2nde partie :

Une dérivation d'un modèle champ de phase par changement d'échelle

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Modelling : different scales

Macroscopic scale

- domains or phases separated by sharp boundaries
- PDE within the domains
- interface tracking

⟶ free-boundary problems

Top-down

regularisation of sharp interfaces

Bottom-up :

- coarse-graining
- homogenisation
- statistical physics

Mesoscopic scale

- fields are continuous
- interfaces are diffuse

⟶ Phase field models

Microscopic scale

- atoms are resolved
- two-body (or many-body) forces

⟶ Atomistic models (Dyn. Mol., Monte Carlo…)

Modelling : different scales

This course :

Bottom-up :

- coarse-graining
- homogenisation
- statistical physics

Mesoscopic scale

- fields are continuous
- interfaces are diffuse

⟶ Phase field models

From "scratch" :

- order parameters
- Laudau rules (symmetry)
- kinetics laws (conserved or non-conserved)

Microscopic scale

- atoms are resolved
- two-body (or many-body) forces

⟶ Atomistic models (Dyn. Mol., Monte Carlo…)

Outline

- Phase Field method : how to get the basic equation ?
- How to compute the Ginzburg-Landau free energy ?

Phase Field method: how to get the basic equation (1)

Starting point : a microscopic master equation

- atomic configuration:

$$\mathcal{C} = (....p_i.....p_j.....) \qquad p_i = 0 \text{ or } 1 \text{ if } A \text{ or } B \text{ on site } i$$

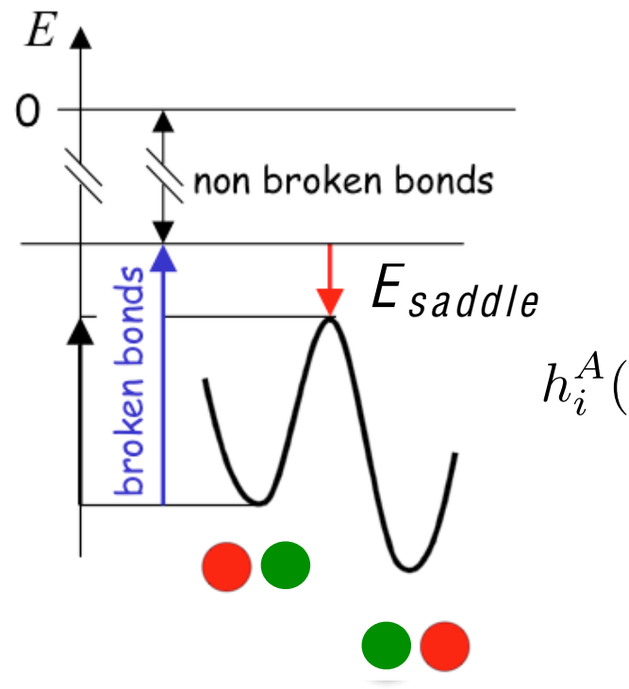
- kinetic model: direct exchange between A and B on 1st neighbor sites

$$\frac{\partial P(\mathcal{C})}{\partial t} = -\sum_{i,j}^{*} W(\mathcal{C} \to \mathcal{C}^{ij}) P(\mathcal{C}) + \sum_{i,j}^{*} W(\mathcal{C}^{ij} \to \mathcal{C}) P(\mathcal{C}^{ij})$$

$\mathcal{C}^{ij}$: $\mathcal{C}$ with i and j exchanged

- transition probability:

local mechanism : direct exchange through saddle point (G. Martin, Phys. Rev. B, 1990)



$$W(\mathcal{C} \to \mathcal{C}^{ij}) = \theta \ \exp -\beta(2E_{saddle} - h_i^A(\mathcal{C}) - h_j^B(\mathcal{C}))\ \delta(p_i)\delta(p_j - 1)$$

$h_i^A(\mathcal{C})$: interaction energy between site *i* and the other sites if *i* is occupied by atom A

if pair interactions only : $h_i^A(\mathcal{C}) = \sum_j V_{ij}^{AA}(1 - p_j) + V_{ij}^{AB} p_j$

easy to verify that W fulfils the detailed balance

$$P_{eq}(\mathcal{C}) W(\mathcal{C} \to \mathcal{C}^{ij}) = P_{eq}(\mathcal{C}^{ij}) W(\mathcal{C}^{ij} \to \mathcal{C})$$ with $$P_{eq}(\mathcal{C}) \sim \exp(-H(C)/kT)$$

$E(\mathcal{C})$: energy of config. $\mathcal{C}$

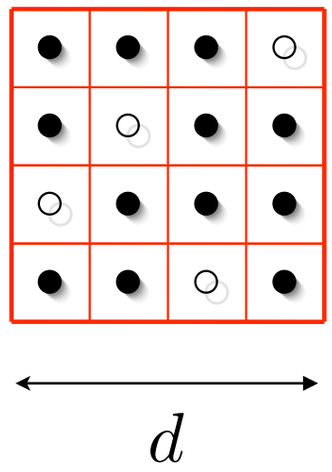
$\longrightarrow$ $P_{eq}(\mathcal{C})$ is a fixed point of the microscopic master equation !

Phase Field method: how to get the basic equation (2)

- Mesoscopic scale :

mesoscopic ← $$c_n = \frac{1}{N_{cell}} \sum_{i \in n} p_i$$ → microscopic

cell of volume d^3



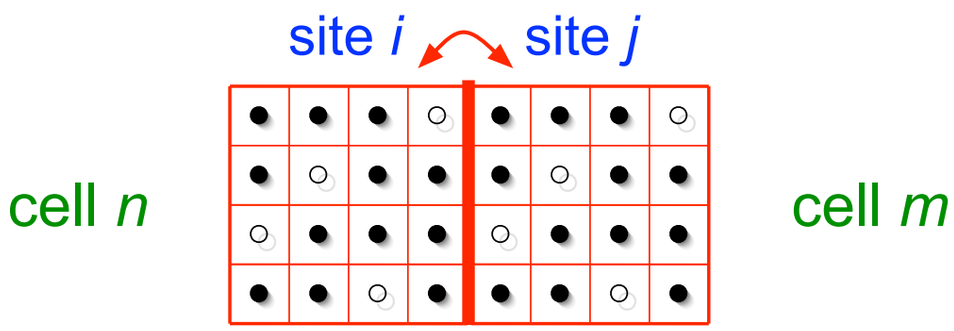
- average out microscopic fluctuations of wavelength < *d*
- keep mesoscopic flustuations of wavelength > *d*

$$\widetilde{\mathcal{C}} = (...c_n....c_m...) \qquad P(\widetilde{\mathcal{C}}) = \mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}}\, P(\mathcal{C})$$

- Mesoscopic master equation :

from:
$$\frac{\partial P(\mathcal{C})}{\partial t} = - \theta\, \exp(-2\beta E_{col}) \sum_{i,j}^{*} \left(\delta(p_i(\mathcal{C}))\, \delta(p_j(\mathcal{C})-1)\, \exp(\beta h_i^A(\mathcal{C}))\, \exp(\beta h_j^B(\mathcal{C}))\, P(\mathcal{C}) \right) + (\text{gain term})$$

to:
$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta\, \exp(-2\beta E_{col}) \sum_{n,m}^{*} \sum_{i \in n, j \in m}^{*} \mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}} \left(\delta(p_i(\mathcal{C}))\, \delta(p_j(\mathcal{C})-1)\, \exp(\beta h_i^A(\mathcal{C}))\, \exp(\beta h_j^B(\mathcal{C}))\, P(\mathcal{C}) \right) + (\text{gain term})$$



Phase Field method: how to get the basic equation (3)

- Mesoscopic master equation :

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta \exp(-2\beta E_{col}) \sum_{n,m}^{*} \sum_{i\in n, j\in m}^{*} \mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}} \left(\delta(p_i(\mathcal{C})) \, \delta(p_j(\mathcal{C})-1) \, \exp(\beta h_i^A(\mathcal{C})) \, \exp(\beta h_j^B(\mathcal{C})) \, P(\mathcal{C}) \right)$$
$$+ \text{(gain term)}$$

- Need simplification :

if N_{cell} large enough

microscopic fast ⟵ $\mathcal{C}$ in quasi-equilibrium with $\widetilde{\mathcal{C}}$ ⟶ mesoscopic slow

$$P(\mathcal{C}) \simeq P(\widetilde{\mathcal{C}}) \, \frac{\exp -\beta H(\mathcal{C})}{\mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}} \exp -\beta H(\mathcal{C})}$$

- Mesoscopic master equation becomes :

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta \exp(-2\beta E_{col}) \sum_{n,m}^{*} \sum_{i\in n, j\in m}^{*} < \delta(p_i(\mathcal{C})) \, \delta(p_j(\mathcal{C})-1) \, \exp(\beta h_i^A(\mathcal{C})) \, \exp(\beta h_j^B(\mathcal{C})) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \, P(\widetilde{\mathcal{C}})$$
$$+ \text{(gain term)}$$

$$< X(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}} = \frac{\mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}} \, X(\mathcal{C}) \, \exp -\beta H(\mathcal{C})}{\mathrm{Tr}_{\mathcal{C}/\widetilde{\mathcal{C}}} \exp -\beta H(\mathcal{C})}$$

Phase Field method: how to get the basic equation (4)

- Mesoscopic master equation:

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta \exp(-2\beta E_{col}) \sum_{n,m}^{*} \sum_{i\in n, j\in m}^{*} < \delta(p_i(\mathcal{C}))\, \delta(p_j(\mathcal{C})-1)\, \exp(\beta h_i^A(\mathcal{C}))\, \exp(\beta h_j^B(\mathcal{C})) >_{\mathcal{C}/\widetilde{\mathcal{C}}}\ P(\widetilde{\mathcal{C}})$$
$$+ \quad (\text{gain term})$$

→ we introduce a mean field approximation :

$$< f(i\in n) f(j\in m) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \sim < f(i\in n) >_{\mathcal{C}/\widetilde{\mathcal{C}}} < f(j\in m) >_{\mathcal{C}/\widetilde{\mathcal{C}}}$$

transition probability becomes:

$$i\in n,\ j\in m: \quad < \delta(p_i(\mathcal{C}))\, \delta(p_j(\mathcal{C})-1)\, \exp(\beta h_i^A(\mathcal{C}))\, \exp(\beta h_j^B(\mathcal{C})) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \sim \exp(\beta g_i^A(\widetilde{\mathcal{C}}))\, \exp(\beta g_j^B(\widetilde{\mathcal{C}}))$$

with:

$$g_i^A(\widetilde{\mathcal{C}}) = kT\, \ln < \delta(p_i(\mathcal{C}))\, \exp \beta h_i^A(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}}$$ chemical potential of A “on” site *i*

$$g_j^B(\widetilde{\mathcal{C}}) = kT\, \ln < \delta(p_j(\mathcal{C})-1)\, \exp \beta h_j^B(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}}$$ chemical potential of B “on” site *j*

Phase Field method: how to get the basic equation (5)

→ mesoscopic master equation becomes:

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta\, e^{-2\beta E_{col}} \sum_{n,m}^{*} \sum_{i\in n, j\in m}^{*} e^{\beta g_i^A(\widetilde{\mathcal{C}})}\, e^{\beta g_j^B(\widetilde{\mathcal{C}})}\, P(\widetilde{\mathcal{C}}) + (\text{gain term})$$

→ form not suitable, because we cannot expand the exponents..... (chemical potential are not small....)

