4.7 Binary mixtures

- This is a first order transition with a conserved order parameter.
- Ising model (with a conserved order parameter).
- We will do a Mean Field treatment of this (cop) Ising model.

Standard treatment in Chemical Physics book by Slater - but beware!

What do we mean by “mean field”?

4.7.1. Basic ideas

- Mixture of two atomic species A and B — in a solid lattice.
- Relative proportions x and $1 - x$.
- Alloy: composition is specified by $\mathrm{A}_x \mathrm{B}_{1-x}$.
- Energy of the system is specified in terms of the nearest neighbour interactions, denote

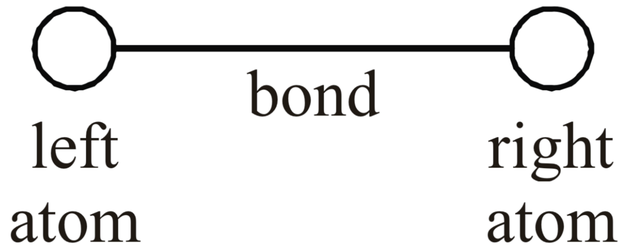
ε_{aa} energy of a single a—a bond

ε_{bb} energy of a single b—b bond

ε_{ab} energy of a single a—b bond

4.7.2. Model calculation (mean field)

- Assumption: the A and B atoms are distributed randomly. Thus we are considering a *homogeneous mixture*.
- Specify temperature and volume so need Landau *Helmholtz* free energy; require to know the *energy* and the *entropy*.
- Considering a *bond* joining two neighbouring atoms. We label one atom as the *left* atom and the other as *the* right.



.

- Each atom may be an A atom or a B atom. Thus there are four different configurations for the bond: a—a, a—b, b—a, b—b.

left atom \ right atom	A	B
A	ε_{aa}	ε_{ab}
B	ε_{ab}	ε_{bb}

configuration energies

- Concentration of the A atoms is x.
- Concentration of the B atoms is $1 - x$.

- — Concentration of the A atoms is x.
  — Concentration of the B atoms is $1 - x$.
- Assume the atoms are distributed randomly so:
- — Probability a site is occupied by an A atom is x.
  — Probability it is occupied by a B atom is $1 - x$.
- In general case concentration varies with position.

  — Probability the left atom is A is x_{l}
  — Probability it is B is $1 - x_{\mathrm{l}}$
  — Probability the right atom is A is x_{r}.
  — Probability it is B is $1 - x_{\mathrm{r}}$

- Four bond configurations a—a, a—b, b—a, b—b, then have the probabilities:

$$x_l x_r,\ x_l(1-x_r),\ (1-x_l)x_r,\ (1-x_l)(1-x_r).$$

left atom \ right atom	A	B
A	$x_l x_r$	$x_l\,(1-x_r)$
B	$(1-x_l)\,x_r$	$(1-x_l)(1-x_r)$

configuration probabilities

4.7.3 System energy

- Have defined the energies $\{\varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{ab}\}$ of the three (four) types of bonds.
- Have the probability of occurrence of each configuration.
- The mean energy for the bond will be the sum of the energy of each state multiplied by its probability:

$$\bar{e}_{lr} = \varepsilon_{aa} x_l x_r + \varepsilon_{ab} x_l \left(1 - x_r\right) + \varepsilon_{ab} \left(1 - x_l\right) x_r + \varepsilon_{bb} \left(1 - x_l\right) \left(1 - x_r\right).$$

- Now assume composition is homogeneous: $x_l = x_r = \text{const}, x$.
- Then mean energy per bond reduces to

$$\bar{e} = x^2 \varepsilon_{aa} + (1 - x)^2 \varepsilon_{bb} + 2x(1 - x)\varepsilon_{ab}$$

- Mean energy per bond

$$\bar{e} = x^2\varepsilon_{\mathrm{aa}} + (1-x)^2\varepsilon_{\mathrm{bb}} + 2x(1-x)\varepsilon_{\mathrm{ab}}$$

- May be rearranged as (why do this?)

$$\bar{e} = x\varepsilon_{\mathrm{aa}} + (1-x)\varepsilon_{\mathrm{bb}} + x(1-x)\Big\{2\varepsilon_{\mathrm{ab}} - \big(\varepsilon_{\mathrm{aa}} + \varepsilon_{\mathrm{bb}}\big)\Big\}.$$

- Internal energy is found by summing over N atomic sites in a lattice where each atom has s neighbours.

