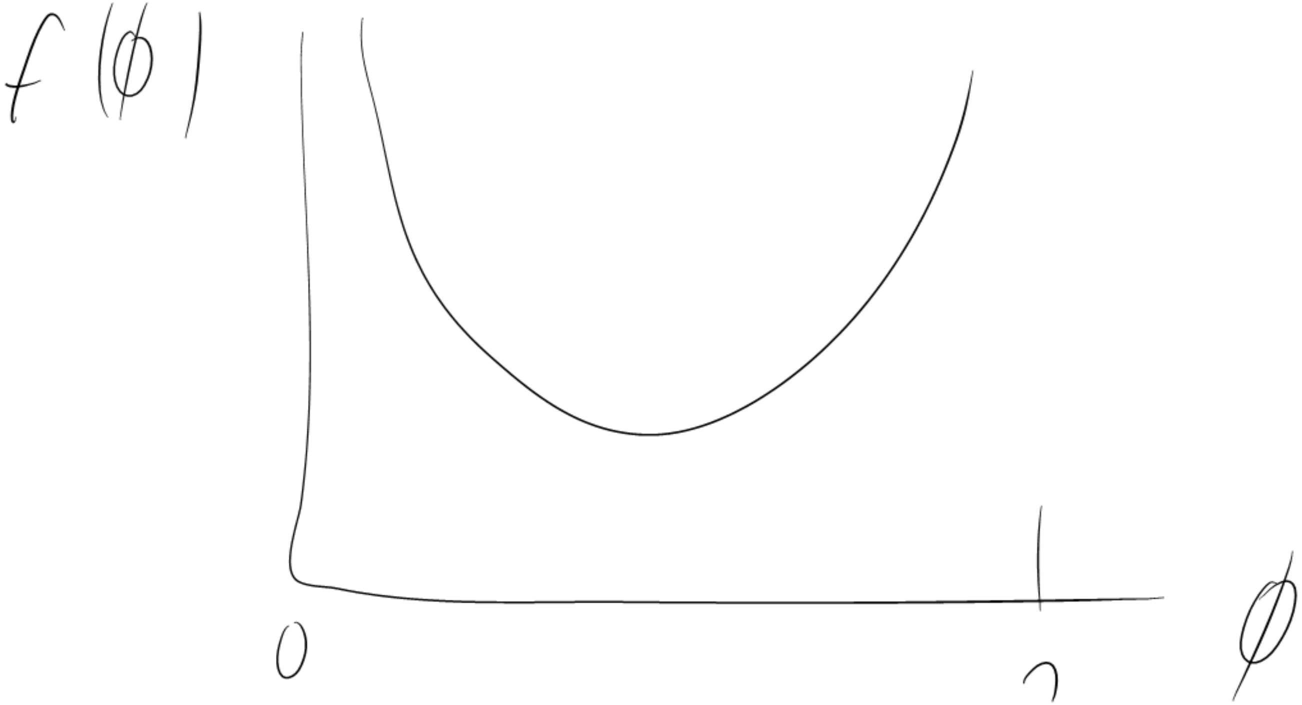
Flory - Huggins free energy (per site) f