→ chemical potential difference (alloy chemical pot.):

$$\mu_i(\widetilde{\mathcal{C}}) = g_i^B(\widetilde{\mathcal{C}}) - g_i^A(\widetilde{\mathcal{C}})$$

→ master equation becomes:

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta\, e^{-2\beta E_{col}} \sum_{n,m}^{*} \sum_{i\in n, j\in m}^{*} e^{\frac{\beta}{2}(g_i^A(\widetilde{\mathcal{C}})+g_i^B(\widetilde{\mathcal{C}})+g_j^A(\widetilde{\mathcal{C}})+g_j^B(\widetilde{\mathcal{C}}))}\, e^{\frac{\beta}{2}(\mu_j(\widetilde{\mathcal{C}})-\mu_i(\widetilde{\mathcal{C}}))}\, P(\widetilde{\mathcal{C}}) + (\text{gain term})$$

mobilities

driving force

Phase Field method: how to get the basic equation (6)

→ define average chemical potentials in cells *n, m :*

$$g_n^A(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}} \sum_{i \in n} g_i^A(\widetilde{\mathcal{C}})$$

$$g_n^B(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}} \sum_{i \in n} g_i^B(\widetilde{\mathcal{C}})$$

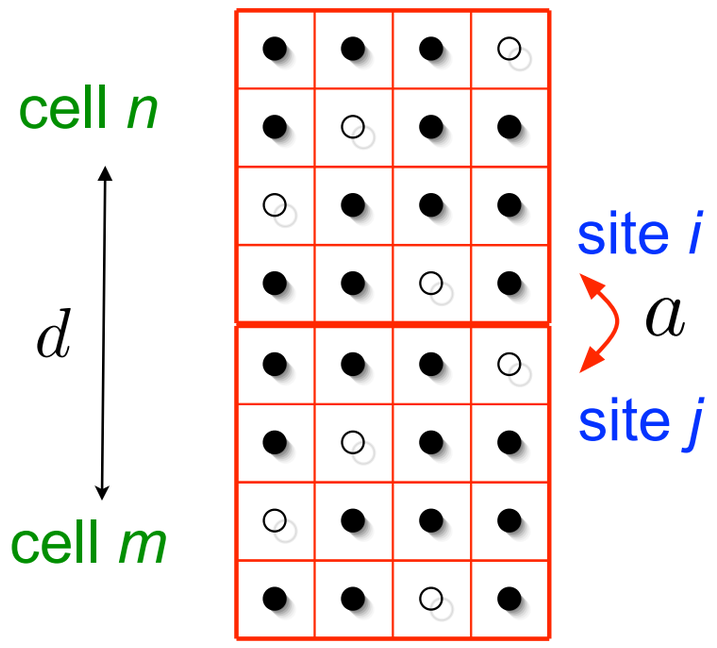
$$\mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

→ Then, if spatial variations of chemical potential are small enough :

to the lowest order in *a/d*, we have:

$$i \in n \ , \ j \in m \ : \quad g_i^A(\widetilde{\mathcal{C}}) + g_j^A(\widetilde{\mathcal{C}}) \simeq g_n^A(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}})$$
$$g_i^B(\widetilde{\mathcal{C}}) + g_j^B(\widetilde{\mathcal{C}}) \simeq g_n^B(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}})$$

$$i \in n \ , \ j \in m \ : \quad \mu_i(\widetilde{\mathcal{C}}) - \mu_j(\widetilde{\mathcal{C}}) \simeq \frac{a}{d} \left(\mu_n(\widetilde{\mathcal{C}}) - \mu_m(\widetilde{\mathcal{C}}) \right)$$



Phase Field method: how to get the basic equation (7)

→ With these 1st order approximations:

$$i \in n \ , \ j \in m \ : \quad \begin{aligned} g_i^A(\widetilde{\mathcal{C}}) + g_j^A(\widetilde{\mathcal{C}}) &\simeq g_n^A(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) \\ g_i^B(\widetilde{\mathcal{C}}) + g_j^B(\widetilde{\mathcal{C}}) &\simeq g_n^B(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}}) \end{aligned}$$

$$\mu_i(\widetilde{\mathcal{C}}) - \mu_j(\widetilde{\mathcal{C}}) \simeq \frac{a}{d} \left(\mu_n(\widetilde{\mathcal{C}}) - \mu_m(\widetilde{\mathcal{C}}) \right)$$

→ the previous master equation:

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - \theta \, e^{-2\beta E_{col}} \sum_{n,m}^{*} \sum_{i \in n, j \in m}^{*} e^{\frac{\beta}{2}(g_i^A(\widetilde{\mathcal{C}}) + g_i^B(\widetilde{\mathcal{C}}) + g_j^A(\widetilde{\mathcal{C}}) + g_j^B(\widetilde{\mathcal{C}}))} \, e^{\frac{\beta}{2}(\mu_j(\widetilde{\mathcal{C}}) - \mu_i(\widetilde{\mathcal{C}}))} \, P(\widetilde{\mathcal{C}}) + (\text{gain term})$$

→ becomes:

with: $$\sum_{i \in n, j \in m}^{*} = \left(\frac{d}{a} \right)^2 = N_{cell} \, \frac{a}{d}$$

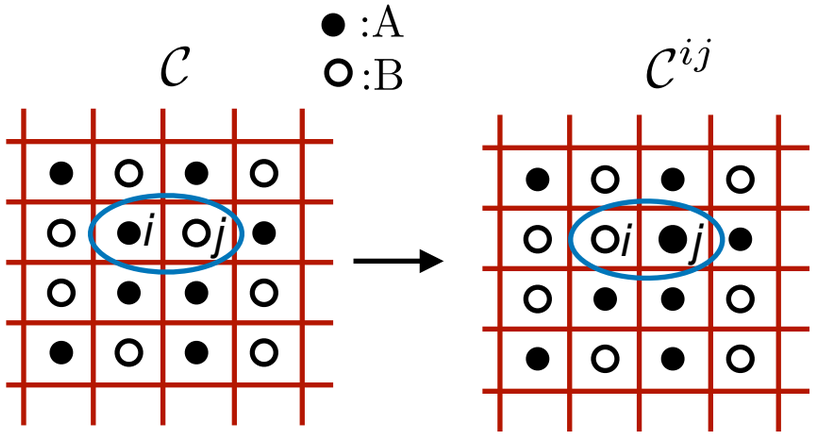
$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - N_{cell} \frac{a}{d} \, \theta \, e^{-2\beta E_{col}} \sum_{n,m}^{*} e^{\frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}}))} \, e^{\frac{\beta}{2}\frac{a}{d}(\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))} \, P(\widetilde{\mathcal{C}}) + (\text{gain term})$$

mobilities

driving force

Où en étions nous hier ?

→ initial scale : microscopic



$$W(\mathcal{C} \to \mathcal{C}^{ij}) = \theta \exp -\beta(2E_{saddle} - h_i^A(\mathcal{C}) - h_j^B(\mathcal{C}))\delta(p_i)\delta(p_j - 1)$$

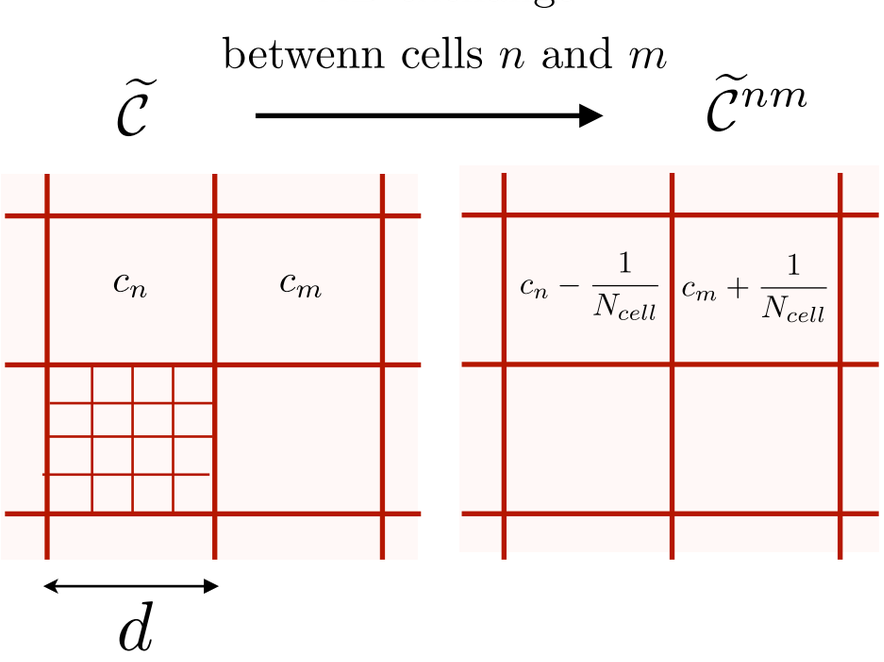
$$\frac{\partial P(\mathcal{C})}{\partial t} = -\sum_{i,j}^{*} W(\mathcal{C} \to \mathcal{C}^{ij})P(\mathcal{C}) + \sum_{i,j}^{*} W(\mathcal{C}^{ij} \to \mathcal{C})P(\mathcal{C}^{ij})$$

if pair interactions only : $h_i^A(\mathcal{C}) = \sum_j V_{ij}^{AA}(1 - p_j) + V_{ij}^{AB} p_j$

→ final scale : mesoscopic

AB exchange

betwenn cells n and m



$$l_{mn}(\widetilde{\mathcal{C}}) = \theta \exp(-2\beta E_{saddle}) \exp \frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}})$$

$$\begin{aligned} \frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} &= -N_{cell}\frac{a}{d}\sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}}) \exp[\frac{\beta}{2}\frac{a}{d}(\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))]P(\widetilde{\mathcal{C}}) \\ &+ N_{cell}\frac{a}{d}\sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}}^{nm}) \exp[\frac{\beta}{2}\frac{a}{d}(\mu_m(\widetilde{\mathcal{C}}^{nm}) - \mu_n(\widetilde{\mathcal{C}}^{nm}))]P(\widetilde{\mathcal{C}}^{nm}) \end{aligned}$$

$$g_n^A(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}} \sum_{i \in n} g_i^A(\widetilde{\mathcal{C}}) \qquad g_n^B(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}} \sum_{i \in n} g_i^B(\widetilde{\mathcal{C}}) \qquad \mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

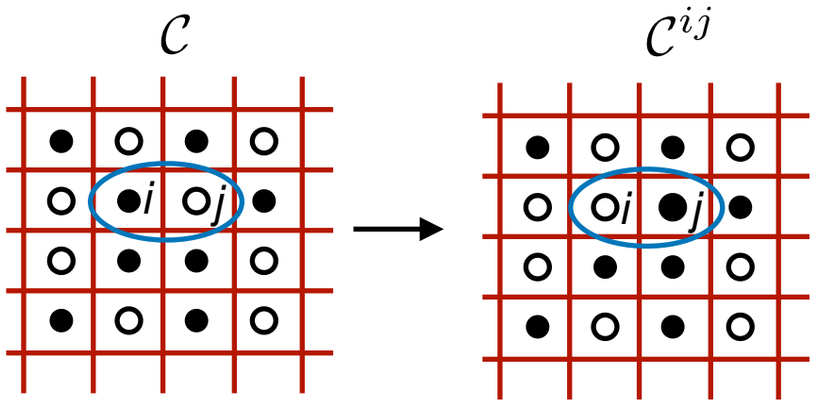
$$\begin{aligned} g_i^A(\widetilde{\mathcal{C}}) &= kT \ \ln < \ \delta(p_i(\mathcal{C})) \ \exp \beta h_i^A(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \\ g_j^B(\widetilde{\mathcal{C}}) &= kT \ \ln < \ \delta(p_j(\mathcal{C}) - 1) \ \exp \beta h_j^B(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \end{aligned}$$

$$g_n^A(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}} \sum_{i \in n} g_i^A(\widetilde{\mathcal{C}})$$

$$\mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

Où en étions nous hier ?

