

Introduction to thermodynamics of phase transformations

Mechanical aspects

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Motivations

Motivations

Transformations at the solid state: ubiquitous in processes

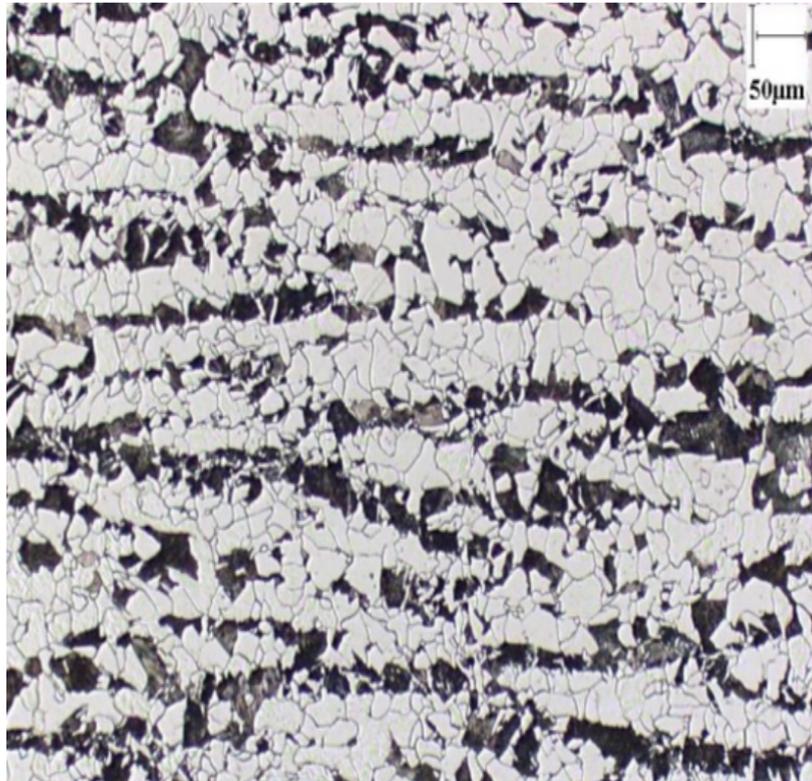
- Heat treatments
- Thermo-mechanical treatments
- Machining
- Additive manufacturing
- Surface treatments
- Hydride precipitation (storage, embrittlement)

Beyond processes: in alloy design (recycling), ageing (sustainability)

Motivations

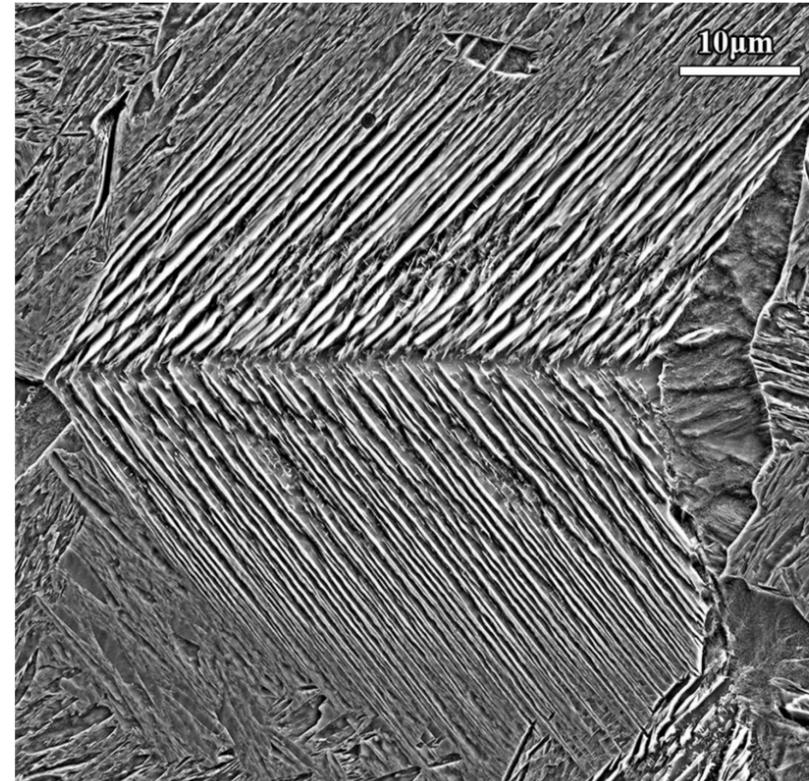
Transformations at the solid state: steels

Ferrite (Fe-C-Mn)



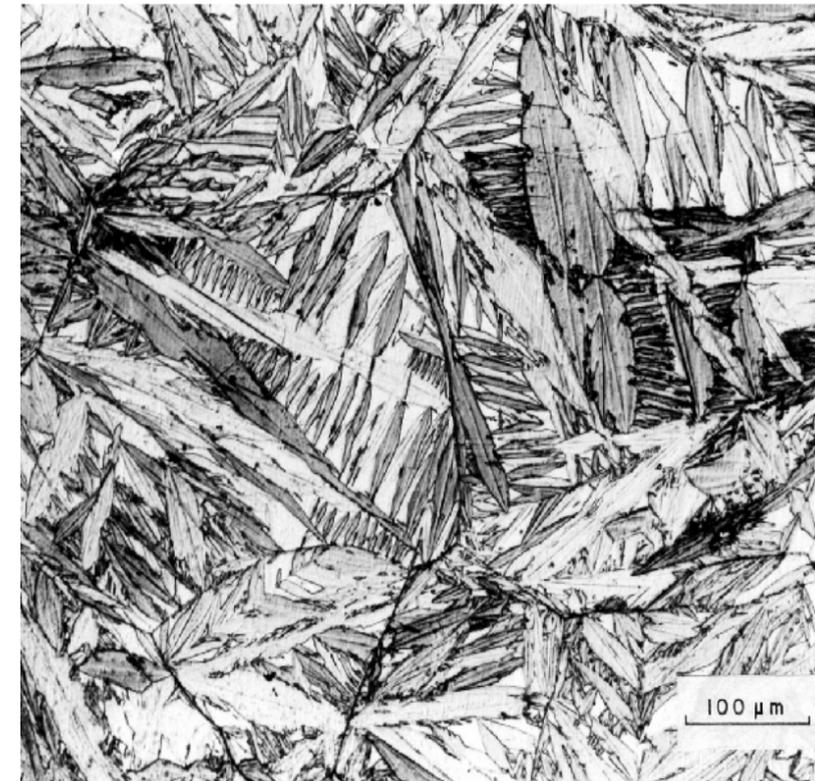
Gouné

Bainite (Fe-0.3C)



Yin, Hillert, and Borgenstam (2017)

Martensite (Fe-31Ni-0.002 C)

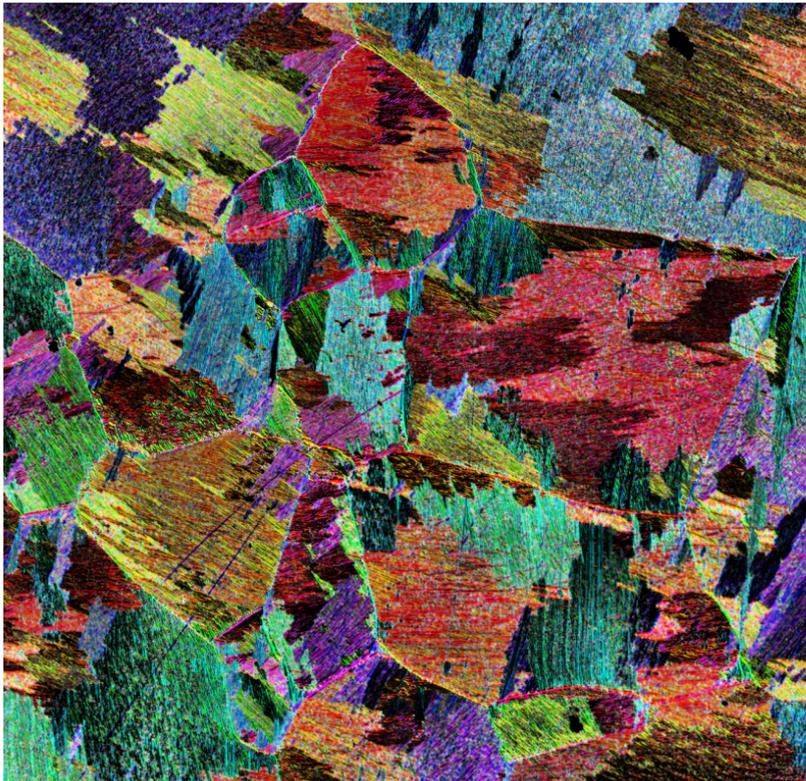


Guimarães and Rios (2015)

Motivations

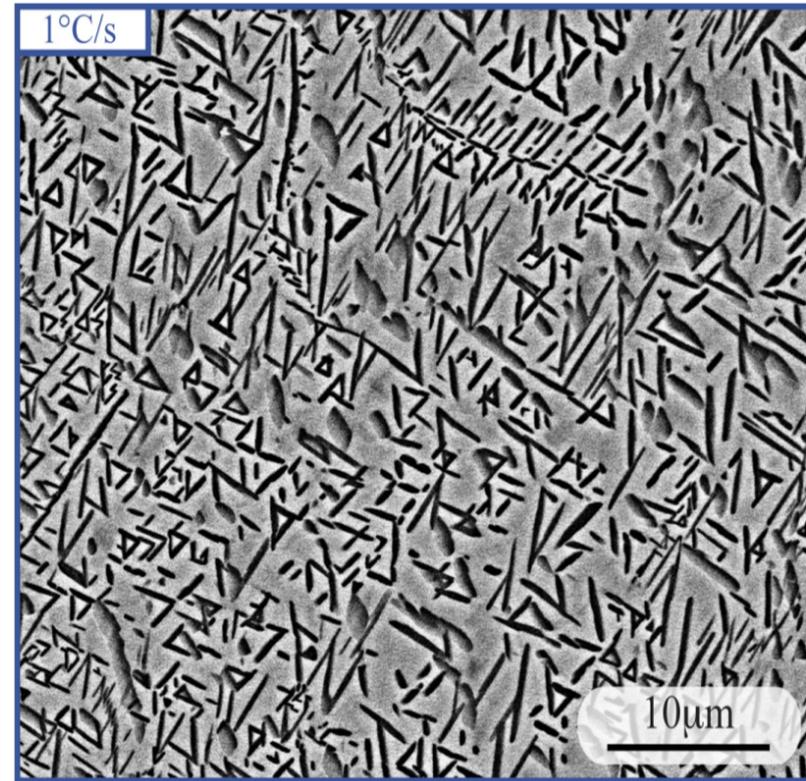
Transformations at the solid state: Ti alloys

Widmanstätten (Ti64)



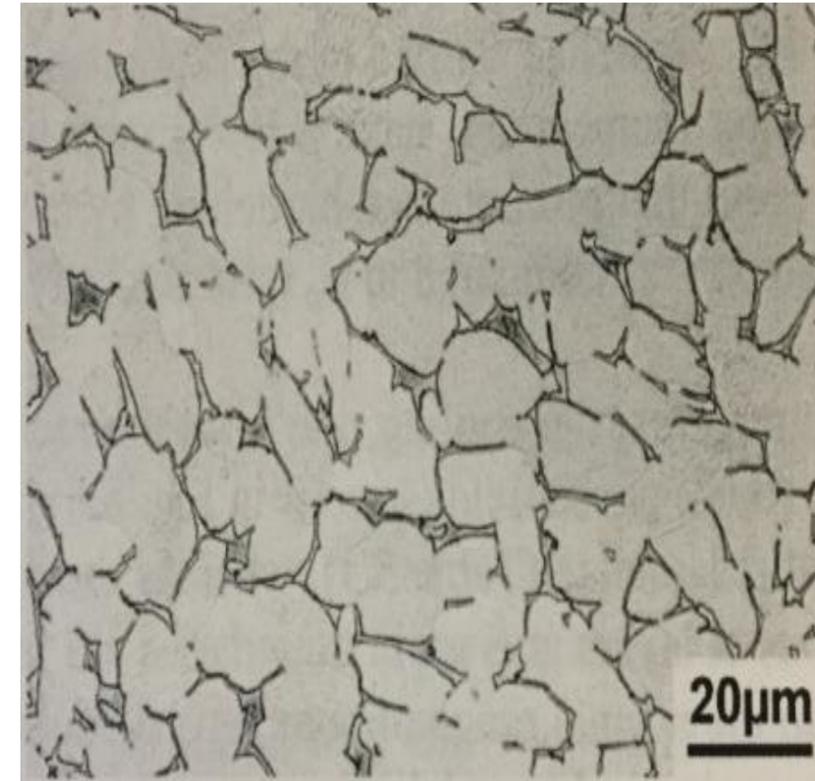
Denand (IJL)

Intragranular (Ti5553)



Settefrati (2012)

Globular (Ti6242)

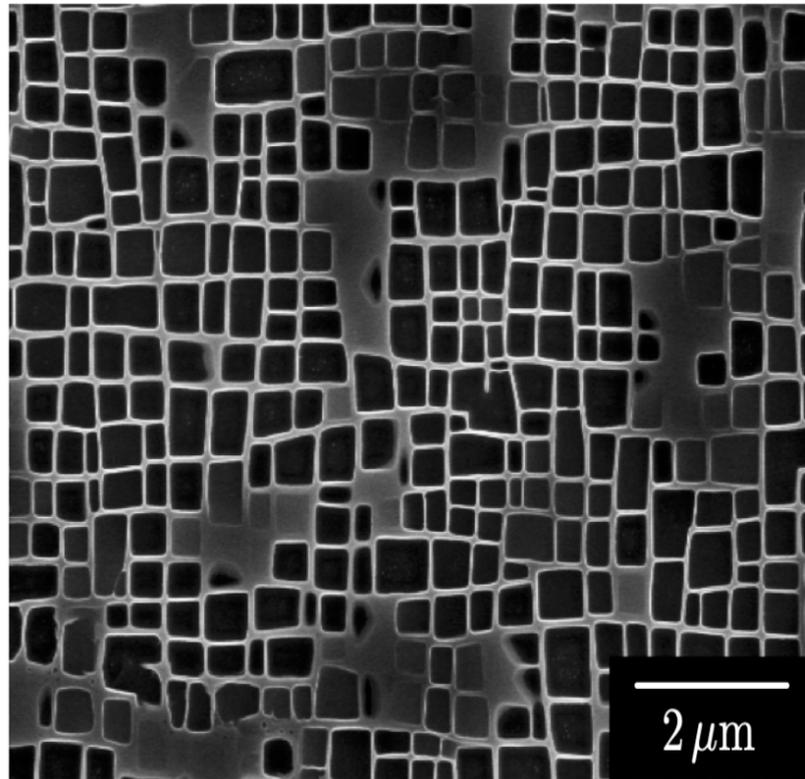


Lütjering and Williams (2003)

Motivations

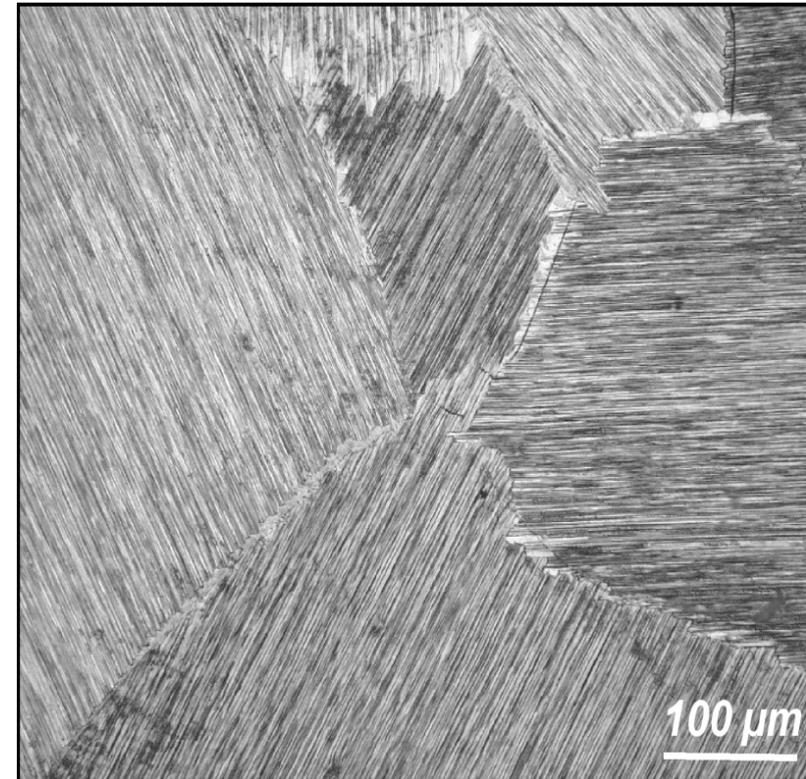
Transformations at the solid state: intermetallics and beyond

Ni-based superalloys



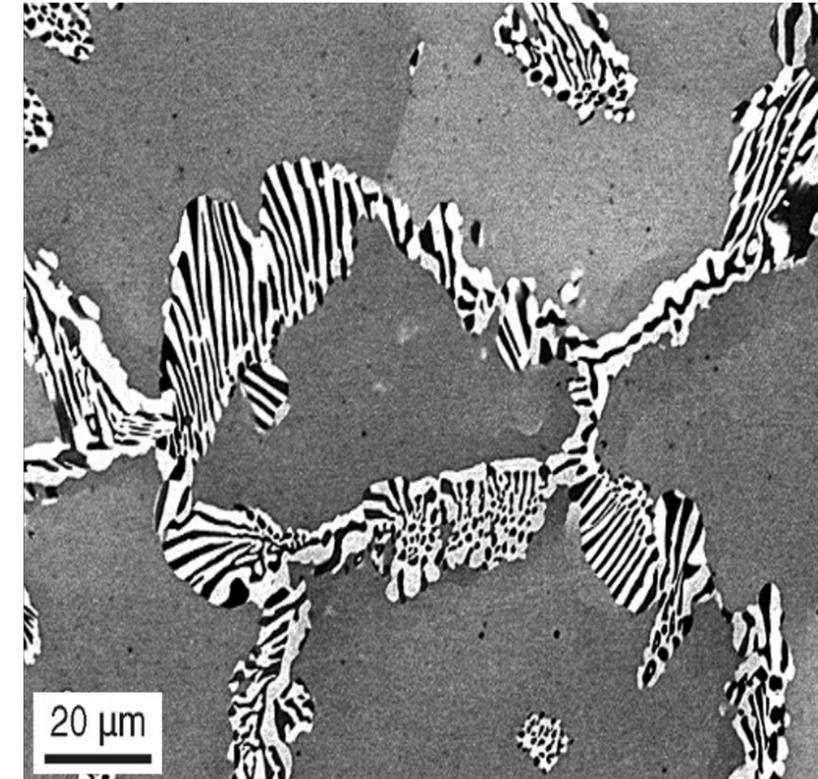
Diologent and Caron (2004)

Ti-Al



Charpentier, Hazotte, and Daloz (2008)

HEA



Poulain (ICMPE)

Motivations

Content

Basic thermodynamic concepts to investigate the role of mechanics on

1. Equilibrium
2. Interfaces
3. Kinetics
4. Morphologies

Many old but excellent (forgotten?) works

Equilibrium

Influence of stress on phase diagrams

Pure materials and displacive transformations



CuAlNi single crystal, from Sittner DoITPoMS, Univ. Cambridge

Influence of stress on phase diagrams

Pure materials and displacive transformations

Driving force for transforming: $\Delta G < 0 \implies T < T_{eq}$

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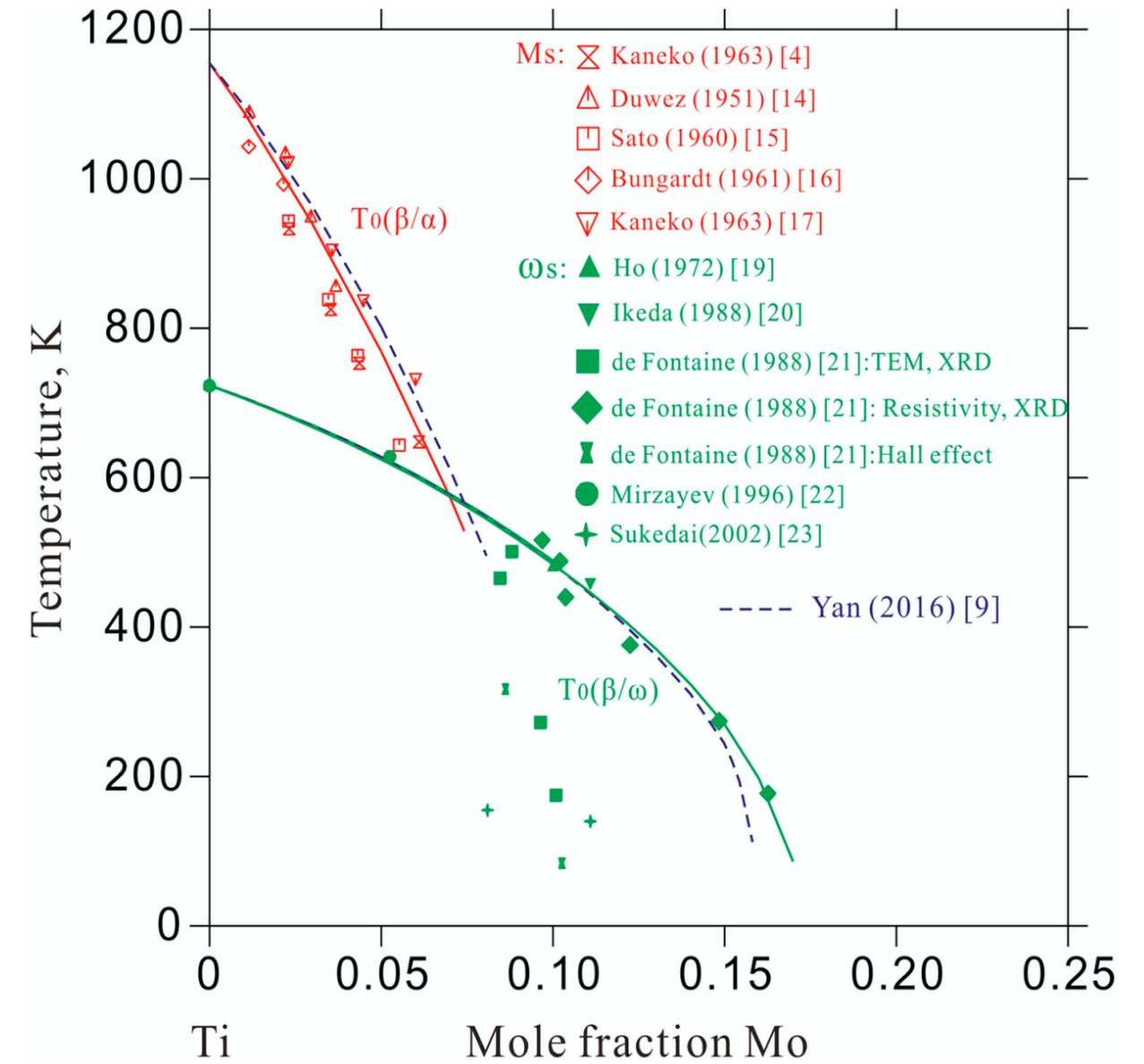
For alloys, T_{eq} is the T_0 temperature

Influence of stress on phase diagrams

Pure materials and displacive transformations

Driving force for transforming: $\Delta G < 0 \implies T < T_{eq}$

For alloys, T_{eq} is the T_0 temperature



ω phase in Ti-Mo Hu et al. (2018)

Influence of stress on phase diagrams

Pure materials and displacive transformations

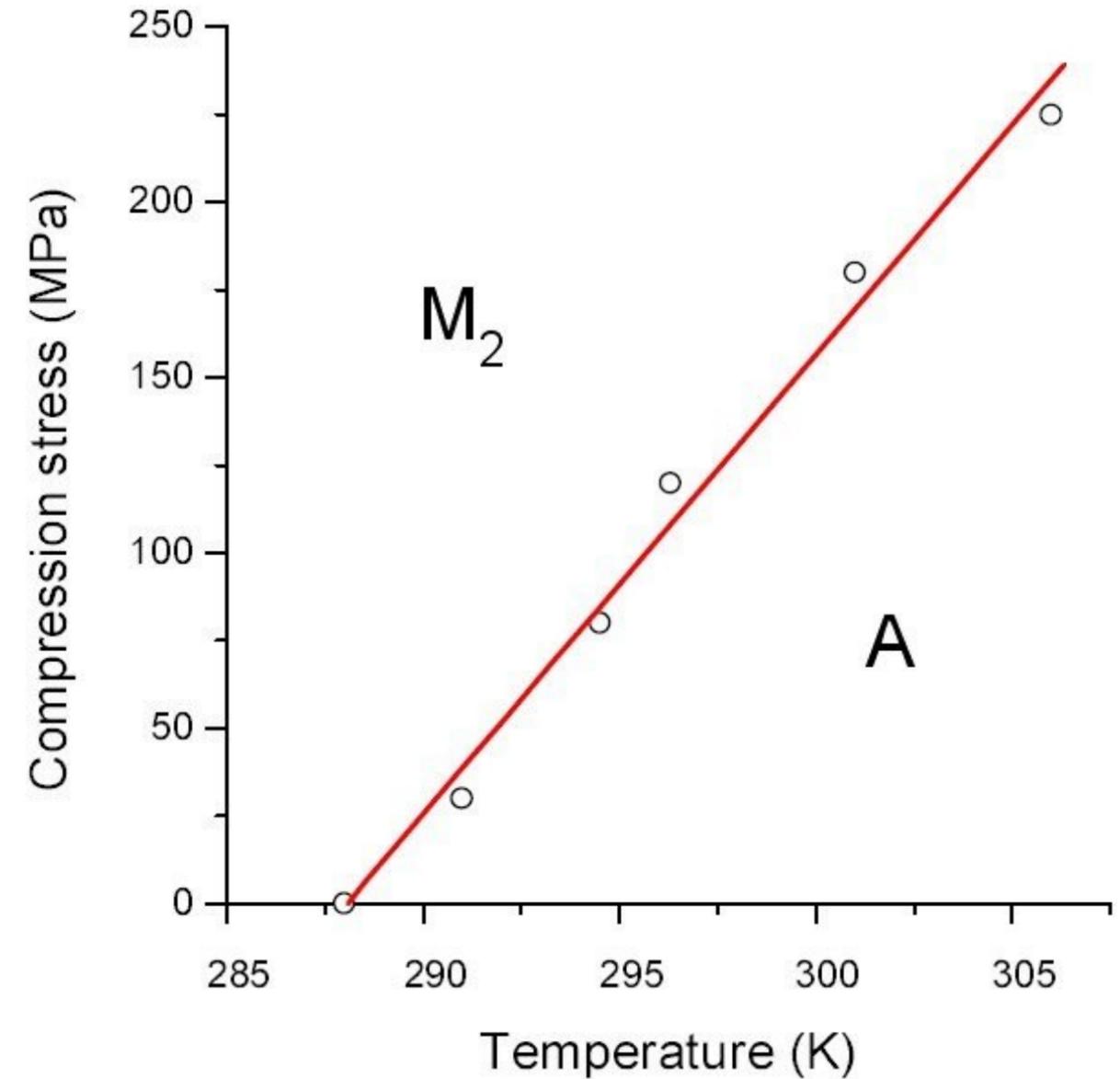
Driving force for transforming: $\Delta G < 0 \implies T < T_{eq}$

Influence of pressure

$$dg = -sdT + vdp$$

Clausius-Clapeyron

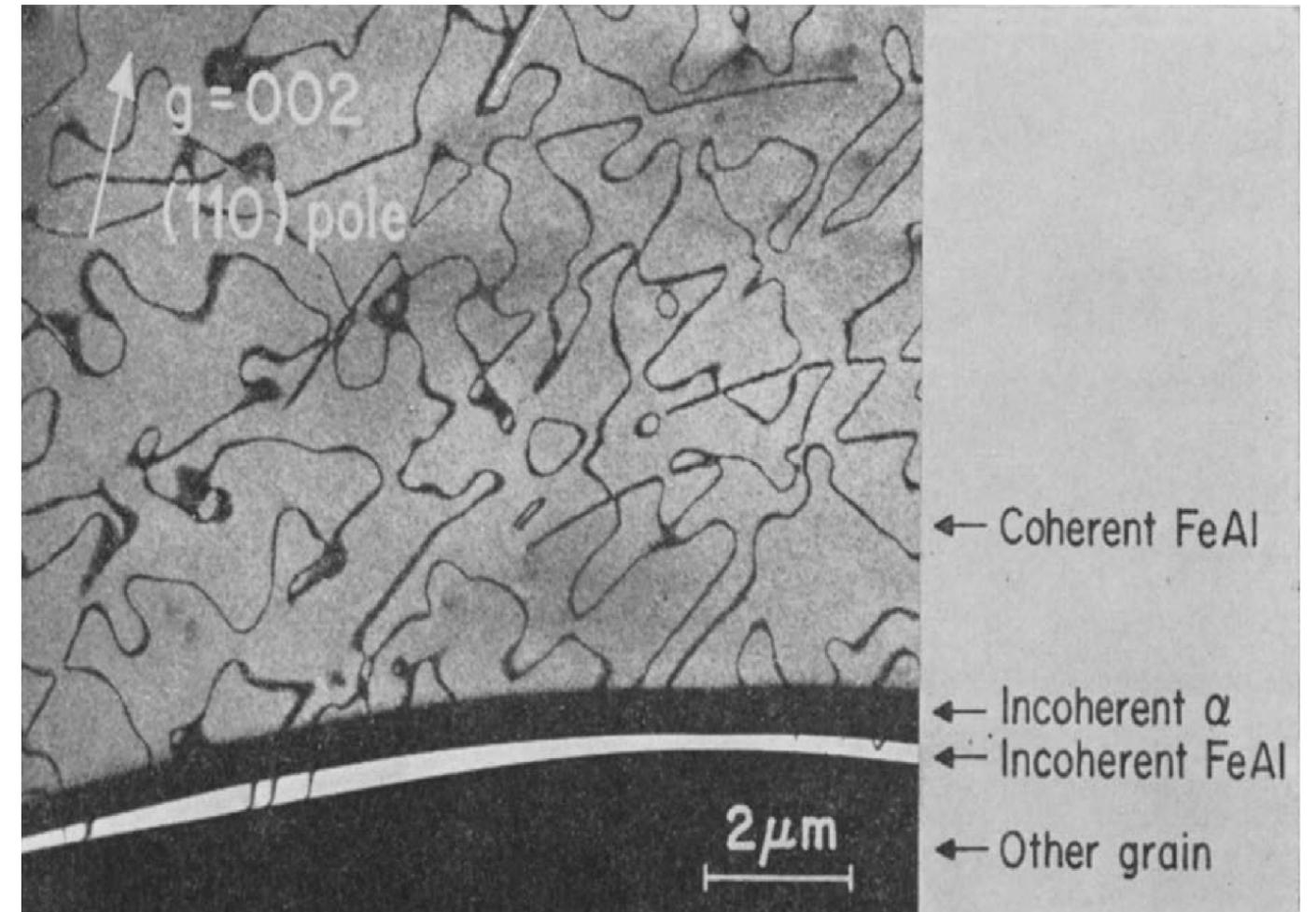
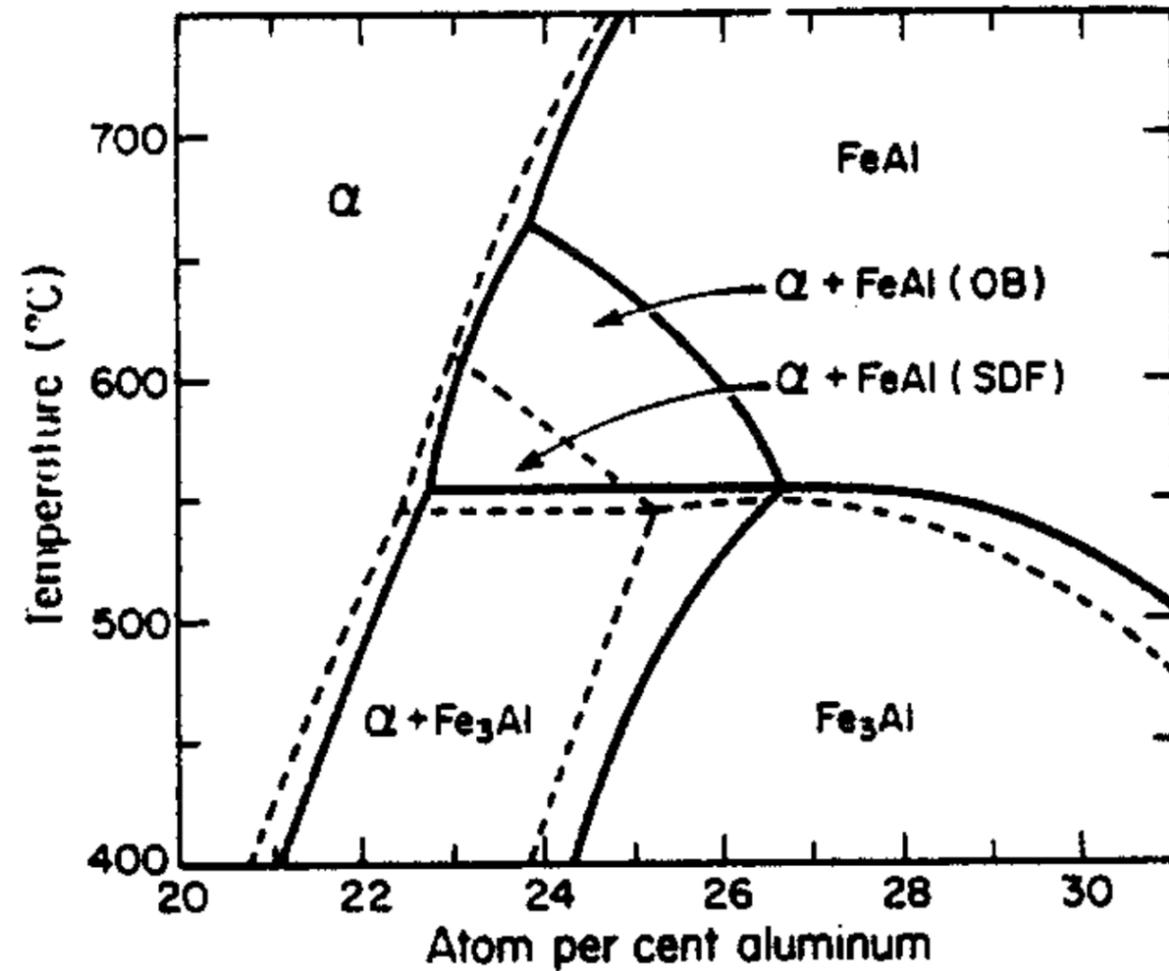
$$\left. \frac{dp}{dT} \right|_{eq} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T_{eq} \Delta v}$$