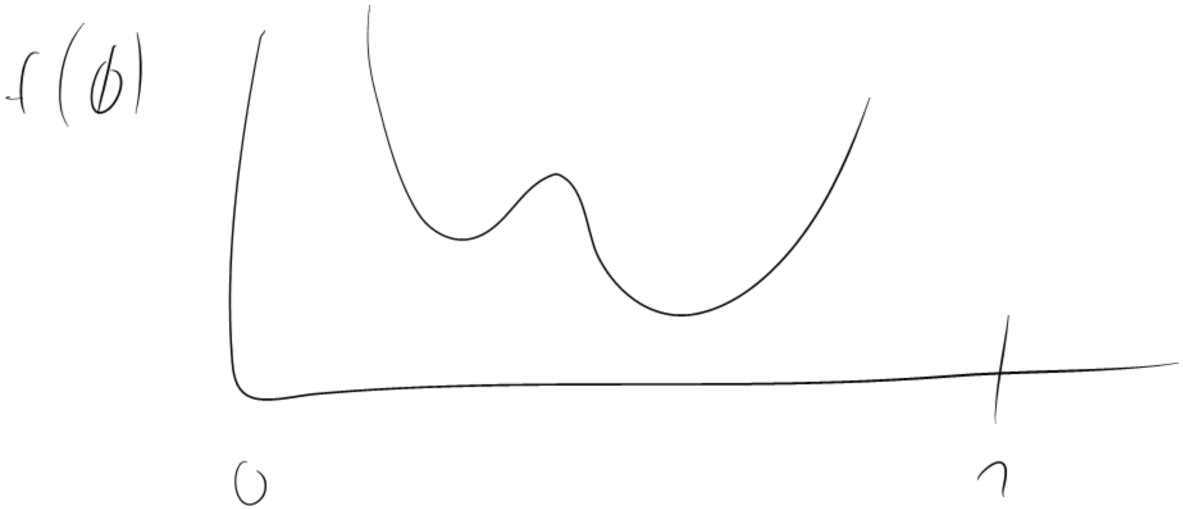
$$\frac{f}{k_B T} = \frac{\phi_A}{N_A} \ln \frac{\phi_A}{N_A} + \frac{\phi_B}{N_B} \ln \frac{\phi_B}{N_B} + \chi \phi_A \phi_B$$

$$+ \underbrace{\text{terms linear in } \phi + \text{const.}}_{\text{do not matter for the phase behavior}}$$

$$\phi = \phi_A = 1 - \phi_B$$



χ small



χ large

$\to$ phase separation

phase separation:

$\lambda \in [0, 1]$

ϕ conservation

"lever rule"

ϕ

$\to f_{FH}(\phi)$

$$\phi = \lambda \phi_{I} + (1-\lambda)\phi_{II}$$

ϕ_{I}, ϕ_{II} determined by thermodynamics

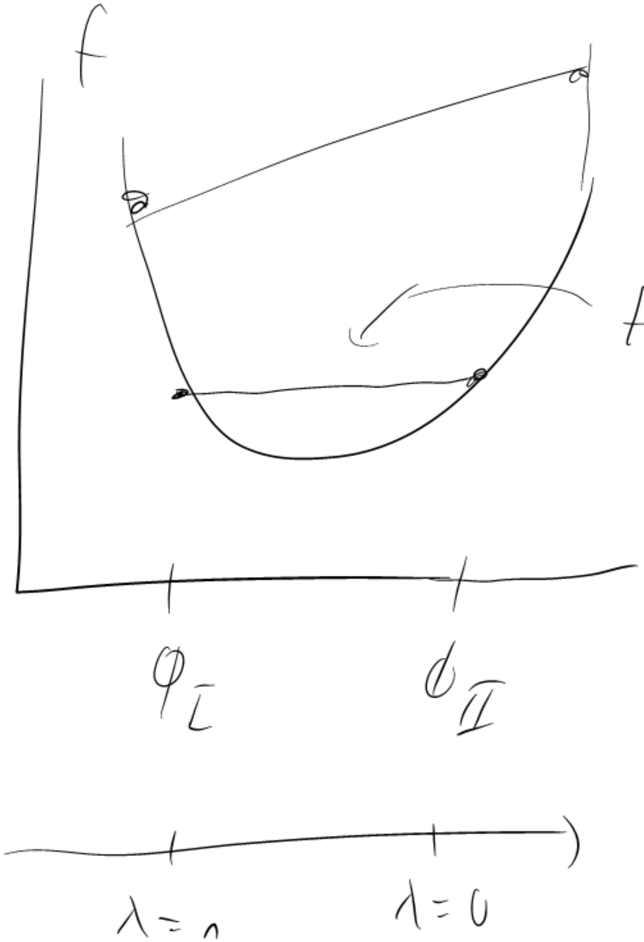
λ | $1-\lambda$

$\phi = \phi_{I}$	$\phi = \phi_{II}$
$f_{FH}(\phi_{I})$	$f_{FH}(\phi_{II})$
phase $\underline{I}$	phase $\underline{II}$

$$f_{FH}\left(\lambda \phi_{I} + (1-\lambda)\phi_{II}\right) > \lambda f_{FH}(\phi_{I}) + (1-\lambda) f_{FH}(\phi_{II})$$

is the condition for phase separation

f convex:



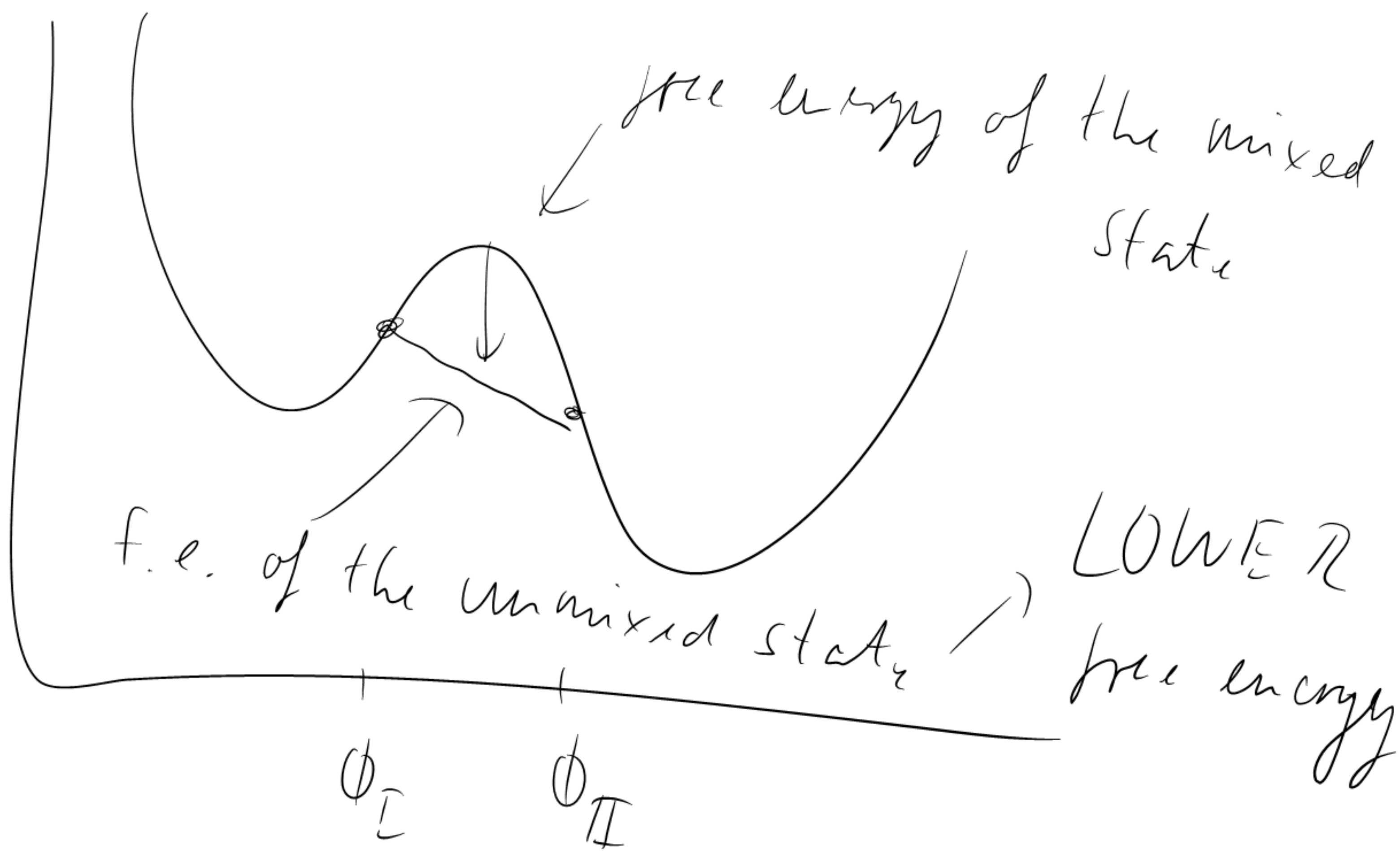
$$\phi = \lambda\, \phi_I + (1-\lambda)\, \phi_{II}$$

