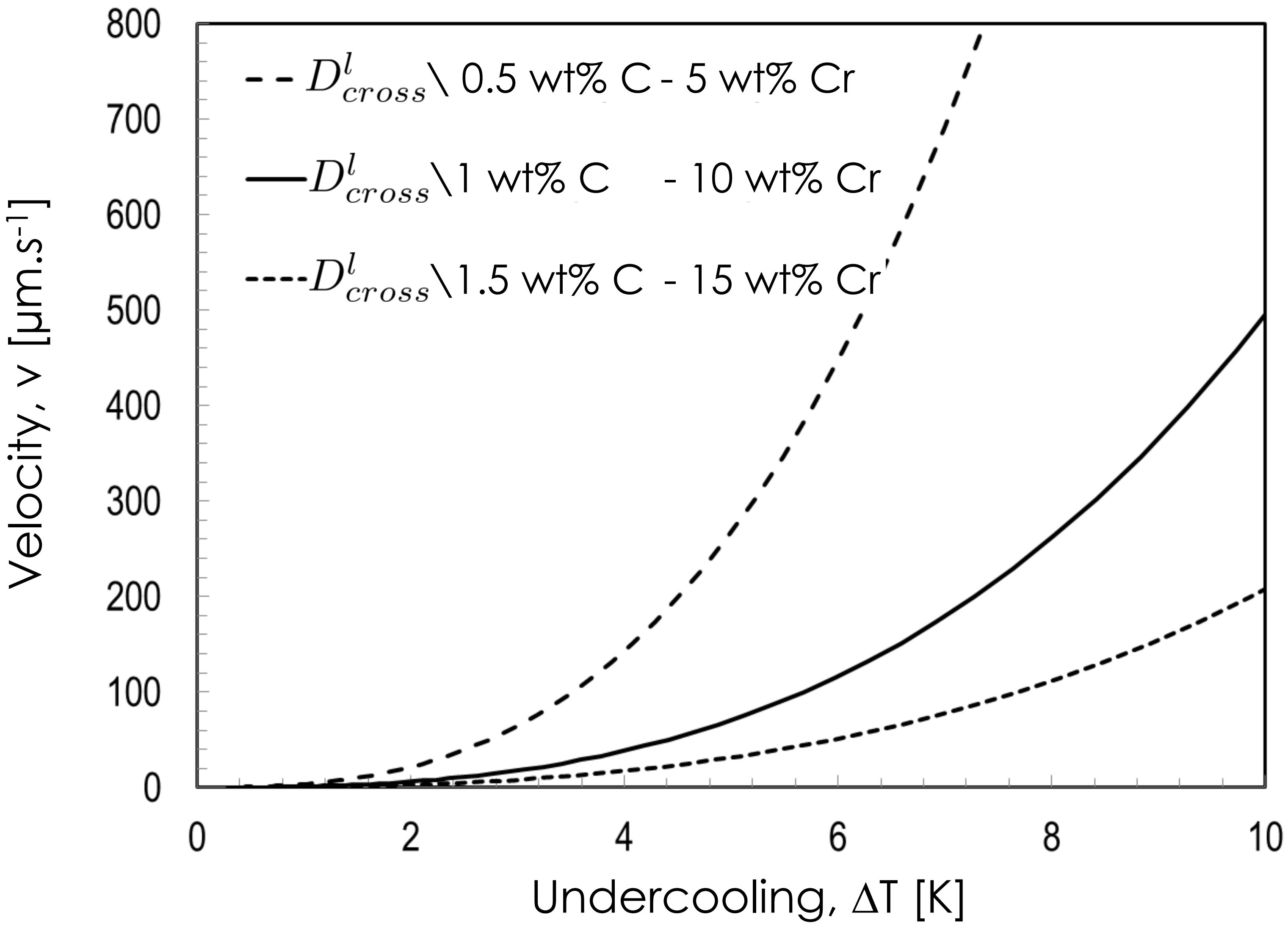
- X_C= 0.5 wt %, X_{Cr} = 5 wt %
- X_C= 1 wt %, X_{Cr} = 10 wt %
- X_C= 5 wt %, X_{Cr} = 15 wt %