NiMnGa single crystal compressed along [110] [Chernenko and L'vov \(1999\)](#)

Influence of stress on phase diagrams

Diffusional (here ordering)



Allen and Cahn (1975)

Influence of stress on phase diagrams

We need simple estimates of stress and strain

In particular, should depend only on

- phase fractions
- concentrations, homogeneous in each phases

Rule out complex microstructures \implies simple microstructures

- laminates
- Eshelby ellipsoids

Indeed, simple strain and stress at least in one of the phase

Influence of stress on phase diagrams

Central concept: eigenstrain

Simplest case, much preferred in oldest works: isotropic

$$\varepsilon^\star = \varepsilon^0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- Relevant for some ordering of cubic phases (bcc \rightarrow B2, fcc \rightarrow L1₂)
- Used very often for austenite \rightarrow ferrite (although not the only contribution)

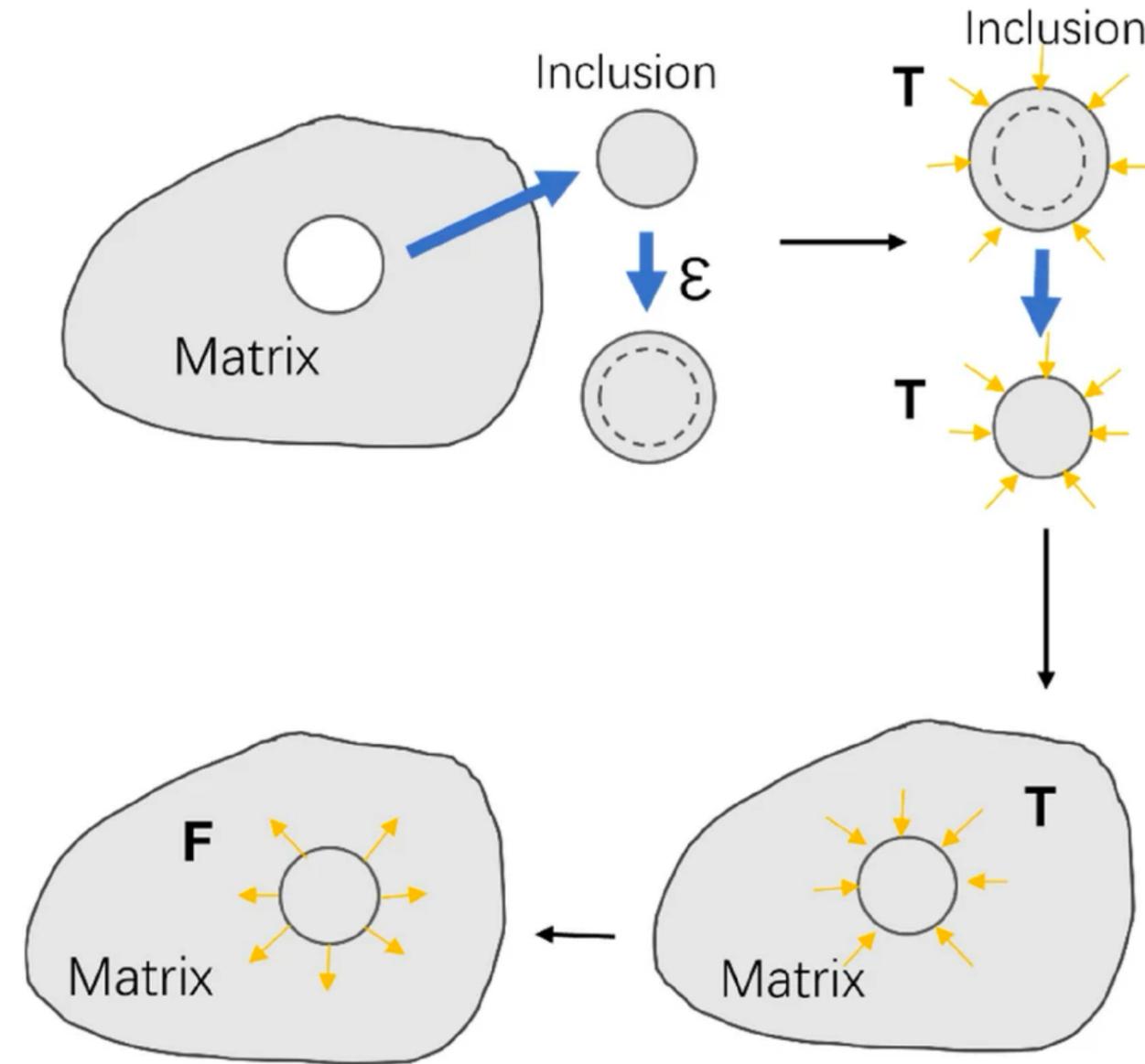


Influence of stress on phase diagrams

Inclusions

$$u_i(\vec{x}) = \int_{\Sigma} G_{il}(\vec{x} - \vec{x}') \sigma_{lk}^* n_k d\Sigma(\vec{x}')$$

with $\sigma_{ij}^* = C_{ijkl} \varepsilon_{kl}^*$



D. Li et al. (2022)

Influence of stress on phase diagrams

Inclusions

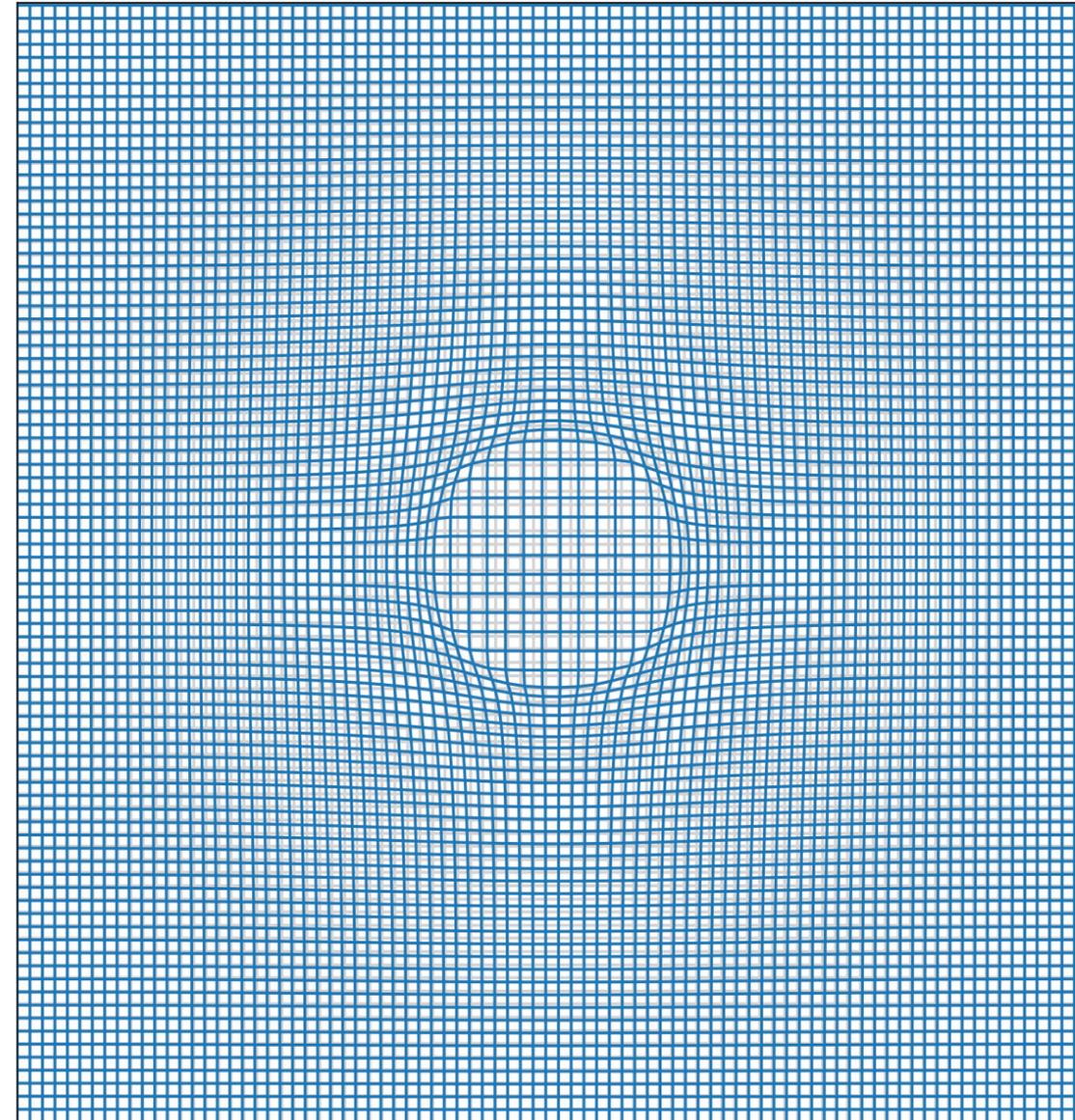
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The magic Eshelby solution

strain and stress homogeneous inside the inclusion!

$$\varepsilon_{ij}^p = S_{ijkl} \varepsilon_{kl}^{\star}$$



Influence of stress on phase diagrams

Inclusions

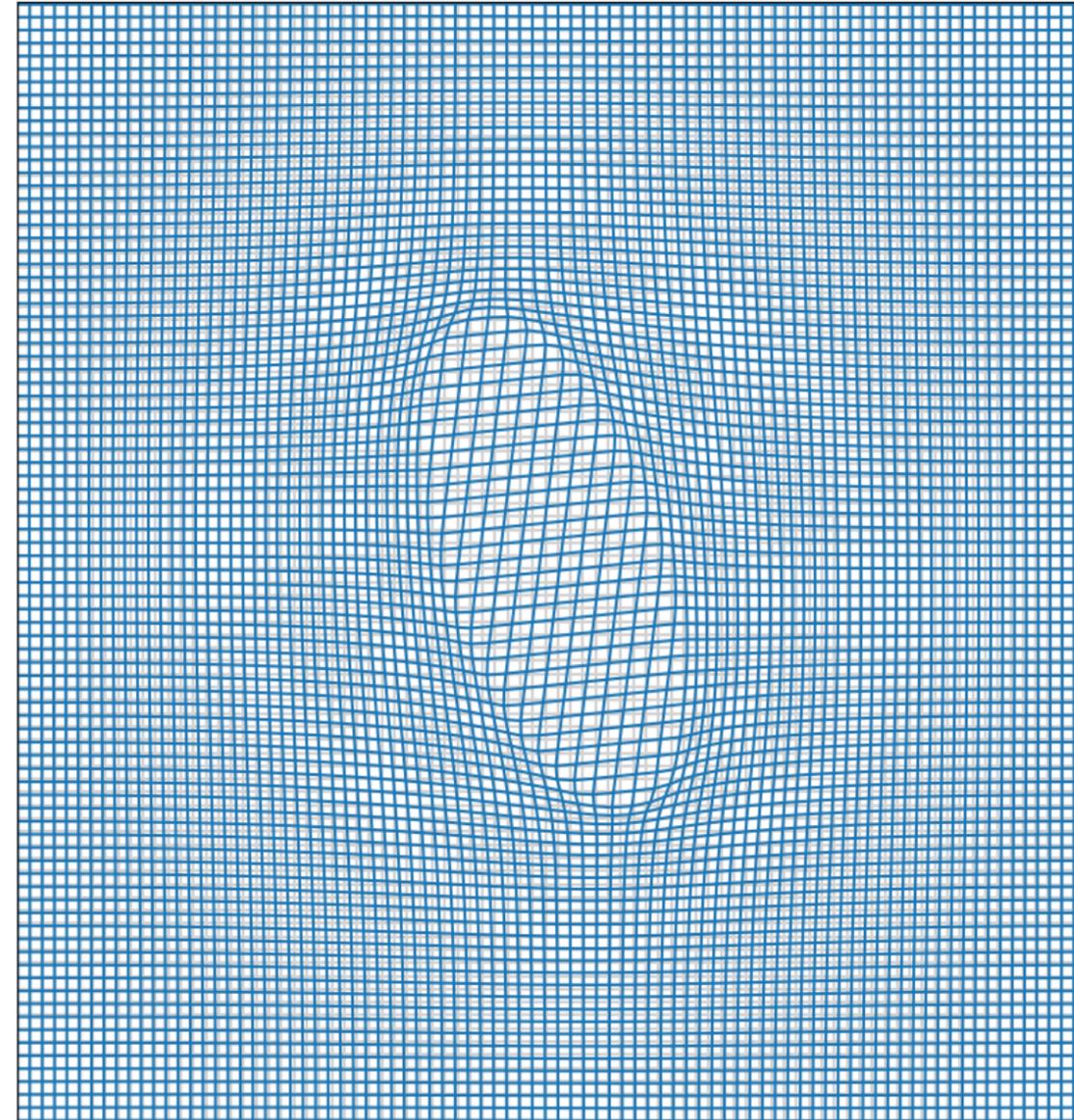
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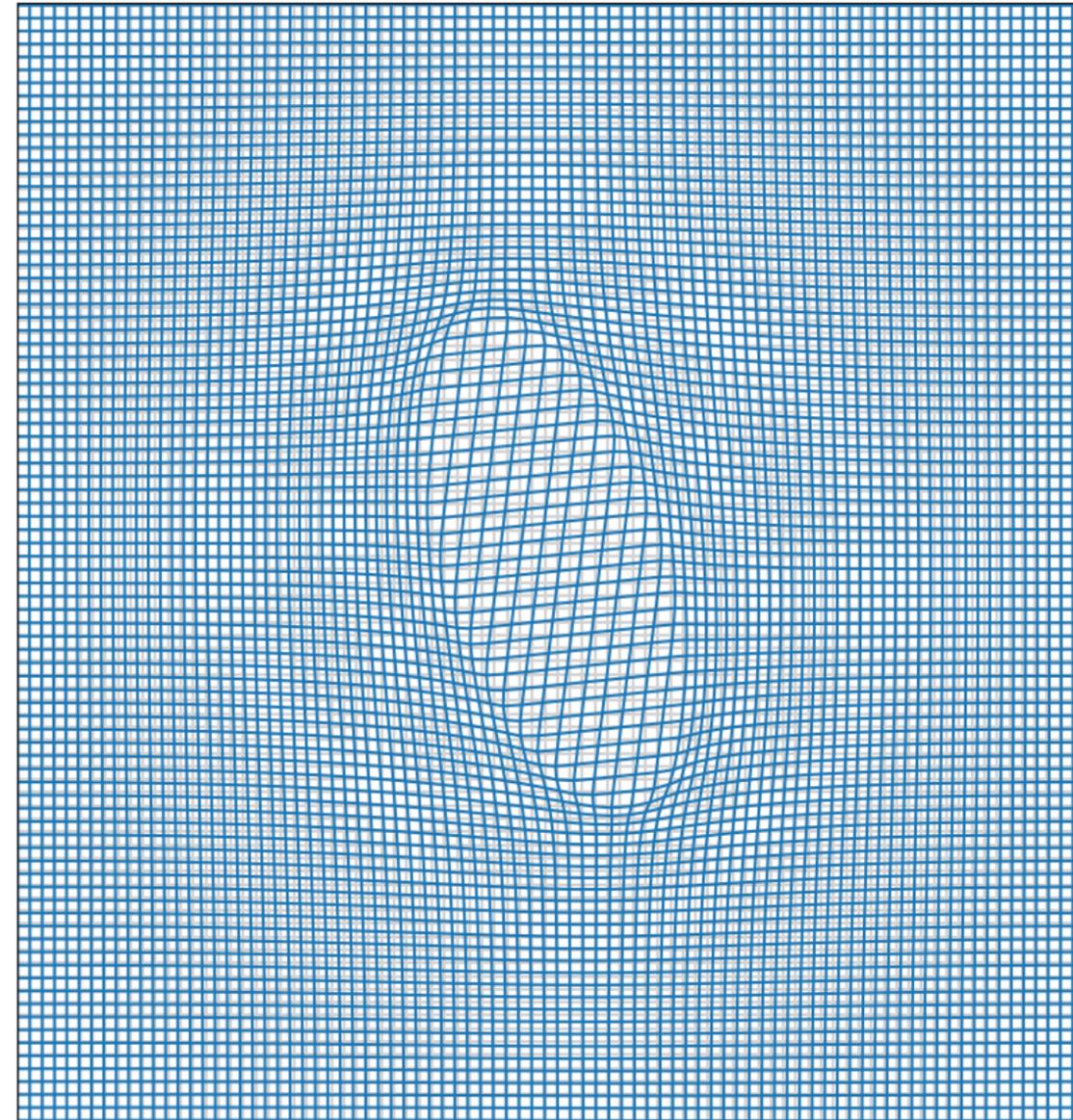
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Elastic energy

$$E_{\text{el}} = \frac{1}{2} \int_V \sigma_{ij} \varepsilon_{ij}^e dV = - \frac{1}{2} \int_{V_0} \sigma_{ij} \varepsilon_{ij}^{\star} dV = - \frac{V_0}{2} \sigma_{ij} \varepsilon_{ij}^{\star}$$



Influence of stress on phase diagrams

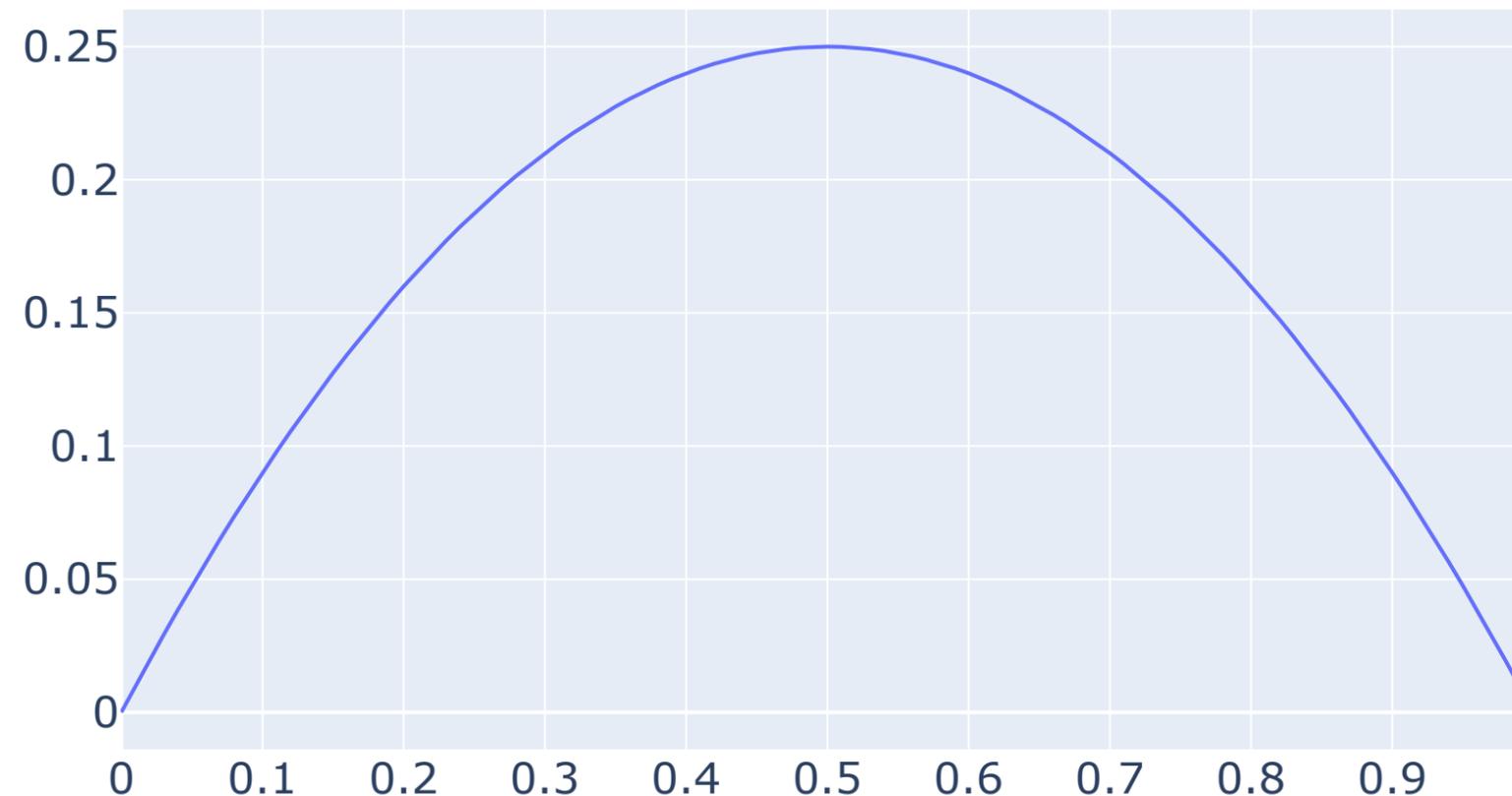
Elastic energy versus phase fraction

Bitter-Crum theorem e.g. [Fratzl, Penrose, and Lebowitz \(1999\)](#) or [Khachaturyan \(1983\)](#)

- homogeneous elastic constants
- homogeneous eigenstrain
- infinite system (vanishing average stress)
- isostropic ε^\star

$$f_{\text{el}} = z(1 - z) \frac{E}{1 - \nu} (\varepsilon^0)^2$$

It does not depend on the pattern, only on the phase fraction



Influence of stress on phase diagrams

Common tangent construction = constrained minimization of f

$$f = zf^\alpha(x) + (1 - z)f^\beta(y)$$

$$L = f - \lambda (w - zx - (1 - z)y)$$

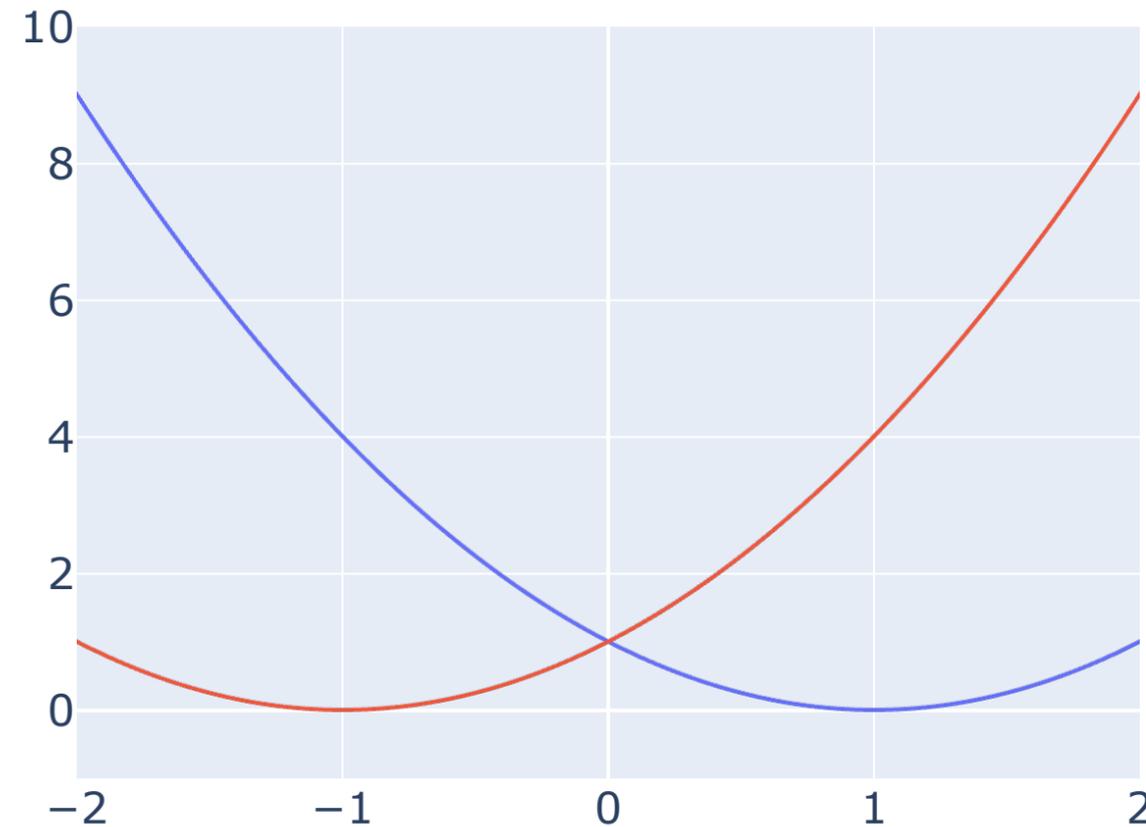
Extremize $\implies \delta L = 0$

$$\frac{\partial L}{\partial x} = 2(1 - x)z - \lambda z = 0$$

$$\frac{\partial L}{\partial y} = 2(1 + y)(1 - z) + \lambda(1 - z) = 0$$

$$\frac{\partial L}{\partial z} = (1 - x)^2 - (1 + y)^2 + \lambda(x - y) = 0$$

$$\frac{\partial L}{\partial \lambda} = w - zx - (1 - z)y = 0$$



The result does not depend on the nominal concentration in binary alloys because it is linear with respect to z

Influence of stress on phase diagrams

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Extremize $\implies \delta L = 0$

$$\lambda = 2(1 - x)$$

$$\lambda = 2(1 + y)$$

$$\lambda = 0$$

$$z = \frac{1}{2} + \frac{w}{2}$$

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Influence of stress on phase diagrams

Common tangent construction = constrained minimization of f

$$f = zf^{\alpha}(x) + (1 - z)f^{\beta}(y)$$

$$L = f - \lambda (w - zx - (1 - z)y)$$

Extremize $\implies \delta L = 0$

$$x = +1$$

$$y = -1$$

$$z = \frac{1}{2} + \frac{w}{2}$$

$$\lambda = 0$$

The result does not depend on the nominal concentration in binary alloys because it is linear with respect to z

Influence of stress on phase diagrams

What happens when elasticity is accounted for?

Williams (1984) Cahn and Larché (1984)

$$f = z f^\alpha(x) + (1 - z) f^\beta(y) + f_{el}(z)$$

$$L = f - \lambda (w - zx - zy)$$

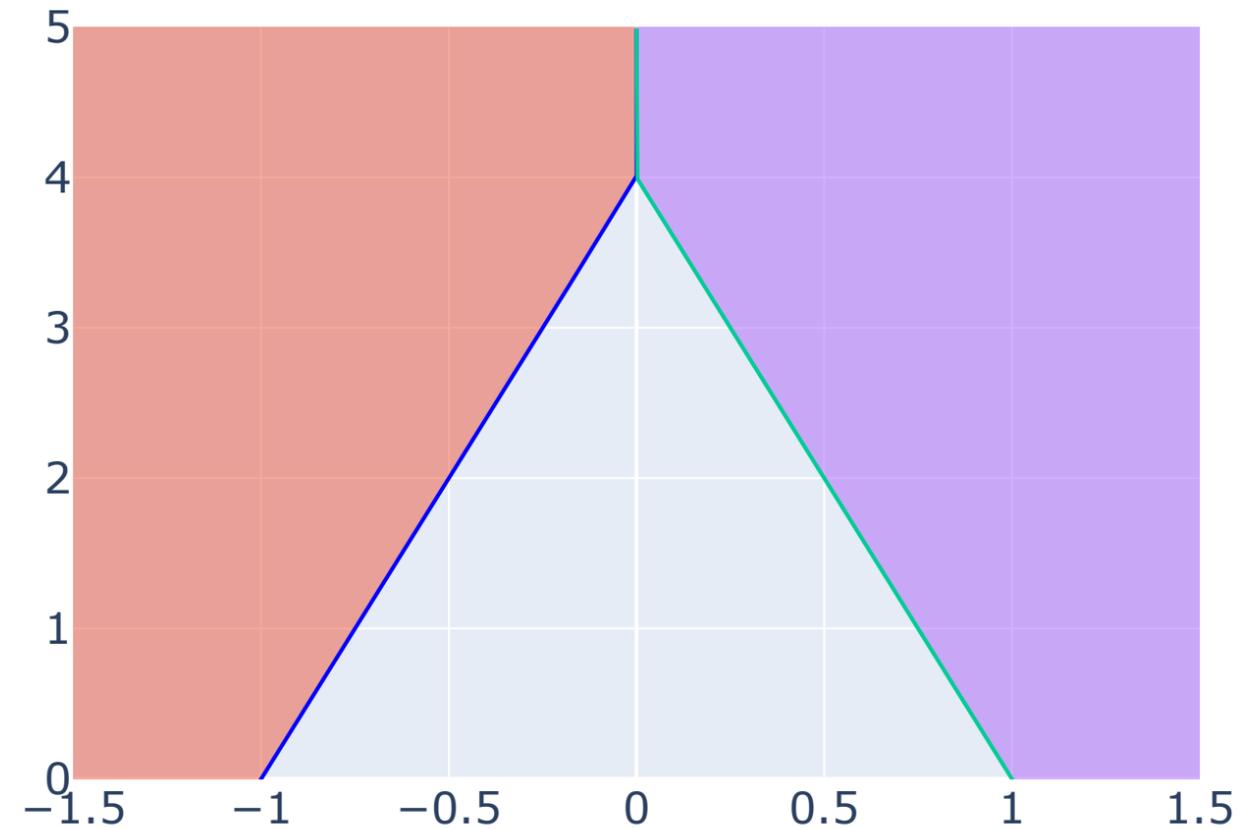
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$$\frac{\partial L}{\partial z} = (1 - x)^2 - (1 + y)^2 + \lambda(x - y) + A(1 - 2z) = 0$$

$$\frac{\partial L}{\partial \lambda} = w - zx - (1 - z)y = 0$$



Influence of stress on phase diagrams

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$$f = z f^\alpha(x) + (1 - z) f^\beta(y) + f_{el}(z)$$

$$L = f - \lambda (w - zx - zy)$$

Extremize $\implies \delta L = 0$

$$z = \frac{1}{2} + \frac{2w}{4 - A}$$

$$x = +1 - \frac{Aw}{4 - A}$$

$$y = -1 - \frac{Aw}{4 - A}$$

Influence of stress on phase diagrams

Questions/issues (personal opinion)

- Are the effects really significant?
- Should we throw out the low temperature parts of phase diagrams?
- Are the rules to read the phase diagrams no longer relevant?
- Is CalPhaD the Alpha and Omega of alloy design?
- Does annealing really remove all these effects?