$$f(\phi_I) \cdot \lambda + f(\phi_{II}) \cdot (1-\lambda)$$

free energy of the unmixed state is <u>larger</u>

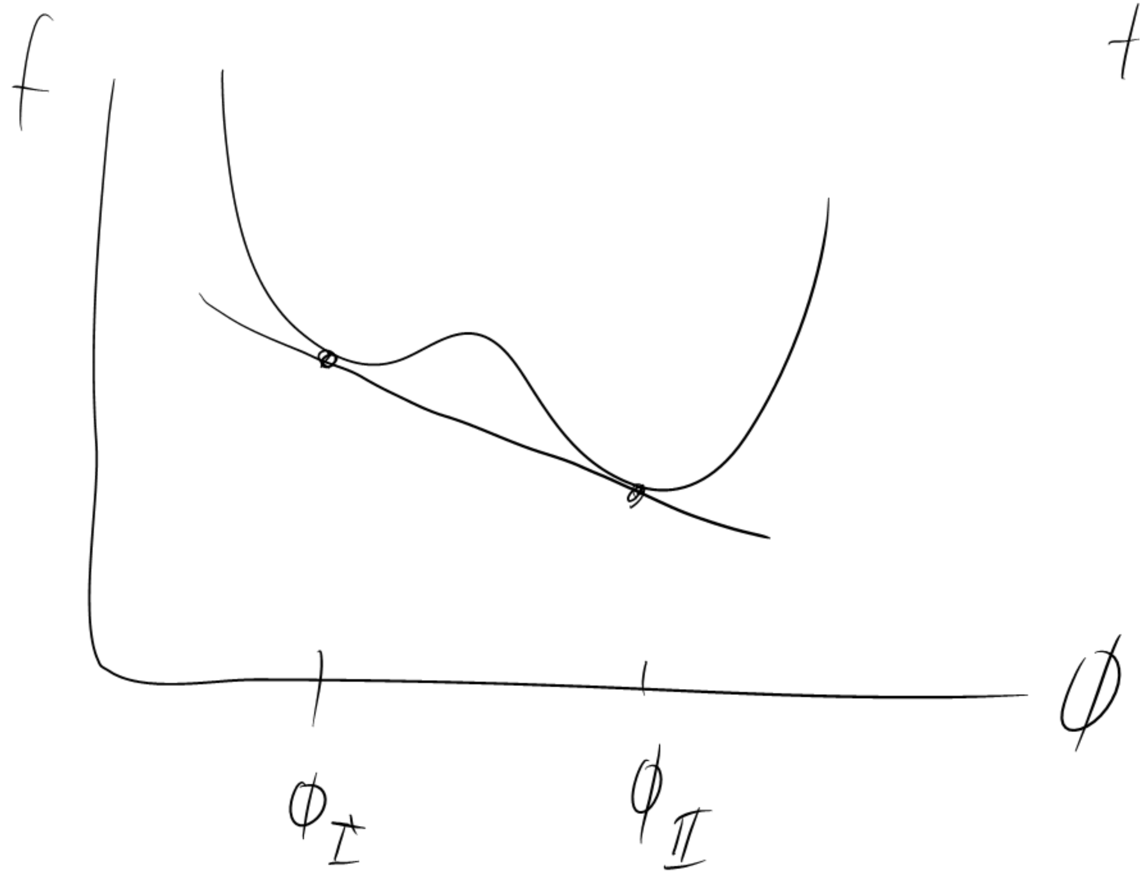
$\rightarrow$ homogeneous state is stable!

f concave


free energy of the mixed state
f.e. of the unmixed state
LOWER free energy
ϕ_I
ϕ_{II}

optimize ϕ_I, ϕ_{II} $\longrightarrow$ common tangent

this determines ϕ_I, ϕ_{II} !



$$\left.\frac{\partial f}{\partial \phi}\right|_{\phi=\phi_I} = \left.\frac{\partial f}{\partial \phi}\right|_{\phi=\phi_{II}} = \frac{f(\phi_I)-f(\phi_{II})}{\phi_I-\phi_{II}}$$

2 eq., 2 unknowns (ϕ_I, ϕ_{II})