Dendrite growth kinetics in multicomponent alloy / Fe-1 wt% C-10wt% Cr



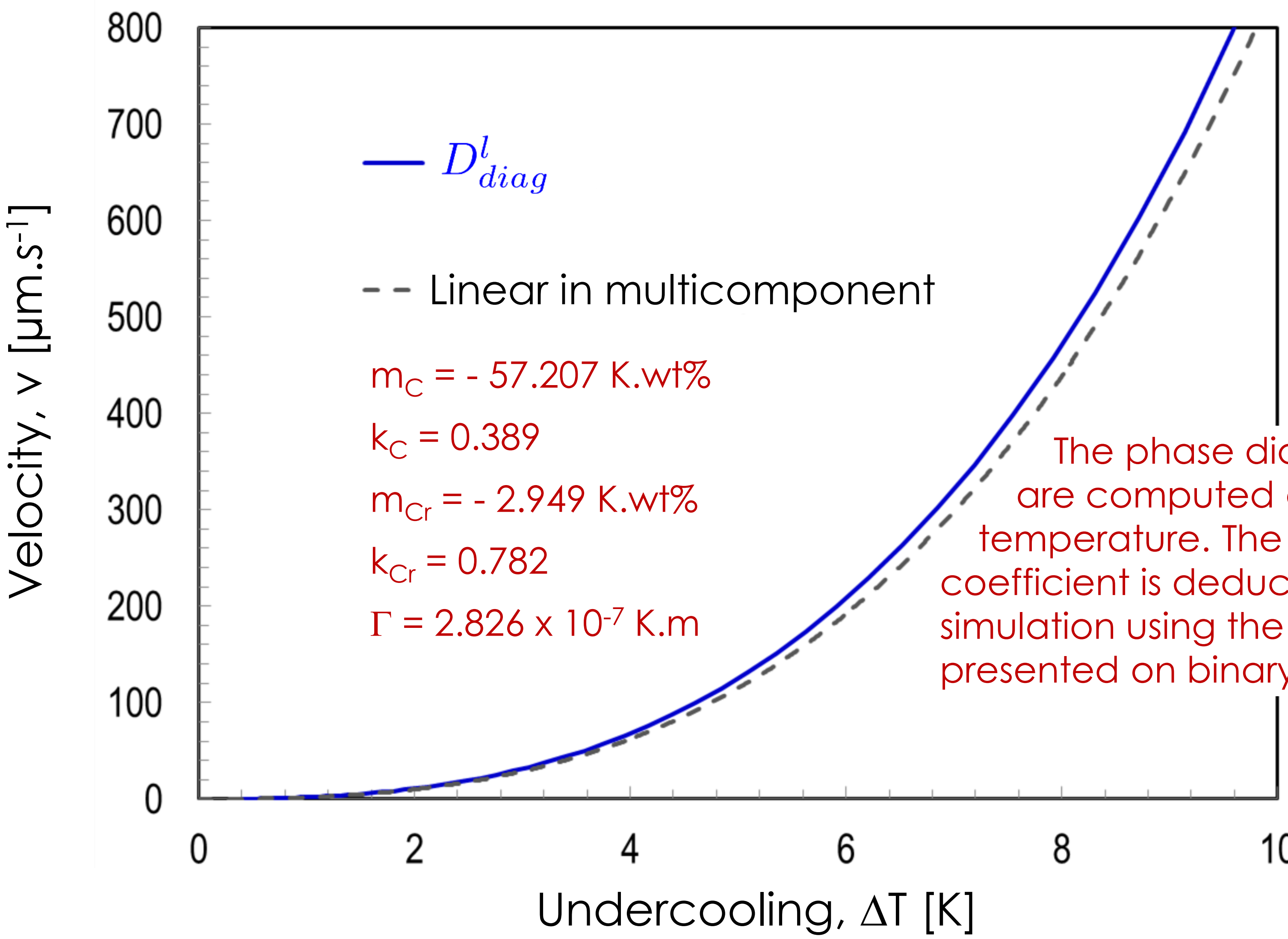
PY\KIND

DENDRITE GROWTH KINETICS IN MULTICOMPONENT ALLOY / FE -[0.5-1.5] WT% C -[5-15] WT% CR



PY\KIND VS. LINEARIZED SOLUTION

DENDRITE GROWTH KINETICS IN MULTICOMPONENT ALLOY / FE-1 WT% C-10WT% CR