→ initial scale : microscopic



$$W(\mathcal{C} \to \mathcal{C}^{ij}) = \theta \exp -\beta(2E_{saddle} - h_i^A(\mathcal{C}) - h_j^B(\mathcal{C}))\delta(p_i)\delta(p_j - 1)$$

$$\frac{\partial P(\mathcal{C})}{\partial t} = -\sum_{i,j}^{*} W(\mathcal{C} \to \mathcal{C}^{ij})P(\mathcal{C}) + \sum_{i,j}^{*} W(\mathcal{C}^{ij} \to \mathcal{C})P(\mathcal{C}^{ij})$$

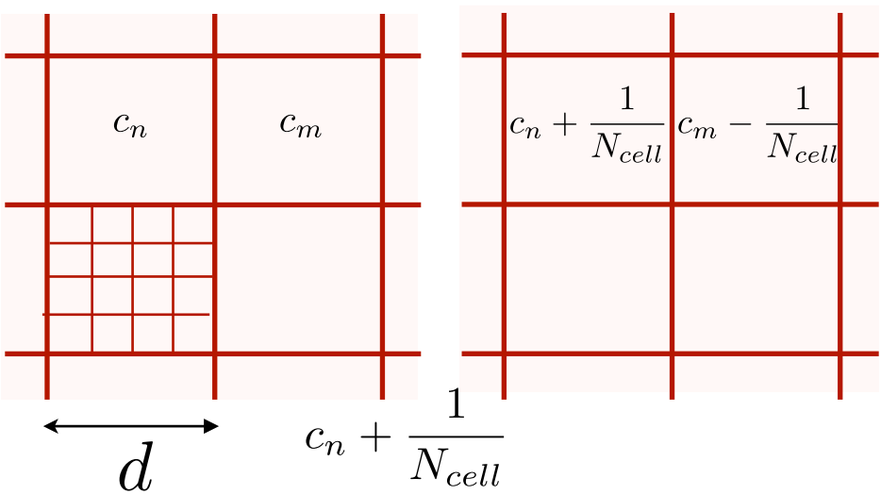
if pair interactions only : $h_i^A(\mathcal{C}) = \sum_j V_{ij}^{AA}(1 - p_j) + V_{ij}^{AB} p_j$

→ final scale : mesoscopic

AB exchange

betwenn cells n and m

$\widetilde{\mathcal{C}} \longrightarrow \widetilde{\mathcal{C}}^{nm}$



$$l_{mn}(\widetilde{\mathcal{C}}) = \theta \exp(-2\beta E_{saddle}) \exp \frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}})$$

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = -N_{cell}\frac{a}{d}\sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}}) \exp[\frac{\beta}{2}\frac{a}{d}(\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))]P(\widetilde{\mathcal{C}})$$

$$+ N_{cell}\frac{a}{d}\sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}}^{nm}) \exp[\frac{\beta}{2}\frac{a}{d}(\mu_m(\widetilde{\mathcal{C}}^{nm}) - \mu_n(\widetilde{\mathcal{C}}^{nm}))]P(\widetilde{\mathcal{C}}^{nm})$$

$$g_n^A(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}}\sum_{i\in n} g_i^A(\widetilde{\mathcal{C}}) \qquad g_n^B(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}}\sum_{i\in n} g_i^B(\widetilde{\mathcal{C}}) \qquad \mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

$$\begin{aligned} g_i^A(\widetilde{\mathcal{C}}) &= kT \ \ln < \ \delta(p_i(\mathcal{C})) \ \exp \beta h_i^A(\mathcal{C}) >_{\mathcal{C}/\widetilde{\mathcal{C}}} \\ &= \widetilde{F}_\Omega(\widetilde{\mathcal{C}}, N_A, N_B) - \widetilde{F}_{\Omega/i}(\widetilde{\mathcal{C}}, N_A - 1, N_B, \text{site } i \text{ empty}) \\ &= \text{free energy increase when an A atom is inserted in } \Omega/i \end{aligned}$$

$$g_n^A(\widetilde{\mathcal{C}}) = \frac{1}{N_{cell}}\sum_{i\in n} g_i^A(\widetilde{\mathcal{C}})$$

$$\mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

Phase Field method: how to get the basic equation (8)

- full mesoscopic master equation :

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = - N_{cell}\ \frac{a}{d}\ \sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}})\ \exp[\frac{\beta}{2}\ \frac{a}{d}\ (\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))]\ P(\widetilde{\mathcal{C}})$$
$$+ N_{cell}\ \frac{a}{d}\ \sum_{n,m}^{*} l_{mn}(\widetilde{\mathcal{C}}_{nm})\ \exp[\frac{\beta}{2}\ \frac{a}{d}\ (\mu_m(\widetilde{\mathcal{C}}_{nm}) - \mu_n(\widetilde{\mathcal{C}}_{nm}))]\ P(\widetilde{\mathcal{C}}_{nm})$$

with : $$\widetilde{\mathcal{C}}_{nm} = \{.....(c_n - \frac{1}{N_{cell}}).....(c_m + \frac{1}{N_{cell}}).....\}$$

and mobilities given by : $$l_{mn}(\widetilde{\mathcal{C}}) = \theta \exp(-2\beta E_{saddle}) \exp \frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}})$$

→ look for a Fokker-Planck equation : Kramers-Moyal expansion to 2nd ordre in *1/N_{cell} !!!*

$$\frac{\partial P(\widetilde{\mathcal{C}}))}{\partial t} = N_{cell}\ \frac{a}{d}\ \sum_{n,m}^{\star}(-\frac{1}{N_{cell}}\frac{\partial}{\partial c_n} + \frac{1}{N_{cell}}\frac{\partial}{\partial c_m} + \frac{1}{2N_{cell}^2}\frac{\partial^2}{\partial c_n^2} + \frac{1}{2N_{cell}^2}\frac{\partial^2}{\partial c_m^2} - \frac{1}{N_{cell}^2}\frac{\partial^2}{\partial c_n \partial c_m})$$
$$\times \{\ l_{nm}(\widetilde{\mathcal{C}})\ \exp[\frac{\beta}{2}\ \frac{a}{d}\ (\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))]\ P(\widetilde{\mathcal{C}})\ \}$$

→ Develop to the lowest order transition probability $\exp[\frac{\beta}{2}\ \frac{a}{d}\ (\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))]$

Phase Field method: how to get the basic equation (10)

→ Fokker-Planck equation

$$\frac{\partial P(\widetilde{\mathcal{C}})}{\partial t} = \frac{a^2}{d^2}\{-\sum_n \frac{\partial}{\partial c_n}\{\, h_n(\widetilde{\mathcal{C}})\, P(\widetilde{\mathcal{C}})\,\} + \sum_{n,m} \frac{1}{N_{cell}} \frac{\partial^2}{\partial c_n \partial c_m}\{\, g_{nm}(\widetilde{\mathcal{C}})\, P(\widetilde{\mathcal{C}})\}\,\}$$

drift term

stochastic term

$$h_n(\widetilde{\mathcal{C}}) = \sum_m^{(n)} l_{nm}(\widetilde{\mathcal{C}})\,\{\,\beta\mu_m(\widetilde{\mathcal{C}}) - \beta\mu_n(\widetilde{\mathcal{C}})\,\}$$

$$g_{nn}(\widetilde{\mathcal{C}}) = \sum_m^{(n)} l_{nm}(\widetilde{\mathcal{C}})$$

$$g_{nm}(\widetilde{\mathcal{C}}) = -\; l_{nm}(\widetilde{\mathcal{C}}) \quad \text{if } n \text{ and } m \text{ are } 1^{st} \text{ neighbors}$$

Phase Field method: how to get the basic equation (I I)

→ Equivalent Langevin equation (Ito calculus) :

$$\frac{\partial c_n}{\partial t} = \frac{a^2}{d^2}\ \frac{1}{kT}\ \sum_m^{(n)} l_{nm}(\widetilde{\mathcal{C}})\ (\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))\ +\ \xi_n(t)$$

Phase Field equation !!!

with multiplicative gaussian noise :

$$\begin{aligned} < \xi_n(t) > &= 0 \\ < \xi_n(t)\ \xi_m(t') > &= 2\ \frac{a^2}{d^2}\ \frac{1}{N_{cell}}\ g_{nm}(\widetilde{\mathcal{C}})\ \delta(t-t') \end{aligned}$$

Phase Field method: how to get the basic equation (12)

→ Results:

$$\frac{\partial c_n}{\partial t} = \frac{a^2}{d^2}\ \frac{1}{kT}\ \sum_m^{(n)} l_{nm}(\widetilde{\mathcal{C}})\ (\mu_m(\widetilde{\mathcal{C}}) - \mu_n(\widetilde{\mathcal{C}}))\ +\ \xi_n(t)$$

- mobilities:

$$l_{mn}(\widetilde{\mathcal{C}}) = \theta \exp(-2\beta E_{saddle}) \exp \frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}}))$$

- alloy chemical potential:

$$\mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

- gaussian noise:

$$\begin{aligned} < \xi_n(t) > &= 0 \\ < \xi_n(t)\ \xi_m(t') > &= 2\ \frac{a^2}{d^2}\ \frac{1}{N}\ g_{nm}(\widetilde{\mathcal{C}})\ \delta(t-t') \\ g_{nn}(\widetilde{\mathcal{C}}) &= \sum_m^{(n)} l_{nm}(\widetilde{\mathcal{C}}) \\ g_{nm}(\widetilde{\mathcal{C}}) &= -\ \ l_{nm}(\widetilde{\mathcal{C}}) \quad \text{if } n \text{ and } m \text{ are } 1^{st} \text{ neighbors} \end{aligned}$$

→ Cahn-Hilliard type equation, but with :

- multiplicative Langevin noise
- cell-size dependant quantities: mobility, chem. potentials, amplitude of noise term

How to get the chemical potentials ?

→ Chemical potentials $g_n^A(\widetilde{\mathcal{C}})$ and $g_n^B(\widetilde{\mathcal{C}})$ are function of all the cell concentrations c_n :

$$g_n^A(\widetilde{\mathcal{C}}) = g_{homo}^A(c_n) + H^A(c_n)||\hat{\nabla} c_n||^2 + K^A(c_n)\hat{\nabla}^2 c_n + \ldots$$

→ $g_n^A(\widetilde{\mathcal{C}})$ and $g_n^B(\widetilde{\mathcal{C}})$ enter into the mobilities and in the alloy chemical potential :

$$l_{mn}(\widetilde{\mathcal{C}}) = \theta \exp(-2\beta E_{saddle}) \exp \frac{\beta}{2}(g_n^A(\widetilde{\mathcal{C}}) + g_n^B(\widetilde{\mathcal{C}}) + g_m^A(\widetilde{\mathcal{C}}) + g_m^B(\widetilde{\mathcal{C}}))$$

$$\mu_n(\widetilde{\mathcal{C}}) = g_n^B(\widetilde{\mathcal{C}}) - g_n^A(\widetilde{\mathcal{C}})$$

→ If cells large enough : inhomo. components can be neglected in mobilities, but are crucial in the alloy chem. potential

- for the mobilities:

$$g_n^A(\widetilde{\mathcal{C}}) \simeq g_{homo}^A(c_n)$$

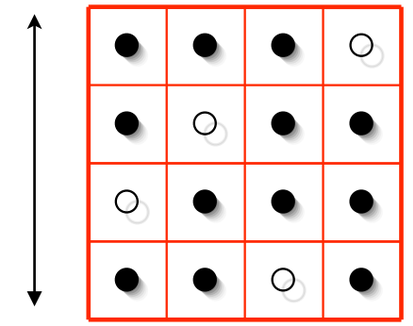
- for the alloys chemical potential:

$$\mu_n(\widetilde{\mathcal{C}}) \simeq g_{homo}^B(c_n) - g_{homo}^A(c_n) + H(c_n)||\hat{\nabla} c_n||^2 + K(c_n)\hat{\nabla}^2 c_n +$$

How to get the chemical potentials (cont.) ?