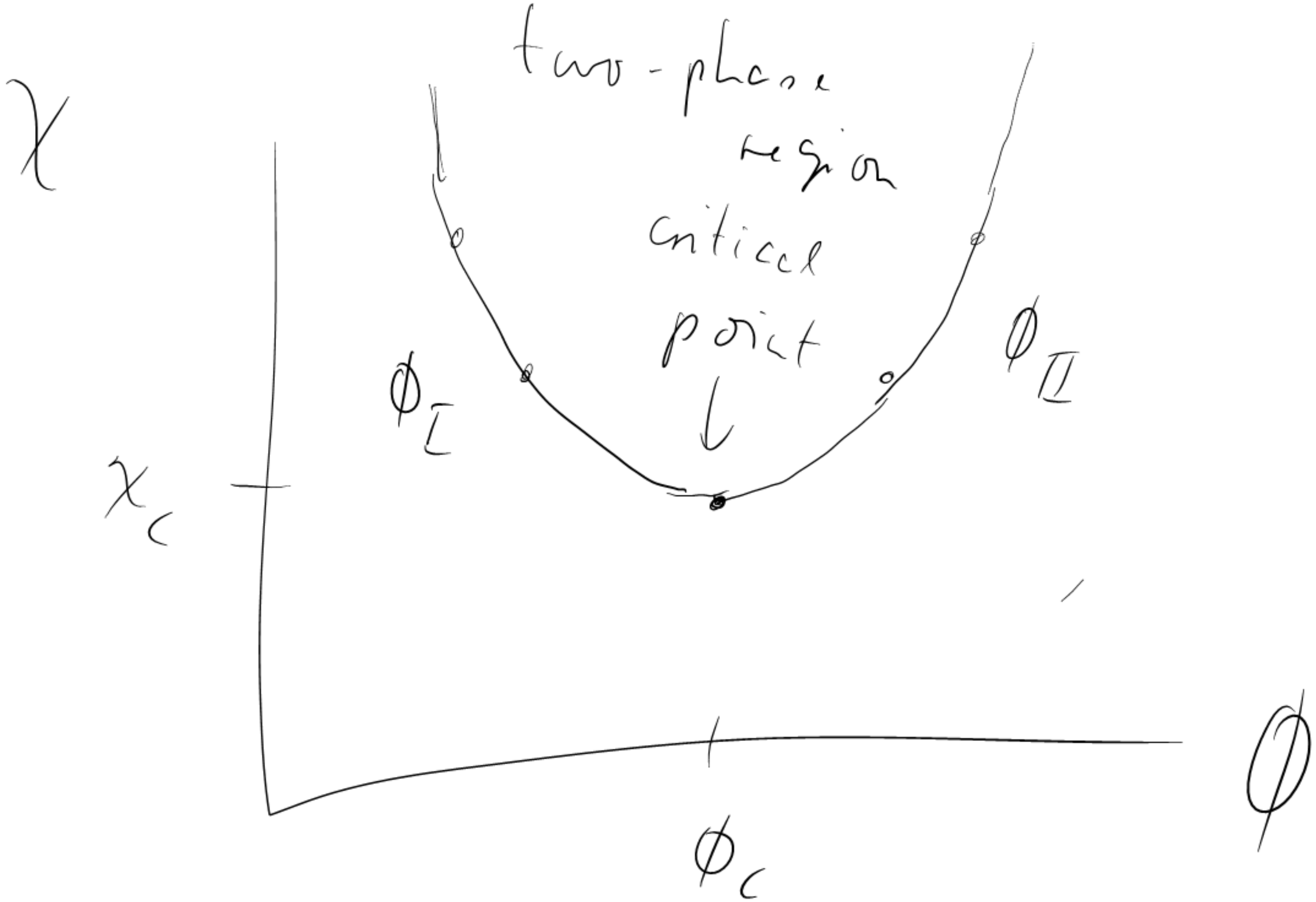
$$f \to f + A\phi + B$$

$$\left.\frac{\partial f}{\partial \phi}\right|_{\phi_I} \to \left.\frac{\partial f}{\partial \phi}\right|_{\phi_I} + A \qquad \left.\frac{\partial f}{\partial \phi}\right|_{\phi_{II}} \to \left.\frac{\partial f}{\partial \phi}\right|_{\phi_{II}} + A$$

$$f(\phi_I) - f(\phi_{II}) \to f(\phi_I) - f(\phi_{II}) + A(\phi_I - \phi_{II})$$

$$\frac{f(\phi_I) - f(\phi_{II})}{\phi_I - \phi_{II}} \to \frac{f(\phi_I) - f(\phi_{II})}{\phi_I - \phi_{II}} + A$$

therefore we can neglect $A\phi + B$ in f!