m_C = - 57.207 K.wt%

k_C = 0.389

m_{Cr} = - 2.949 K.wt%

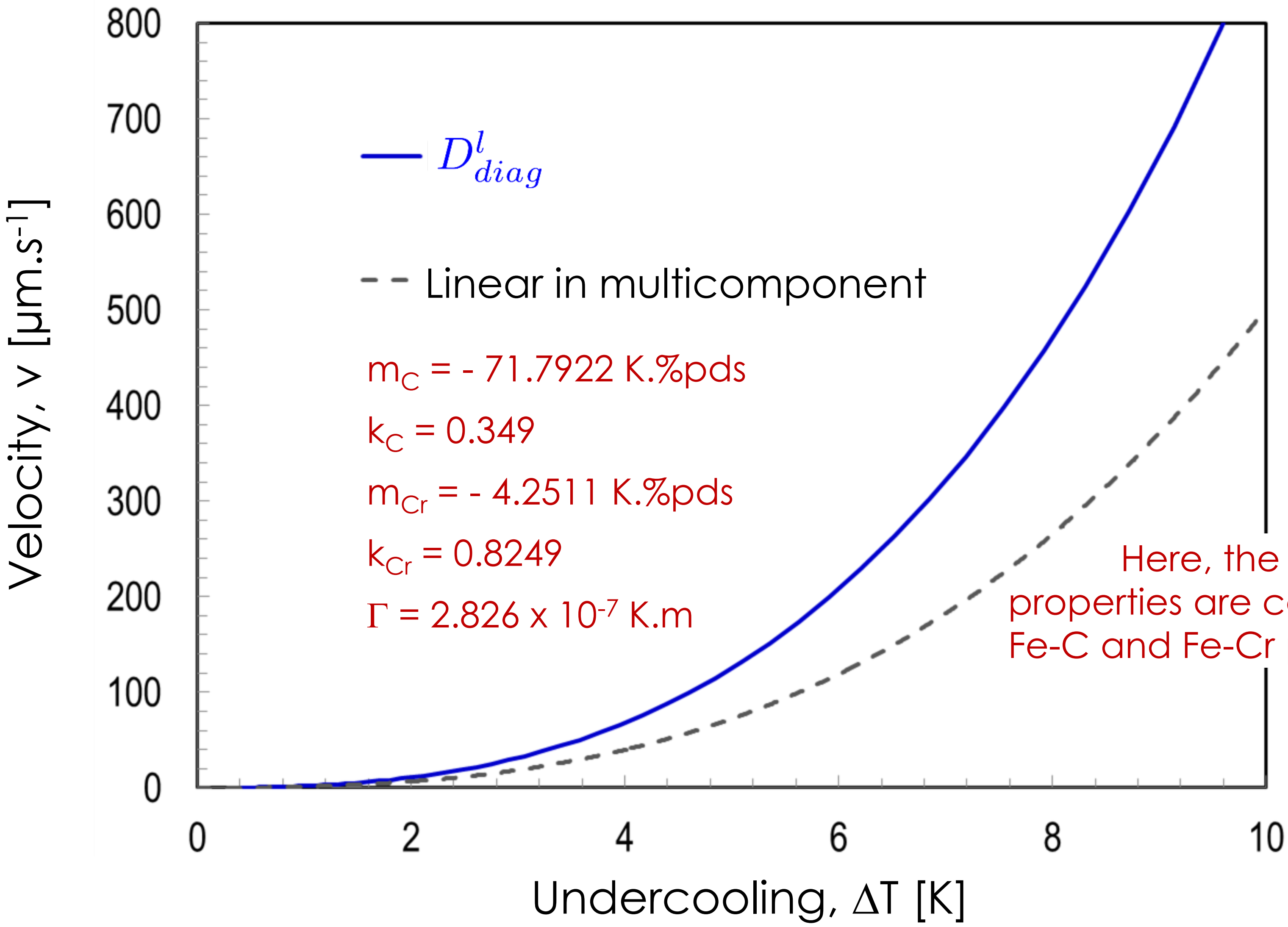
k_{Cr} = 0.782

Γ = 2.826 x 10^{-7} K.m

The phase diagram properties are computed at the liquidus temperature. The Gibbs Thomson coefficient is deduced from the PY\KIND simulation using the methodology previously presented on binary alloy.