Issues rising again with HEA (e.g. [Lass \(2022\)](#))

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Beyond (before) the phase diagrams

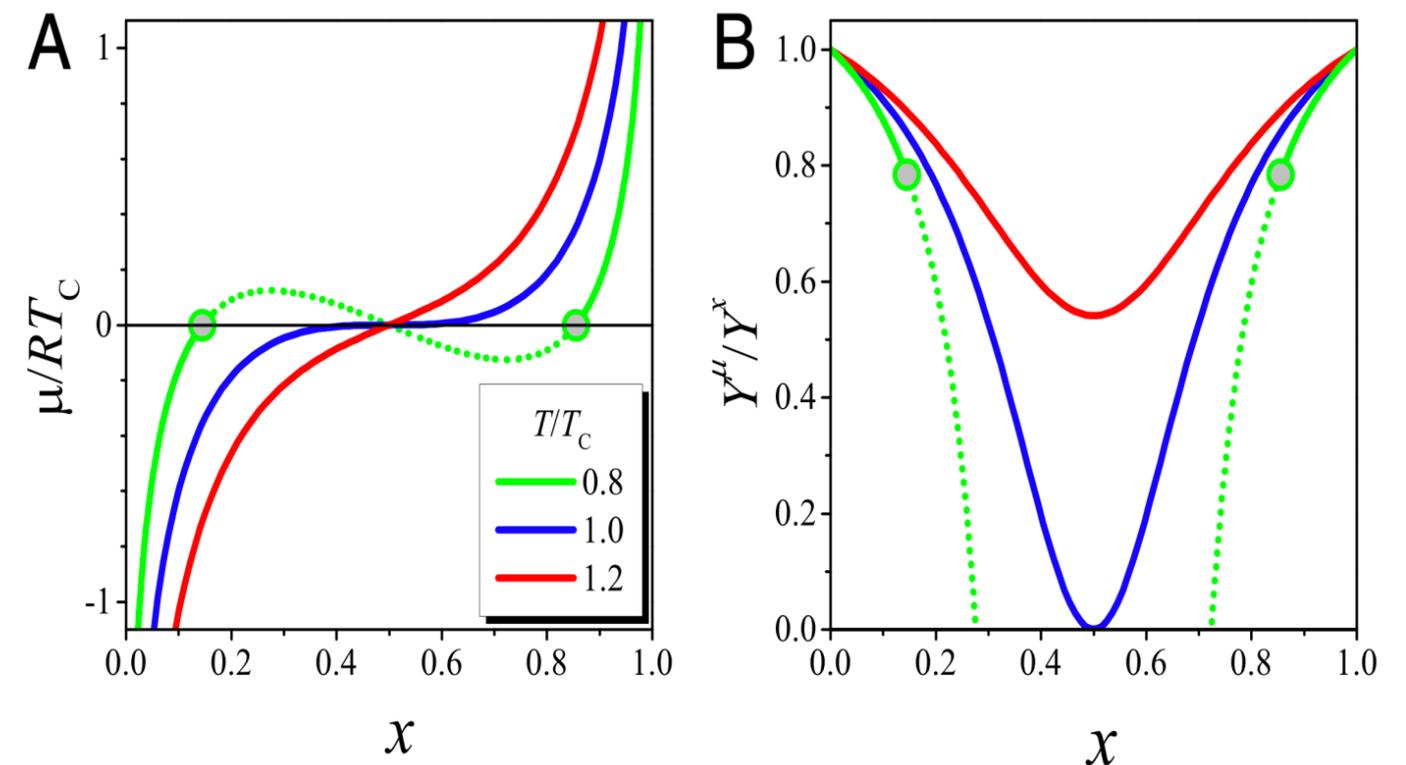
Open system elasticity Larché and Cahn (1985)

Verifying Larché–Cahn elasticity, a milestone of 20th-century thermodynamics

[Shi, Markmann, and Weissmuller \(2018\)](#)

$$G^\mu = G^c$$

$$E^\mu = \frac{E^c}{1 + \chi\eta^2 E^c}$$



Interfaces

Influence of stress on interfaces

Dislocation emission from an austenite lath growing in a ferrite matrix [Du, Momprou, and Zhang \(2017\)](#)

Influence of stress on interfaces

Variational calculation of Larché and Cahn (1978) see also Voorhees and Johnson (2004)

Insulated system with 2 phases containing 2 substitutional species joined at a coherent interface

Minimize (everything in the reference frame)

$$E = \int_{V^\alpha} e^\alpha(F^\alpha, s^\alpha, c_A^\alpha, c_B^\alpha) dV + \int_{V^\beta} e^\beta(F^\beta, s^\beta, c_A^\beta, c_B^\beta) dV + \int_{\Sigma} e^\Sigma(s^\Sigma) d\Sigma$$

constrained by:

- constant total entropy (insulated system) $S = \int_{V^\alpha} s^\alpha dV + \int_{V^\beta} s^\beta dV + \int_{\Sigma} s^\Sigma d\Sigma$
- constant numbers of A and B atoms (no interface segregation) $N_i = \int_{V^\alpha} c_i^\alpha dV + \int_{V^\beta} c_i^\beta dV$

Lagrangian to extremize

$$\delta L = \delta E - \theta \delta S - \mu_A \delta N_A - \mu_B \delta N_B = 0$$

with θ , μ_A and μ_B Lagrange multipliers

Influence of stress on interfaces

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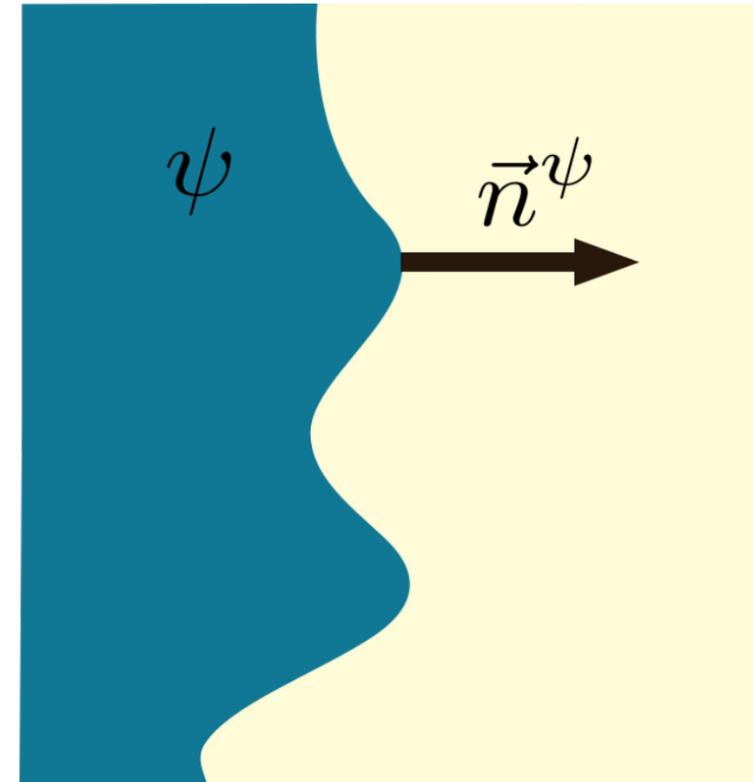
For any Λ and ψ

$$\delta A^\psi = \int_{V^\psi} \delta a^\psi dV + \int_{\Sigma} a^\psi \delta y^\psi d\Sigma$$

For the interface Σ

$$\delta A^\Sigma = \int_{\Sigma} \delta a^\Sigma d\Sigma + \int_{\Sigma} a^\Sigma 2\bar{\kappa} \delta y^\beta d\Sigma$$

for β convex



$$\delta y^\psi = \delta \vec{y}^\psi \cdot \vec{n}^\psi$$

Influence of stress on interfaces

Variational calculation of Larché and Cahn (1978) see also Voorhees and Johnson (2004)

First variation of internal energy (any phase)

$$\delta e^\psi = \theta^\psi \delta s^\psi + T_{ij}^\psi \delta F_{ij}^\psi + M_{AV}^\psi \delta c_A^\psi + M_{BV}^\psi \delta c_B^\psi$$

$$\delta e^\Sigma = \theta^\Sigma \delta s^\Sigma$$

- where diffusion of A and B is mediated by vacancies V
- where the Gibbs dividing surface eliminates $\partial e^\Sigma / \partial \kappa_i$

The mechanical work can be integrated by parts

$$\int_{V^\psi} T_{ij}^\psi \delta F_{ij}^\psi dV = \int_{\Sigma} T_{ij} \delta u_i n_j d\Sigma - \int_{V^\psi} \frac{\partial T_{ij}}{\partial x_j} \delta u_i dV$$

Influence of stress on interfaces

Variational calculation of Larché and Cahn (1978) see also Voorhees and Johnson (2004)

Putting all together and because all variations are independent

$$0 = \int_{V^\psi} dV \left[(\theta^\psi - \theta) \delta s^\psi + (M_{AV}^\psi - \mu_A) \delta c_A^\psi + (M_{BV}^\psi - \mu_B) \delta c_B^\psi - T_{ij,j}^\psi \delta u_i^\psi \right]$$

$$0 = \int_{\Sigma} d\Sigma (\theta^\Sigma - \theta) \delta s^\Sigma$$

$$0 = \int_{\Sigma} d\Sigma \left[\omega^\alpha \delta y^\alpha + \omega^\beta \delta y^\beta + 2\bar{\kappa} \gamma \delta y^\beta + T_{ij}^\alpha n_j^\alpha \delta u_i^\alpha + T_{ij}^\beta n_j^\beta \delta u_i^\beta \right]$$

with grand potentials $\omega^\psi = e - \theta s^\psi - \mu_A c_A^\psi - \mu_B c_B^\psi$ and interface energy $\gamma = e^\Sigma - \theta^\Sigma$

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with grand potentials $\omega^\psi = e - \theta s^\psi - \mu_A c_A^\psi - \mu_B c_B^\psi$ and interface energy $\gamma = e^\Sigma - \theta^\Sigma$

Usual equilibrium conditions

$$\theta^\alpha = \theta^\beta = \theta^\Sigma = \theta$$

$$M_{AV}^\alpha = M_{AV}^\beta = \mu_A$$

$$M_{BV}^\alpha = M_{BV}^\beta = \mu_B$$

$$\frac{\partial T_{ij}^\psi}{\partial x_j} = 0 \quad \forall \psi$$

Influence of stress on interfaces

Variational calculation of Larché and Cahn (1978) see also Voorhees and Johnson (2004)

At the interface

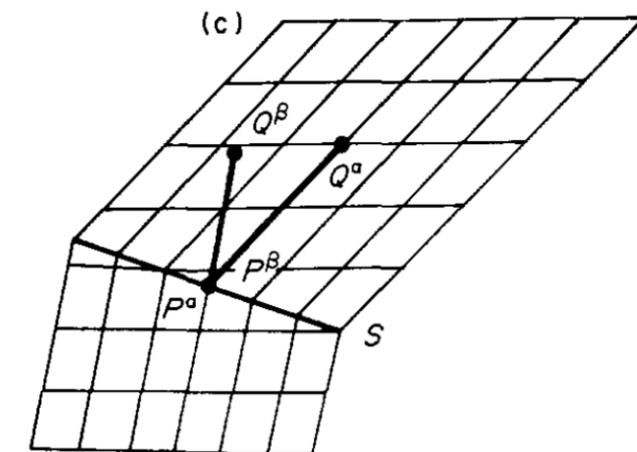
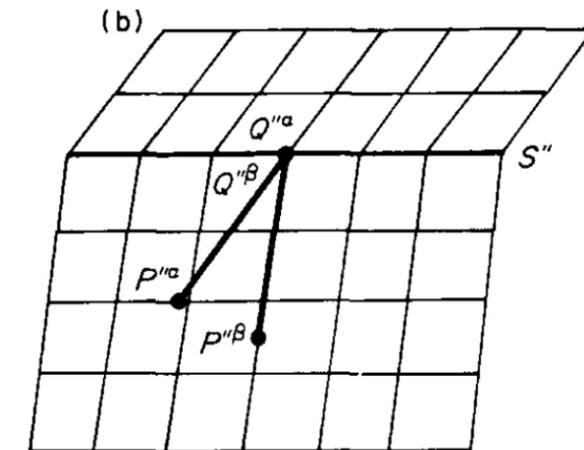
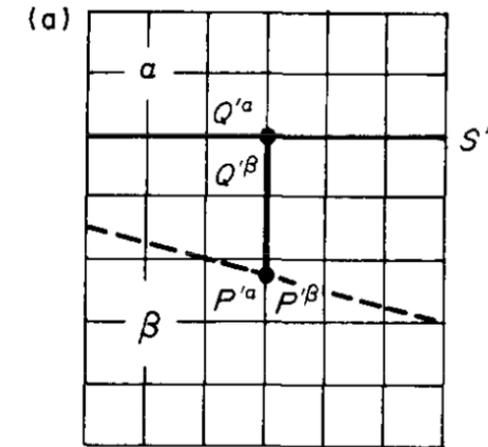
$$0 = \int_{\Sigma} d\Sigma \left[\omega^{\alpha} \delta y^{\alpha} + \omega^{\beta} \delta y^{\beta} + 2\bar{\kappa} \gamma \delta y^{\beta} + T_{ij}^{\alpha} n_j^{\alpha} \delta u_i^{\alpha} + T_{ij}^{\beta} n_j^{\beta} \delta u_i^{\beta} \right]$$

- We have $\delta y^{\alpha} = -\delta y^{\beta}$
- and the $\delta \vec{u}^{\psi}$ are not independent

For a coherent interface $\delta u_i^{\alpha} = \delta u_i^{\beta} + \left(F_{ij}^{\beta} - F_{ij}^{\alpha} \right) n_j^{\beta} \delta y^{\beta}$

$$0 = \int_{\Sigma} d\Sigma \left[T_{ij}^{\alpha} n_j^{\alpha} + T_{ij}^{\beta} n_j^{\beta} \right] \delta u_i^{\alpha}$$

$$0 = \int_{\Sigma} d\Sigma \left[\omega^{\beta} - \omega^{\alpha} + T_{ij}^{\alpha} n_j^{\alpha} \left(F_{ik}^{\beta} - F_{ik}^{\alpha} \right) n_k^{\beta} + 2\bar{\kappa} \gamma \right] \delta y^{\beta}$$



Influence of stress on interfaces

Variational calculation of Larché and Cahn (1978) see also Voorhees and Johnson (2004)

Finally

$$T_{ij}^{\alpha} n_j^{\beta} = T_{ij}^{\beta} n_j^{\beta}$$
$$\omega^{\beta} - \omega^{\alpha} - T_{ij}^{\beta} n_j^{\beta} \left(F_{ik}^{\beta} - F_{ik}^{\alpha} \right) n_k^{\beta} + 2\bar{\kappa} \gamma = 0$$

Small strain version

$$\sigma_{ij}^{\alpha} n_j^{\beta} = \sigma_{ij}^{\beta} n_j^{\beta}$$
$$\omega^{\beta} - \omega^{\alpha} - \sigma_{ij}^{\beta} \left(\varepsilon_{ij}^{\beta} - \varepsilon_{ij}^{\alpha} \right) + 2\bar{\kappa} \gamma = 0$$

- The grand potential contains the elastic energy
- Extra energy required to keep coherency upon accretion

Influence of stress on interfaces

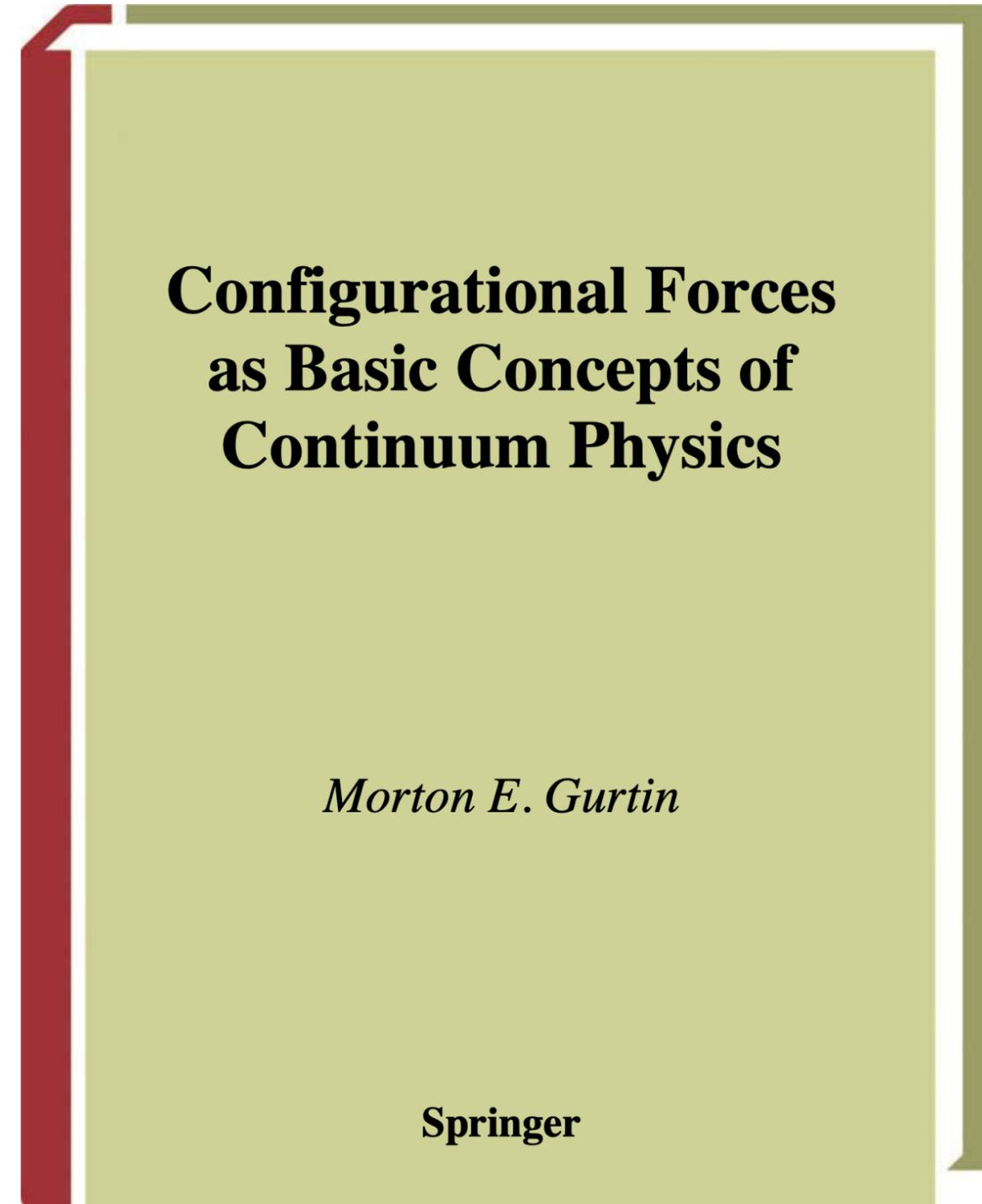
Beyond variational calculations

1. In fact $\omega\delta_{ij} - F_{ki}T_{kj}$ is the energy-momentum Eshelby tensor (Peach-Koehler, J integral) \implies configurational mechanics

Read [Gurtin and Voorhees \(1996\)](#), [Gurtin \(2000\)](#), [Maugin \(2011\)](#) and [Fischer et al. \(2008\)](#)

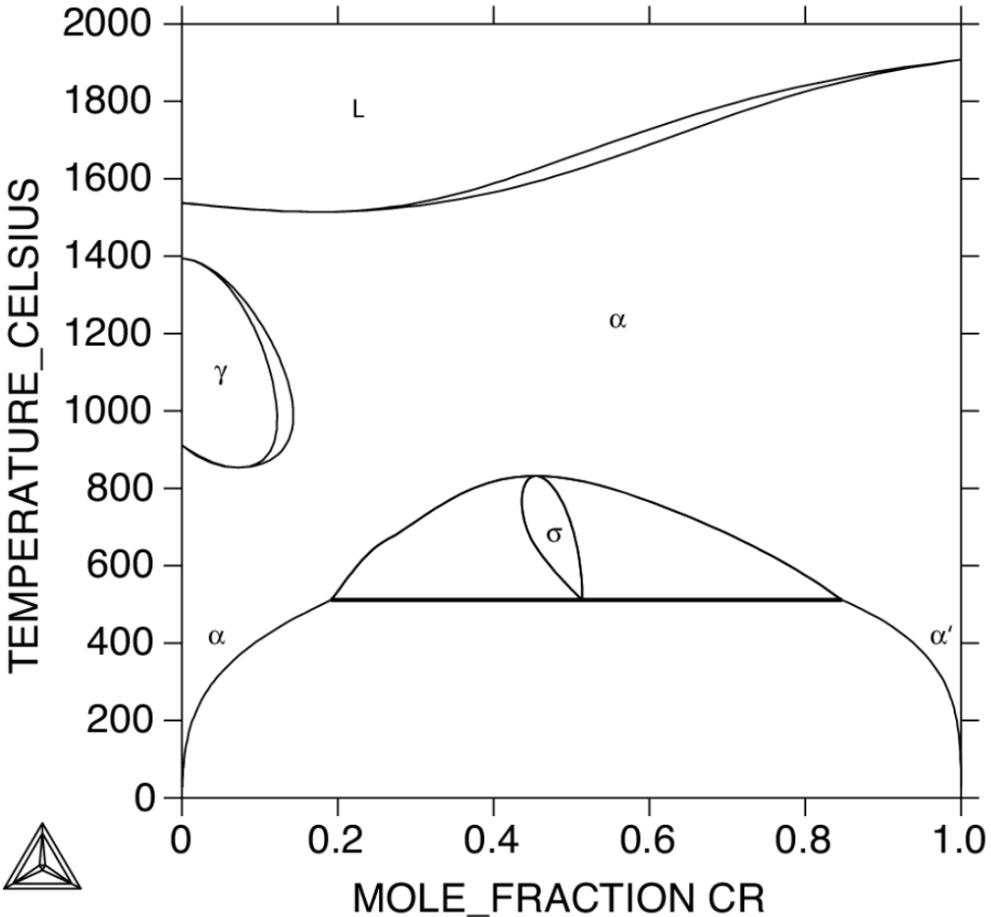
2. Nonetheless, computing the dissipation combining 1st and 2nd principles with a moving sharp interface is sufficient for finding the usual interfacial constitutive laws

Talk to J.F. Ganghoffer (in the room) and read his old papers

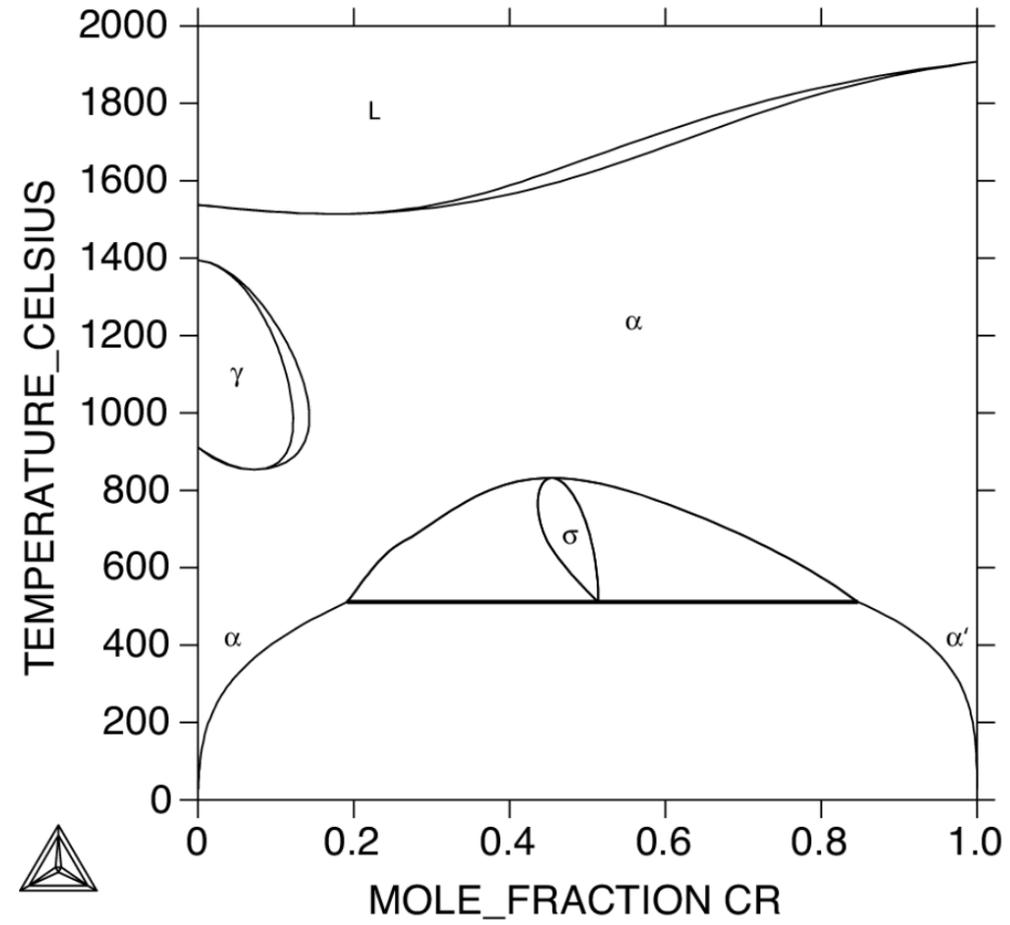


Kinetics

Nucleation or spinodal decomposition?

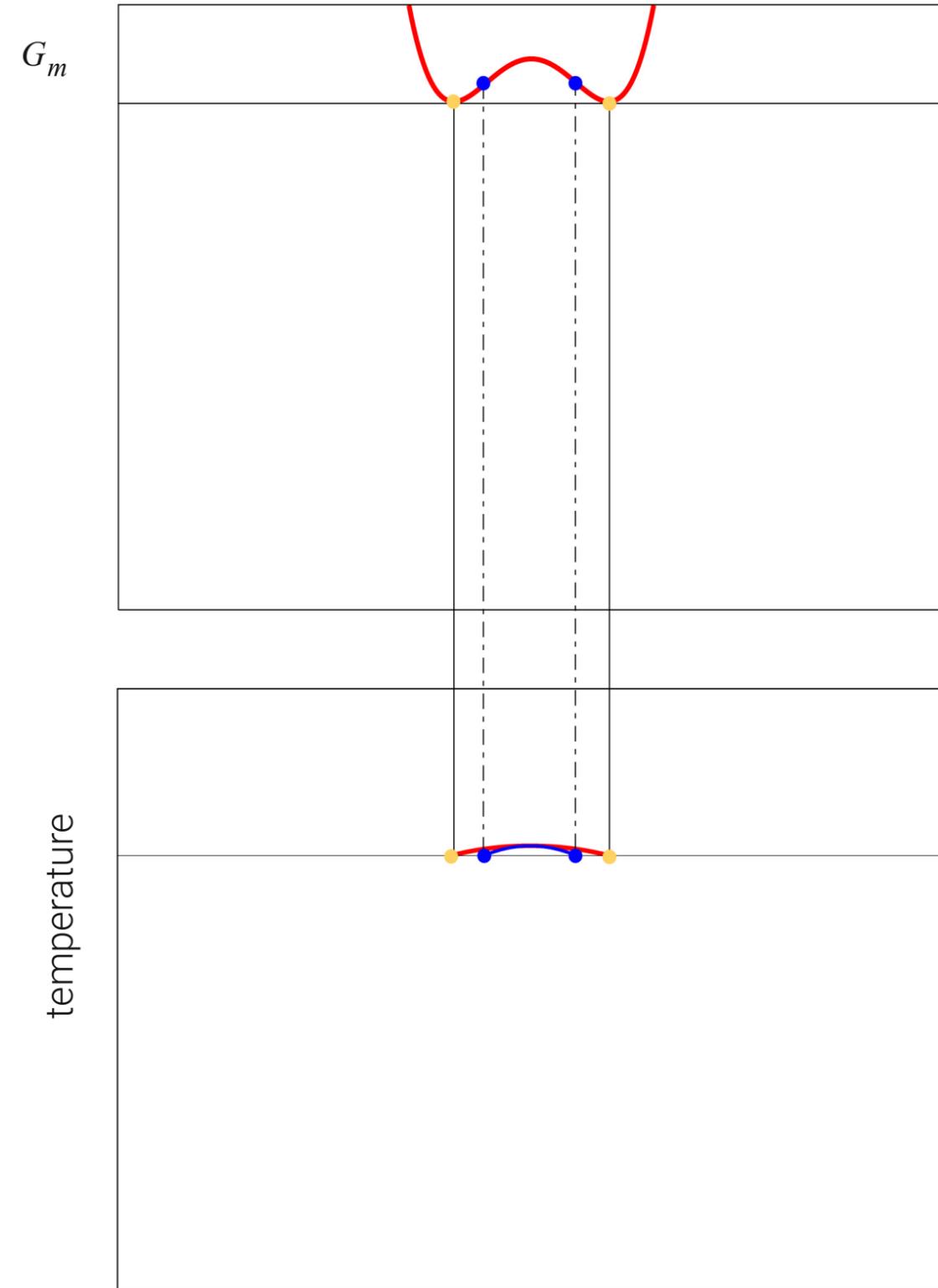


Nucleation or spinodal decomposition?

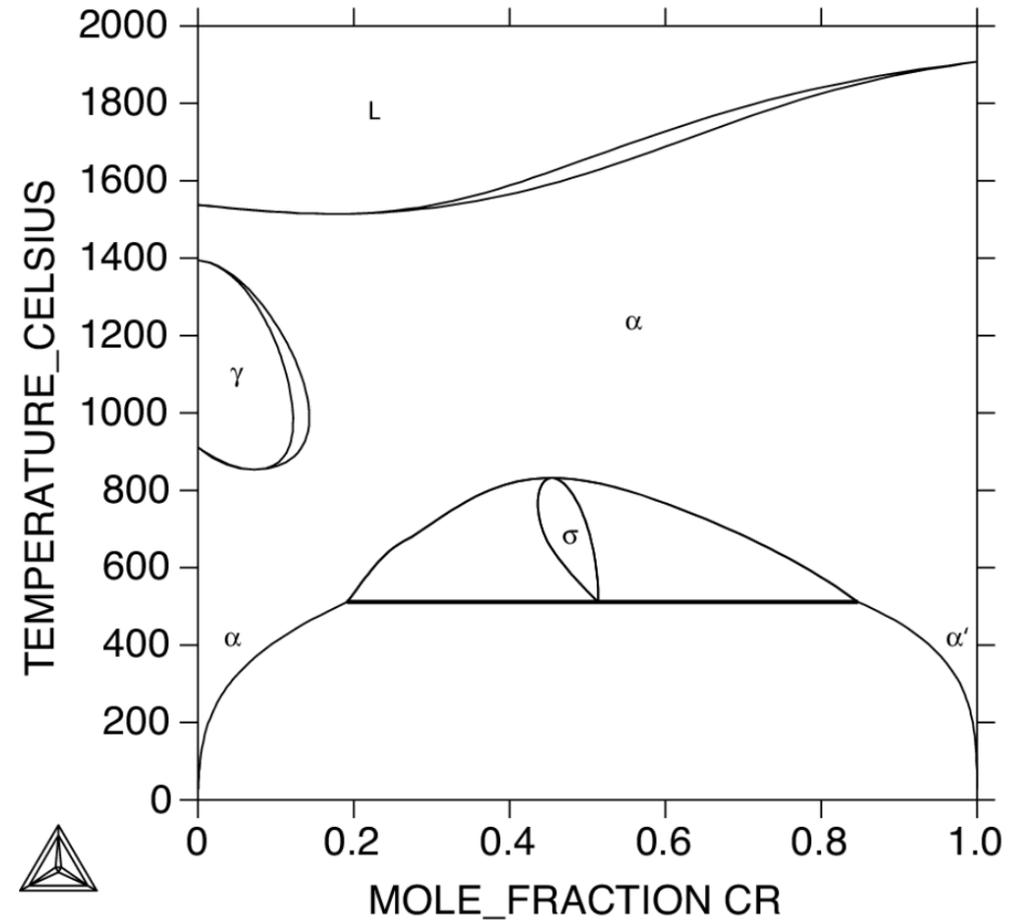


For ex. regular solid solution

$$G_m = RT[c \ln c + (1 - c) \ln(1 - c)] + Ac(1 - c)$$

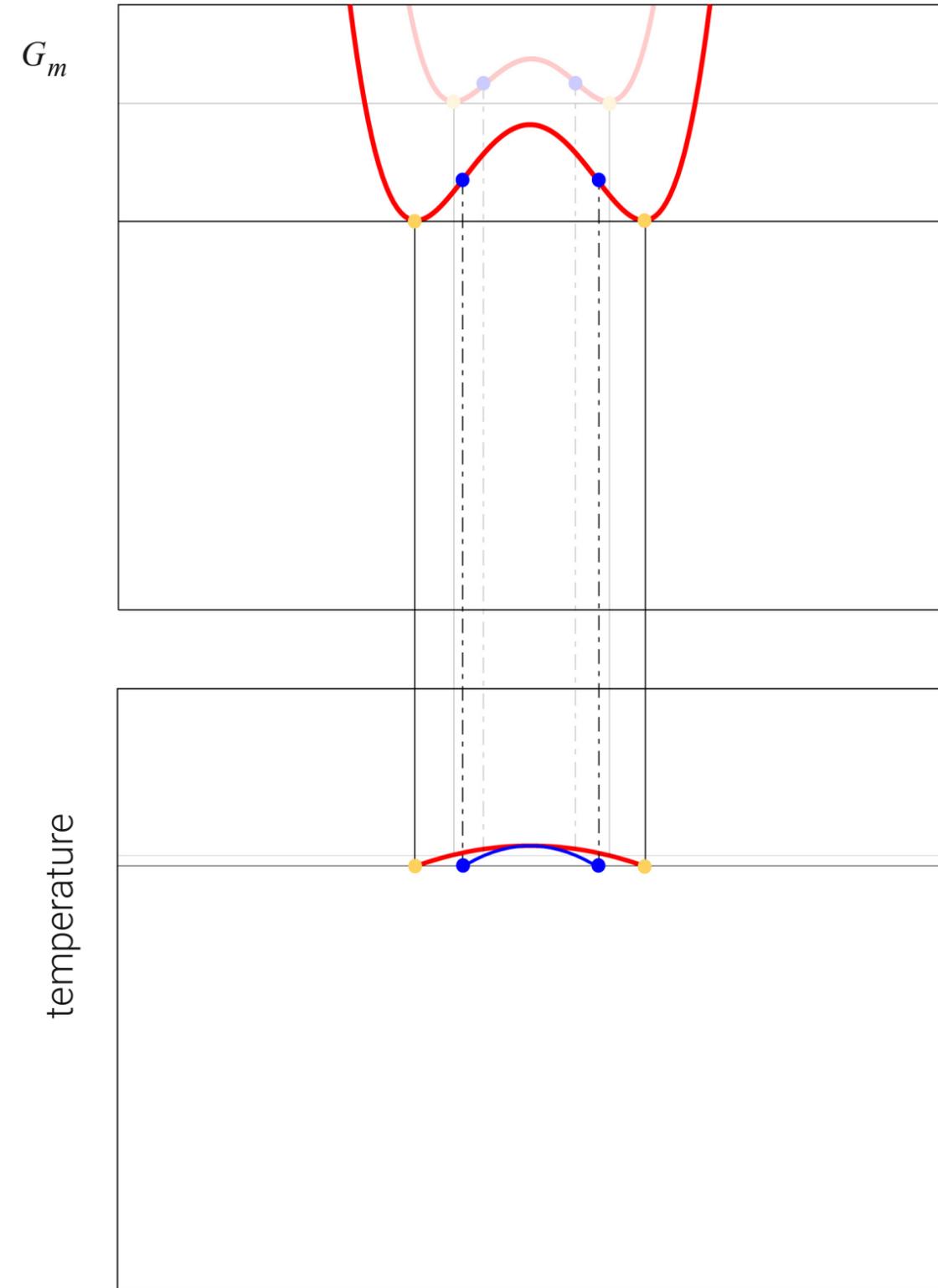


Nucleation or spinodal decomposition?