→ Numerical procedure for homogeneous chemical potentials $g^A_{homo}(c_n)$ and $g^B_{homo}(c_n)$

Widom-like method by Monte Carlo on a single cell

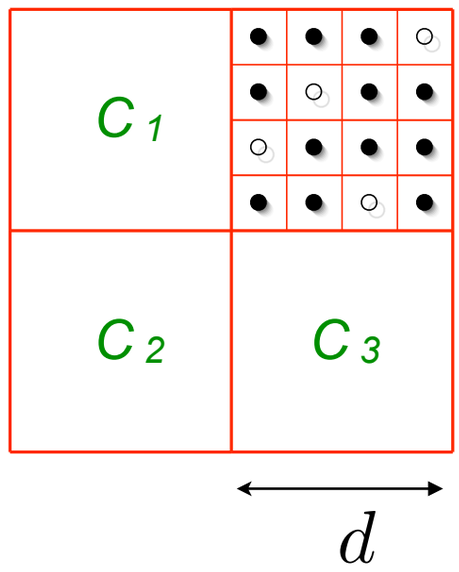


→ Numerical procedure for the inhomogeneous component of $\mu_n(\widetilde{\mathcal{C}})$

we expect $$F_{tot}(\widetilde{\mathcal{C}}) = N_d \sum_n \{f^d_{homo}(c_n) + \frac{1}{2}\lambda^d(c_n)||\hat{\nabla}c_n||^2\}$$ with $$\mu_n(\widetilde{\mathcal{C}}) = \frac{1}{N_d}\frac{dF_{tot}(\widetilde{\mathcal{C}})}{dc_n},$$

thus : $$\mu^d_n(\widetilde{\mathcal{C}}) = \mu^d_{homo}(c_n) - \lambda^d(c_n)\hat{\nabla}^2 c_n + \frac{1}{2}\frac{\partial\lambda^d(c_n)}{\partial c_n}||\hat{\nabla}c_n||^2$$

→ Procedure for $\lambda^d(c_n)$: gaussian fluctuations between cells



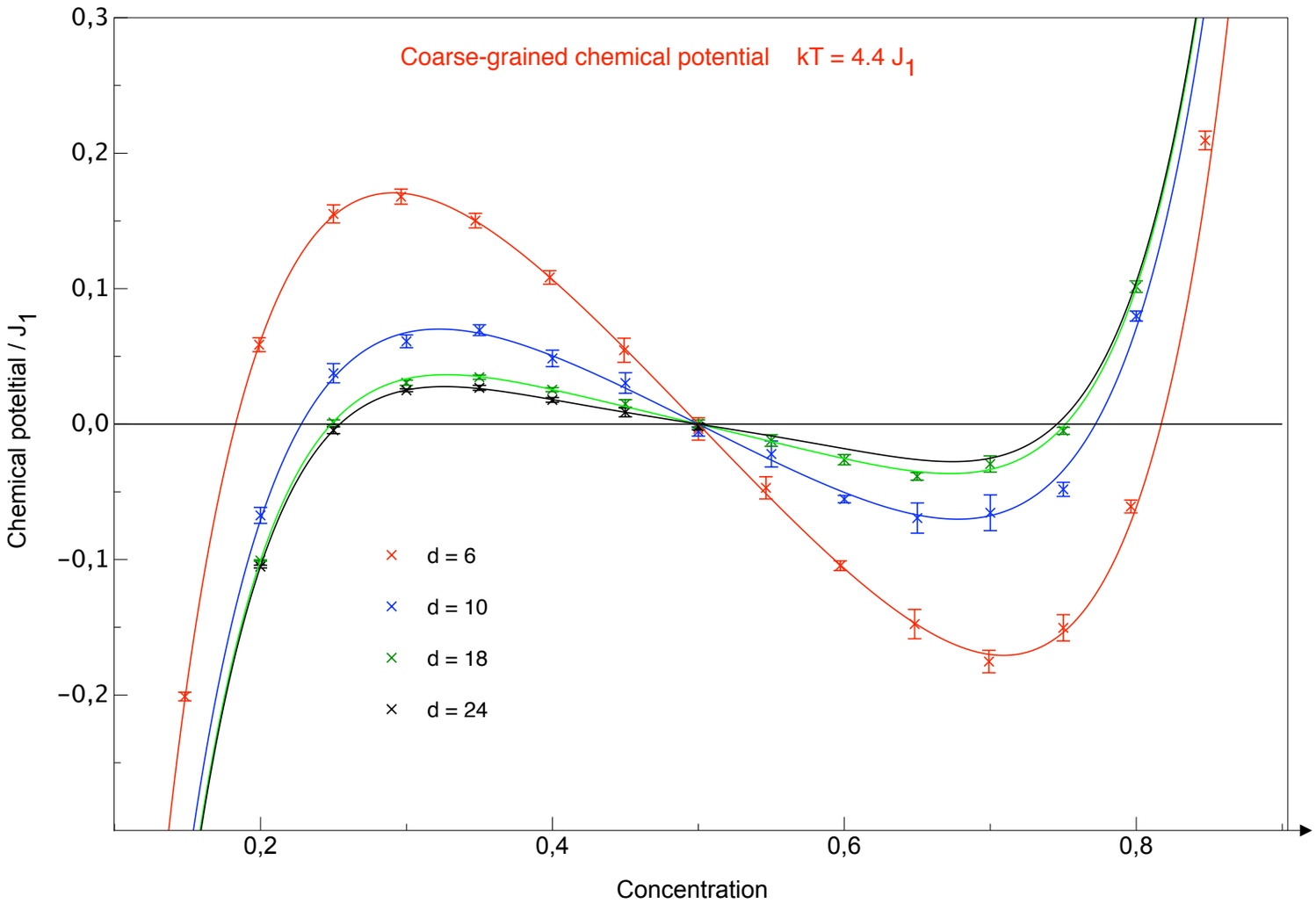
How to get the chemical potentials (cont.) ?

simple cubic lattice

→ Simple cubic lattice, 1st neighbor interactions J1

$$H = \frac{1}{2} \sum_{n,m} \sigma_n \, \sigma_m \qquad \sigma_n = +/-1 \qquad T_c \sim 4.51 J_1$$

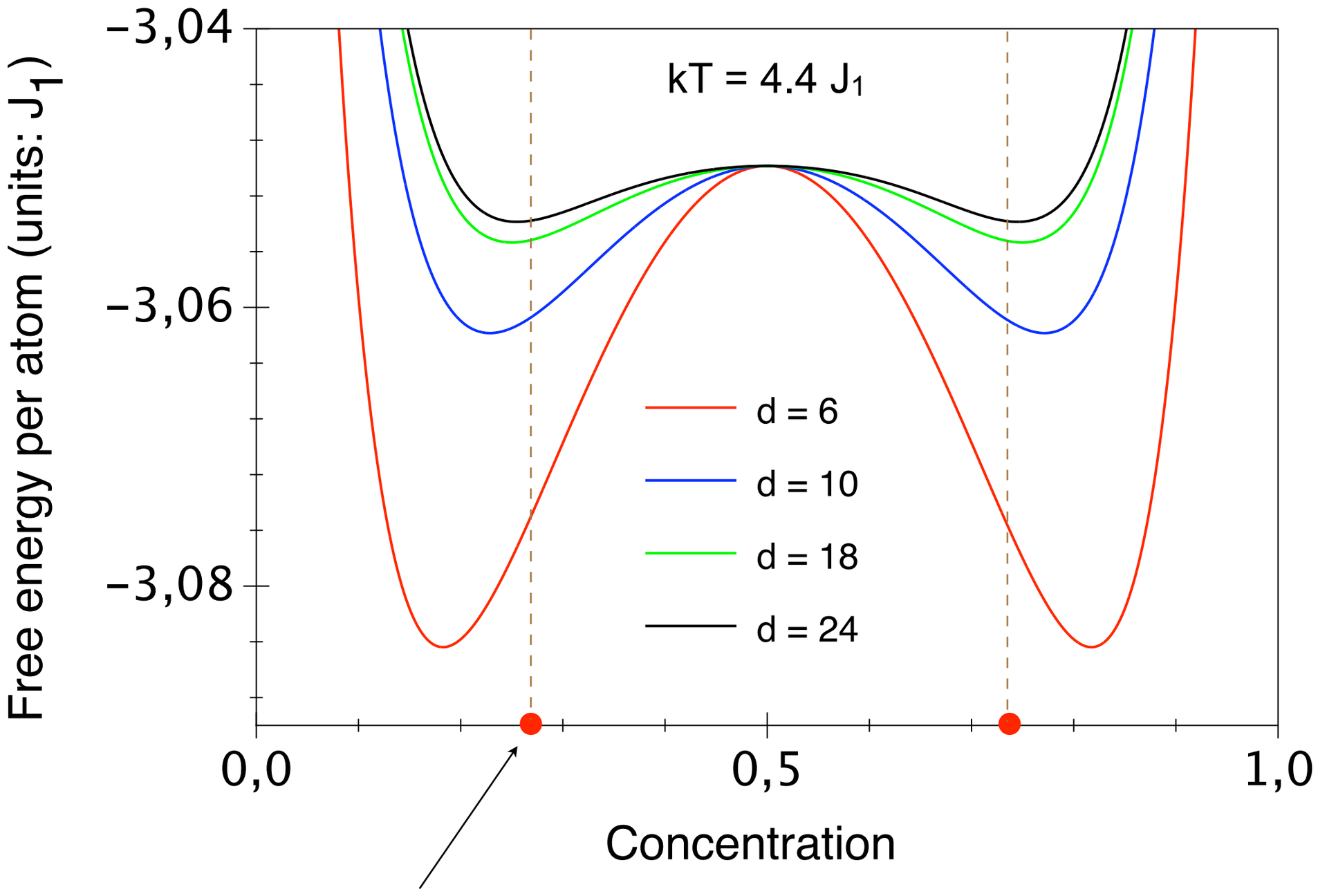
→ chemical potential : homogeneous part $\mu^d_{homo}(c)$ by Monte Carlo on a single cell + fit



$$\mu_d(c) = 2pJ_1(2c-1) + Ac(1-c)(c-0.5)\{1 + B(c-0.5)^2\} \; + kT \; \ln \frac{c}{1-c}$$