PY\KIND VS. LINEARIZED SOLUTION

DENDRITE GROWTH KINETICS IN MULTICOMPONENT ALLOY / FE-1 WT% C-10WT% CR



Here, the thermodynamic properties are computed from the single Fe-C and Fe-Cr phase diagram

PY\KIND – OVERVIEW

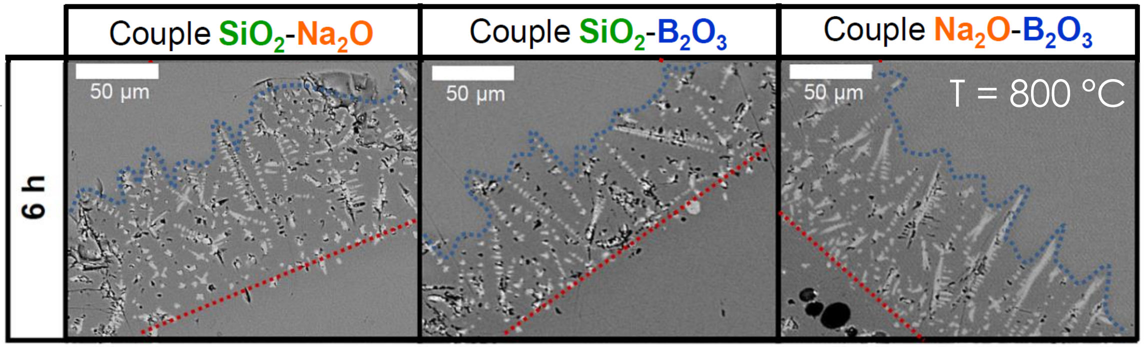
ADVANTAGES FOR COMPUTATION OF DENDRITE TIP GROWTH KINETICS

- Generalized approach applied for any alloy described with a CALPHAD database (*non restricted to a ternary system*)
- Large range of compositions and growth velocities can be assessed
- Efficient computation model
- Main dependencies with databases
  - Equilibrium compositions
  - Diffusion coefficients (Thermodynamic database – Dictra)
  - Solid/liquid interfacial energy