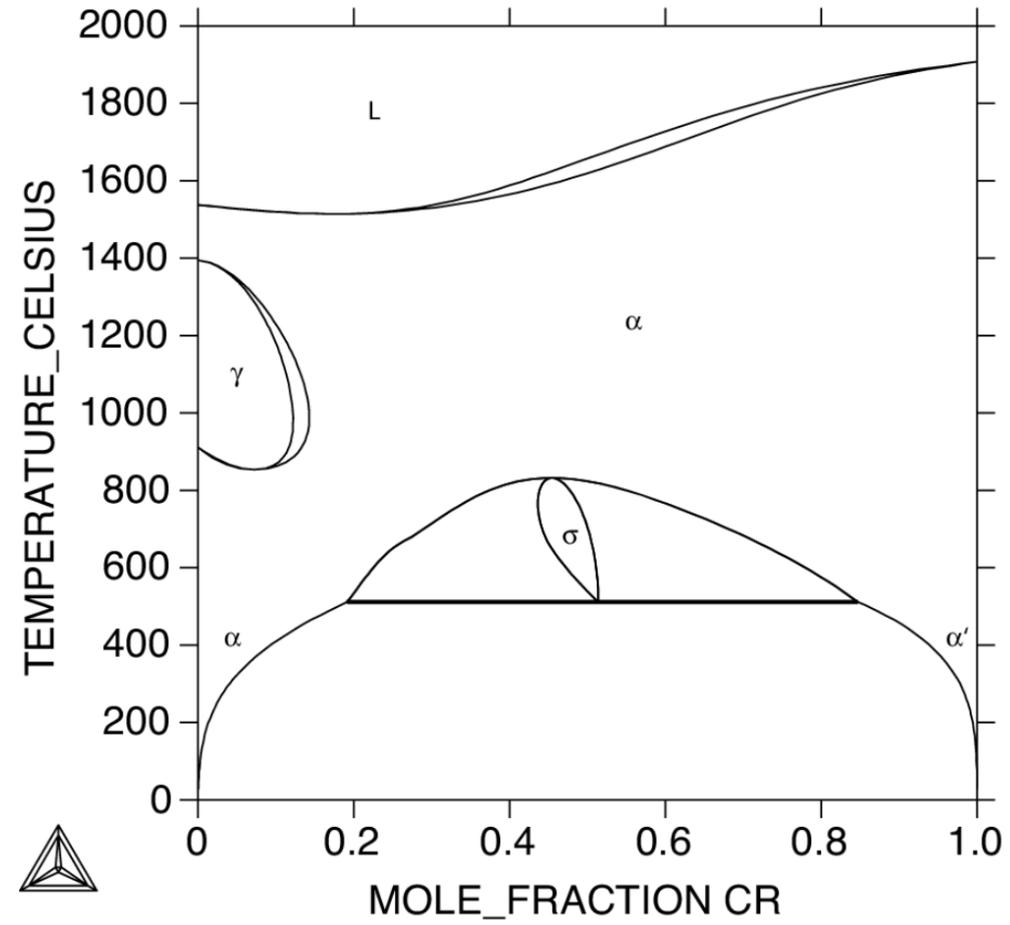


For ex. regular solid solution

$$G_m = RT[c \ln c + (1 - c) \ln(1 - c)] + Ac(1 - c)$$

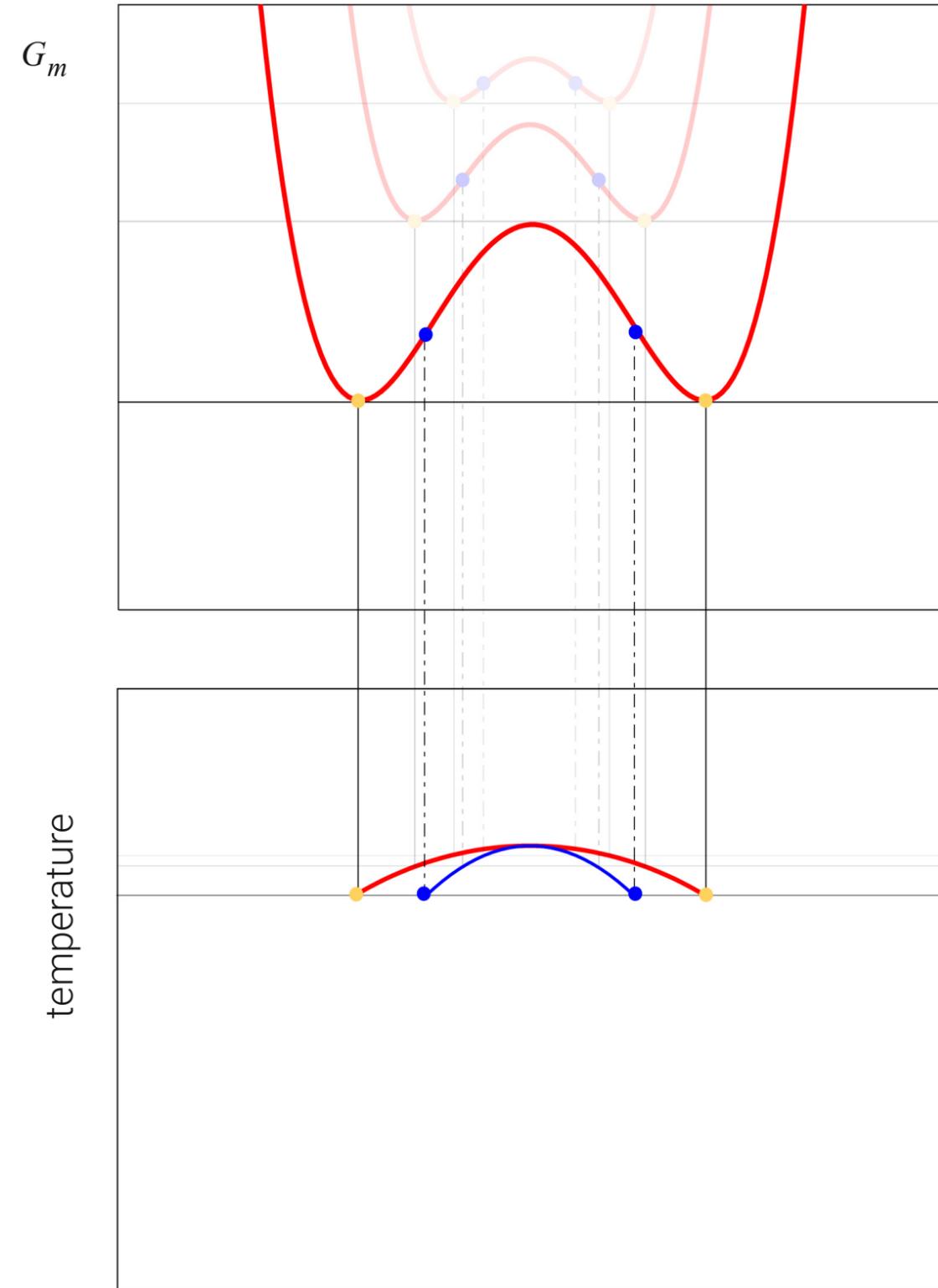


Nucleation or spinodal decomposition?

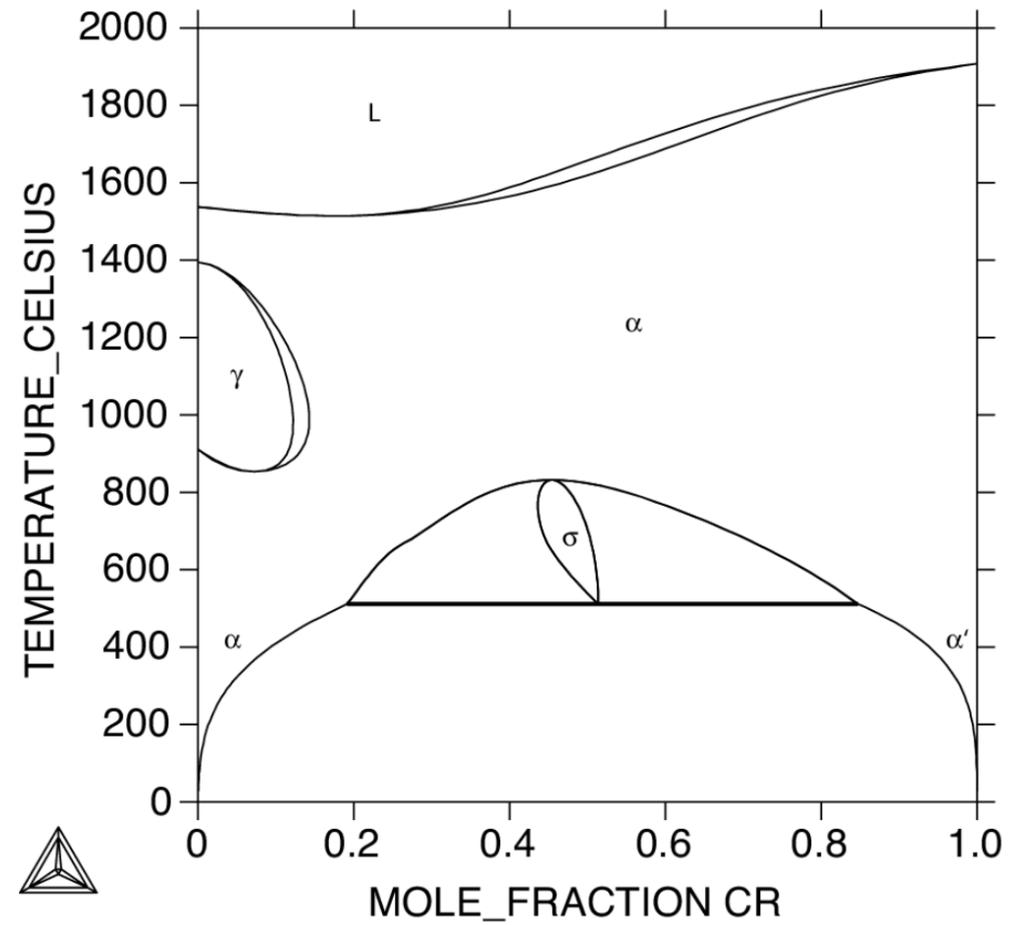


For ex. regular solid solution

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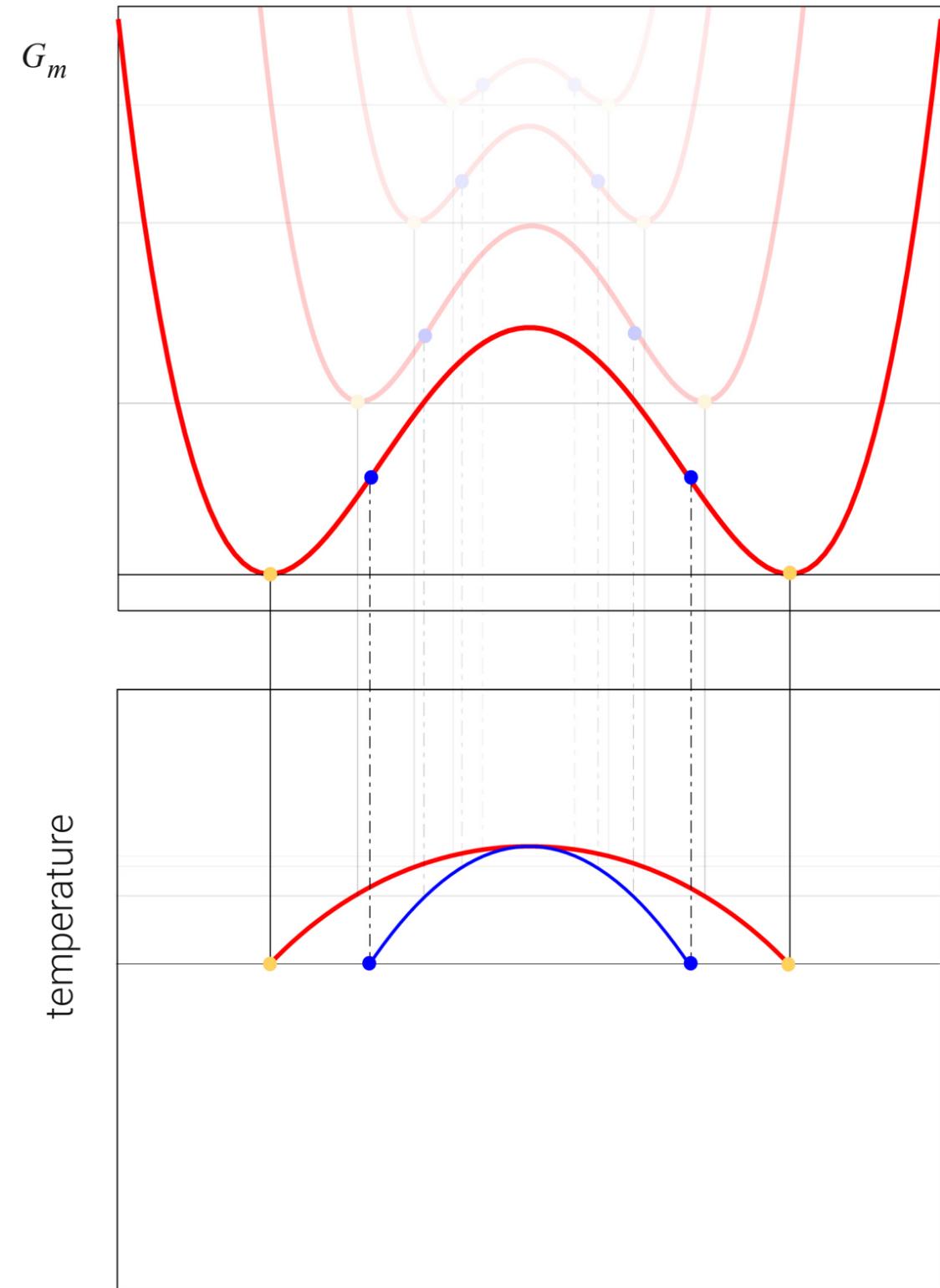


Nucleation or spinodal decomposition?

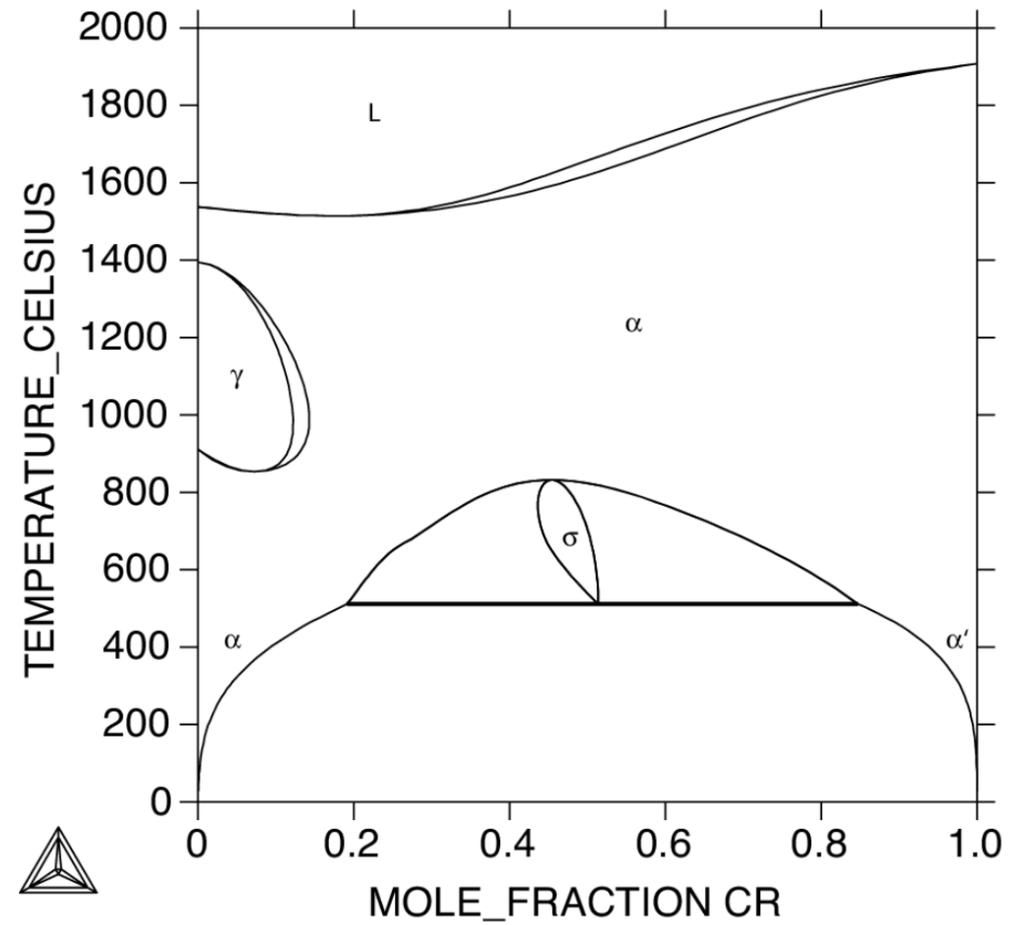


For ex. regular solid solution

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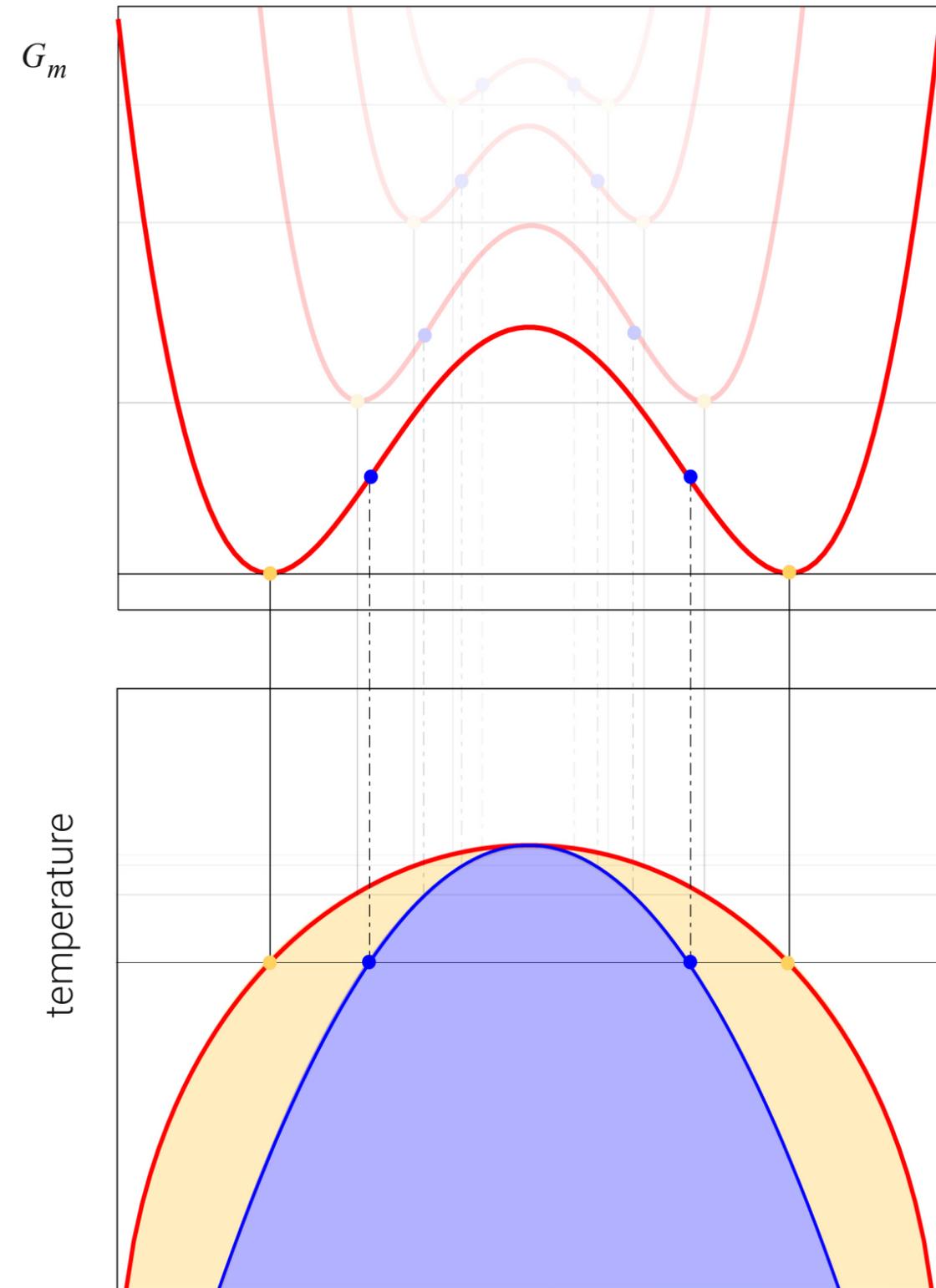


Nucleation or spinodal decomposition?

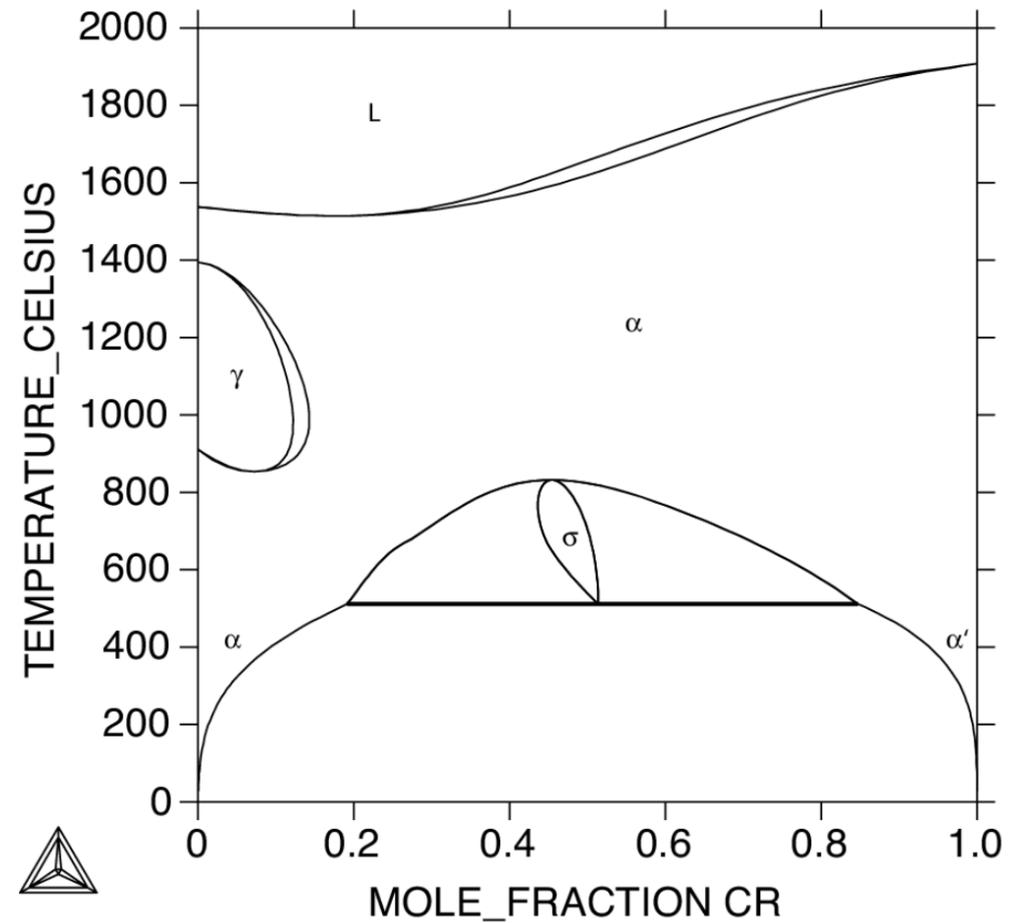


For ex. regular solid solution

$$G_m = RT[c \ln c + (1 - c) \ln(1 - c)] + Ac(1 - c)$$



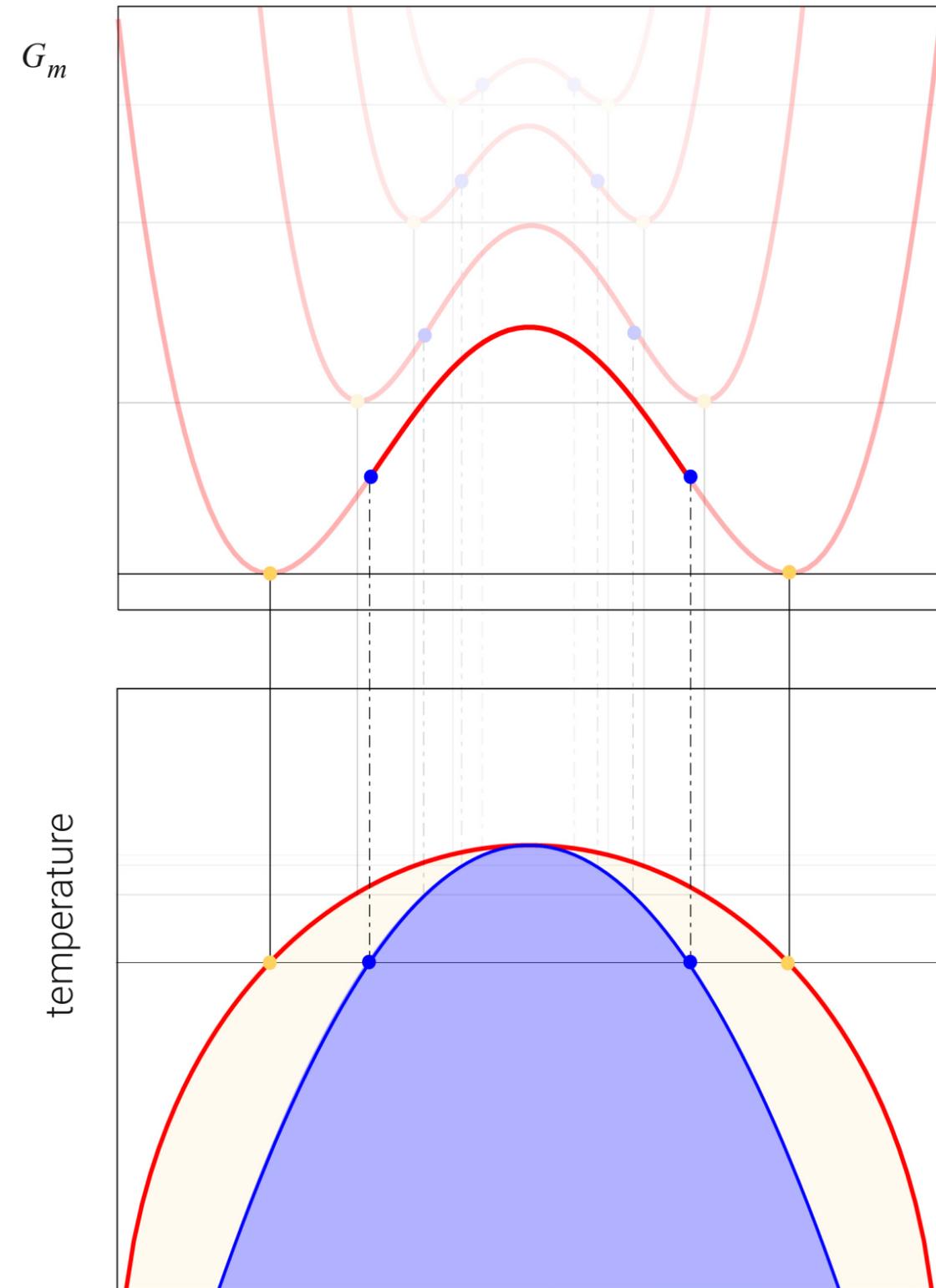
Nucleation or spinodal decomposition?



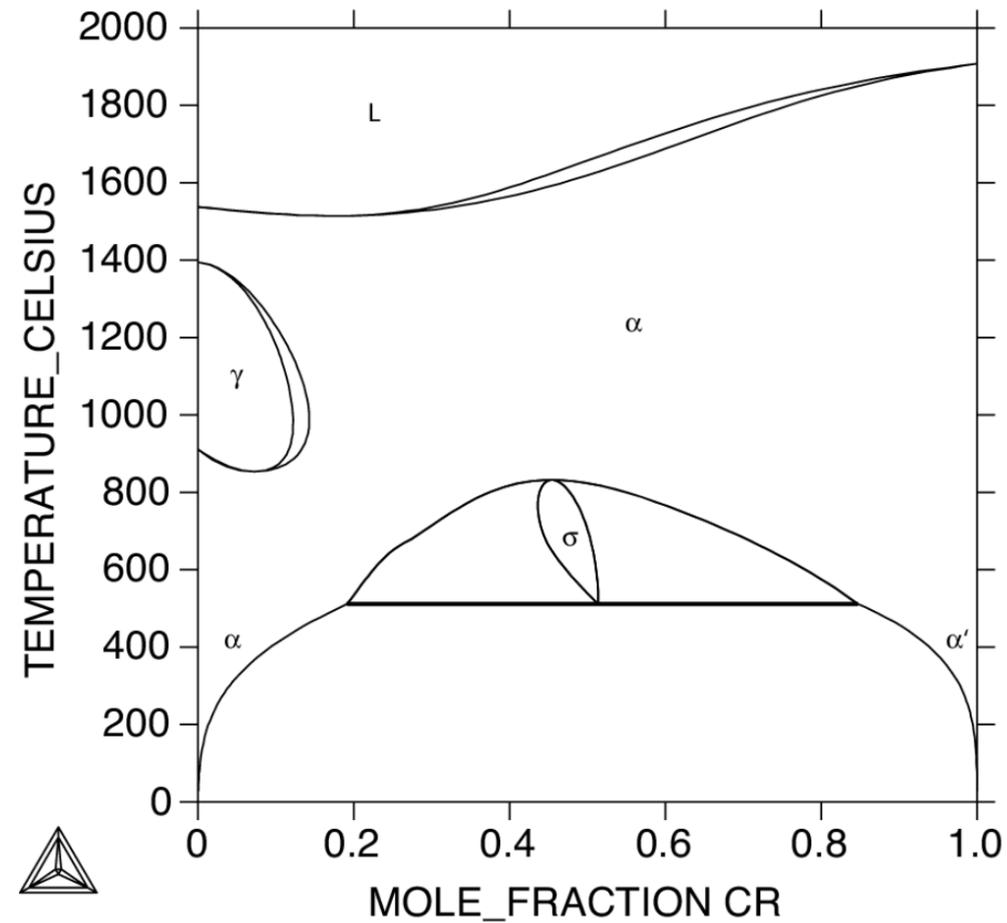
For ex. regular solid solution

$$G_m = RT[c \ln c + (1 - c) \ln(1 - c)] + Ac(1 - c)$$

- Inside the spinodal $\partial^2 G_m / \partial c^2 < 0$: unstable homog. syst.



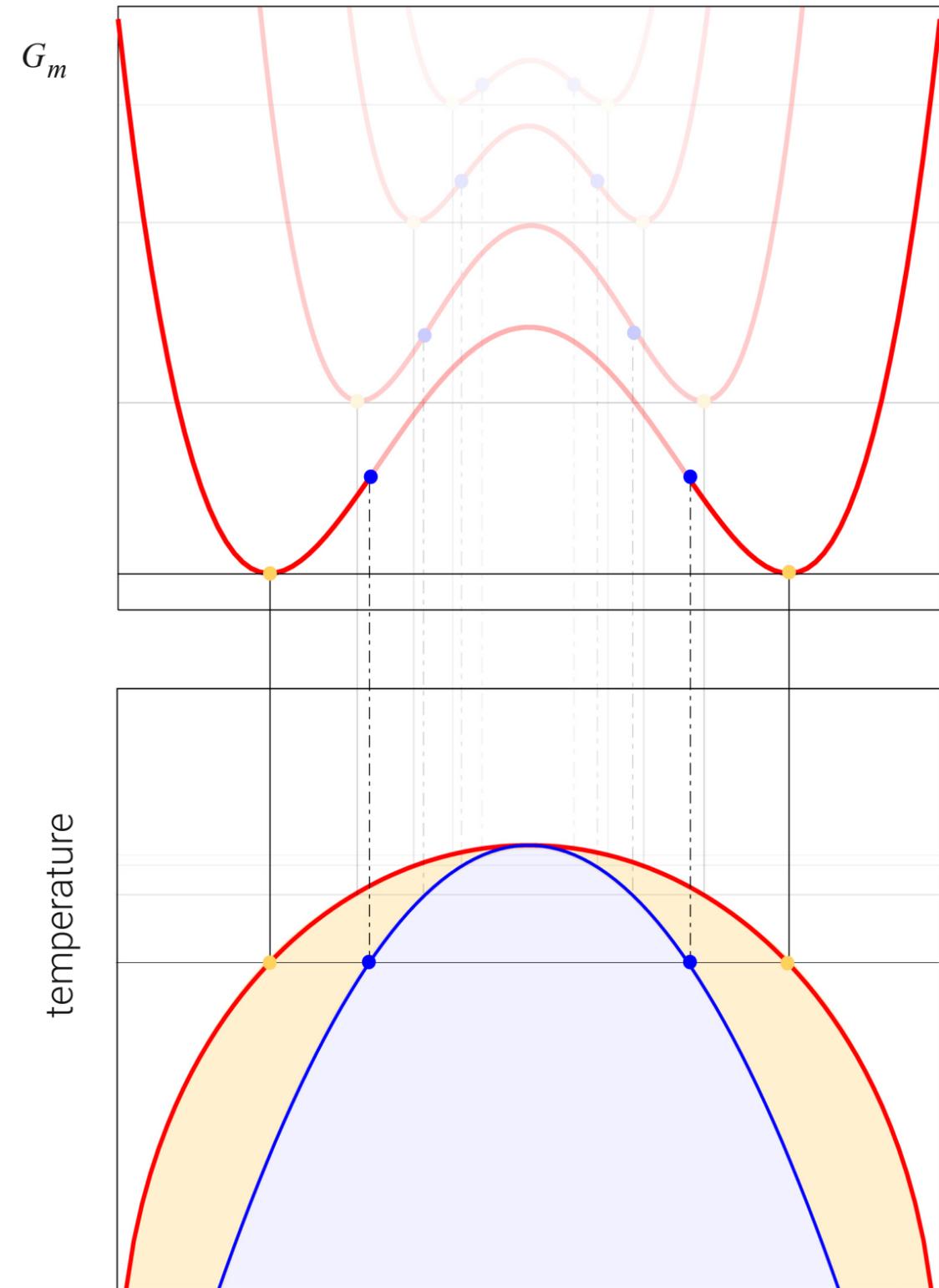
Nucleation or spinodal decomposition?