- Number of neighbour bonds will be $Ns/2$; the divisor of 2 removes double counting.

- Internal energy is then $E = Ns\bar{e}/2$

- Internal energy is $E = Ns\bar{e}/2$ or

$$E = \frac{Ns}{2}\left\{ x\varepsilon_{\mathrm{aa}} + (1-x)\varepsilon_{\mathrm{bb}} + 2x(1-x)\left[\varepsilon_{\mathrm{ab}} - \left(\frac{\varepsilon_{\mathrm{aa}} + \varepsilon_{\mathrm{bb}}}{2}\right)\right]\right\}$$

- First two terms represent the energy of the separated pure phases E_0.

$$E_0 = \frac{Ns}{2}\left[x\varepsilon_{\mathrm{aa}} + (1-x)\varepsilon_{\mathrm{bb}}\right]$$

- Third term gives the *energy of mixing* E_{m}.

$$E_{\mathrm{m}} = Nsx(1-x)\left[\varepsilon_{ab} - \left(\frac{\varepsilon_{aa} + \varepsilon_{bb}}{2}\right)\right].$$

Simplify . . .

- We will see that that E_{m} is the only energy that counts.

$$E_{\mathrm{m}} = Nsx(1-x)\left[\varepsilon_{ab} - \frac{1}{2}\left(\varepsilon_{aa} + \varepsilon_{bb}\right)\right] .$$

- Define the energy ε

$$\varepsilon = \varepsilon_{ab} - \frac{1}{2}\left(\varepsilon_{aa} + \varepsilon_{bb}\right)$$

  the difference between the ‘unlike’ neighbour energy and the mean of the two ‘like’ neighbour energies. This is the *characteristic energy* of the system.

- Then the energy of mixing takes the simple form

$$E_{\mathrm{m}} = Ns\, x(1-x)\, \varepsilon.$$

- $$E_{\mathrm{m}} = Ns\, x(1-x)\, \varepsilon$$

- Observe that E_{m} is invariant under the transformation $x \to 1 - x$

  E_{m} is symmetric about the line $x = \frac{1}{2}$.

- System whose energy satisfies this condition are *strictly regular* solutions.

- An ideal solution has $\varepsilon = 0$; its energy of mixing is zero. It cannot lower its energy by changing its structure.

- But when $\varepsilon \neq 0$ then the solution can lower its energy by transforming to an ordered structure.

  — When $\varepsilon < 0$ then a—b bonds are preferred; ordered state will be a superlattice. (Clearly this would only happen in a solid.)

  — When $\varepsilon > 0$ then a—a and b—b bonds are preferred; ordered state will comprise separate a-rich and of b-rich atoms. (This would happen in both solids and liquids.)

4.7.4. Entropy

- Each site can be occupied by an A atom or a B atom; it has two states.

  — The probability that it is an A atom is x.

  — The probability that it is a B atom is $(1-x)$.

- The (Gibbs) entropy is

$$S = -Nk\left[x\ln x + (1-x)\ln(1-x)\right].$$

- Recognise: standard entropy for 2-state system. Identical to that for the spin $^1/_2$ magnet.