phase diagram

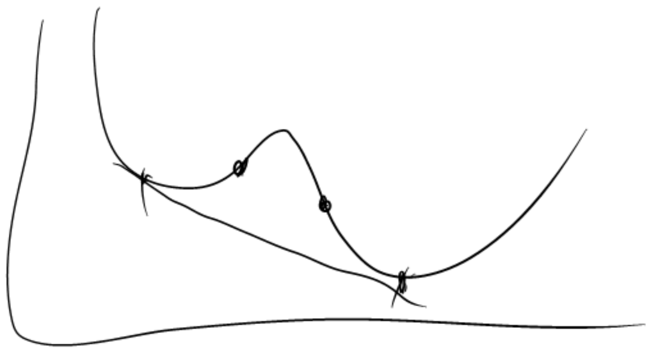
$$\frac{\partial^2 f}{\partial \phi^2} > 0$$ locally convex

→ system is stable w.r.t.

infinitesimal fluctuations

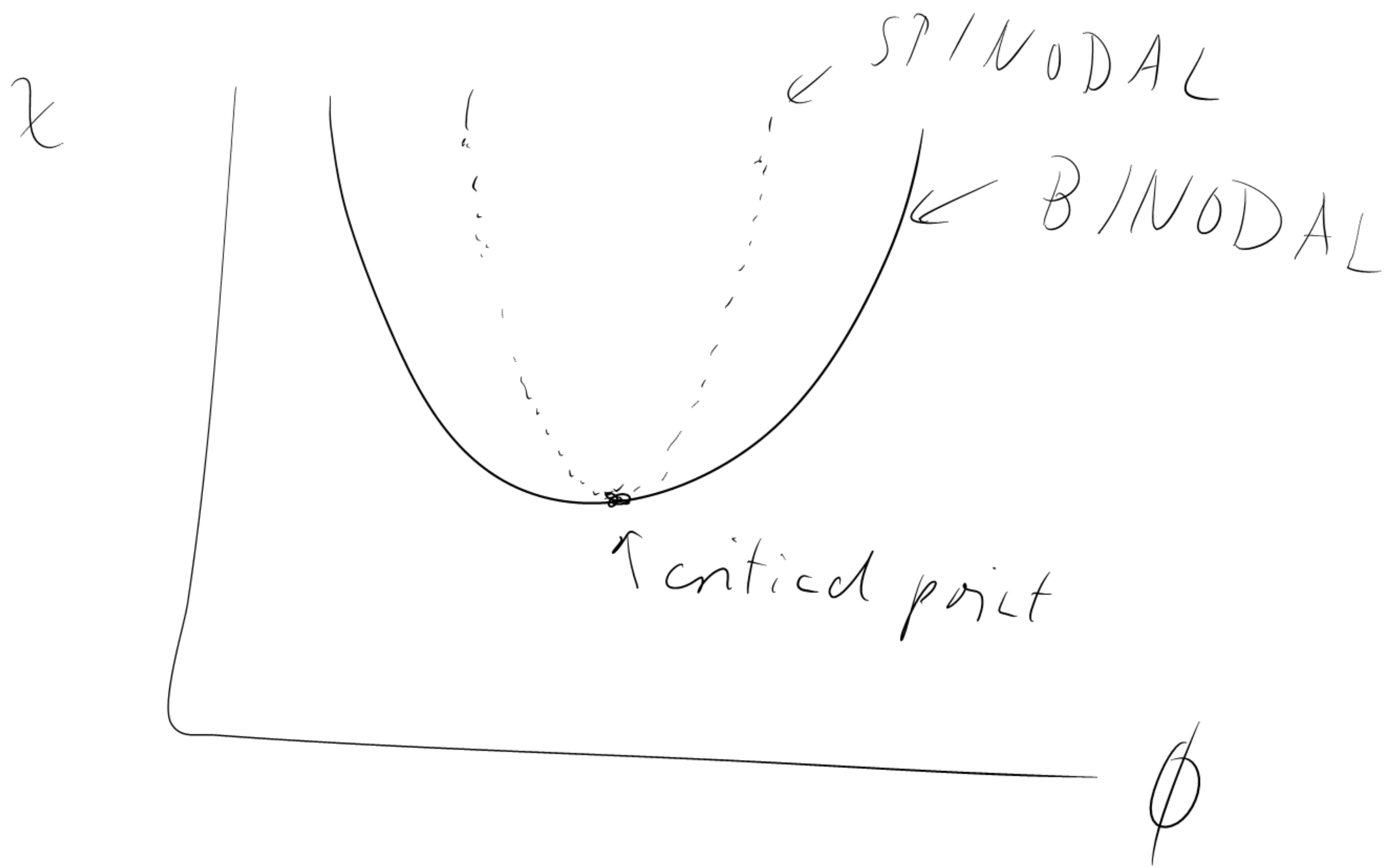
$$\frac{\partial^2 f}{\partial \phi^2} < 0$$ locally concave → instable