For ex. regular solid solution

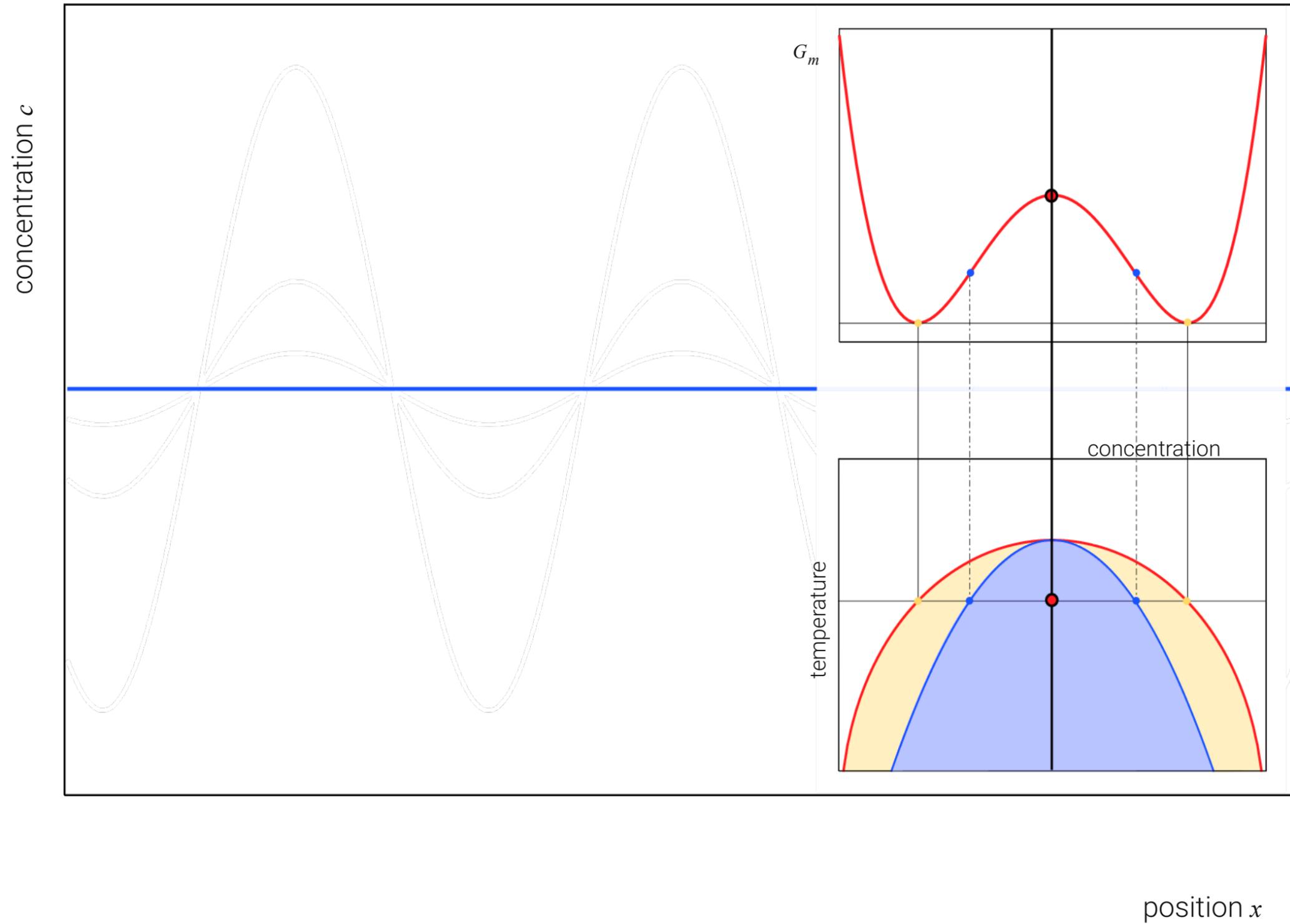
$$G_m = RT[c \ln c + (1 - c) \ln(1 - c)] + Ac(1 - c)$$

- Inside the spinodal $\partial^2 G_m / \partial c^2 < 0$: unstable homog. syst.
- In between the solubility gap and the spinodal $\partial^2 G_m / \partial c^2 > 0$: metastable homog. syst.



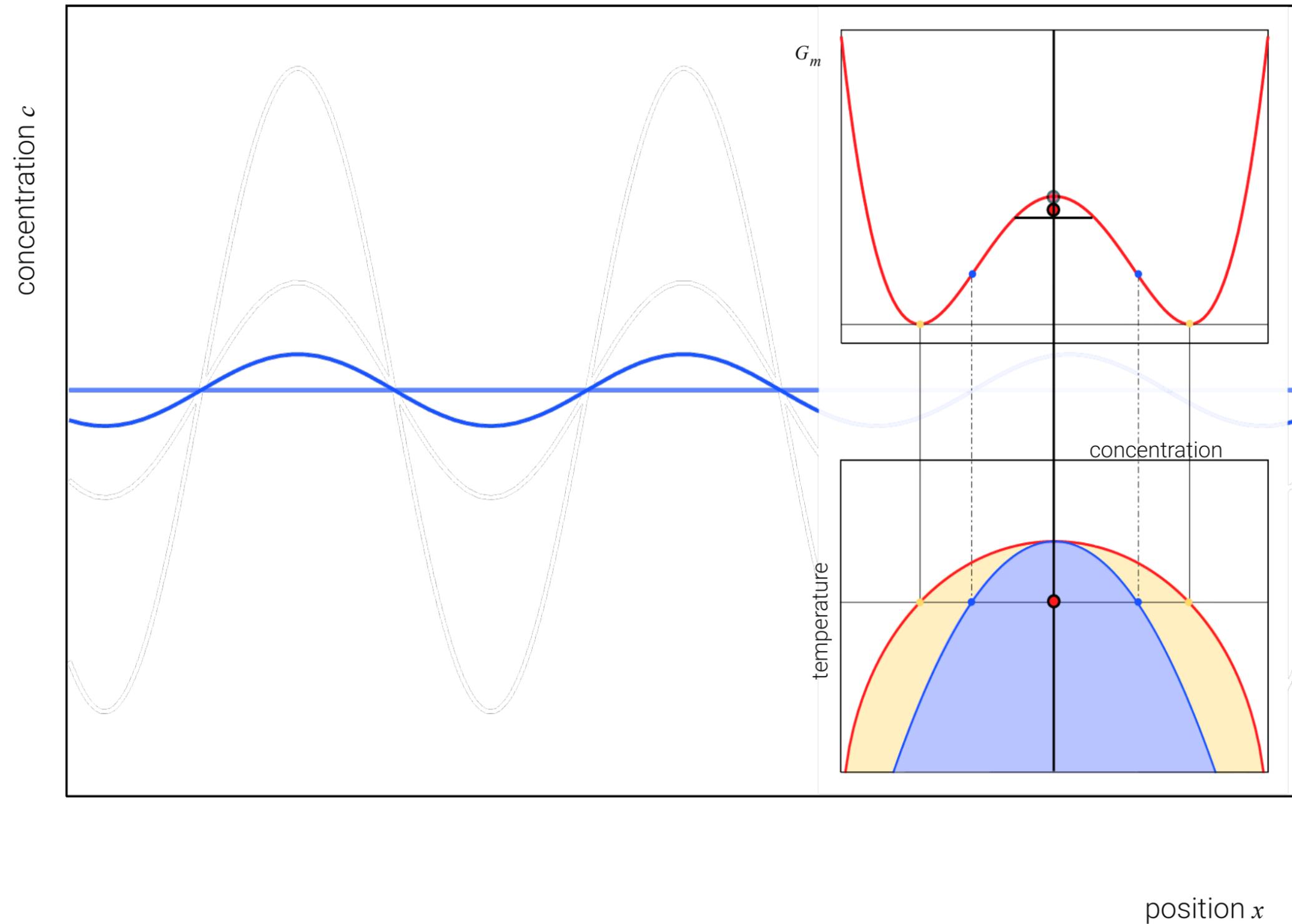
Nucleation or spinodal decomposition?

Inside the spinodal



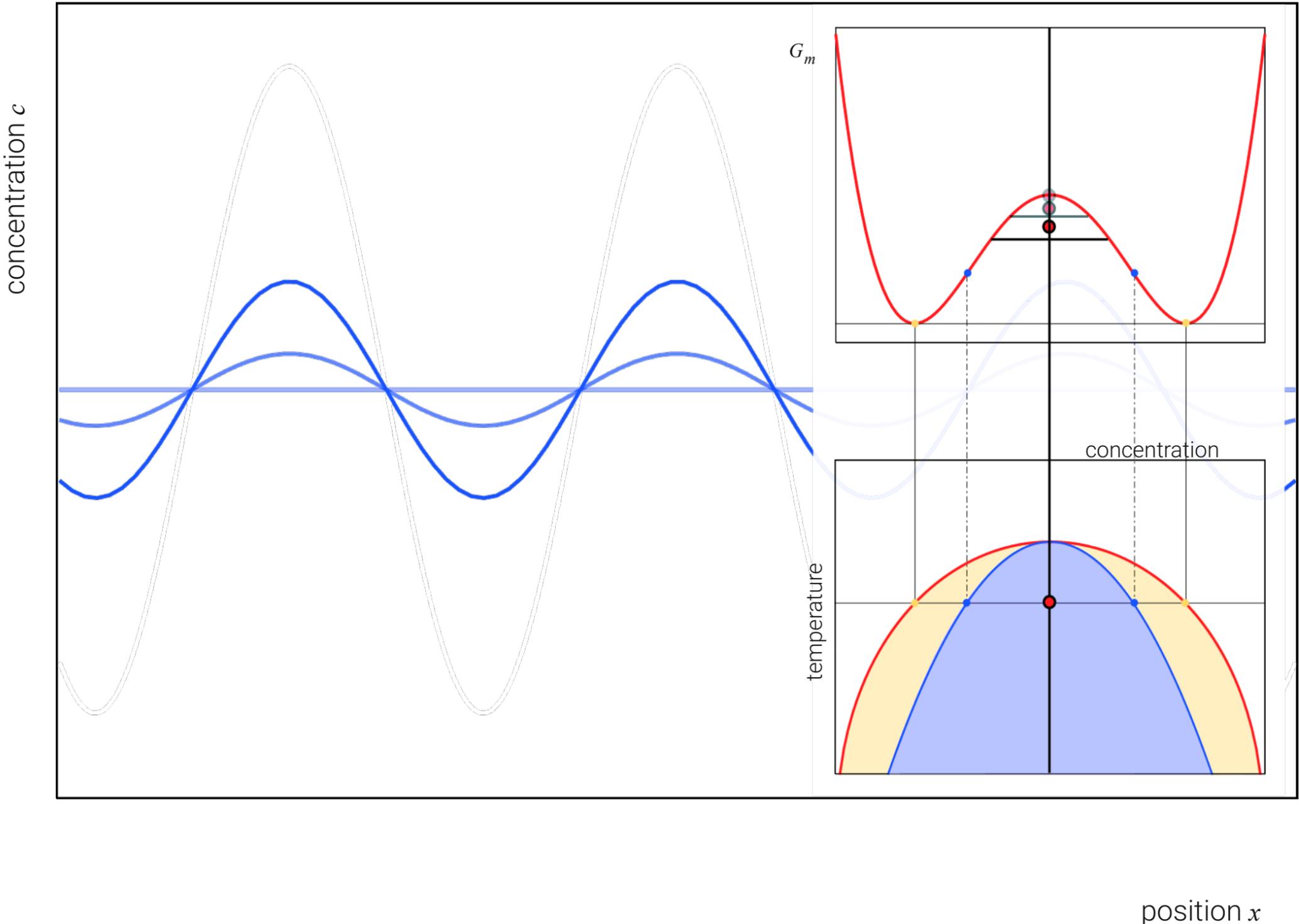
Nucleation or spinodal decomposition?

Inside the spinodal



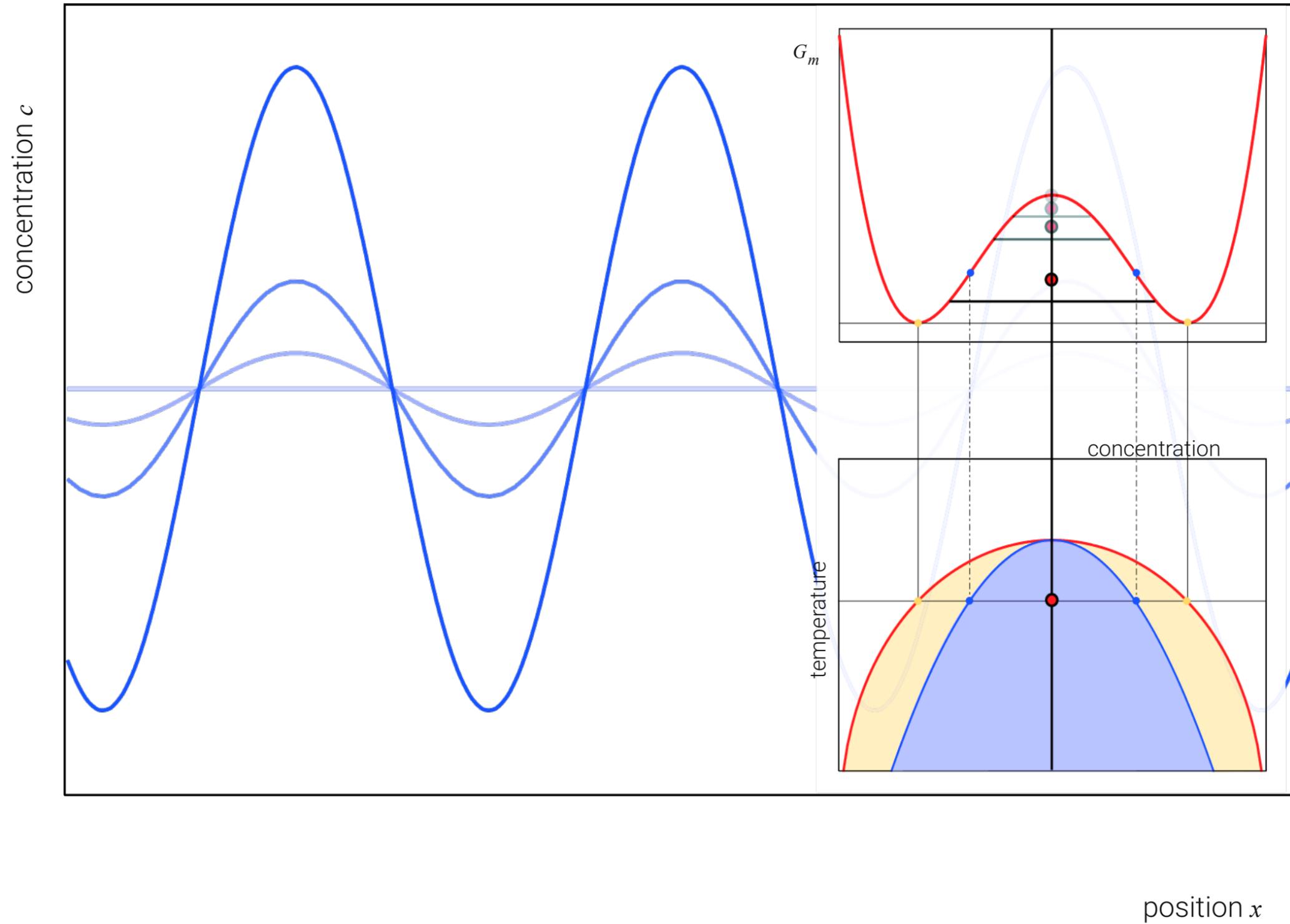
Nucleation or spinodal decomposition?

Inside the spinodal



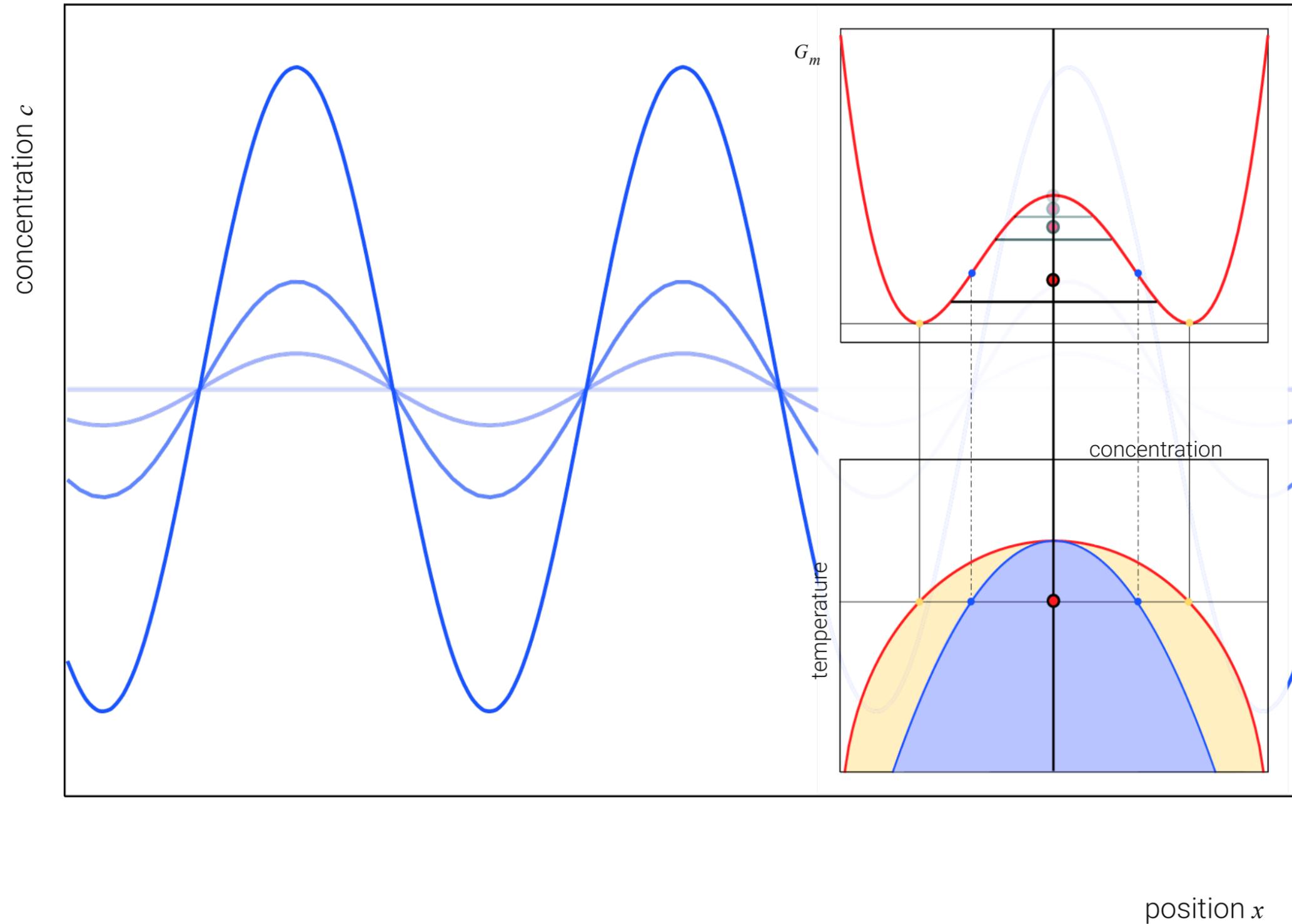
Nucleation or spinodal decomposition?

Inside the spinodal



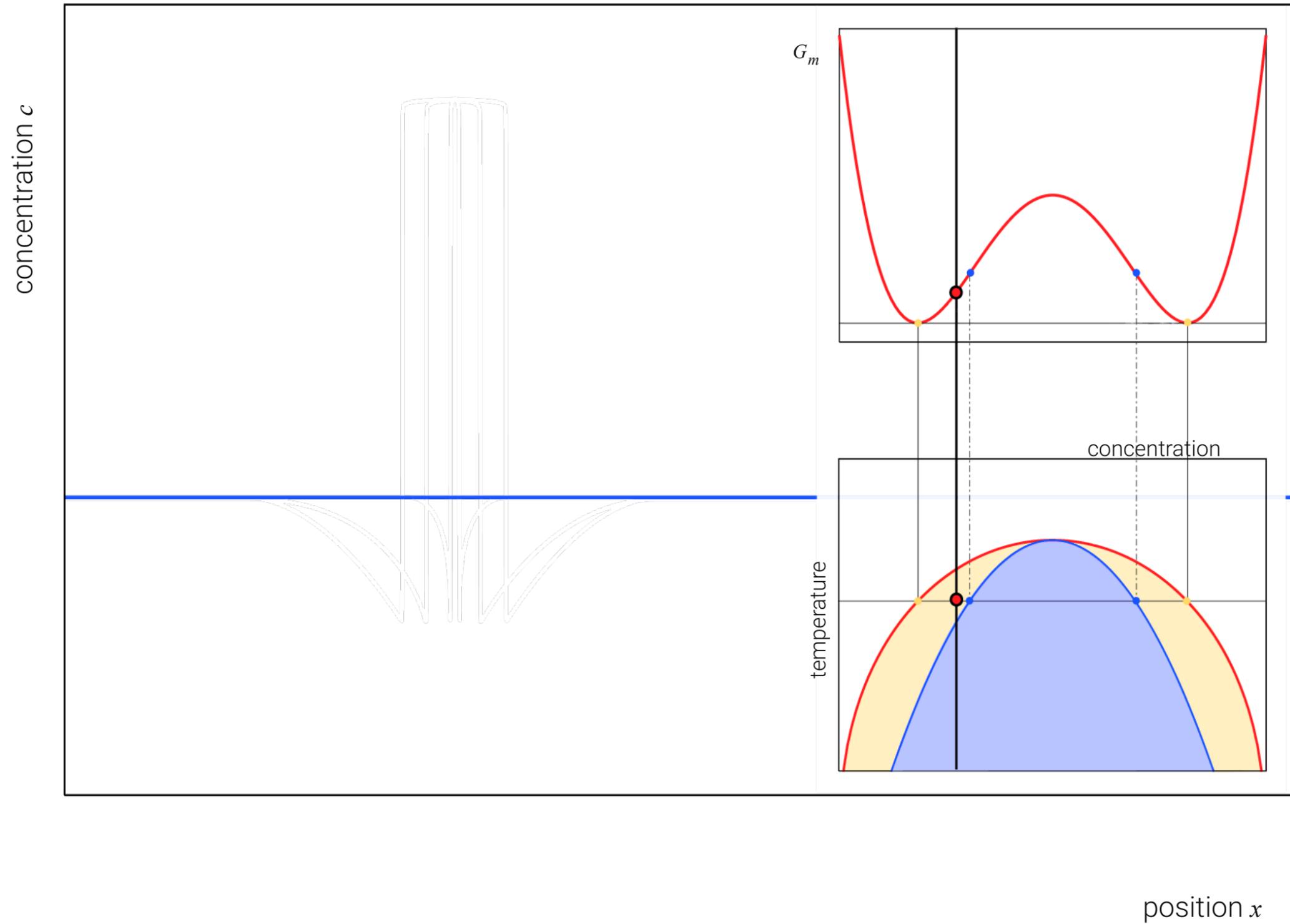
Nucleation or spinodal decomposition?

Inside the spinodal



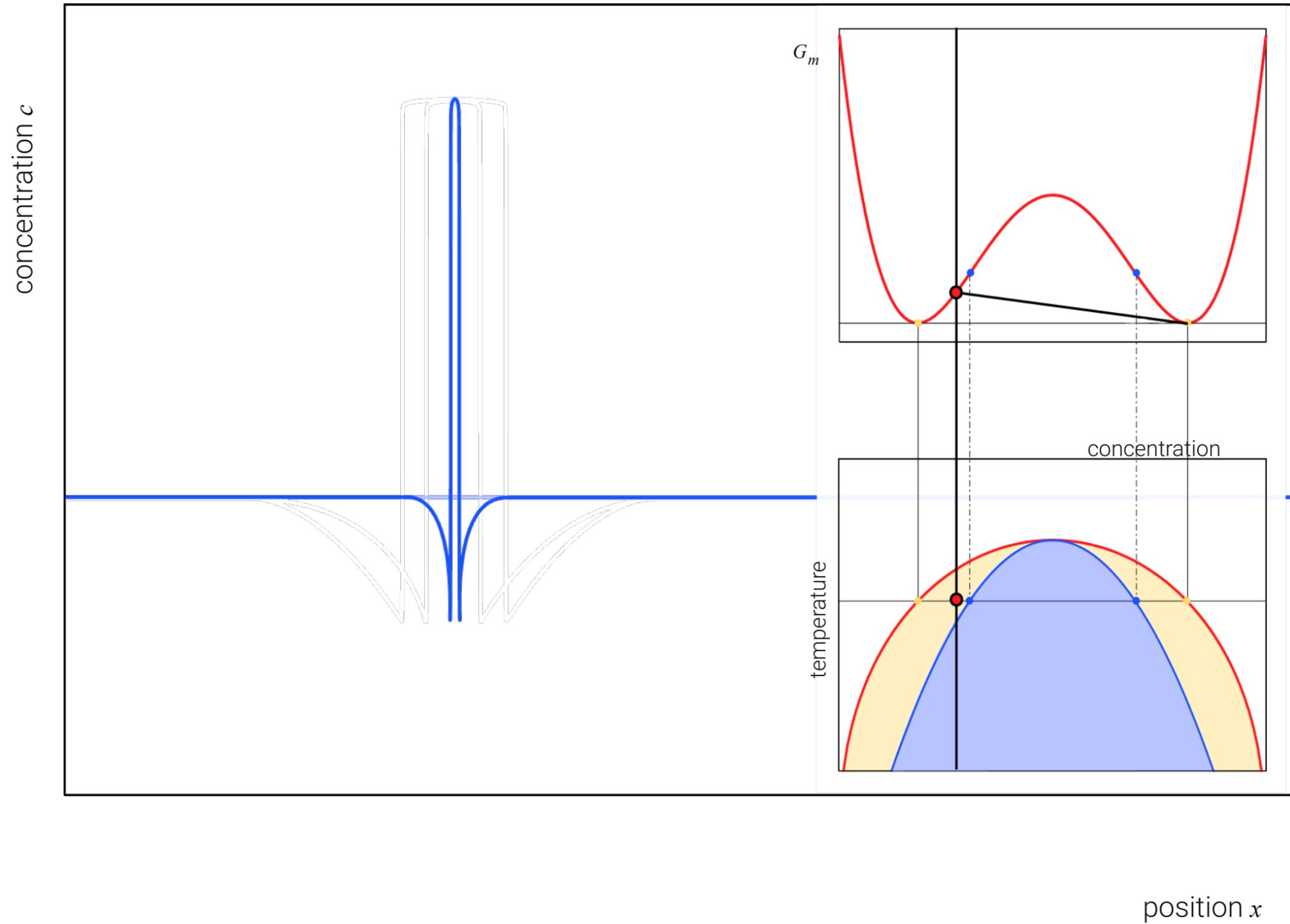
Nucleation or spinodal decomposition?

Outside the spinodal



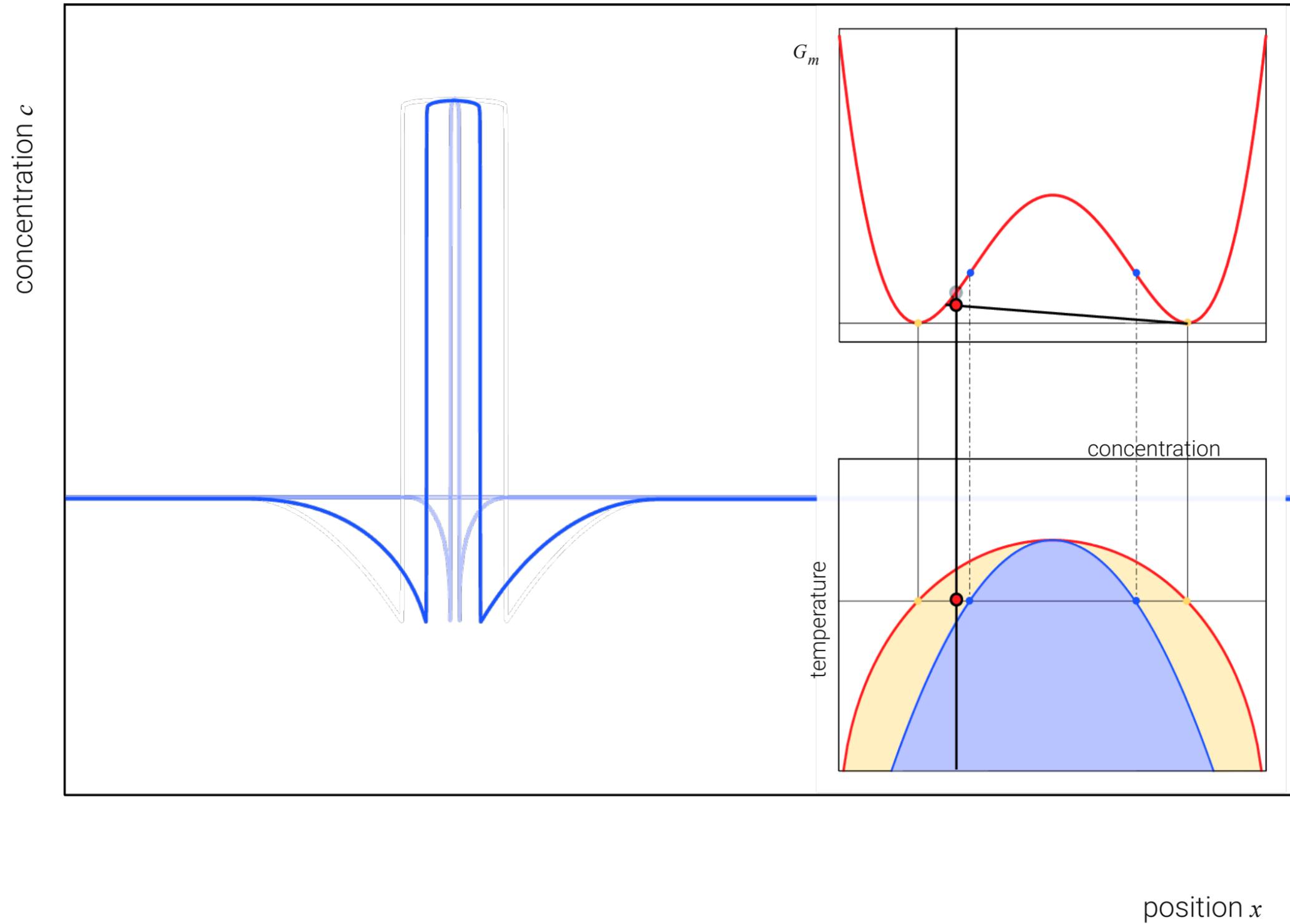
Nucleation or spinodal decomposition?

Outside the spinodal



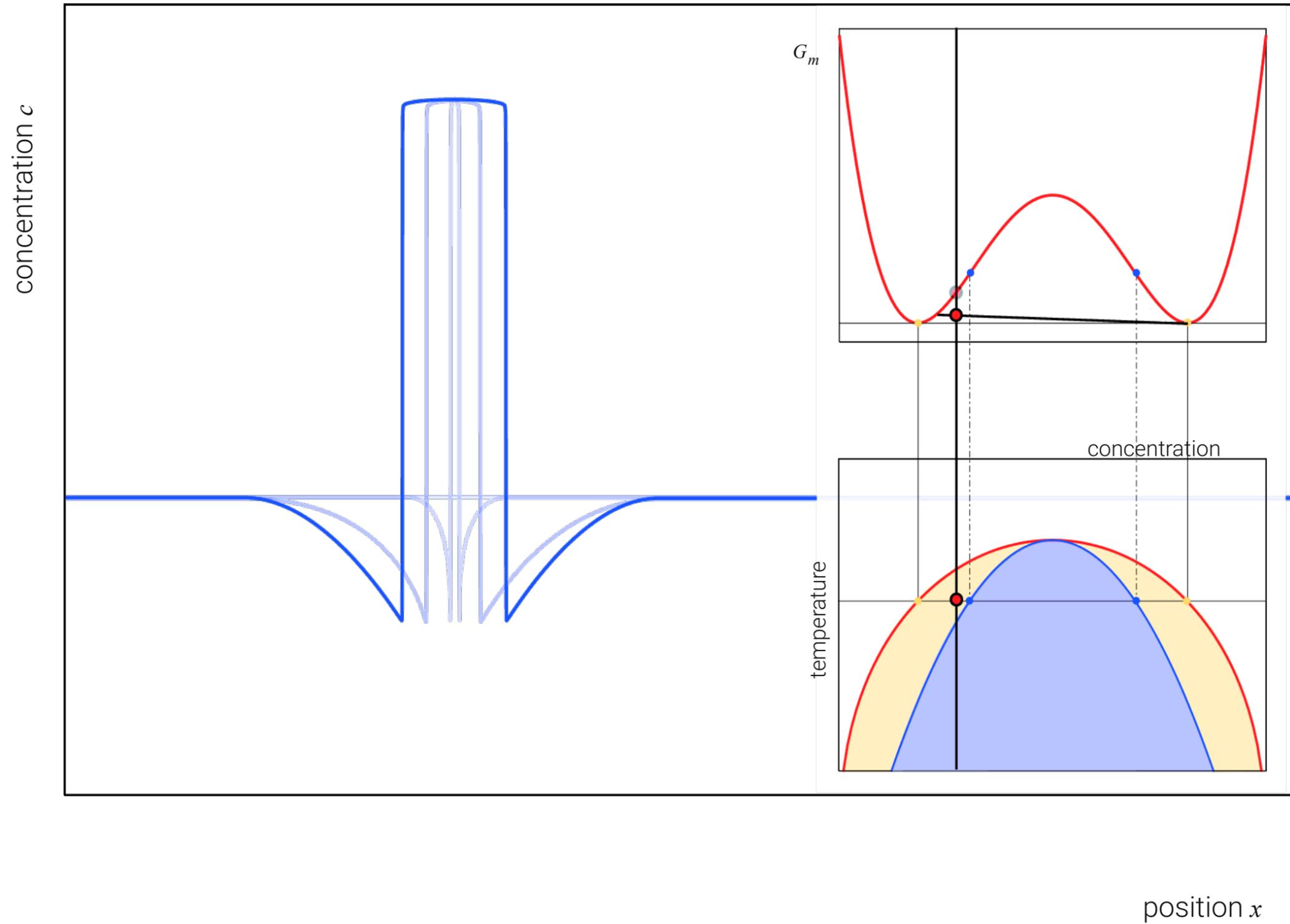
Nucleation or spinodal decomposition?