Free energies as a function of the coarse-graining size

simple cubic lattice



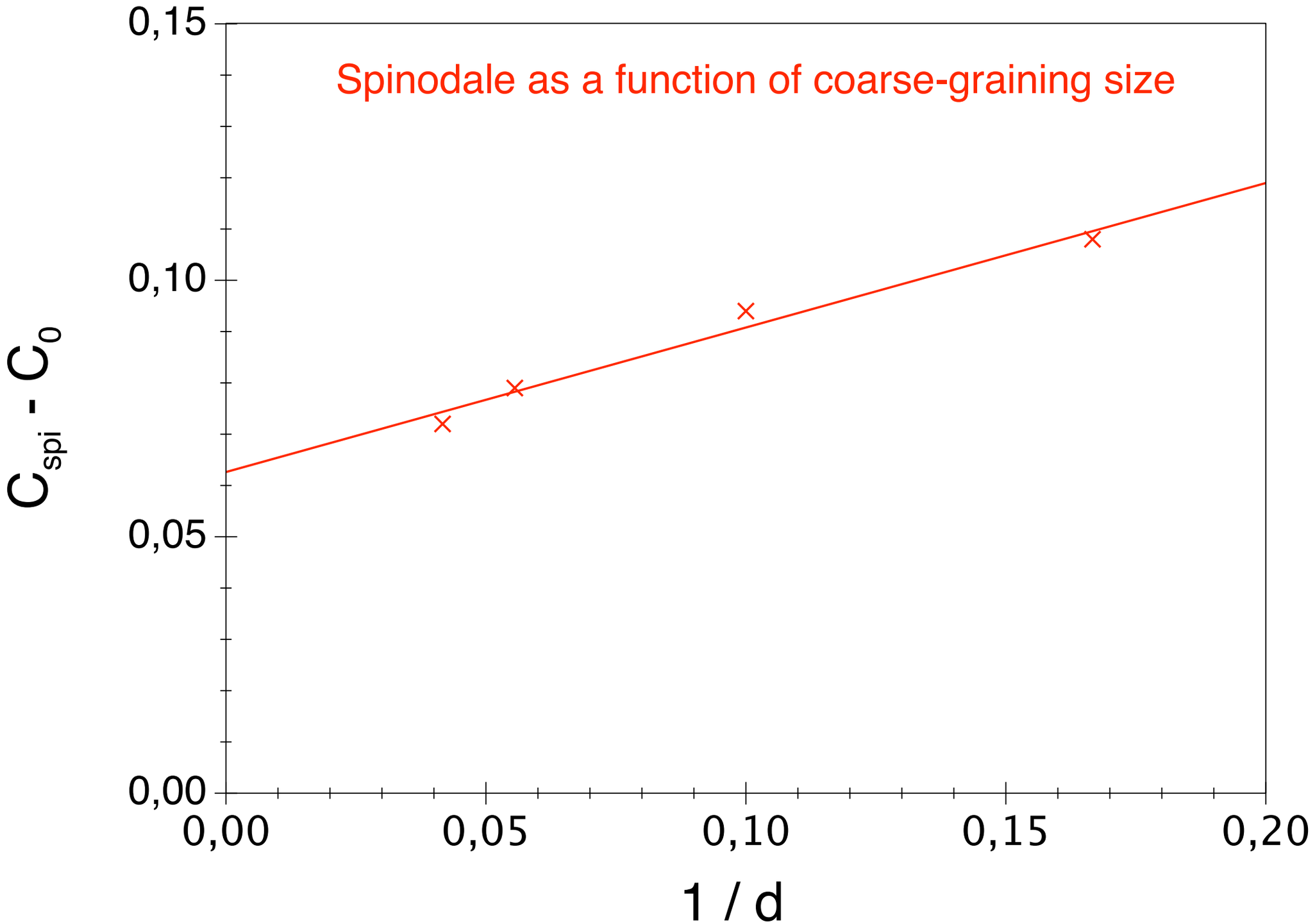
$c_0 = 0.273...$

phase diagram for infinite system

Free energies as a function of the coarse-graining size (cont.)

simple cubic lattice

→ by-product : spinodal as a function of the coarse graining size....



→ How to get the stiffness coefficient $\lambda^d(c)$?

$$F^d_{tot}(\{c_n\}) = \sum_n \{ \; f^d_{homo}(c_n) + \frac{\lambda_d}{2} ||\tilde{\nabla} c_n||^2 \; \}$$

→ if “gaussian” fluctuations :

- small fluctuations around the average concentration : $\bar{c}$ $\qquad \delta c_n = c_n - \bar{c} \ll \bar{c}$

$$\sum_n \delta c_n = 0 \quad \rightarrow \quad F^d_{tot}(\{c_n\}) = \sum_n \{ \; f^d_{homo}(\bar{c}) + \frac{1}{2} f''(\bar{c}) \, \delta c_n^2 + \frac{\lambda_d}{2} ||\tilde{\nabla} c_n||^2 \; \}$$

- Fourier modes:

$$\delta c(q) = \frac{1}{N_{cell}} \sum_n \delta c_n \; \exp -iq.R_n$$

$$F_{tot} \sim cte + \frac{1}{2} \sum_{q \neq 0} \{ \tilde{f}''(\bar{c}) + \lambda_d \, q^2 \} \, ||\delta c(q)||^2$$

- équipartition:

$$< ||\delta c(q)||^2 >= \frac{kT}{\tilde{f}''(\bar{c}) + \lambda_d \, q^2}$$

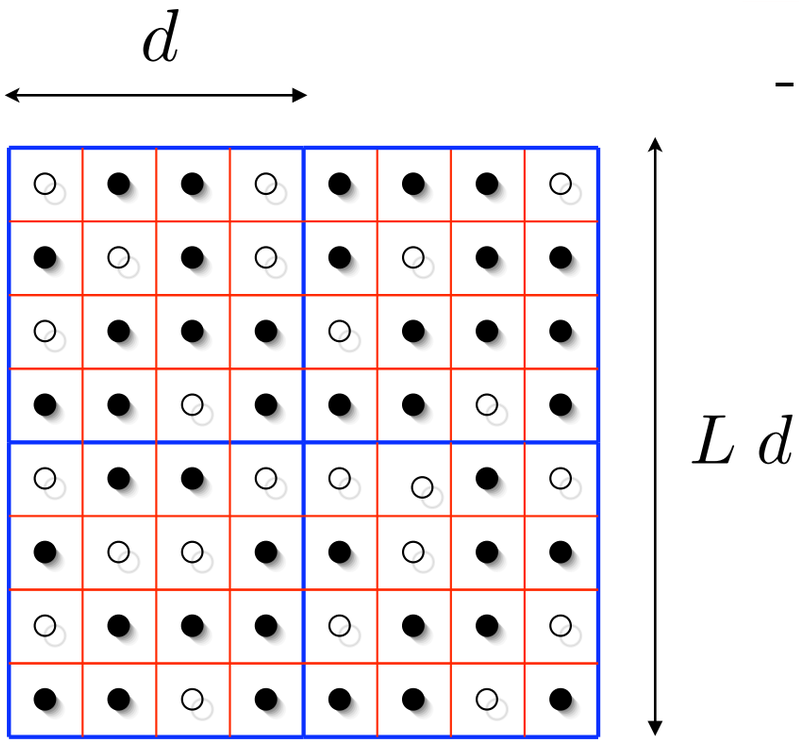
→ How to get the stiffness coefficient $\lambda^d(c)$ (cont.) ?

→ simple method to calculate λ_d :

get fluctuations with Monte Carlo simulations ←

$$\frac{kT}{N_{cell}\, d^3} < ||\delta c(q)||^2 >^{-1} = \tilde{f}''(\bar{c}) + \lambda^d(\bar{c})\, q^2$$

→ linear fit in q²

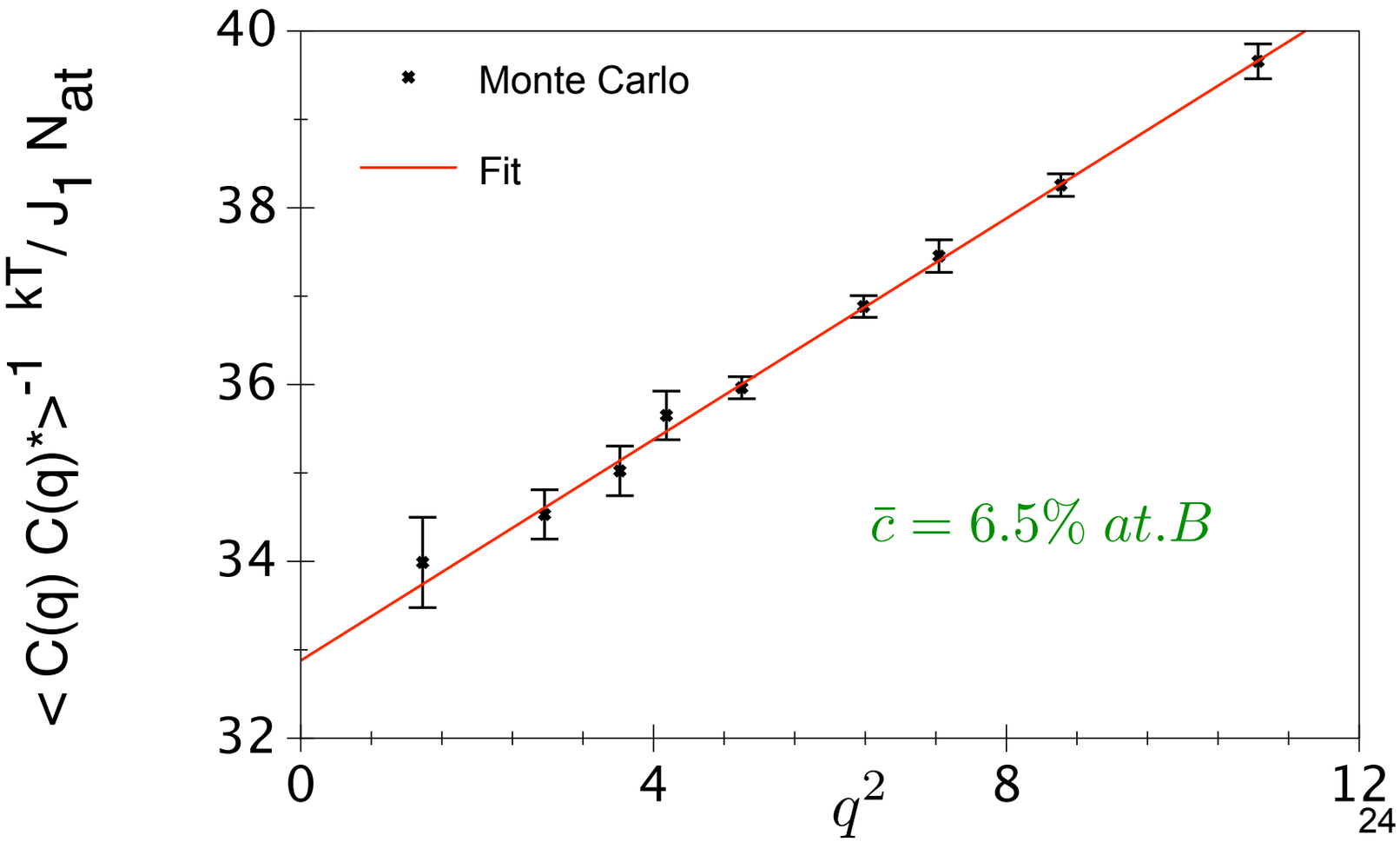


- for a given $\bar{c}$

→ compute a "coarse-grained" concentration field $\quad c_n^d(c) = \frac{1}{d^3} \sum_{k \in n} p_k$

→ get its fluctuations (in q-space)