even w.r.t. infinitesimal fluctuations



$$\frac{\partial^2 f}{\partial \phi^2} = 0$$ inflection points

→ SPINODAL

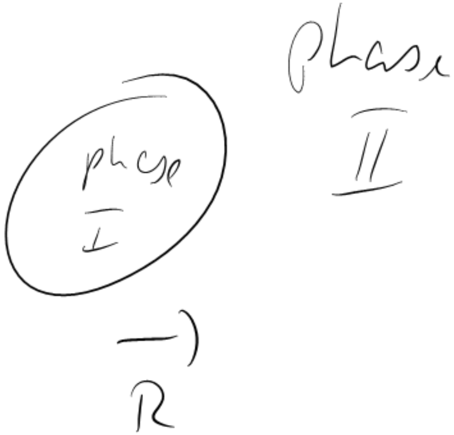


(phase diagram again)

Nucleation

(excursion)

Becker-Döring



$$\Delta F = -\frac{4\pi}{3} R^3 \cdot \underbrace{\Delta\mu}_{>0} + 4\pi R^2 \cdot \gamma \leftarrow \text{interfacial tension}$$

time ~

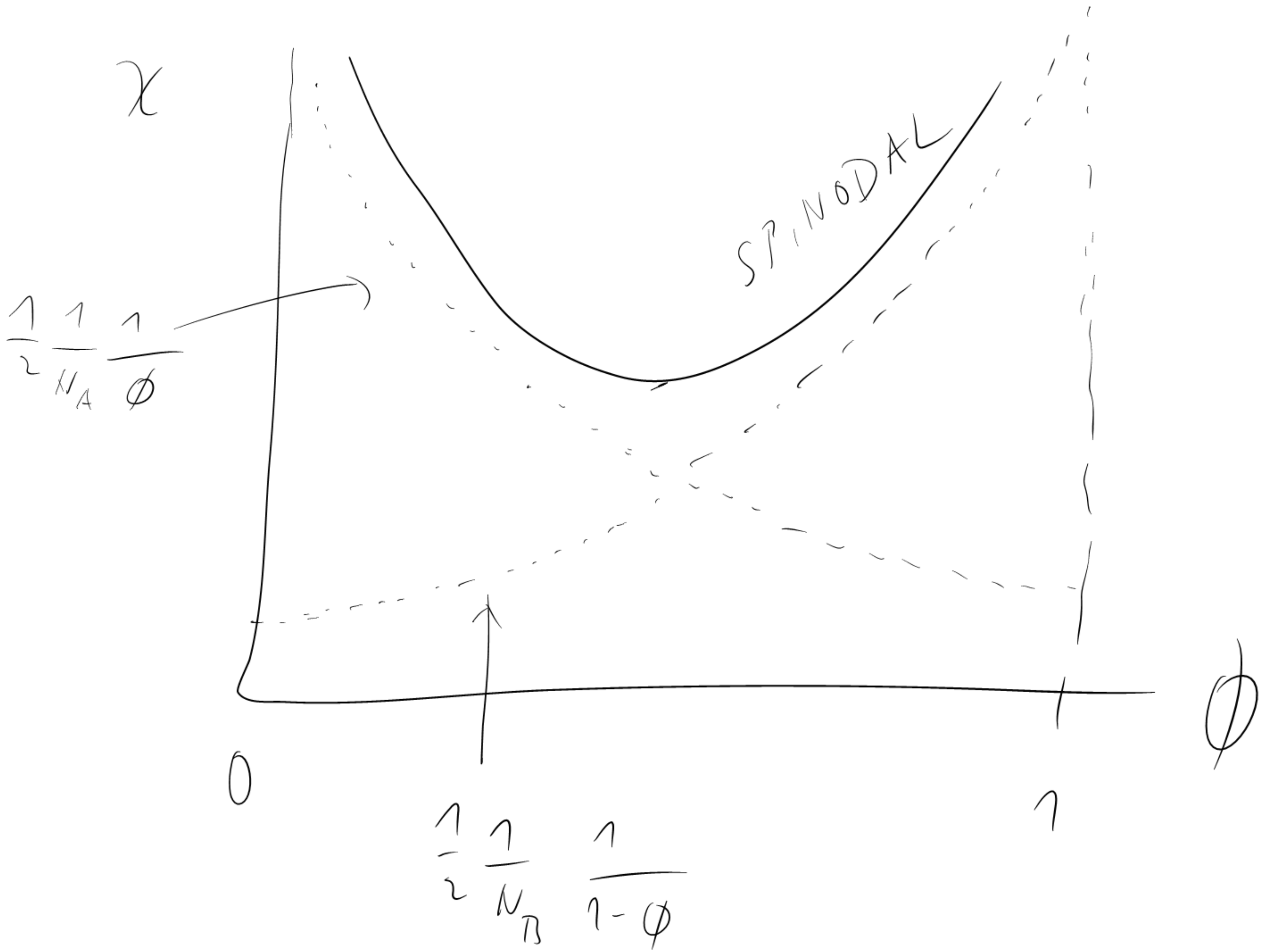
$$\tau \propto \exp\left[+ \frac{\Delta F^*}{k_B T} \right]$$