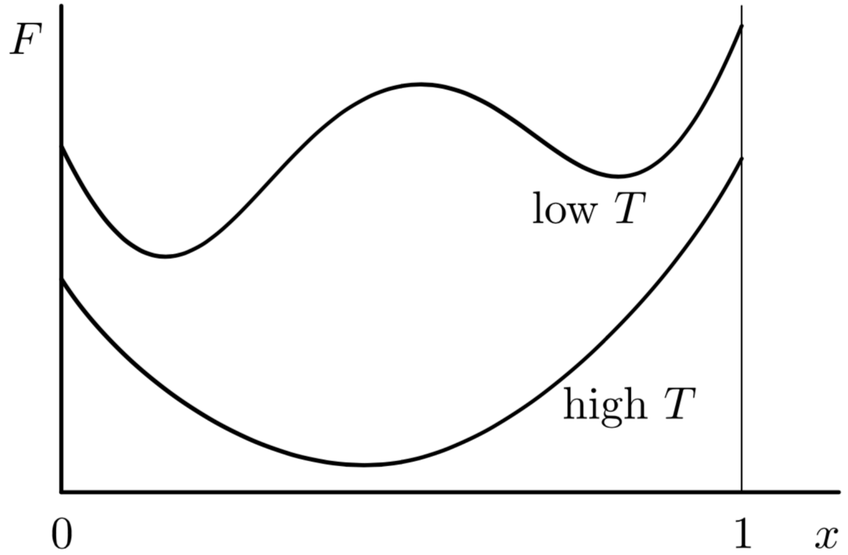
4.7.5. Free energy

- System has its *temperature* and *volume* fixed thus the *Helmholtz* free energy is the appropriate thermodynamic potential to use.

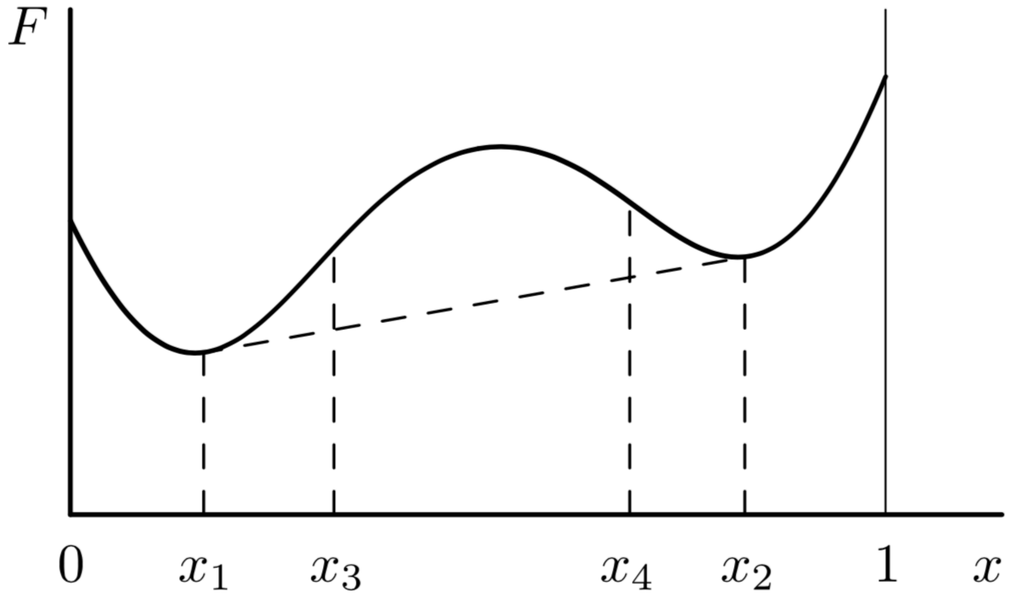
$$F = E - TS.$$

So we have

$$F = \frac{Ns}{2}\left[\underbrace{x\varepsilon_{\mathrm{aa}} + (1-x)\varepsilon_{\mathrm{bb}}}_{\text{vertical shear}} + \underbrace{2x(1-x)\varepsilon}_{\text{energy of mixing}}\right] + NkT\left[x\ln x + (1-x)\ln(1-x)\right]$$



- Between $x = x_1$ and $x = x_2$ it is possible to lower the free energy by phase separation by dropping down from the curve to the double tangent line, with a mixture of phases at densities x_1 and x_2. This is analogous to the situation with the liquid-gas system treated in the van der Waals approach. And as with the fluid case, in the phase separation region some parts are *metastable* while some parts are *unstable*.