- kT / J1 = 4
- cell size: d = 8

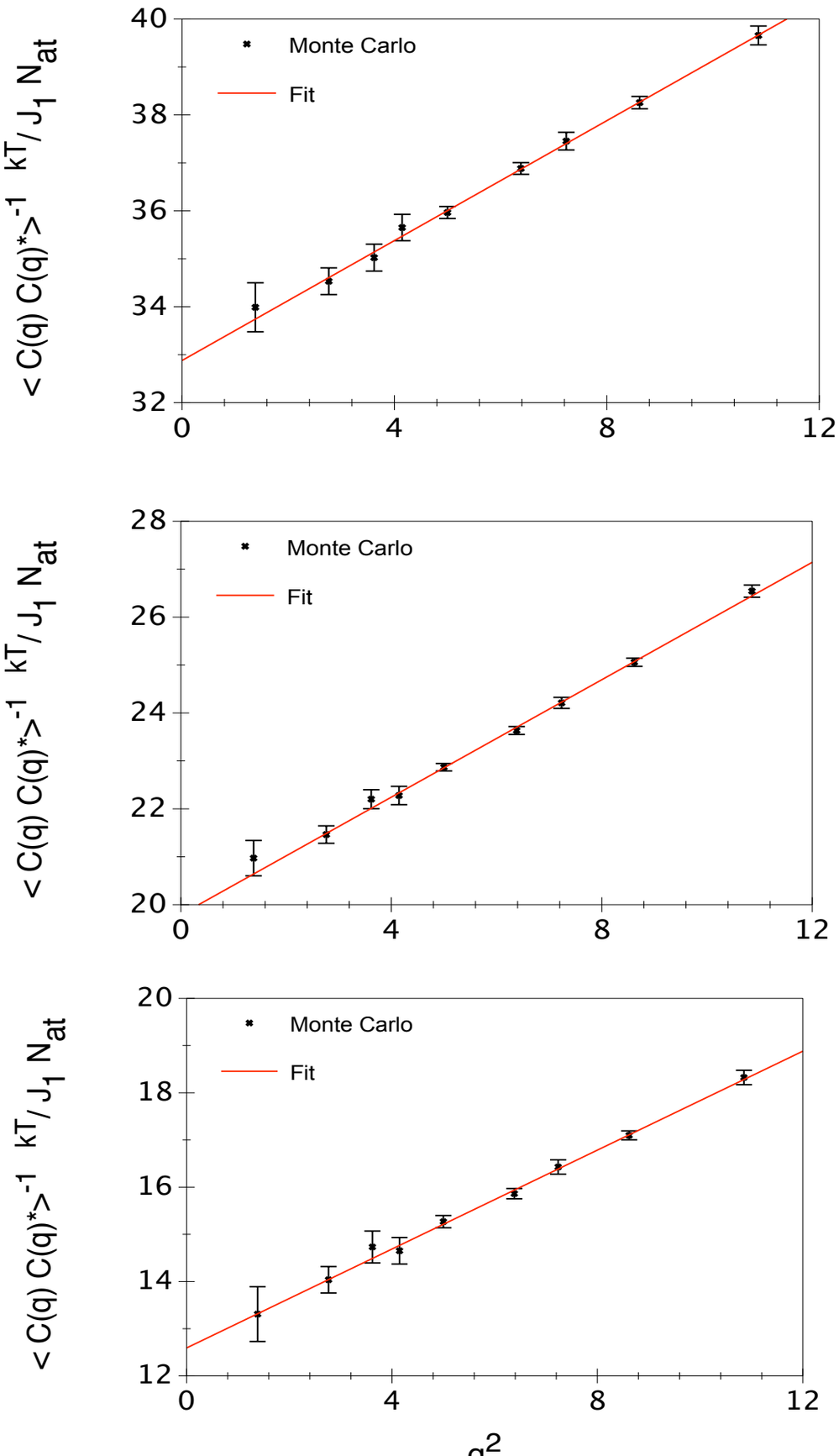


$\rightarrow$ How to get the stiffness coefficient $\lambda^d(c)$ (cont.) ?

- kT / J1 = 4
- cell size: d = 8

c	λ_d	$\tilde{f}''(\bar{c})$	$\frac{\partial \mu_d(\bar{c})}{\partial \bar{c}}$
0.065	0.62 ± 0.01	32.9 ± 0.1	33.23
0.075	0.60 ± 0.01	25.6 ± 0.1	25.80
0.085	0.59 ± 0.01	20.0 ± 0.1	20.27
0.095	0.57 ± 0.01	15.7 ± 0.1	16.05
0.105	0.54 ± 0.01	12.3 ± 0.1	12.75
0.115	0.52 ± 0.02	9.70 ± 0.1	10.13
0.125	0.50 ± 0.01	7.54 ± 0.1	8.04

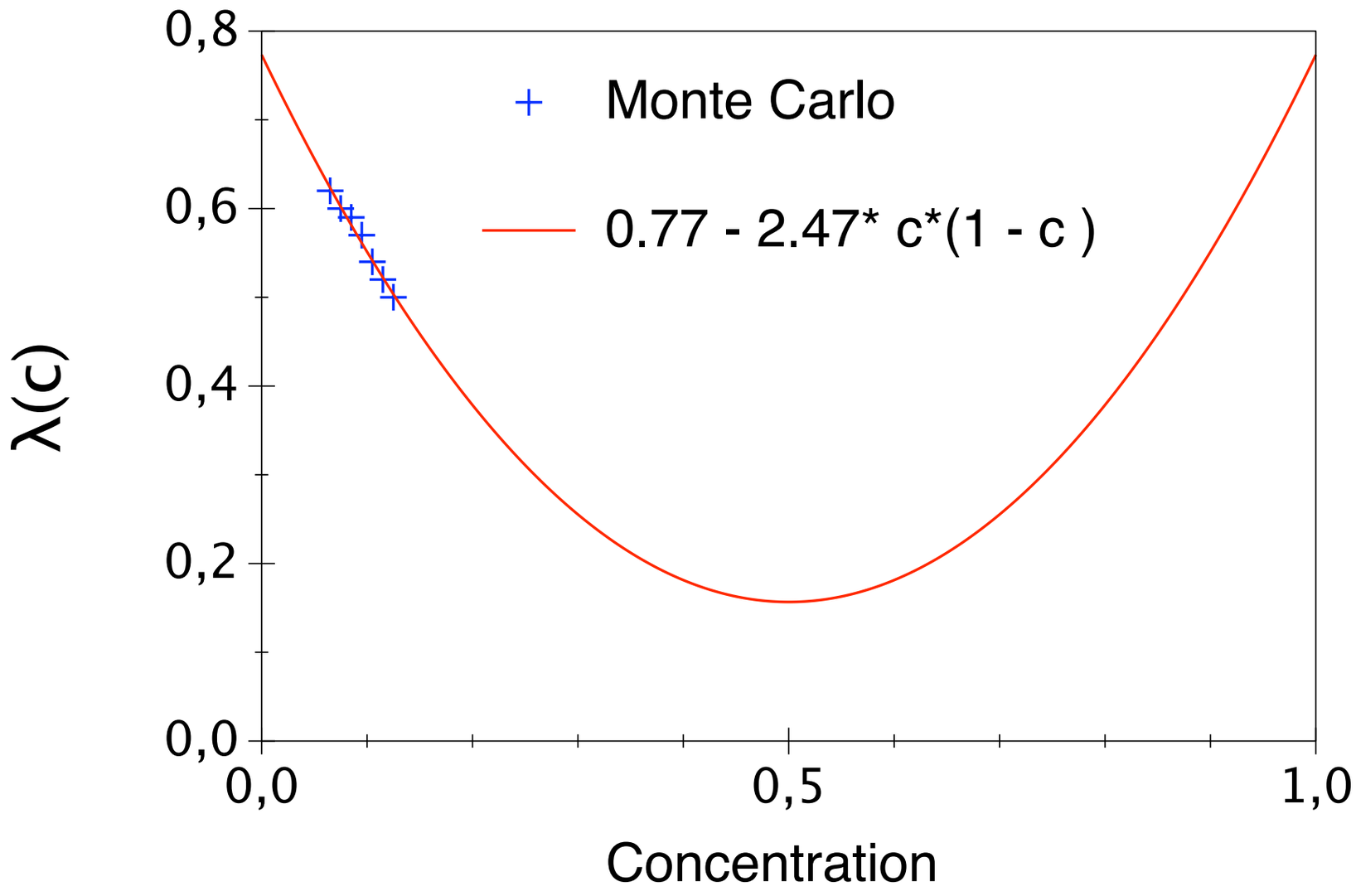
λ_d varies with $\bar{c} \rightarrow \lambda_d(\bar{c})$!!!



$\rightarrow$ How to get the stiffness coefficient $\lambda^d(c)$ (cont.) ?

$\rightarrow$ To the lowest order, symmetry implies:

$$\lambda_d(\bar{c}) = A + B\ \bar{c}(1-\bar{c})$$



All together !!!

→ Inhomogeneous Ginzburg-Landau free energy :

$$F^d_{tot}(\{c_n\}) \;=\; \sum_n \{\;\; f^d_{homo}(c_n) \;+\; \frac{\lambda_d(c_n)}{2}\;||\tilde{\nabla} c_n||^2 \;\}$$

→ Inhomogeneous chemical potential :

$$\mu_d^{inhomo}(\{c_n\}) \;=\; \frac{\delta F^d_{tot}(\{c_n\})}{\delta c_n} \;=\; \mu_d^{homo}(c_n) - \lambda_d(c_n)\tilde{\nabla}^2 c_n + \frac{1}{2}\frac{\partial \lambda_d(c_n)}{\partial c_n}||\tilde{\nabla} c_n||^2$$

Monte Carlo coarse-graining:
(only 1 cell)

(gaussian) fluctuations:
between cells

→ Continuous limit of kinetic equation (not needed…) :

$$\frac{\partial\, c}{\partial\, t} = \nabla M(c)\;\vec{\nabla}\{\;\mu_d(c) \;-\; \lambda_d\;\nabla^2 c \;+\; \frac{1}{2}\frac{\partial \lambda_d(c)}{\partial c}||\tilde{\nabla} c||^2\} \;+\; \eta(r,t)$$

“new” inhomogeneous term

with a mobility $M_d(c)$:

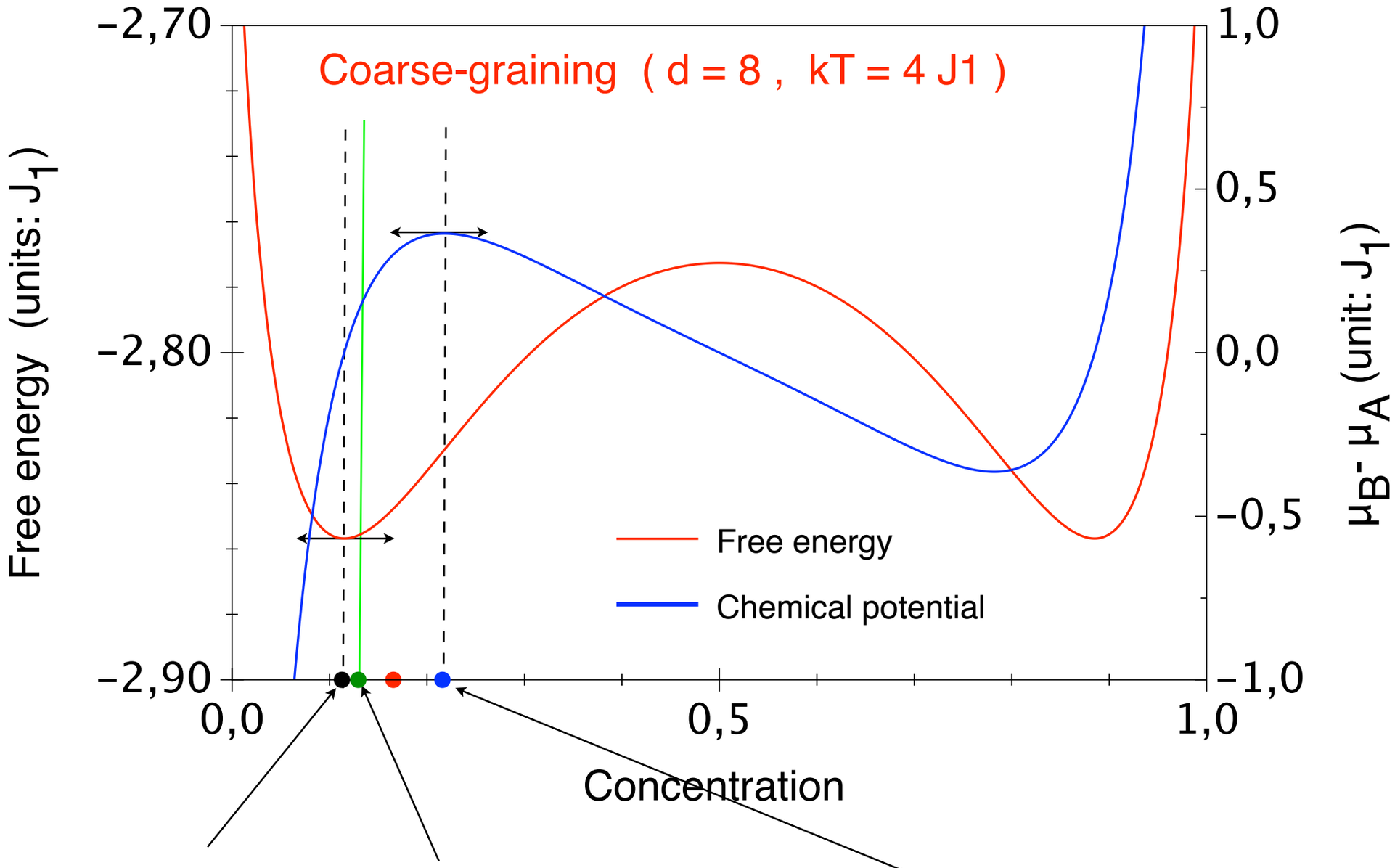
$$M_d(c) = \theta a^2 \;\exp -2\beta E_{saddle} \;\exp \beta(g^A_d(c) + g^B_d(c))$$