back to FH: calculate spinodal

$$\frac{f}{k_BT} = \frac{\phi}{N_A} \ln \frac{\phi}{N_A} + \frac{1-\phi}{N_B} \ln \frac{1-\phi}{N_B} + \chi \phi (1-\phi)$$

$$\frac{\partial^2}{\partial \phi^2} \frac{f}{k_BT} = \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi \overset{!}{=} 0$$

$$\chi = \frac{1}{2}\left(\frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)}\right)$$



χ
SPINODAL
$\frac{1}{2}\frac{1}{N_A}\frac{1}{\phi}$
ϕ
0
1
$\frac{1}{2}\frac{1}{N_B}\frac{1}{1-\phi}$

Critical point?

$$0 \overset{!}{=} \frac{\partial}{\partial\phi}\left\{\frac{1}{2}\left(\frac{1}{N_A\,\phi}+\frac{1}{N_B\,(1-\phi)}\right)\right\}$$

$$= \frac{\partial}{\partial\phi}\left\{\frac{1}{N_A\,\phi}+\frac{1}{N_B\,(1-\phi)}\right\} = -\frac{1}{N_A\,\phi^2}+\frac{1}{N_B\,(1-\phi)^2}$$

$$\Rightarrow \quad \phi = \phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A}+\sqrt{N_B}} \longrightarrow$$ into spinodal

$$\Rightarrow \quad \chi_c = \frac{1}{2}\left(\frac{1}{N_A}+\frac{1}{N_B}\right)+\frac{1}{\sqrt{N_A\,N_B}}$$

Symmetric polymer mixture: $N_A = N_B = N$

$$\chi_c = \frac{1}{N} + \frac{1}{N} = \underline{\underline{\frac{2}{N}}} \qquad \phi_c = \frac{1}{2}$$

$$\downarrow$$

$$\propto \frac{1}{k_B T_c} \longrightarrow \boxed{k_B T_c \propto N}$$

polymers mix very poorly!

polymer solution $N_B = 1$ $N_A \gg 1$

$N_A = N$

$$\phi_c \simeq \frac{1}{\sqrt{N}} = N^{-1/2}$$

$$\chi_c \cong \frac{1}{2} + \frac{1}{\sqrt{N}} = \frac{1}{2} + N^{-1/2}$$