Outside the spinodal



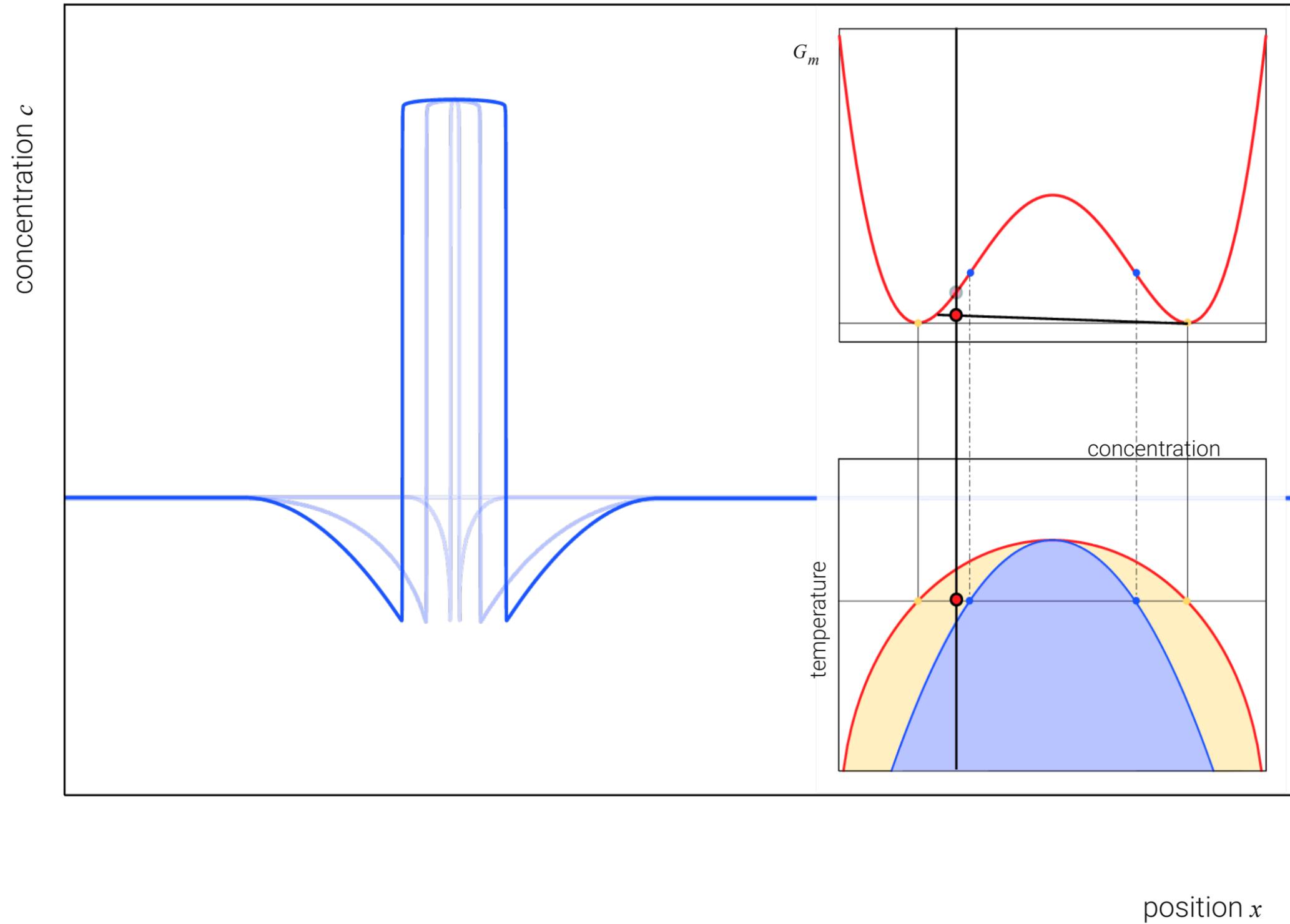
Nucleation or spinodal decomposition?

Outside the spinodal



Nucleation or spinodal decomposition?

Outside the spinodal



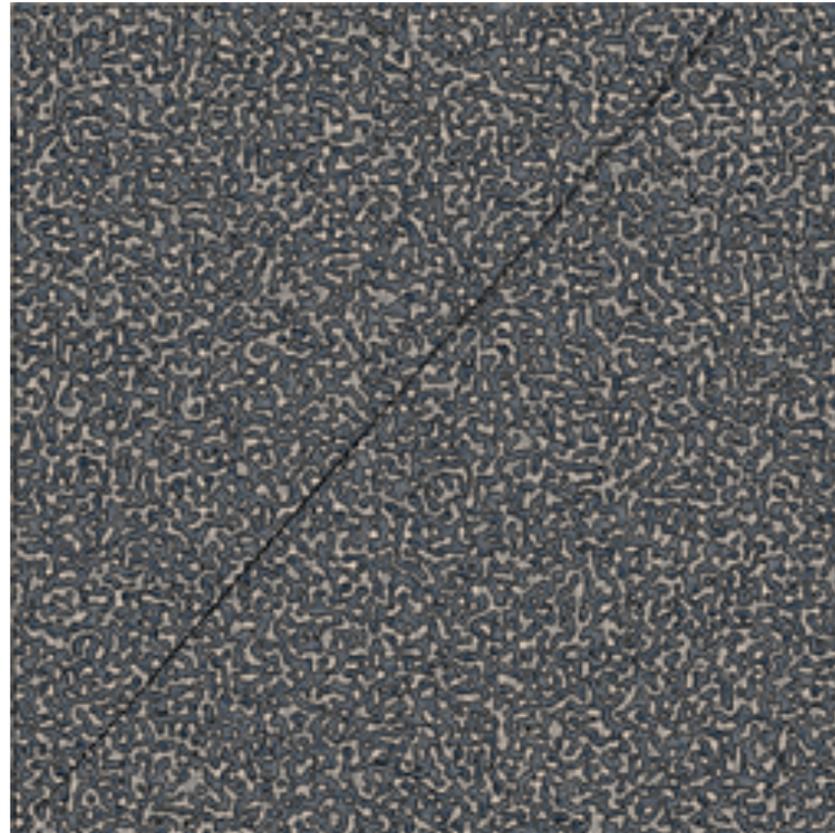
Nucleation or spinodal decomposition?

Inside the spinodal

Cahn-Hilliard model (Cahn and Hilliard 1958)

$$F = \int f_0(c) + \frac{\alpha}{2} |\nabla c|^2 dV$$

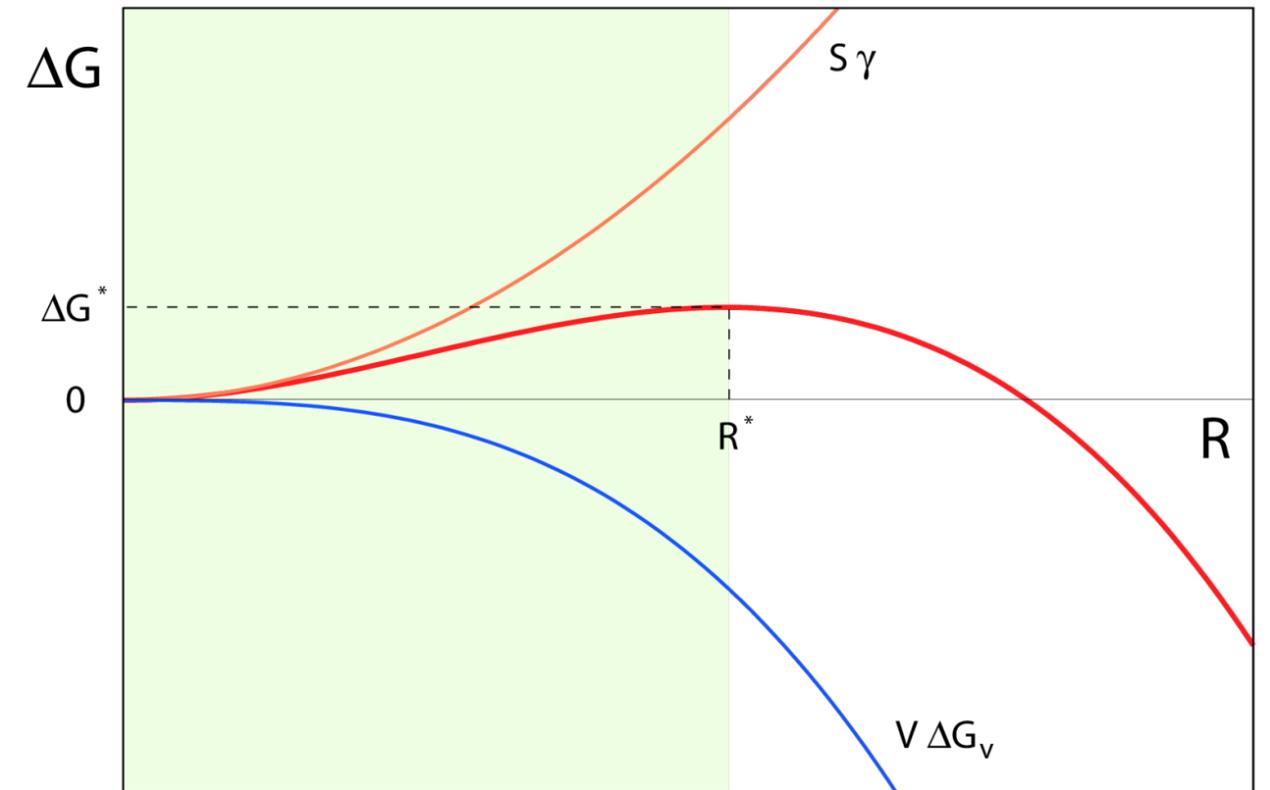
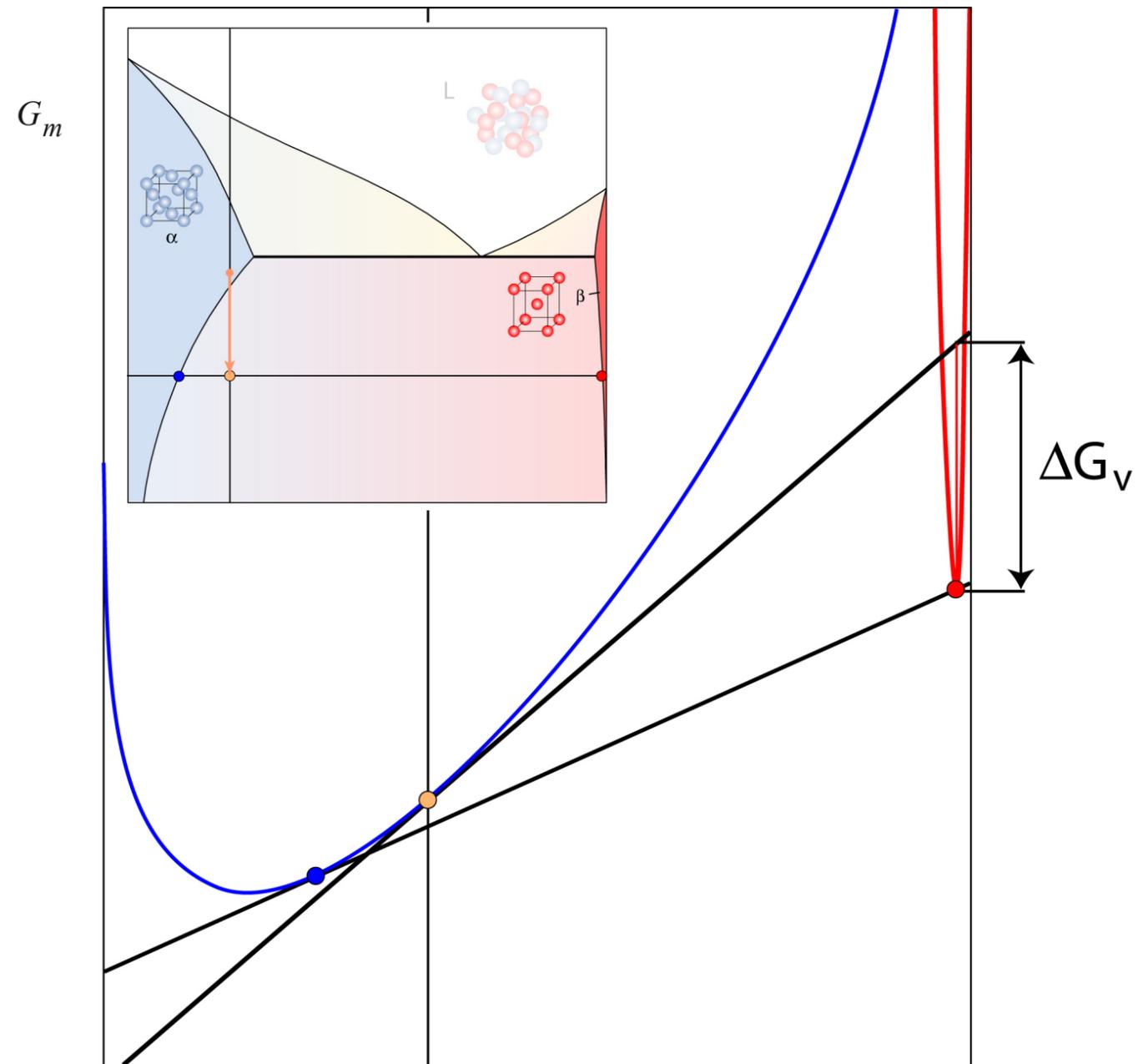
Homework



Nucleation or spinodal decomposition?

Outside the spinodal

Classical Nucleation Theory: thermodynamics [Volmer, Weber 1926]

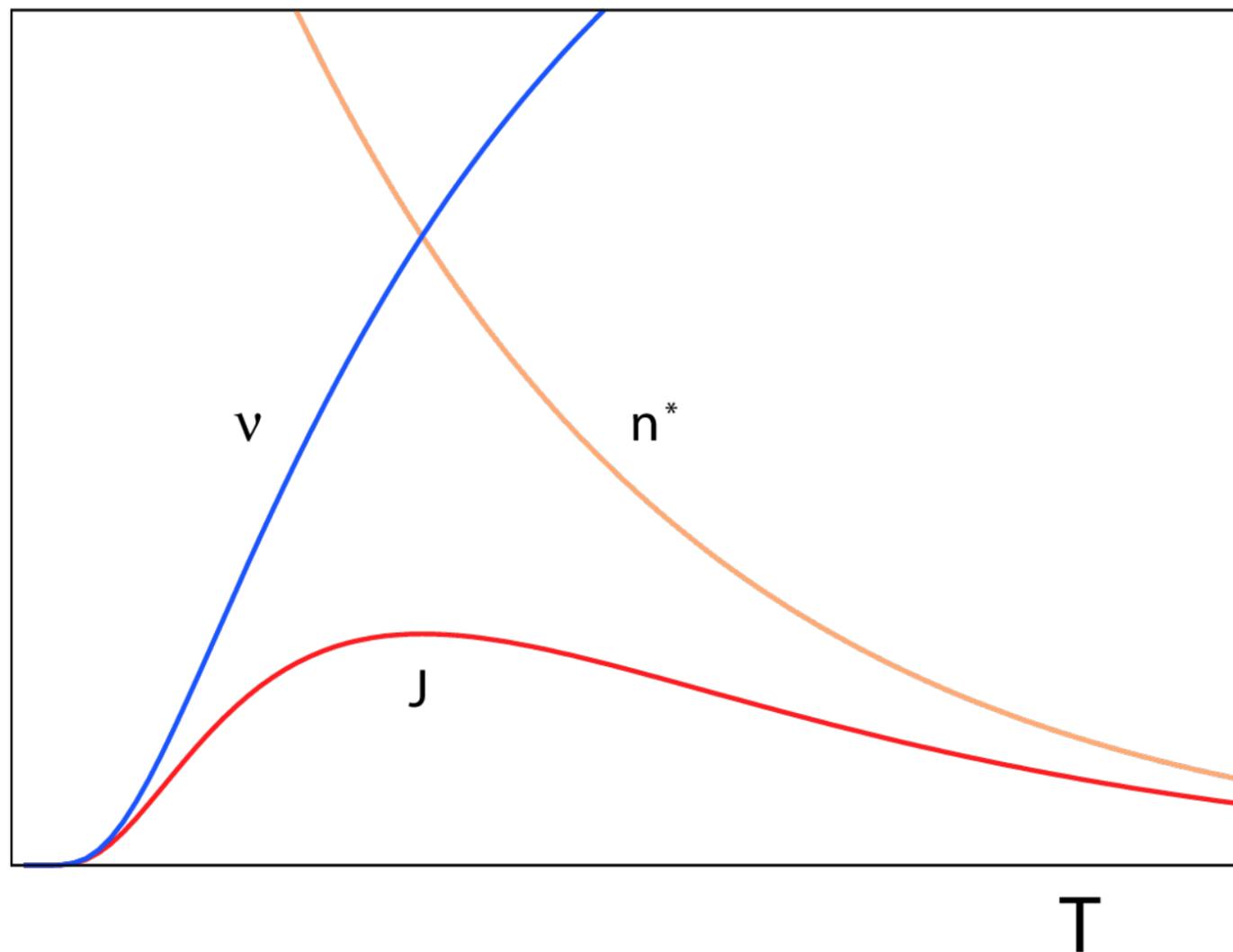


Homework

Nucleation or spinodal decomposition?

Outside the spinodal

Classical Nucleation Theory: kinetics [Becker, Döring 1935] 



- Nucleation rate $J \propto \nu n^*$

- Attachment frequency $\nu = \frac{D}{\lambda^2} = \nu_0 \exp\left(\frac{-Q}{RT}\right)$

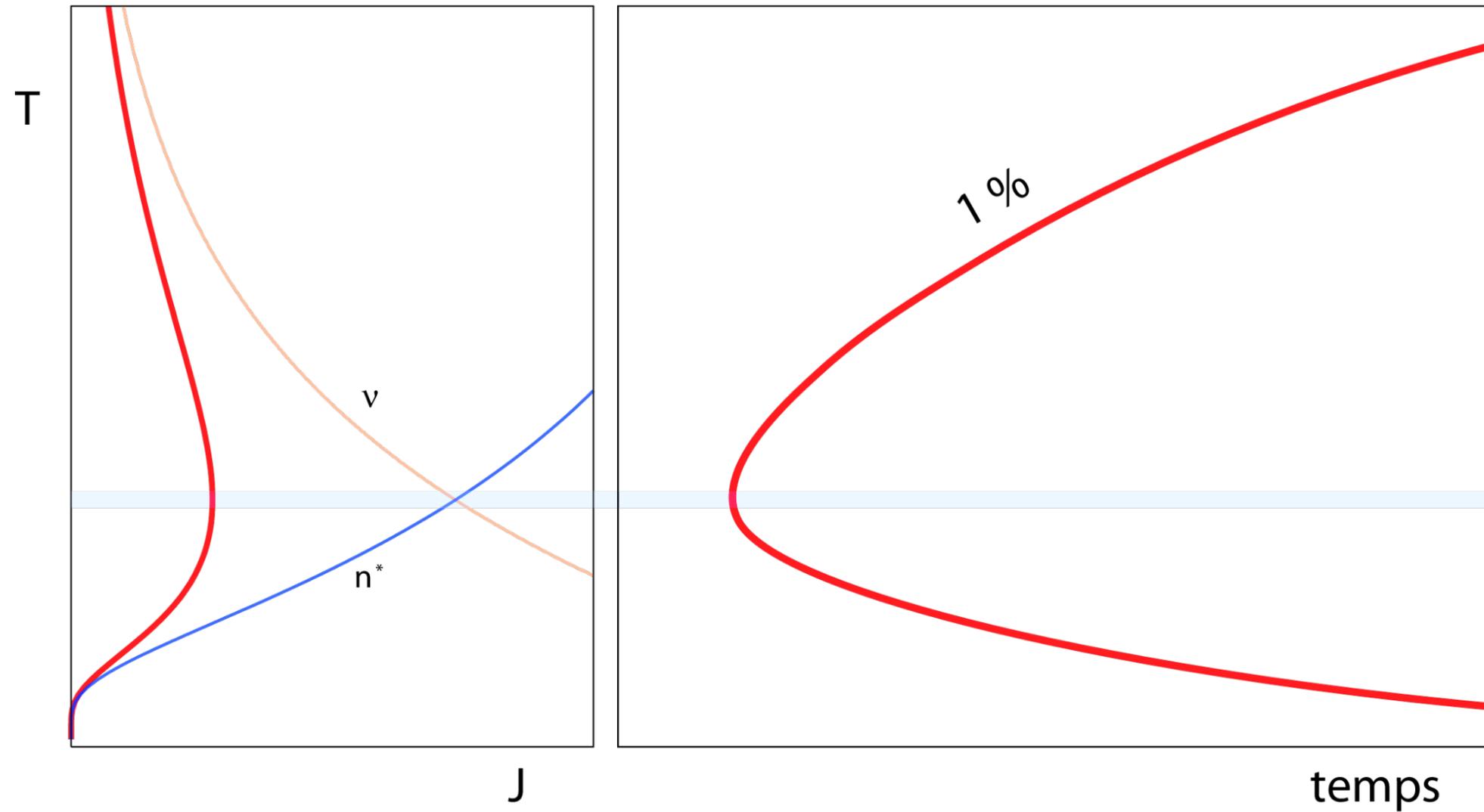
- Number of critical nuclei $n^* = n^0 \exp\left(\frac{-\Delta G^*}{RT}\right)$

Validity [Clouet 2010] [Ryu, Cai 2010]

Nucleation or spinodal decomposition?

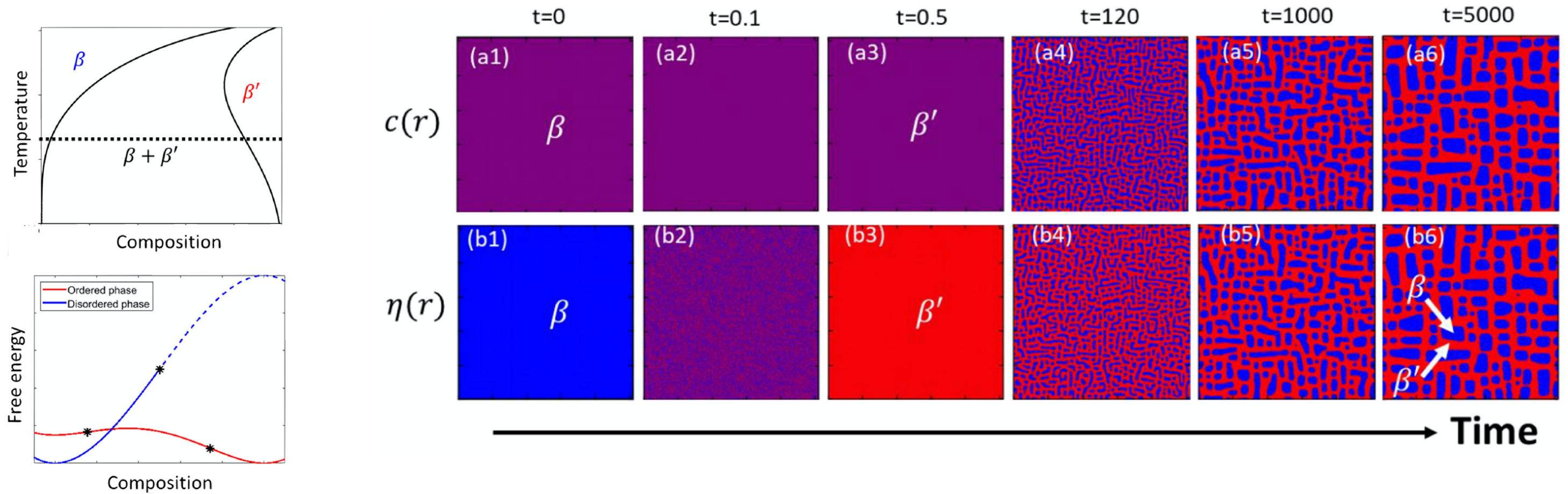
Outside the spinodal

Classical Nucleation Theory: kinetics [Becker, Döring 1935]



Nucleation or spinodal decomposition?

bcc → *bcc in B2* (e.g. Al-Mo_{0.5}-Nb-Ta_{0.5}-Ti-Zr) Kadirvel, Fraser, and Wang (2023)



Configuration of the free energies would explain bcc in B2

Influence of stress on nucleation

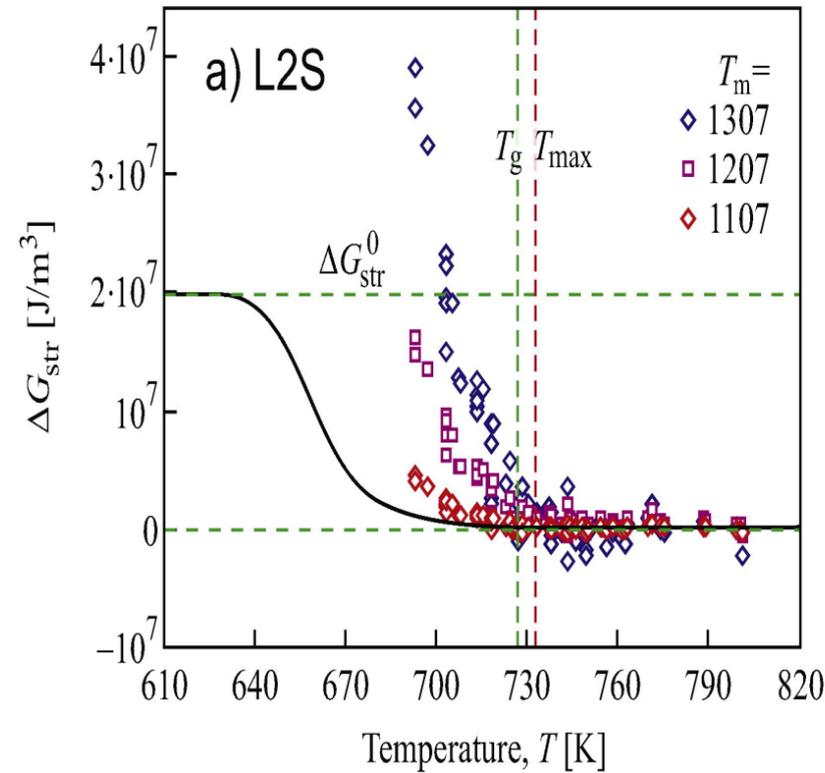
Modify the driving force (most obvious)

Crystallization of glass during cooling

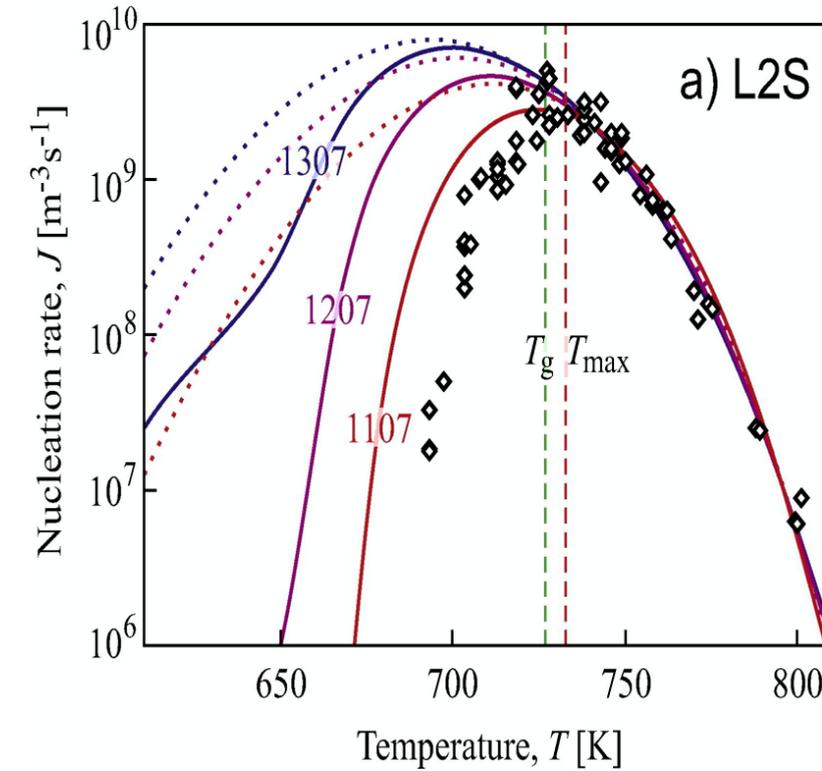
$$\Delta G^{\star} = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_v + F_{el}}$$

with $|\Delta G_v + F_{el}| < |\Delta G_v|$

That's all (almost)



Li₂O-2 SiO₂

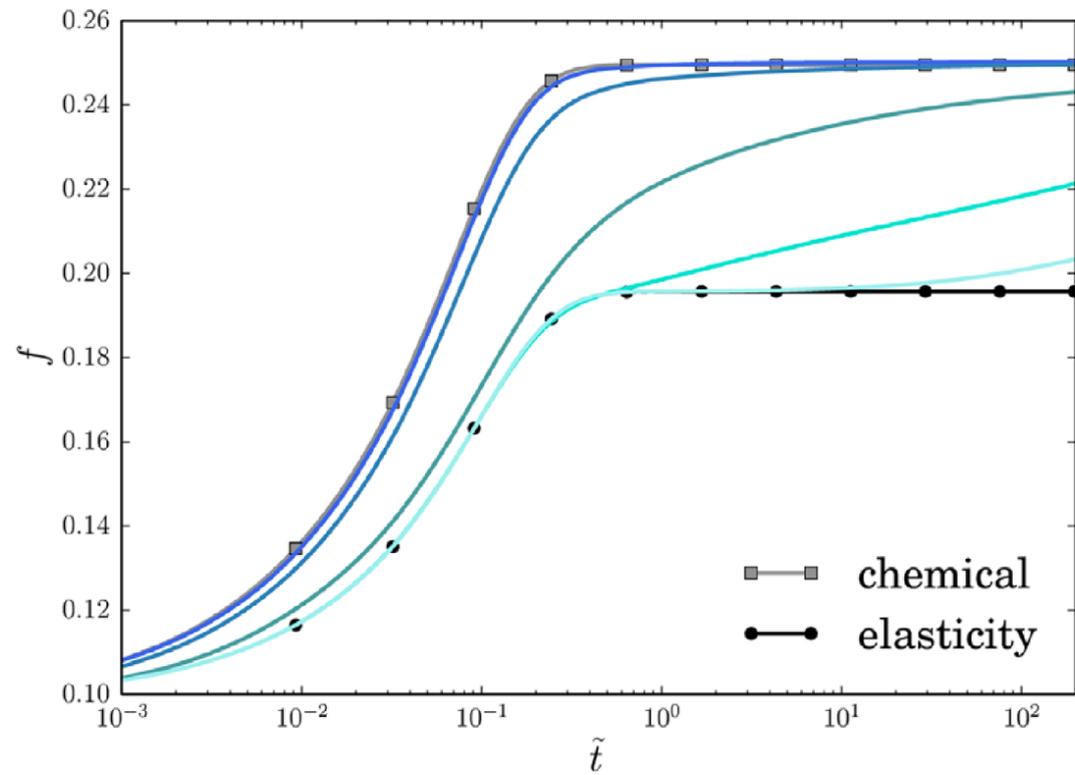


Abyzov et al. (2016)

Influence of stress on growth

Change the interfacial concentrations

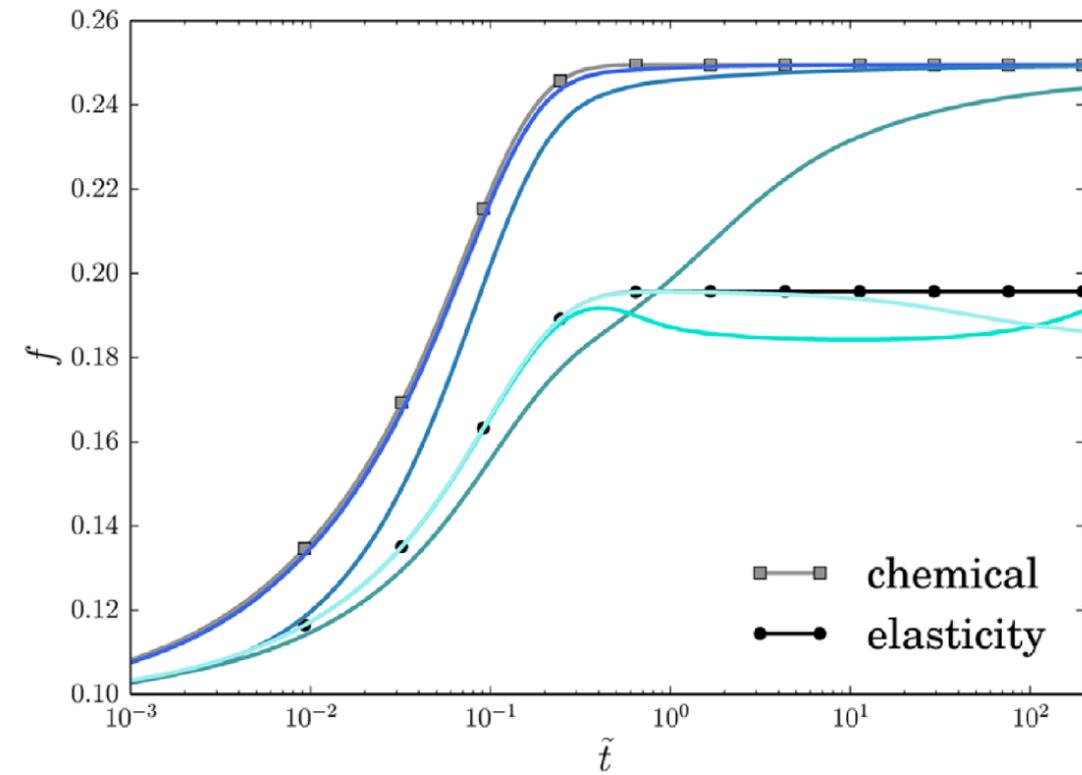
Planar precipitate growing in a supersaturated matrix



viscoplastic precipitate

$$c^\psi = c^{\psi 0} + \llbracket f_{el} \rrbracket - \sigma_{ij}^\beta \llbracket \varepsilon_{ij} \rrbracket + 2\bar{\kappa} \gamma$$