and Langevin noise :

$$< \eta(r,t)\;\eta(r',t') >= -2\;kT\;\nabla M(c)\;\nabla\delta(r-r')\;\delta(t-t')$$

Precipitation : from nucleation and growth to coalescence

→ coarse-grained free energy (chemical potential) from Monte Carlo (d = 8) and kT = 4 J1:



coarse-grained free energy minimum: $c_1 = 0.115...$

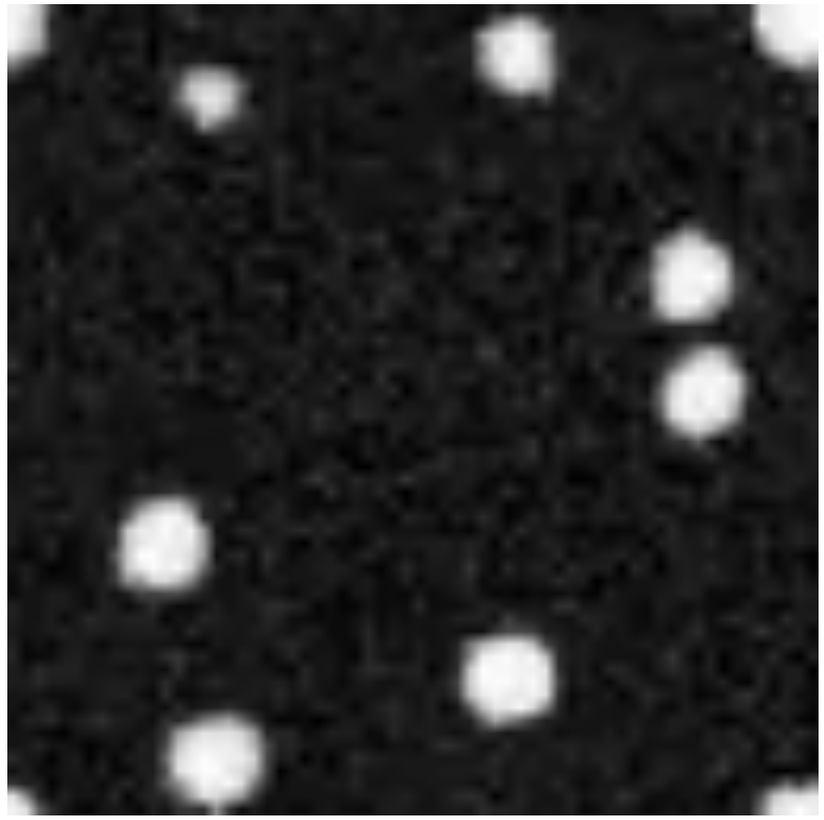
Solubility limit: $c_0 = 0.125...$
$c_0 > c_1$ because of fluctuations..... !!!!!

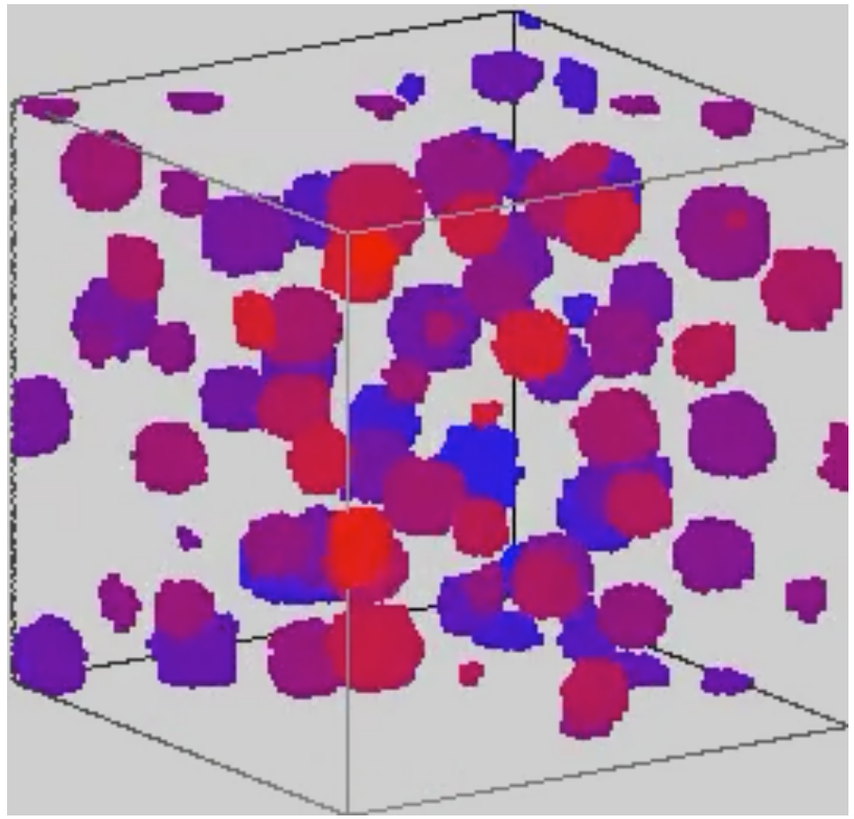
Spinodale: $c_{spi} = 0.218....$

- → precipitation for c = 0.17 ($c_0 < c < c_s$): nucleation and growth mechanism....

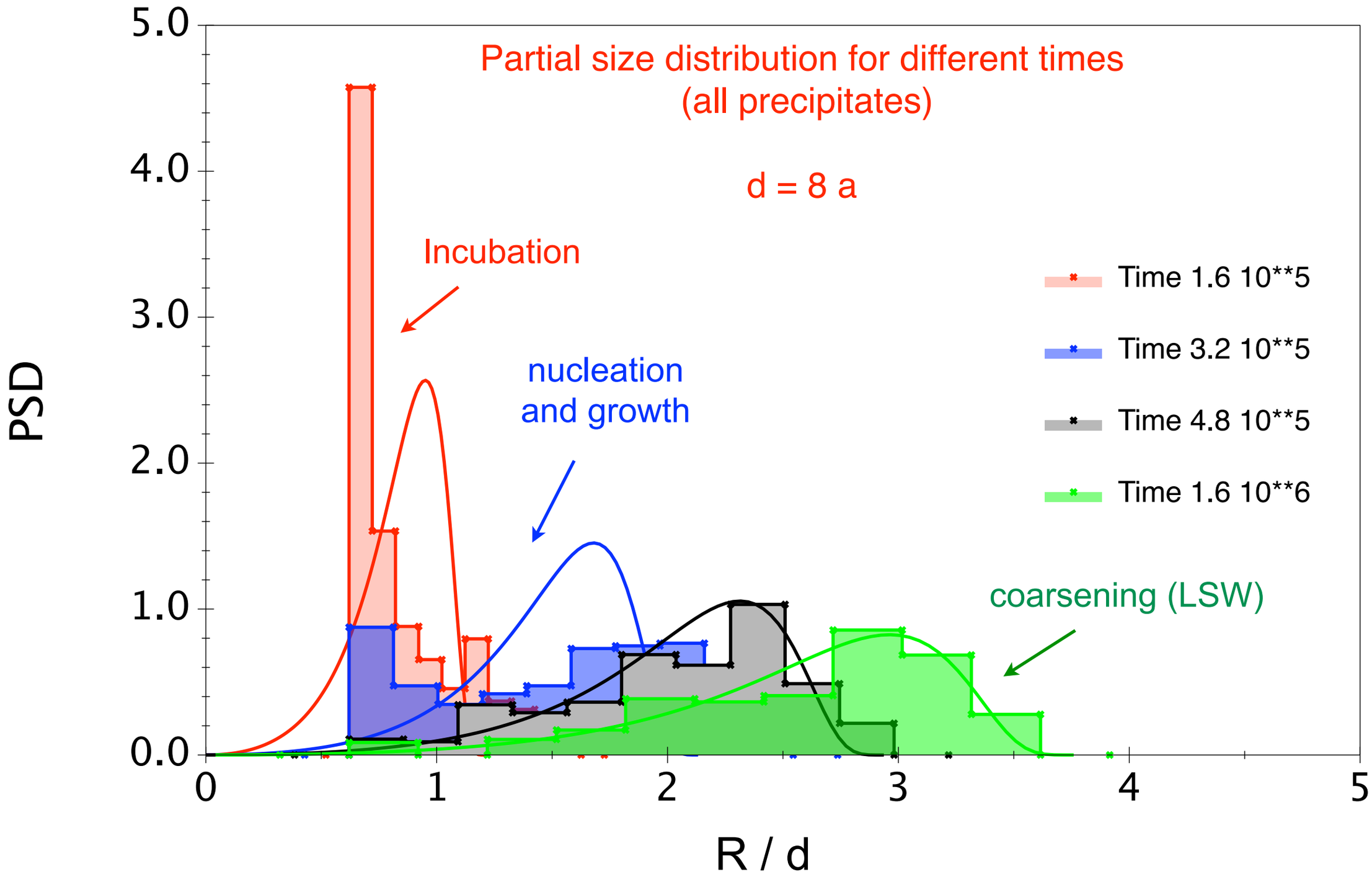
Precipitation : from nucleation and growth to coalescence