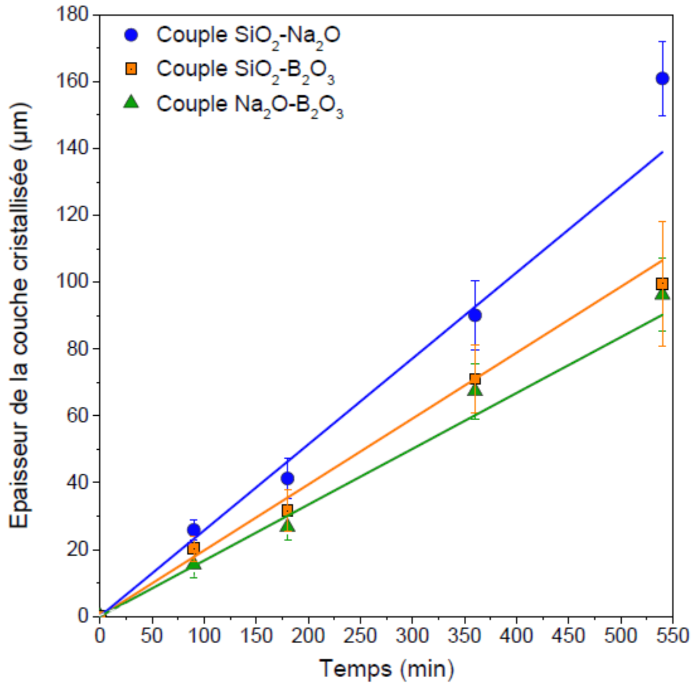
PY\KIND – Perspectives

Observations in $SiO_2 – Na_2O – B_2O_3$

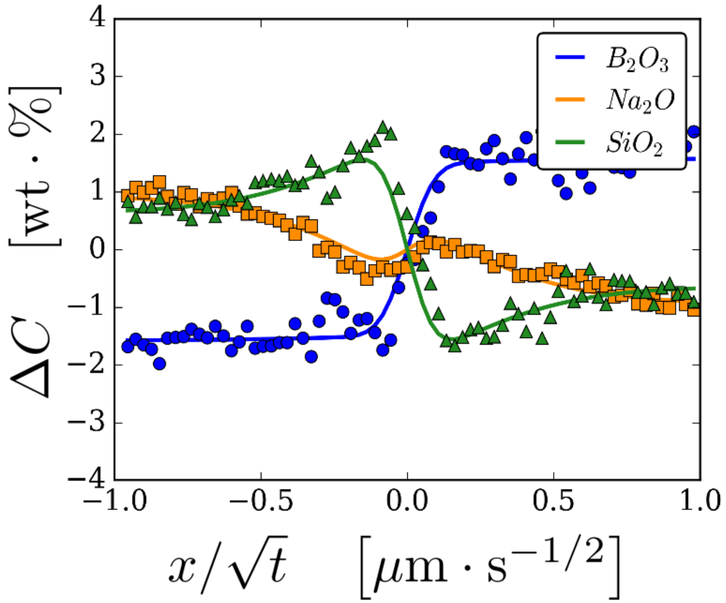
- Constant growth velocity of the cristobalite dendritic layer
- Known equilibrium data and diffusion matrix as a function of temperature and composition

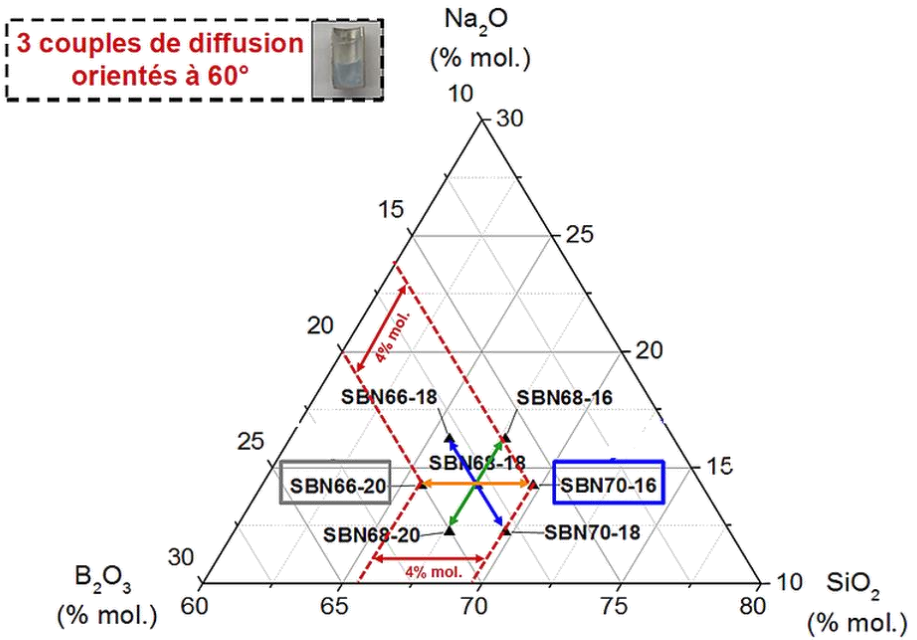


Evolution of the cristobalite dendritic layer for various diffusion couples



e.g. couple $Na_2O – B_2O_3$





PY\KIND – PERSPECTIVES

APPLICATIONS TO SiO_2 – Na_2O – B_2O_3

- Computation of growth kinetics associated to dendritic structures observed on cristobalite based on :
  - Equilibrium compositions ✓
  - Diffusion coefficients ✓
  - Cristobalite/glass interfacial energy **?**

- Investigation of temperature and solutal effects on interface evolutions for future experiments & simulations in borosilicate glasses !

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[The] TCFE6+MOBFE4, Thermo-Calc Database, Thermo-Calc Software AB

Merci de votre attention,

Questions ?