- Two competing time scales

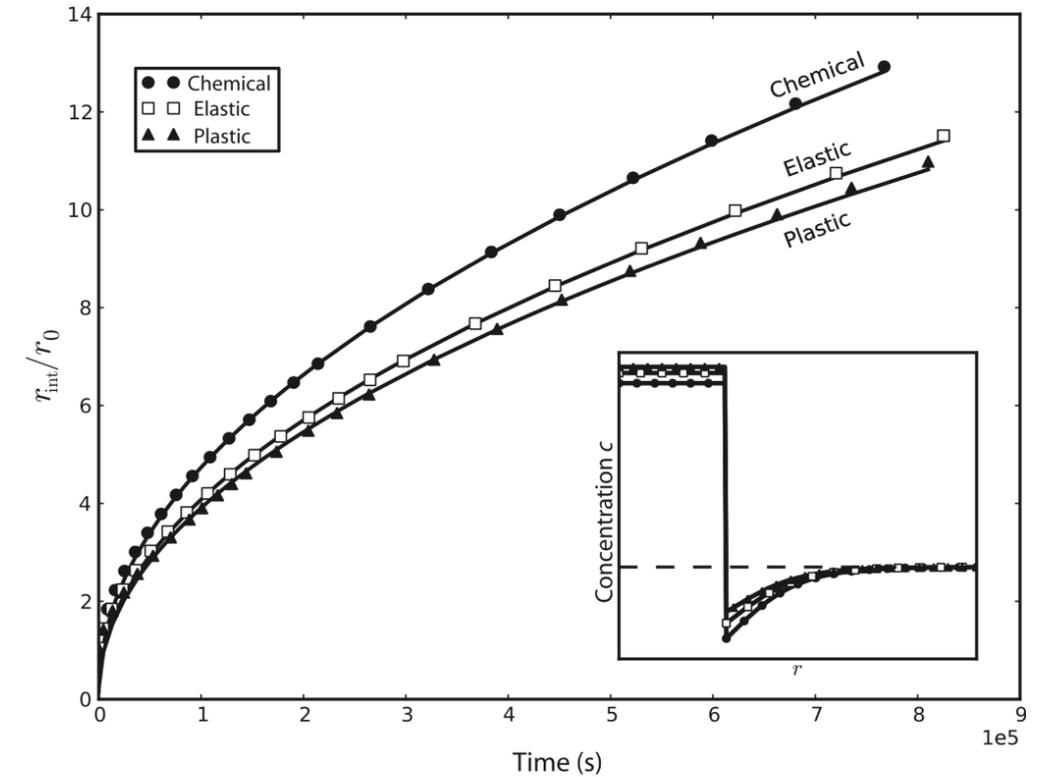
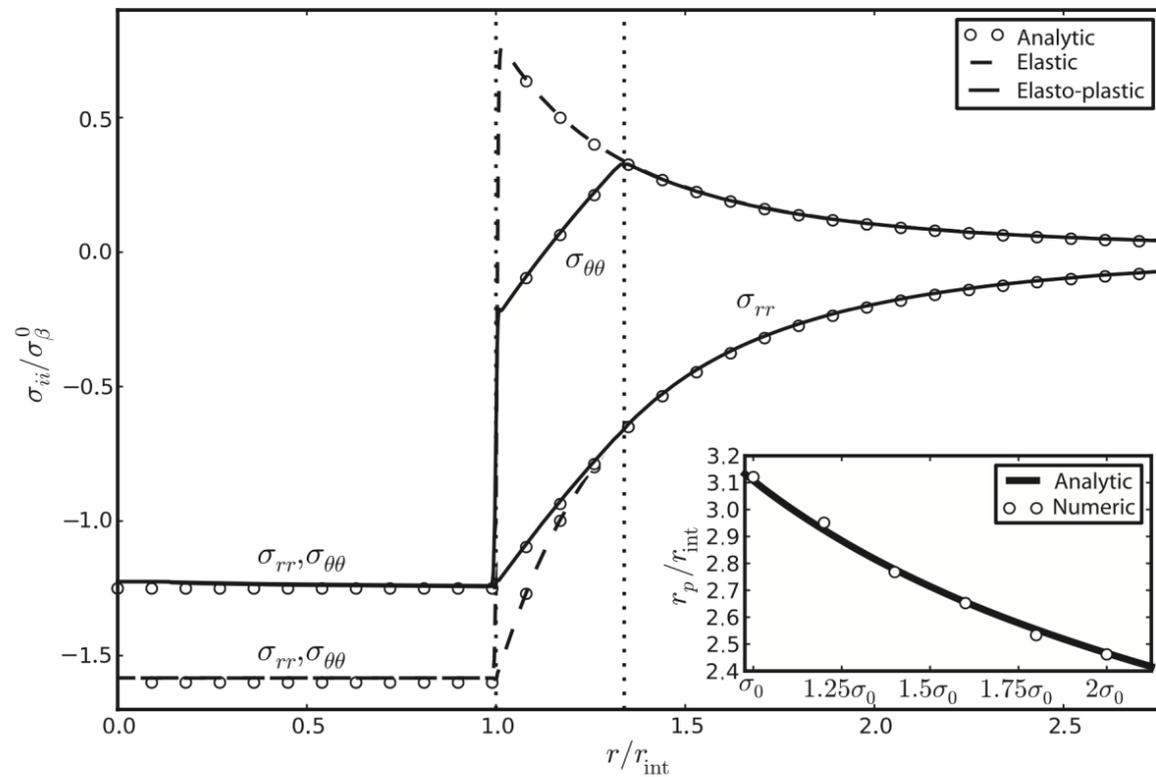


viscoplastic matrix [de Rancourt et al. \(2016\)](#)

Influence of stress on growth

Change the interfacial concentrations

Spherical precipitate growing in a supersaturated matrix



Ammar et al. (2011)

$$c^\psi = c^{\psi 0} + \llbracket f_{el} \rrbracket - \sigma_{ij}^\beta \llbracket \varepsilon_{ij} \rrbracket + 2\bar{\kappa}\gamma$$

- plasticity hinders growth for some morphologies!!
- May also change the bulk diffusion (cf. open elastic constants)

Morphologies

Elasticity selects the shape

The elastic kernel

In Fourier space

- The elastic energy is a simple product

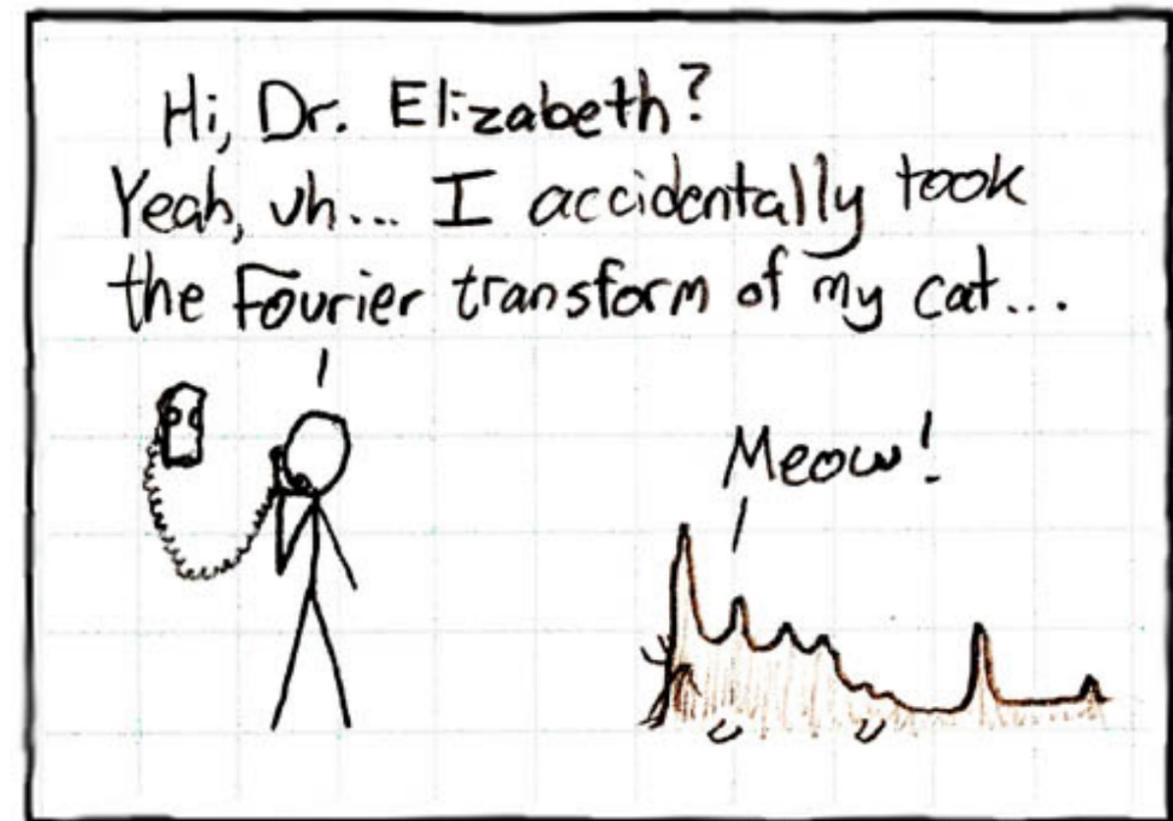
$$E_{\text{el}} = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} B(\vec{n}) \times |\theta(\vec{q})|^2$$

→ distribution of the second phase $|\theta(\vec{q})|^2$

→ elastic kernel $B(\vec{n}) = \varepsilon^* : C : \varepsilon^* - \vec{n} \cdot \varepsilon^* : \Omega : \varepsilon^* \cdot \vec{n}$

$$\Omega^{-1}(\vec{n}) = \vec{n} \cdot C \cdot \vec{n}$$

Eq. to laminates

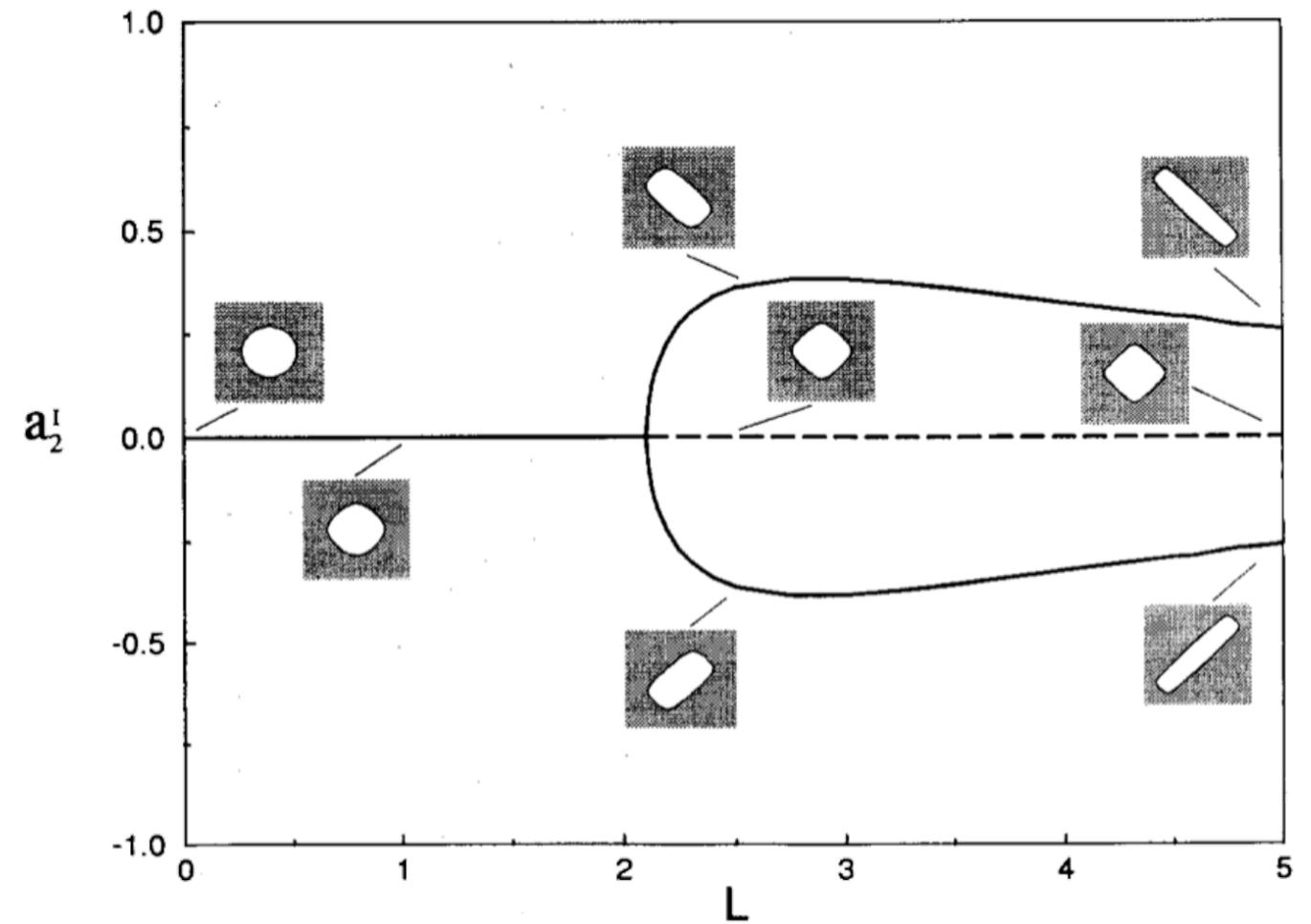
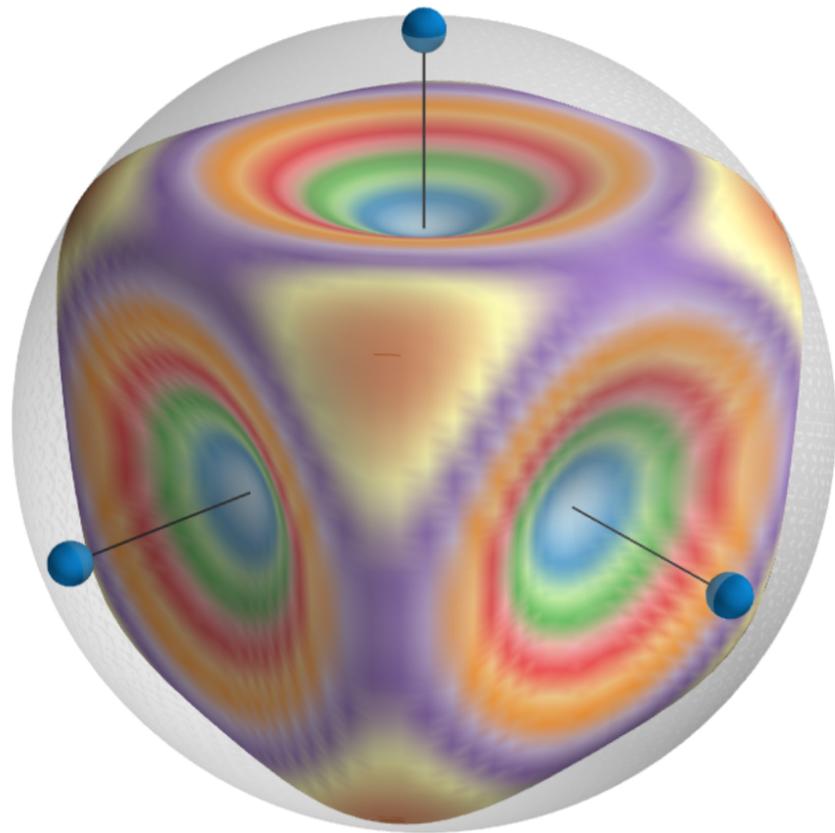


Analyzing $B(\vec{n})$: soft directions (preferred planes) and hard ones

Elasticity selects the shape

Isotropic eigenstrain

- Isotropic elastic constants but inhomogeneous: sphere or plate
- Anisotropic elastic constants: sides normal to soft directions

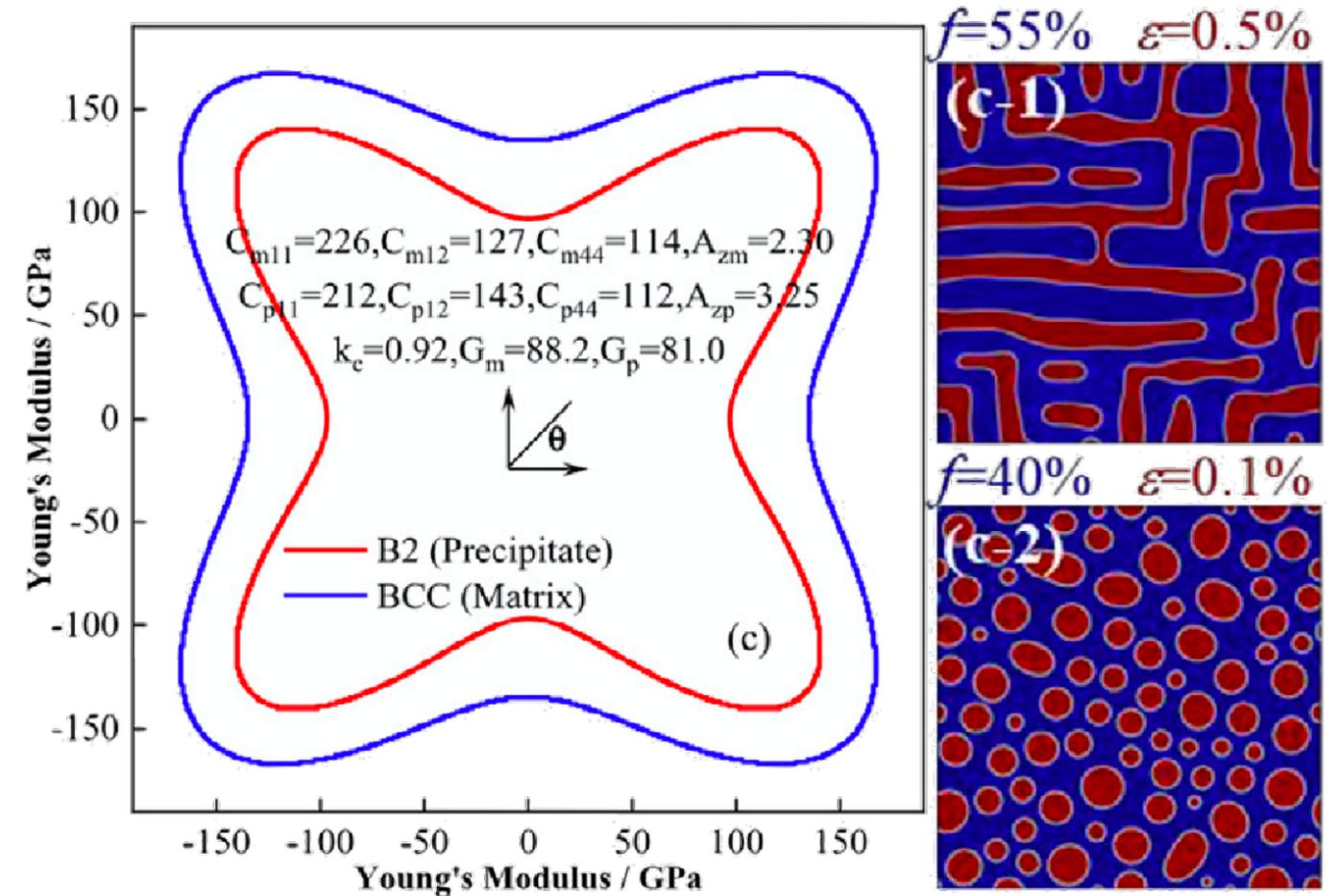
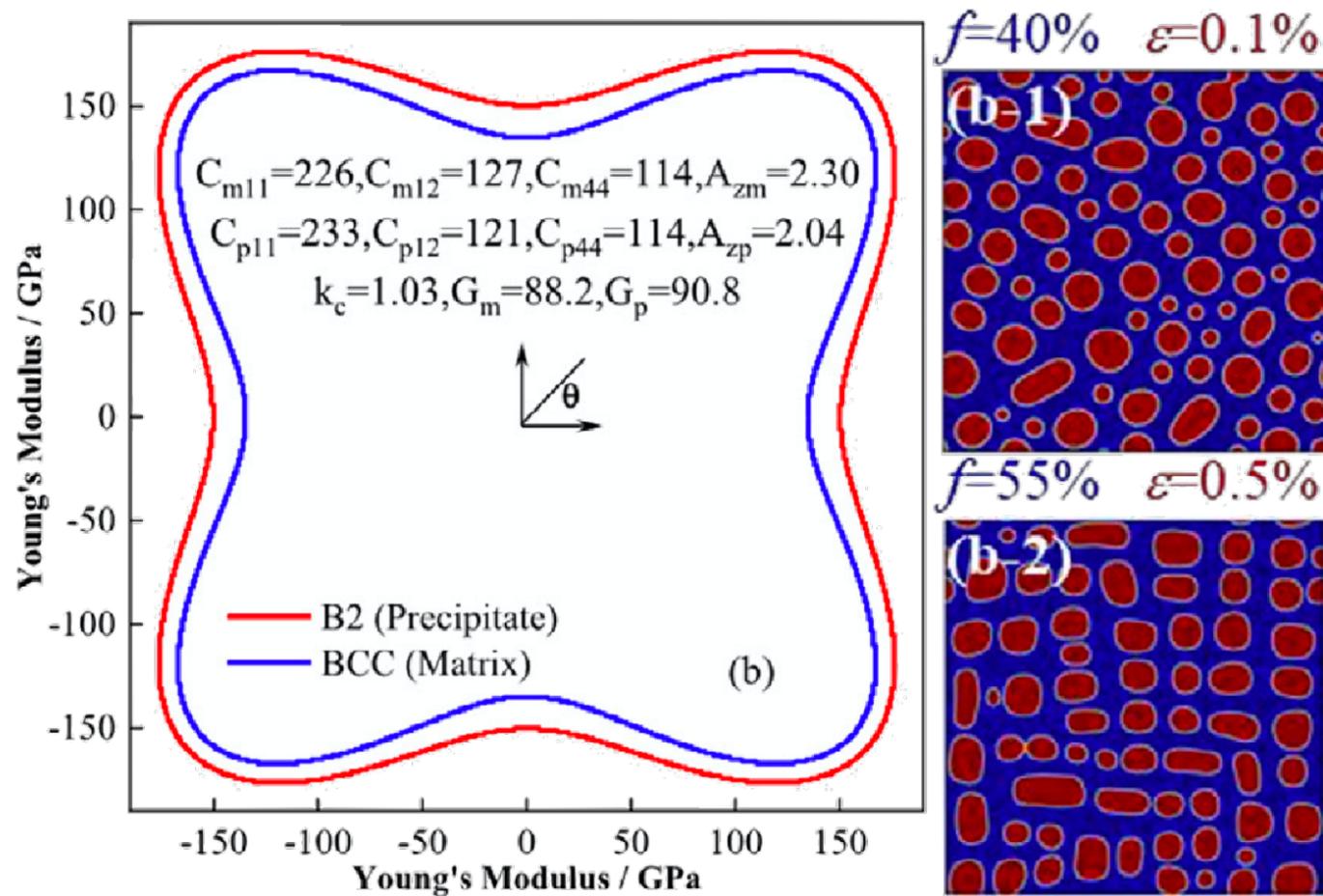


Thompson, Su, and Voorhees (1994)

Elasticity selects the shape

Isotropic eigenstrain

Al-Co-Cr-Fe-Ni J. L. Li et al. (2020)

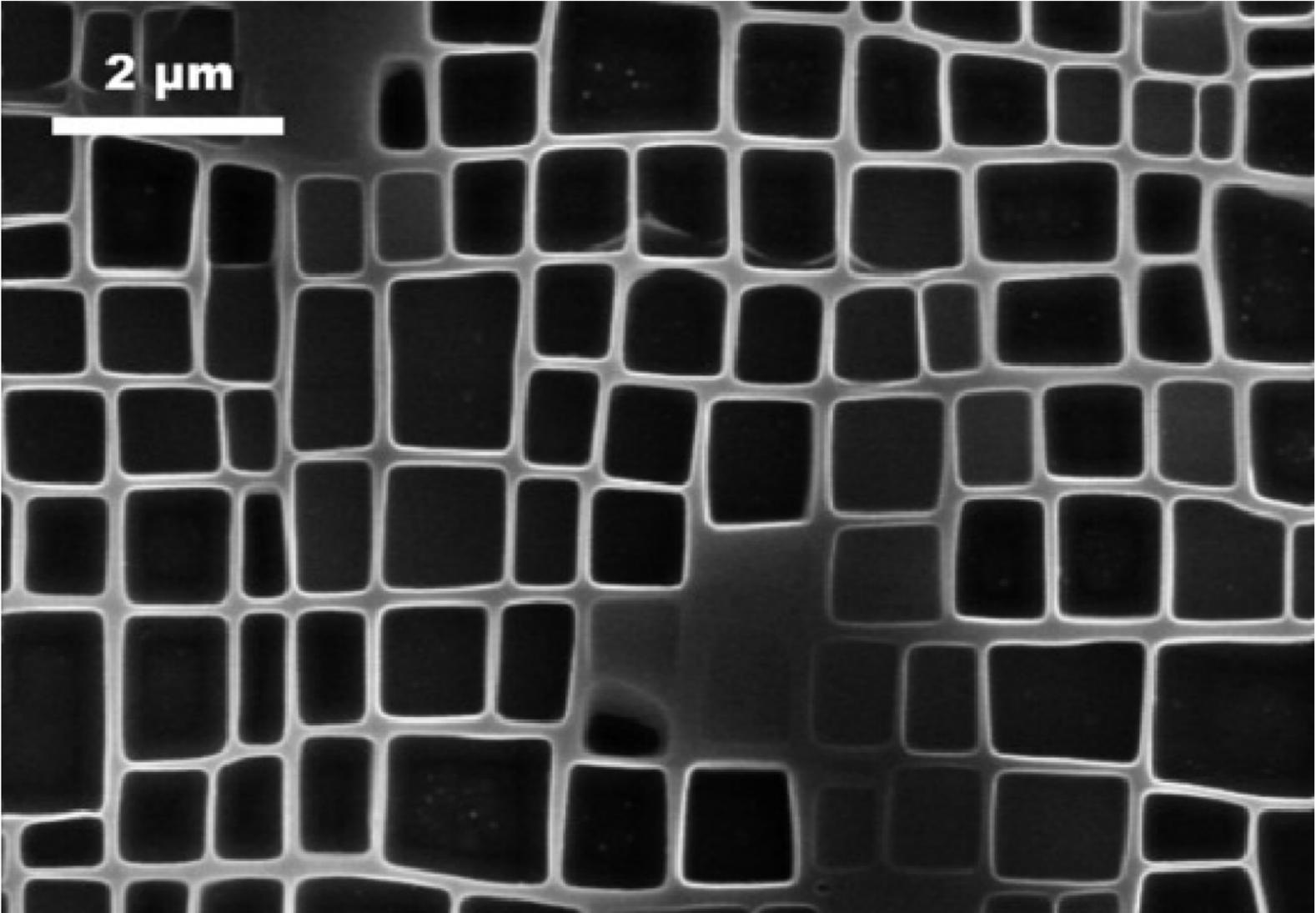


- For small $F_{el} \Rightarrow$ spheres

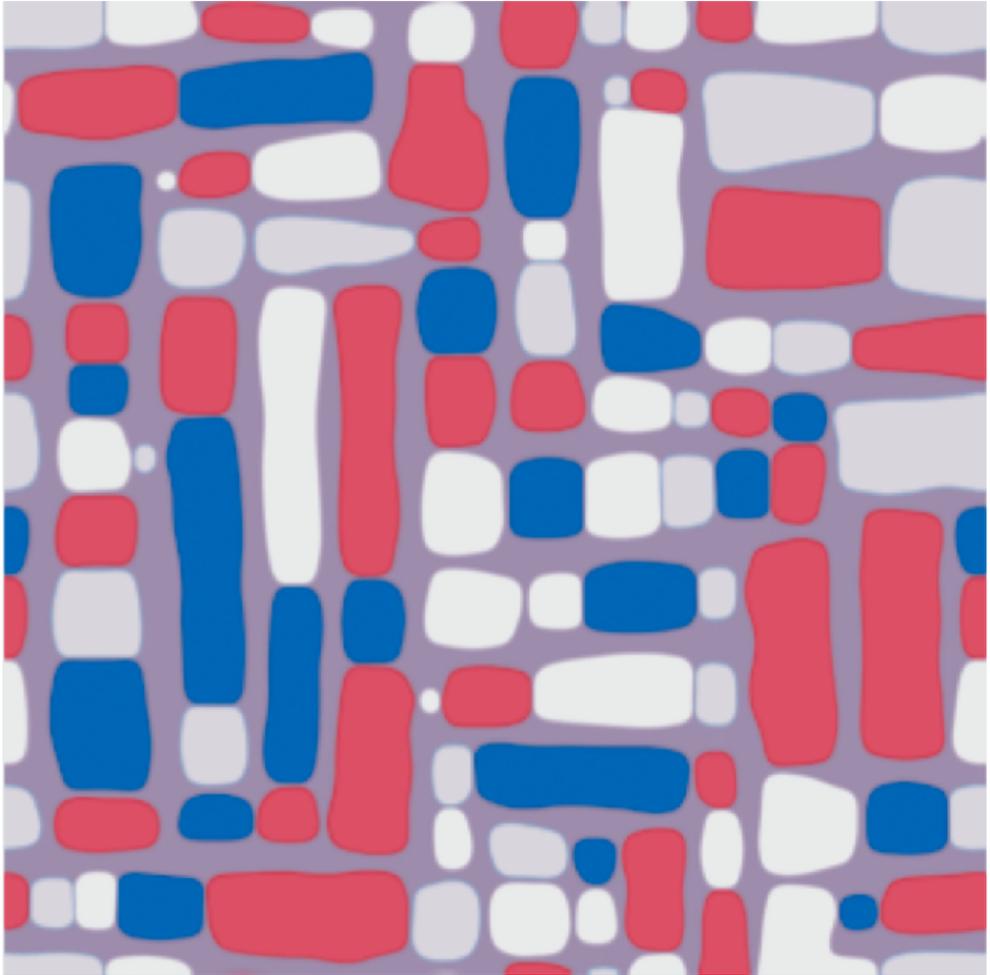
- For large F_{el}
 - \rightarrow hard in soft \Rightarrow cubes
 - \rightarrow soft in hard \Rightarrow plates

Elasticity selects the shape

Elastic constants are not always easy to know



AM1 Diologent and Caron (2004)



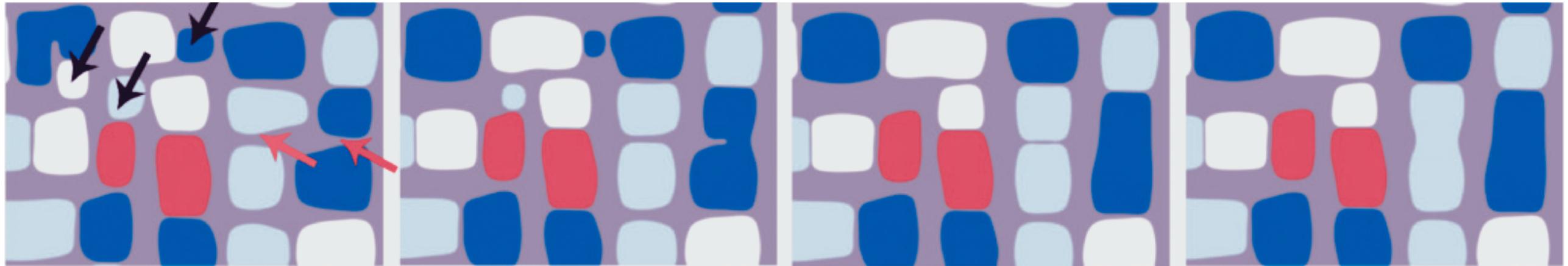
Cottura et al. (2015)

Elasticity selects the shape

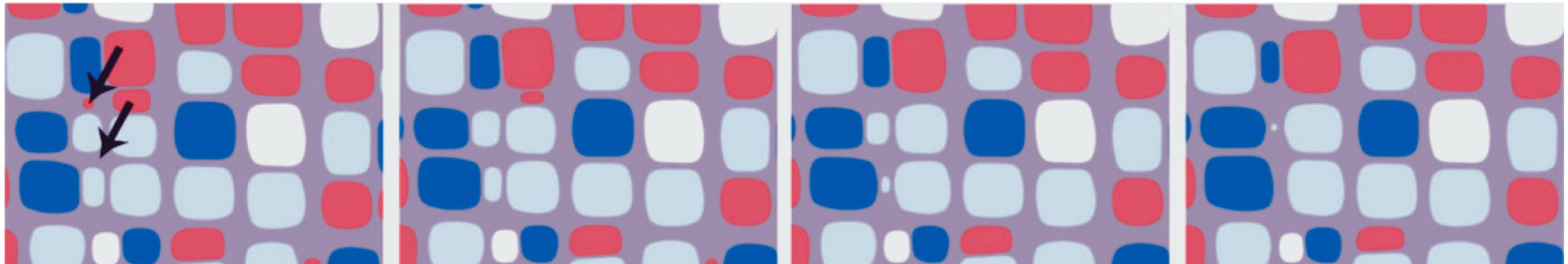
Elastic constants are not always easy to know

Importance of $\Delta C' = (C_{11} - C_{12})/2$ to get cubes

$\Delta C' = 17\%$ (reverse engineering)