Precipitation : from nucleation and growth to coalescence





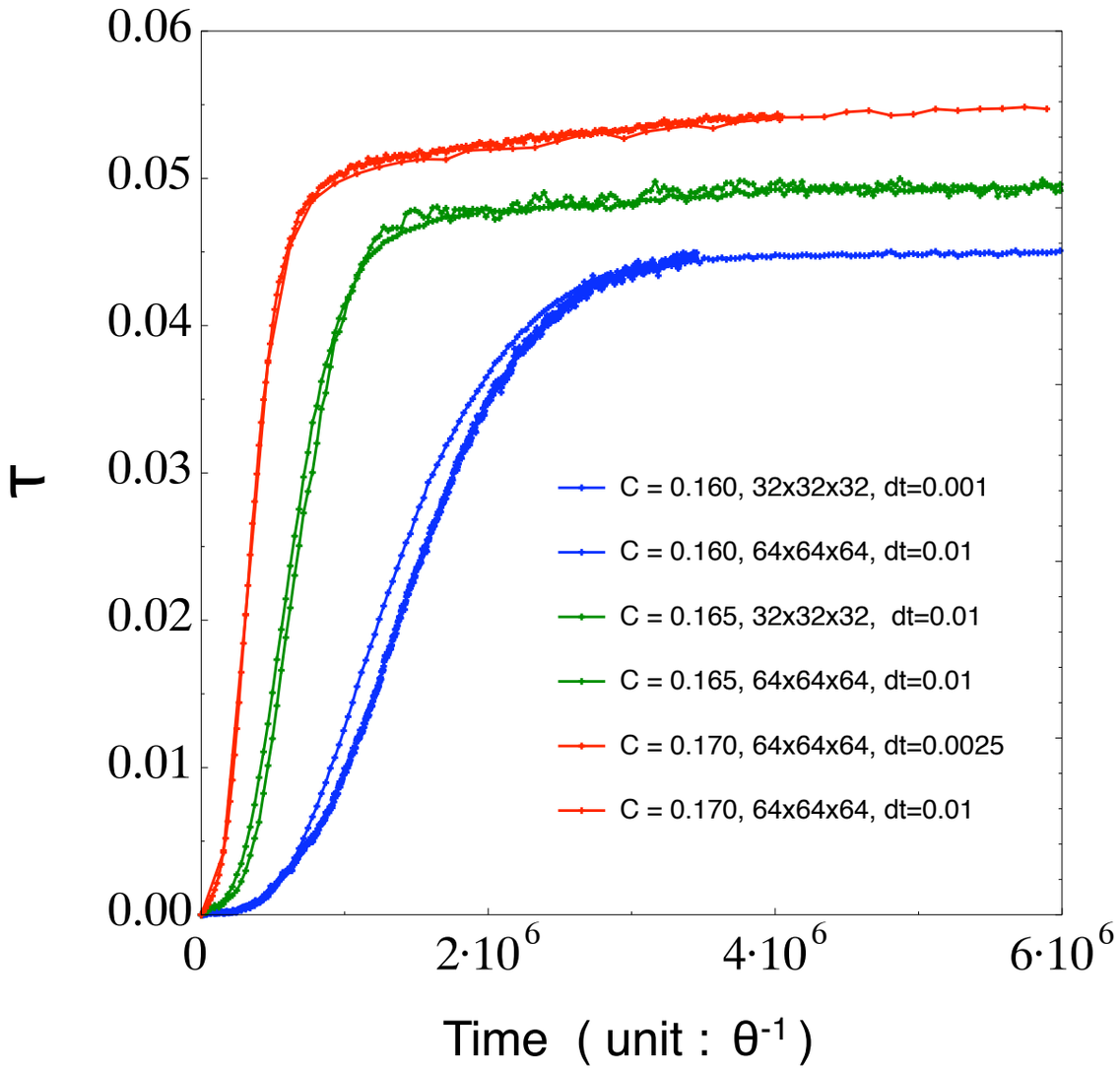
Precipitation : from nucleation and growth to coalescence

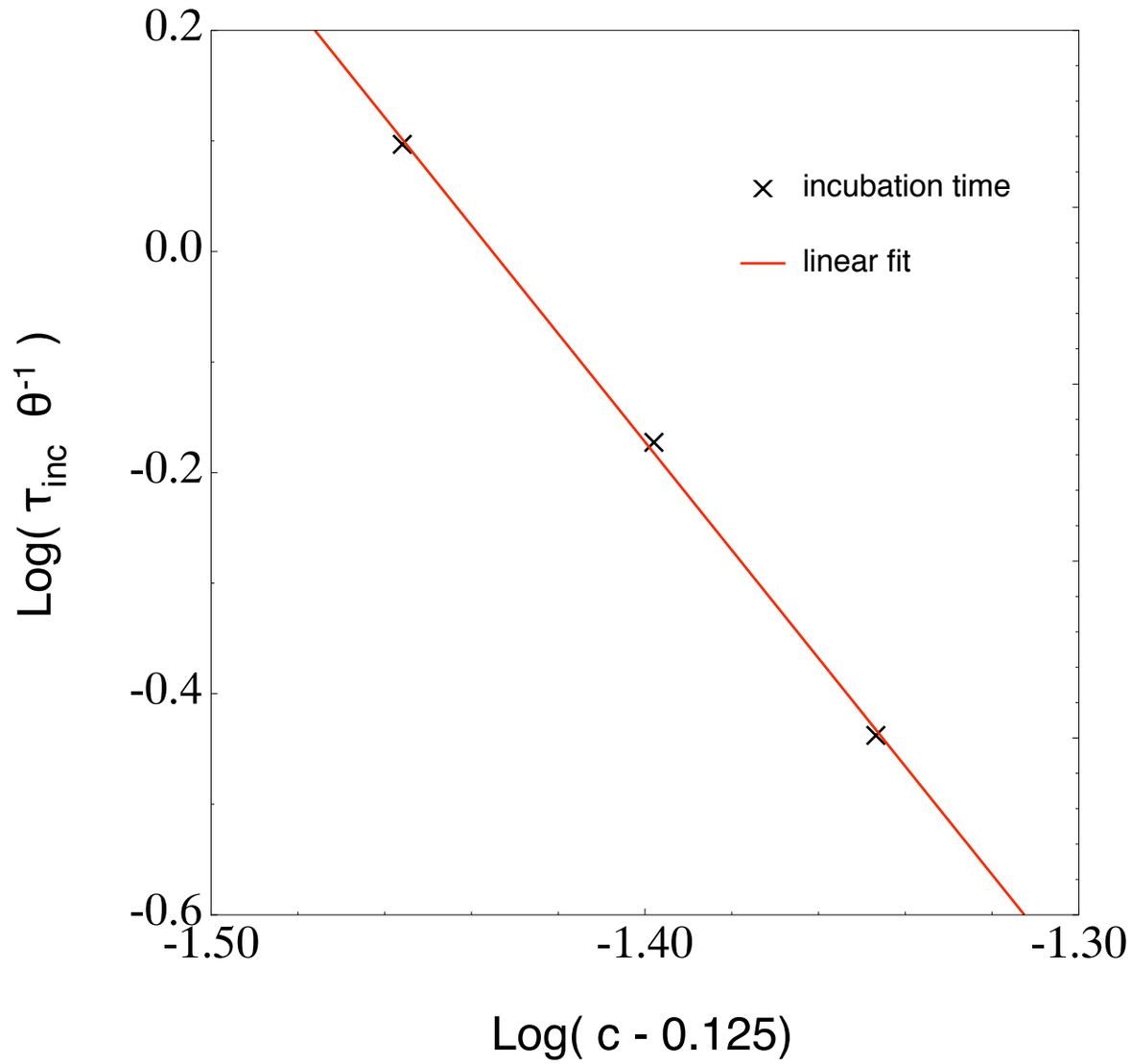


→ Critical radius : $R_c \sim 1\, d$

Comparaison with classical nucleation theory

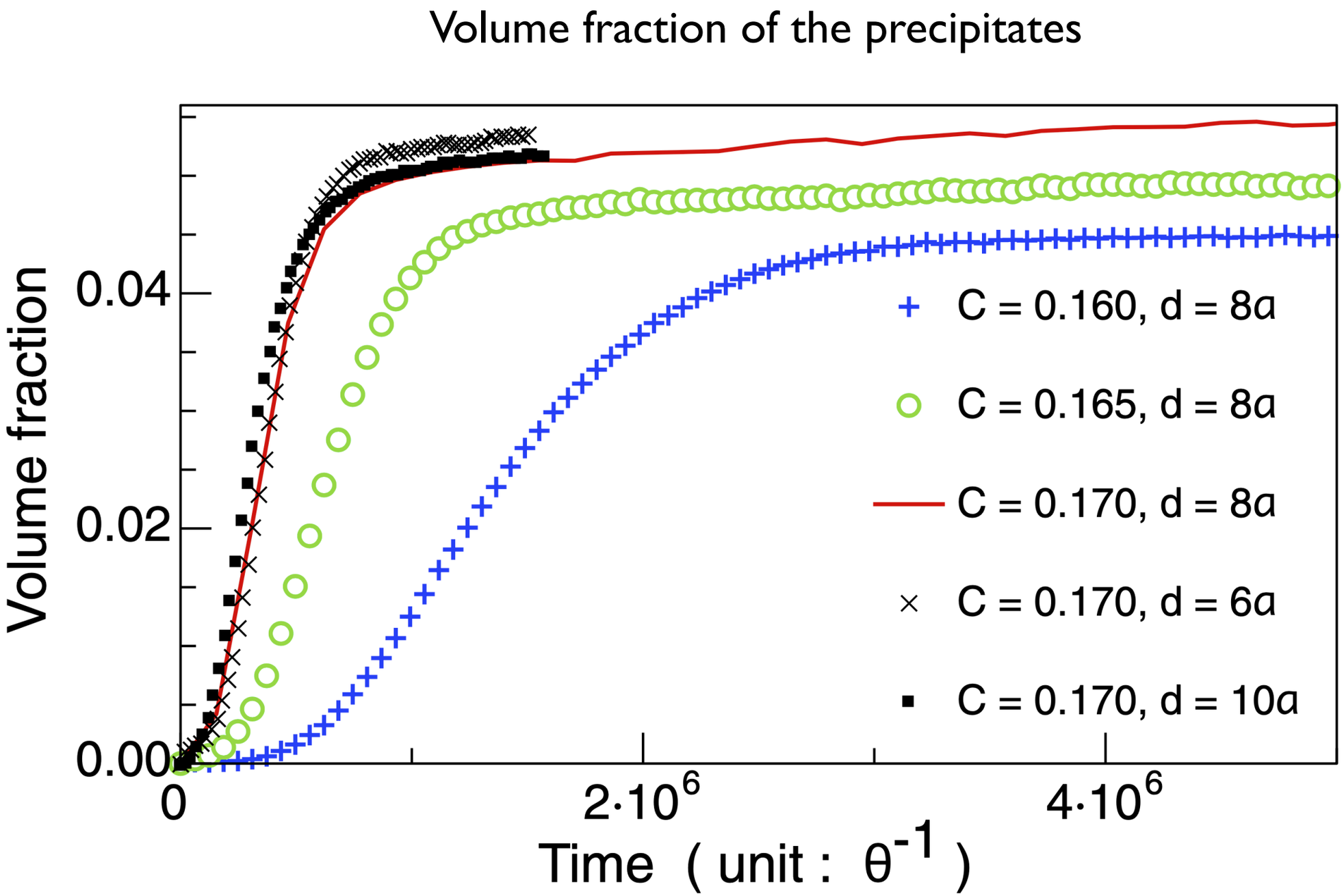
→ Incubation time as a function of sursaturation $(c - c_0)$





$$\tau \sim (c - c_0)^{-\alpha} \qquad \alpha \simeq 4.8 \pm 0.1 \qquad CNT : \alpha = 4$$

On the influence of the coarse-graining size



Conclusion

a Phase Field model by coarse-graining…

- generates simultaneously a coarse-grained GL free energy and a coarse-grained CH kinetics
- a stochastic equation with a multiplicative noise term (with a fluctuation theorem)
- Mobility M(c) and noise correlations depend on coarse-graining size and on local concentration
- "stiffness" constant $\lambda^d(c)$ depend on coarse-graining size and on local concentration
- reproduces equilibrium fluctuations as well as precipitation