$\Delta C' = 50\%$

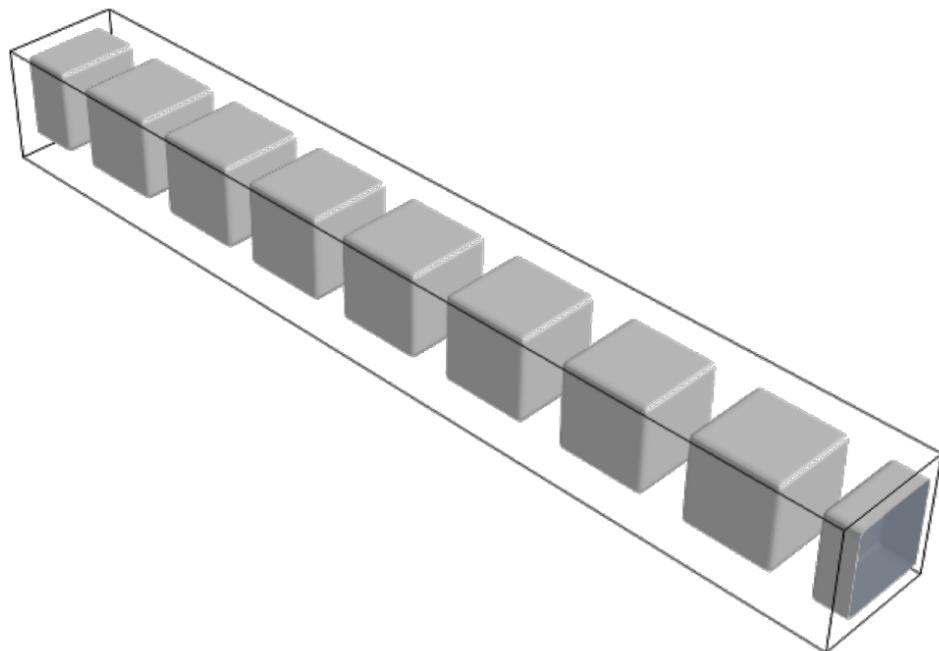


Elasticity selects the shape

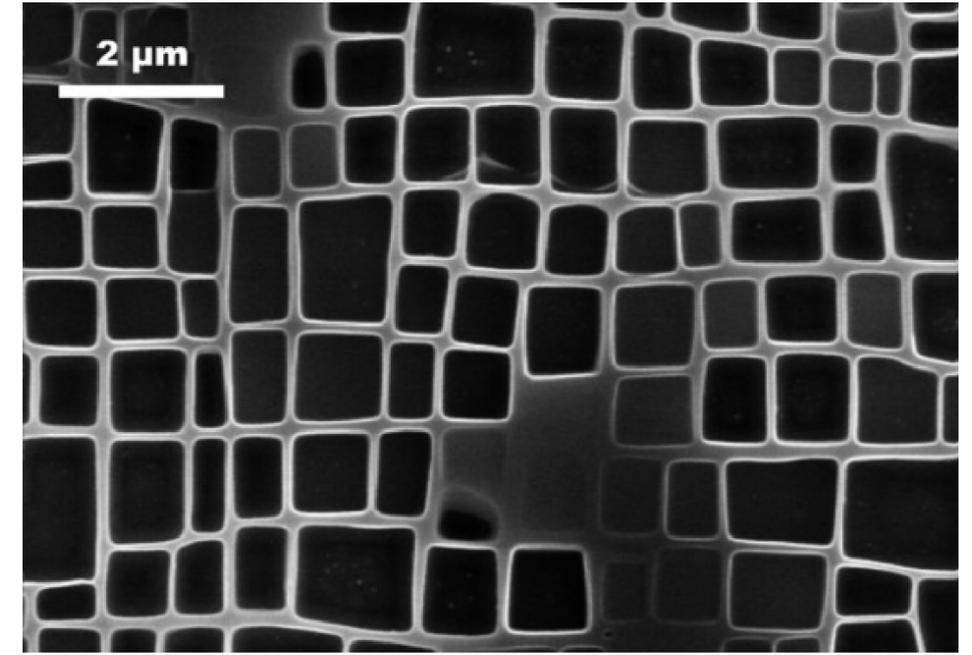
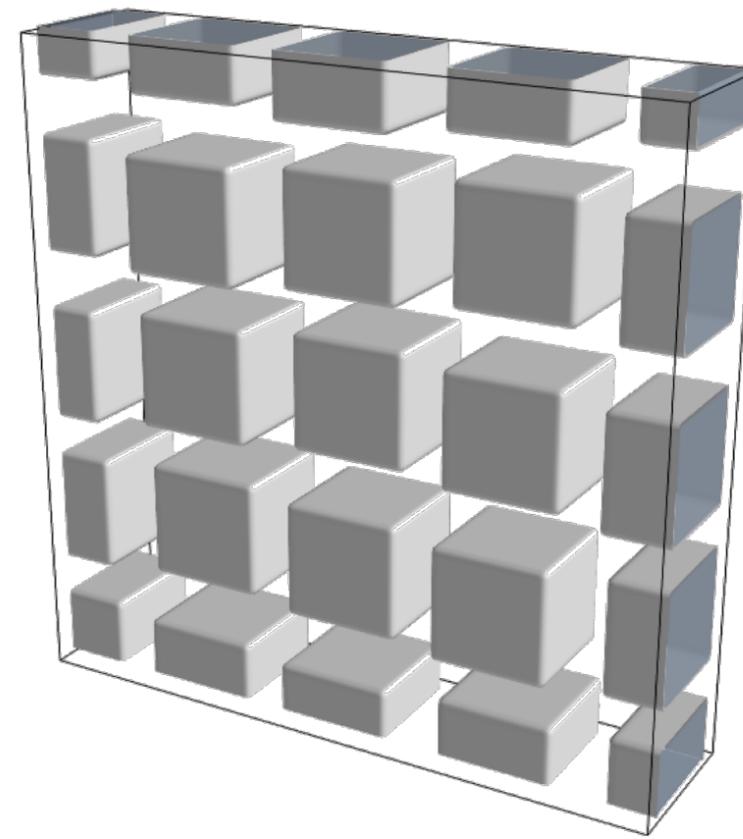
Why no perfect rows and columns? [Degeiter et al. (2020)]

- perfect array of spheres = stable
- perfect array of cubes = unstable

Squeezed mode



Zigzag mode

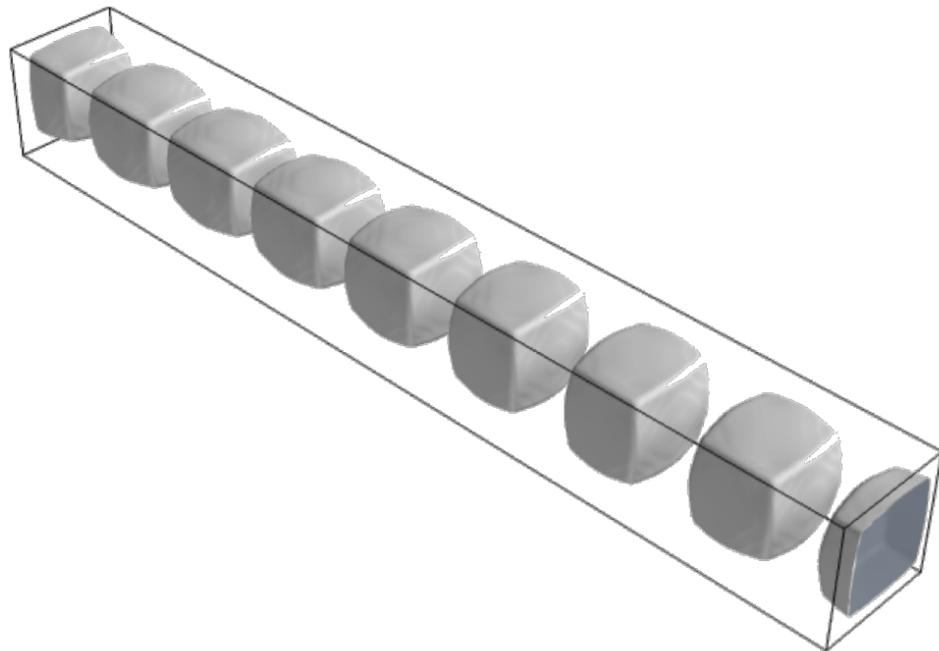


Elasticity selects the shape

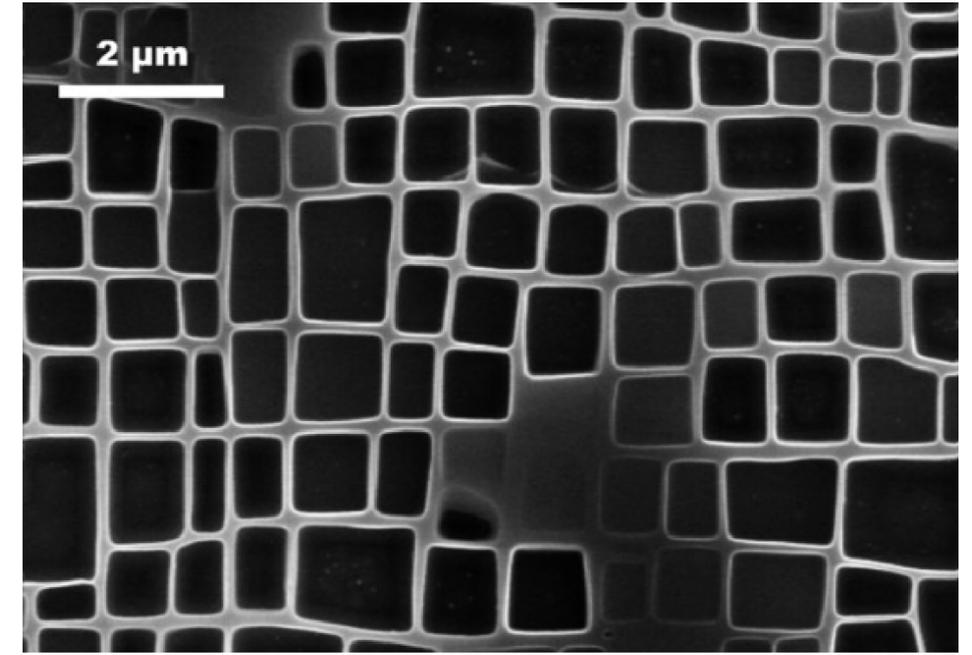
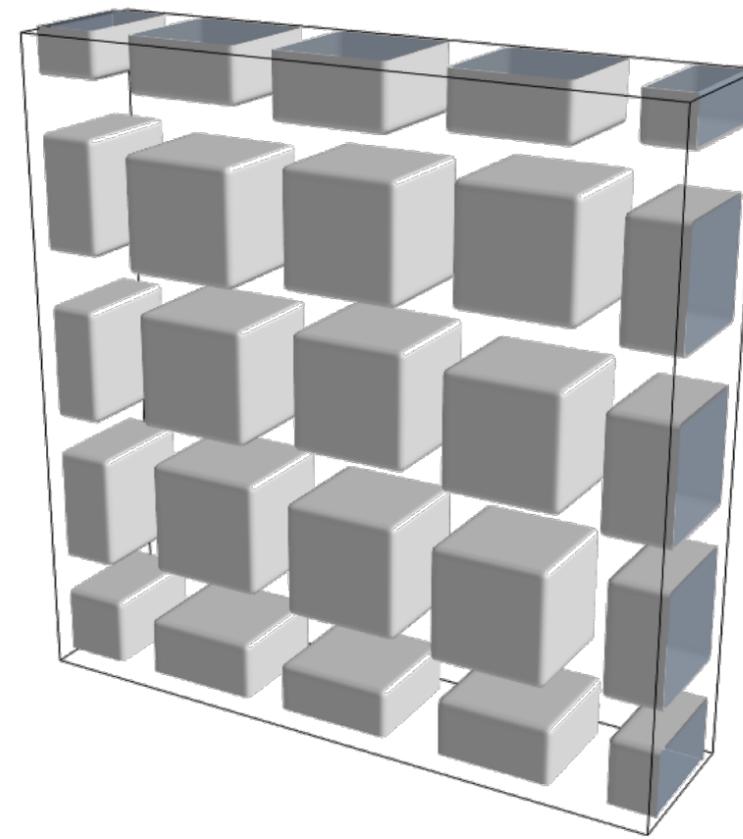
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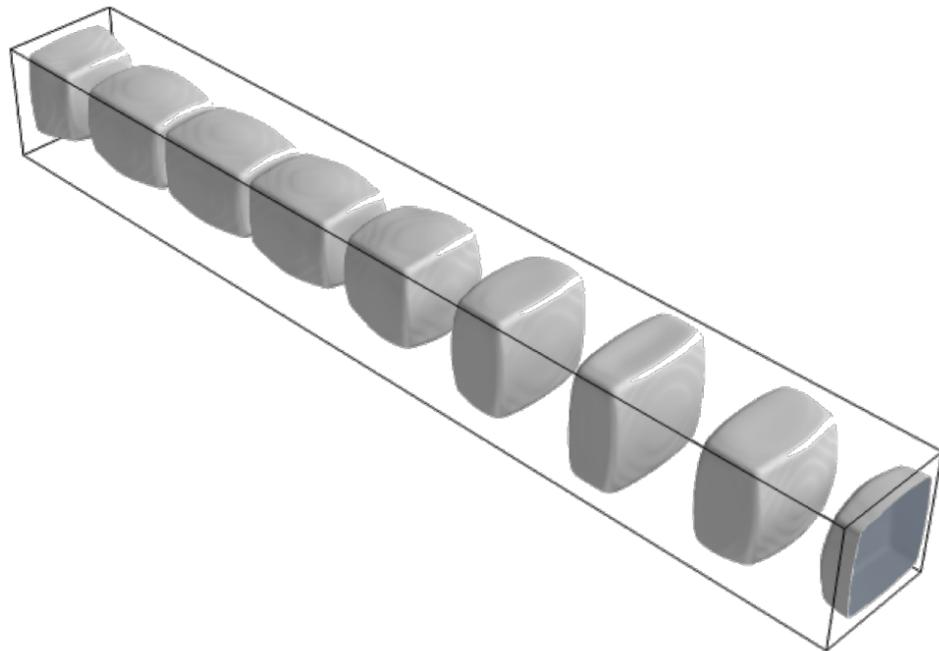


Elasticity selects the shape

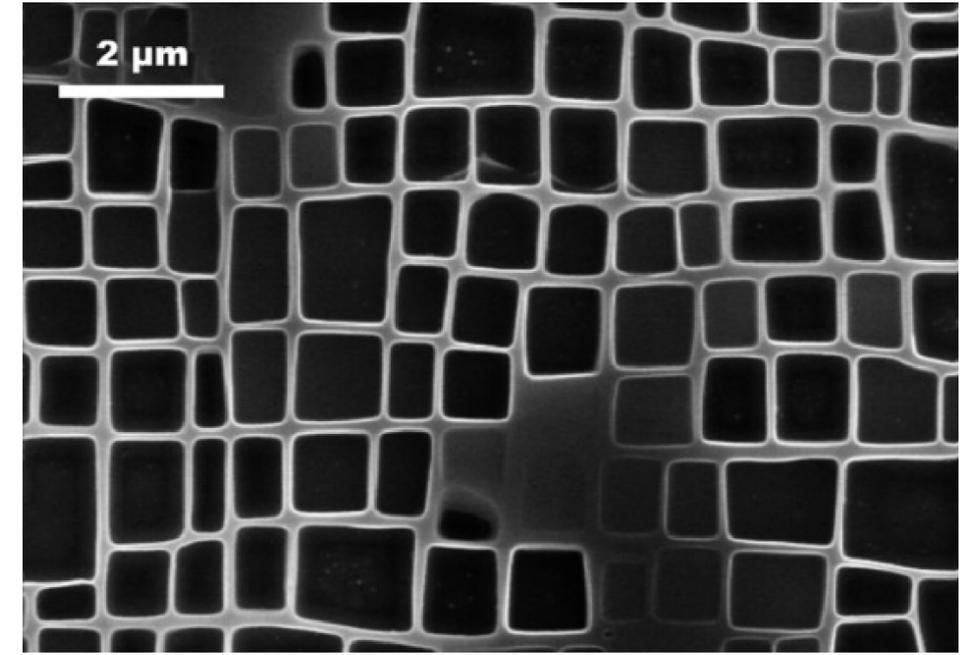
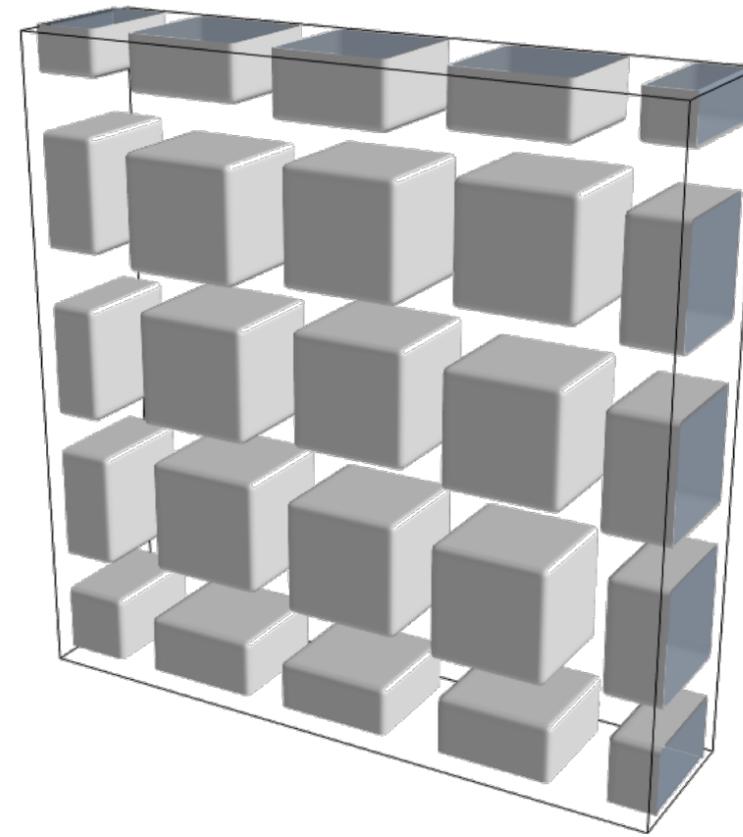
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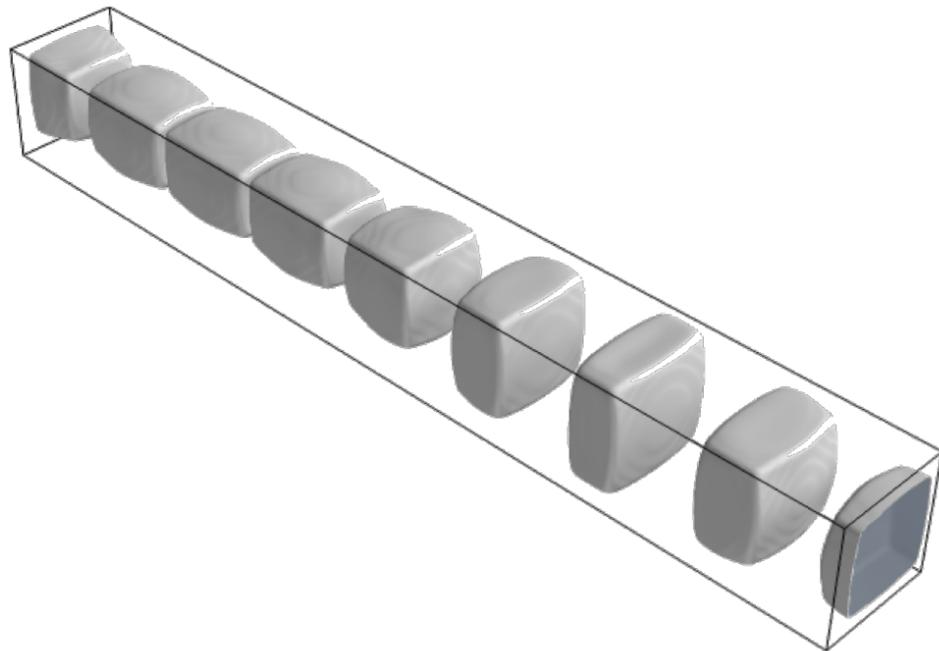


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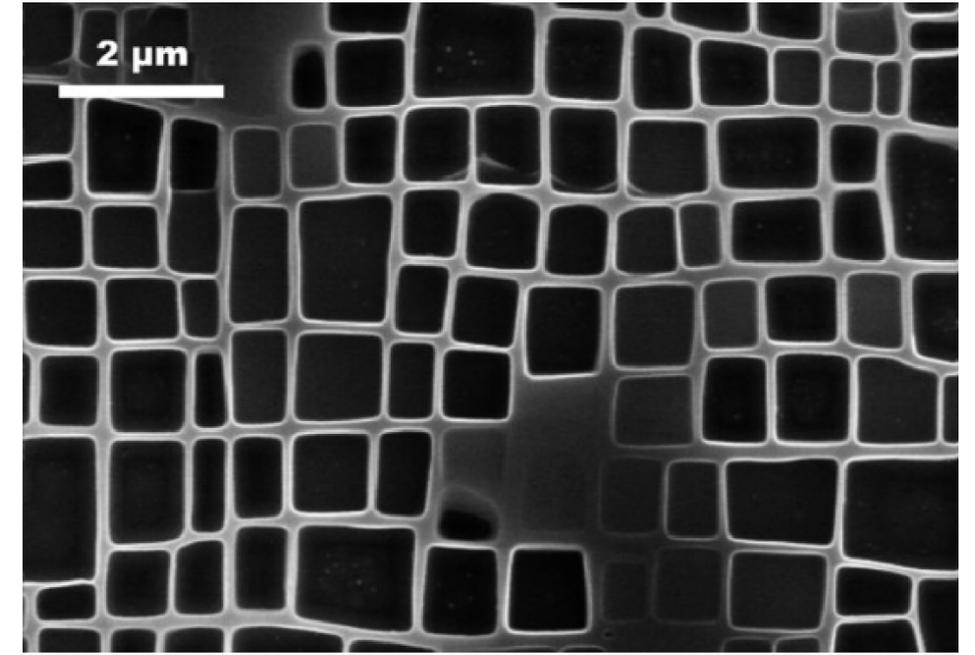
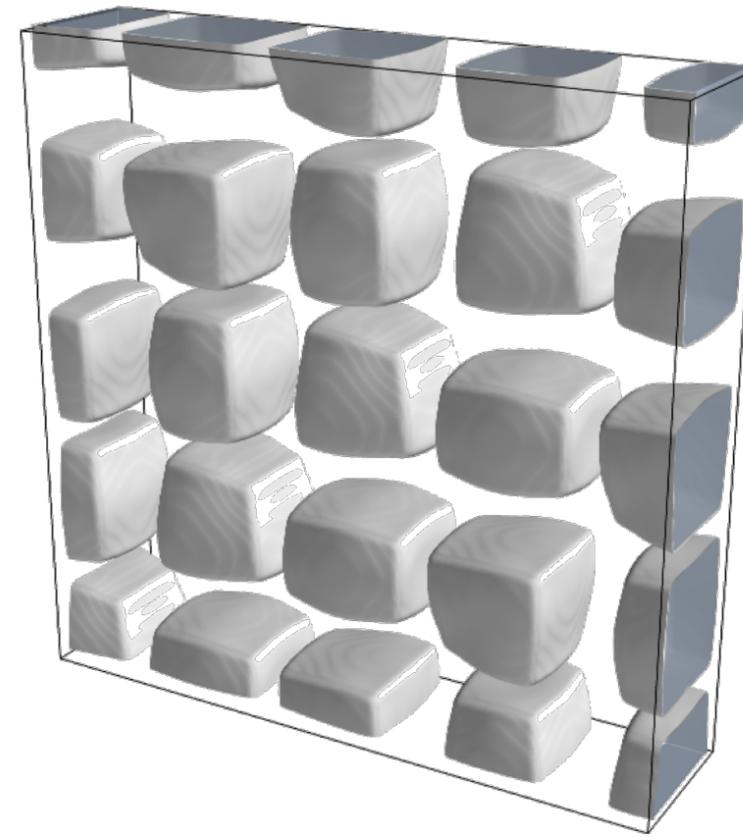
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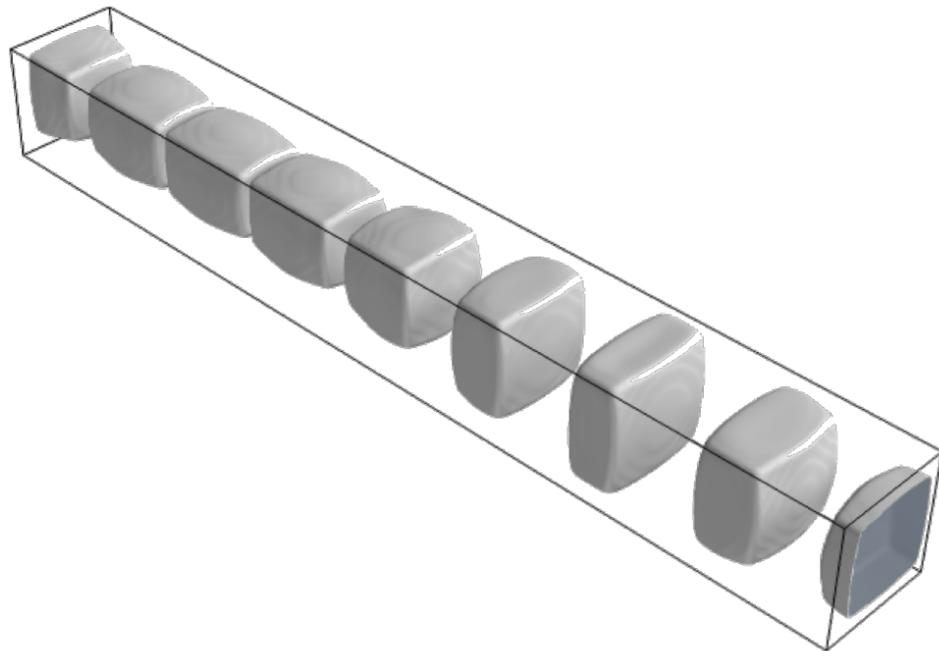


Elasticity selects the shape

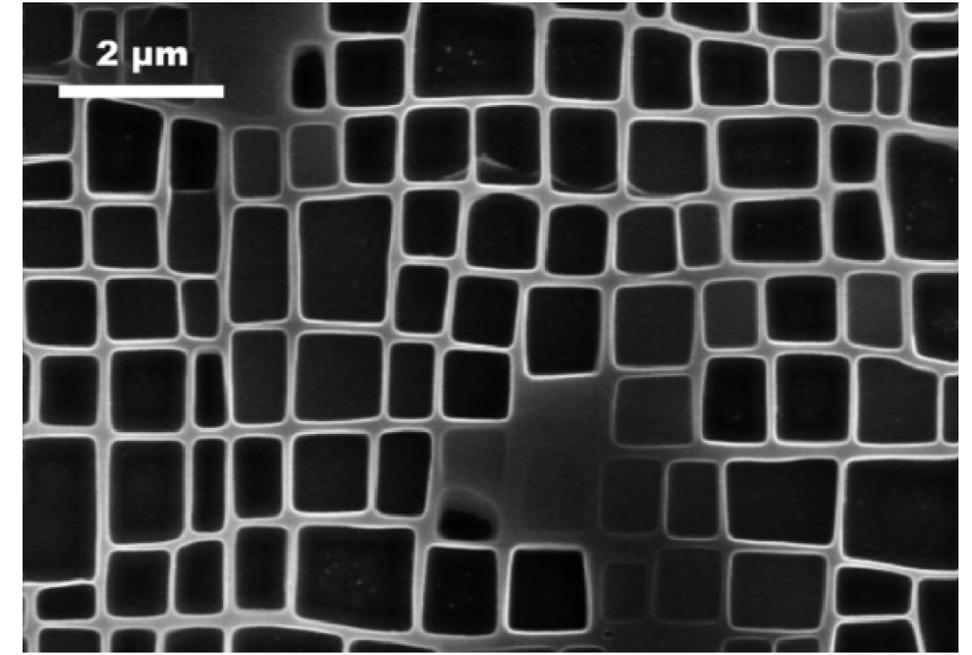
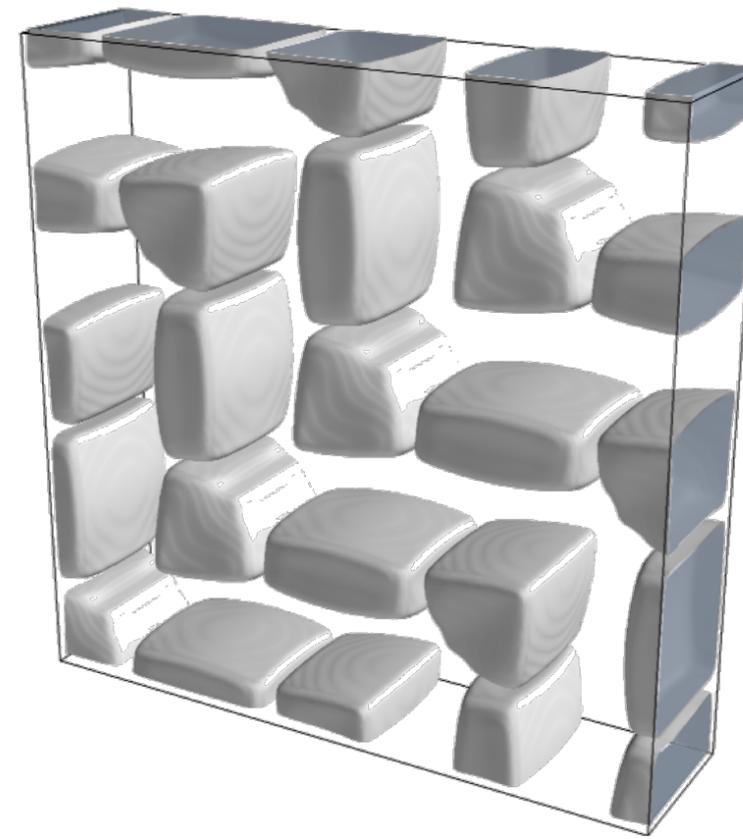
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Squeezed mode



Zigzag mode



Conclusion

No more time (read good papers)

A few points

- Kinetics and shape of acicular precipitates (Widmanstätten and beyond) Struggling against solidification like solution
- Plasticity may promote shape change
 - isotropic: competition between time scales of loading and diffusion
 - anisotropic: impact for moderate
- Kinetics is related to morphology

Is there anything to do at the process scale?

- Coupling mechanics and phase transformation (except for SMA) has been the realm of full-field computations because of the morphological evolutions
- But it is maybe time to upscale these calculations, although there is surely not a universal strategy

References

- Abyzov, Alexander S., Vladimir M. Fokin, Alisson Mendes Rodrigues, Edgar D. Zanotto, and Jörn W. P. Schmelzer. 2016. "The Effect of Elastic Stresses on the Thermodynamic Barrier for Crystal Nucleation." *Journal of Non-Crystalline Solids* 432: 325–33.
- Allen, S. M., and J. W. Cahn. 1975. "Coherent and Incoherent Equilibria in Iron-Rich Iron-Aluminium Alloys." *Acta Metallurgica* 23: 1017–17.
- Ammar, K., B. Appolaire, G. Cailletaud, and S. Forest. 2011. "Phase Field Modeling of Elasto-Plastic Deformation Induced by Diffusion Controlled Growth of a Misfitting Spherical Precipitate." *Philosophical Magazine Letters* 91 (3): 164–72.
- Cahn, J. W., and J. E. Hilliard. 1958. "Free Energy of a Nonuniform System. I. Interfacial Free Energy." *Journal of Chemical Physics* 28 (2): 258–67. <https://doi.org/10.1063/1.1744102>.
- Cahn, J. W., and F. Larché. 1984. "A Simple Model for Coherent Equilibrium." *Acta Metallurgica* 32 (11): 1915–23.
- Charpentier, M., A. Hazotte, and D. Daloz. 2008. "Lamellar Transformation in Near- γ TiAl Alloys – Quantitative Analysis of Kinetics and Microstructure." *Materials Science and Engineering A* 491: 321–30.
- Chernenko, V. A., and V. A. L'vov. 1999. "Thermodynamics of Stress Induced Martensitic Transformation: Application to Ni–Mn–Ga Alloys." *The European Physical Journal - Applied Physics* 8 (1): 25–28.
- Cottura, M., Y. Le Bouar, B. Appolaire, and A. Finel. 2015. "Rôle of Elastic Inhomogeneity in the Development of Cuboidal Microstructures in Ni-Based Superalloys." *Acta Materialia* 94: 15–25.
- de Rancourt, V., K. Ammar, B. Appolaire, and S. Forest. 2016. "Homogenization of Viscoplastic Constitutive Laws Within a Phase Field Approach." *Journal of the Mechanics and Physics of Solids* 88: 291–319.
- Degeiter, M., Y. Le Bouar, B. Appolaire, M. Perrut, and A. Finel. 2020. "Instabilities in the Periodic Arrangement of Elastically Interacting Precipitates in Nickel-Base Superalloys." *Acta Materialia* 187: 41–50.
- Diologent, F., and P. Caron. 2004. "On the Creep Behavior at 1033 K of New Generation Single-Crystal Superalloys." *Materials Science and Engineering A* 385: 245–57.
- Du, J., F. Momprou, and W. Z. Zhang. 2017. "A TEM Study of the Crystallography of Lath-Shaped Austenite Precipitates in a Duplex Stainless Steel." *Journal of Materials Science* 52: 11688–700.
- Fischer, F. D., T. Waitz, D. Vollath, and N. K. Simha. 2008. "On the Role of Surface Energy and Surface Stress in Phase-Transforming Nanoparticles." *Progress in Materials Science* 53: 481–527.

- Fratzl, P., O. Penrose, and J. L. Lebowitz. 1999. "Modelling of Phase Separation in Alloys with Coherent Elastic Misfit." *Journal of Statistical Physics* 95 (5-6): 1429–1503.
- Guimarães, José Roberto Costa, and Paulo Rangel Rios. 2015. "Microstructural Path Analysis of Martensite Dimensions in FeNiC and FeC Alloys." *Materials Research* 18 (3): 595–601. <https://doi.org/10.1590/1516-1439.000215> .
- Gurtin, M. E. 2000. *Configurational Forces as Basic Concepts of Continuum Physics*. Edited by J. E. Marsden and L. Sirovich. Vol. 137. Applied Mathematical Sciences. Springer.
- Gurtin, M. E., and P. W. Voorhees. 1996. "The Thermodynamics of Evolving Interfaces Far from Equilibrium." *Acta Mater.* 44 (1): 235–47.
- Hu, B., Y. Jiang, J. Wang, B. Yao, F. Min, and Y. Du. 2018. "Thermodynamic Calculation of the T_0 Curve and Metastable Phase Diagrams of the Ti–M (M = Mo, V, Nb, Cr, Al) Binary Systems." *Calphad* 62: 75–82.
- Kadirvel, K., H. L. Fraser, and Y. Wang. 2023. "Microstructural Design via Spinodal-Mediated Phase Transformation Pathways in High-Entropy Alloys (HEAs) Using Phase-Field Modelling." *Acta Materialia* 243: 118438.
- Khachaturyan, A. G. 1983. *Theory of Structural Transformations in Solids*. John Wiley & Sons.
- Larché, F., and J. W. Cahn. 1978. "Thermochemical Equilibrium of Multiphase Solids Under Stress." *Acta Metallurgica* 26 (10): 1579–89.
- . 1985. "Overview No. 41 the Interactions of Composition and Stress in Crystalline Solids." *Acta Metallurgica* 33 (3): 331–57.
- Lass, Eric A. 2022. "On the Thermodynamics and Phase Transformation Pathways in BCC-B2 Refractory Compositionally Complex Superalloys." *Metallurgical and Materials Transactions A* 53 (12): 4481–98.
- Li, Danning, James Barrington, Stephen James, David Ayre, Marcin Słoma, Meng-Fang Lin, and Hamed Yazdani Nezhad. 2022. "Electromagnetic Field Controlled Domain Wall Displacement for Induced Strain Tailoring in BaTiO₃-Epoxy Nanocomposite." *Scientific Reports* 12 (1): 7504.
- Li, J. L., Z. Li, Q. Wang, C. Dong, and P. K. Liaw. 2020. "Phase-Field Simulation of Coherent BCC/B2 Microstructures in High Entropy Alloys." *Acta Materialia* 197: 10–19.
- Lütjering, G., and J. C. Williams. 2003. *Titanium*. Engineering Materials and Processes. Springer.
- Maugin, G. A. 2011. *Configurational Forces – Thermomechanics, Physics, Mathematics, and Numerics*. CRC Press.
- Settefrati, A. 2012. "Étude Expérimentale Et Modélisation Par Champ de Phase de La Formation de α Dans Les Alliages de Titane β -Métastable." PhD thesis, Université de Lorraine.
- Shi, S., J. Markmann, and J. Weissmuller. 2018. "Verifying Larché–Cahn Elasticity, a Milestone of 20th-Century Thermodynamics." *Proceedings of the National Academy of Sciences of the United States of America* 115 (43).
- Thompson, M. E., C. S. Su, and P. W. Voorhees. 1994. "The Equilibrium Shape of a Misfitting Precipitate." *Acta Metallurgica and*