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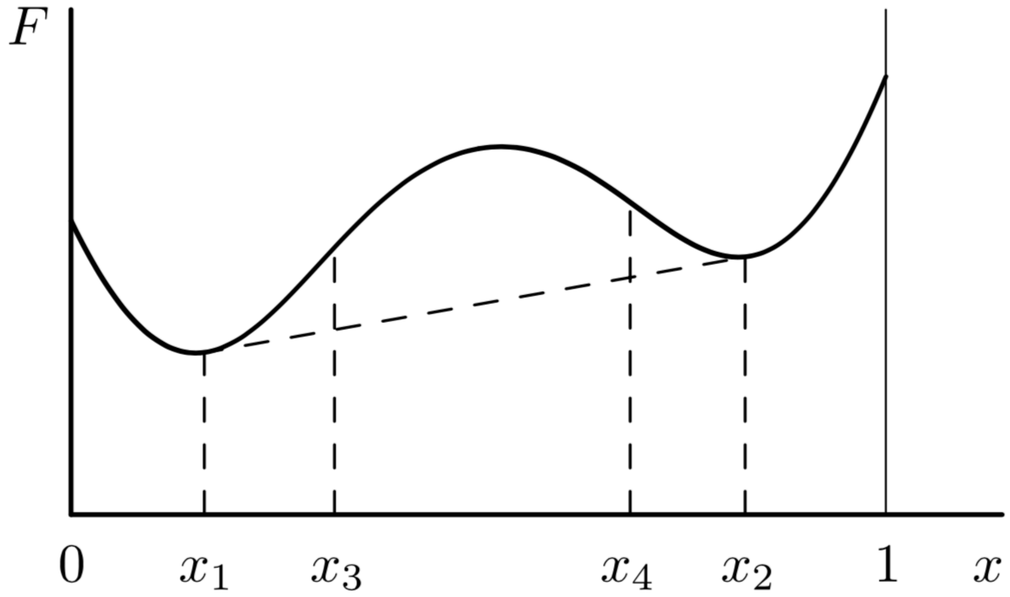
- Instability occurs whenever $\partial F/\partial x$ is a *decreasing* function of x, that is, when $\partial^2 F/\partial x^2 < 0$. Then the system is unstable with respect to infinitesimal concentration fluctuations. This happens in the region x_3 to x_4. This is known as the *spinodal* region. If the temperature is quenched into this region then one has spontaneous phase separation, referred to as *spinodal decomposition*.



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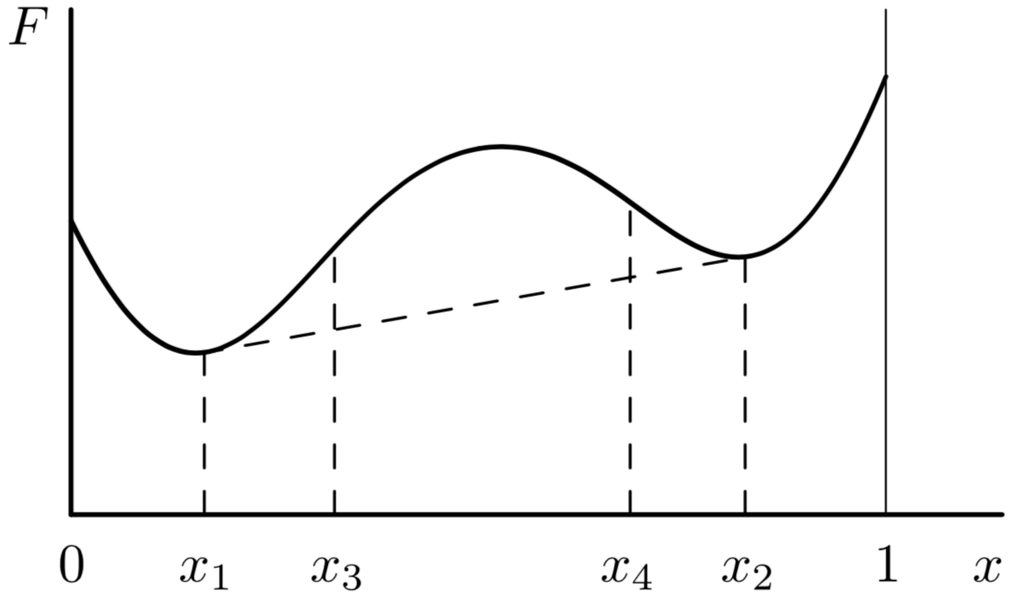
- By contrast the regions x_1 to x_3 and x_4 to x_2 are *metastable*. Here it is possible to remain in the inhomogeneous phase unless a concentration fluctuation of sufficient magnitude occurs. The system is unstable with respect to *finite* concentration fluctuations. Clearly if one waits long enough a fluctuation of sufficient magnitude will occur (but it might be a very long wait indeed).



—(Look at Section 4.7.6 Lever rule)

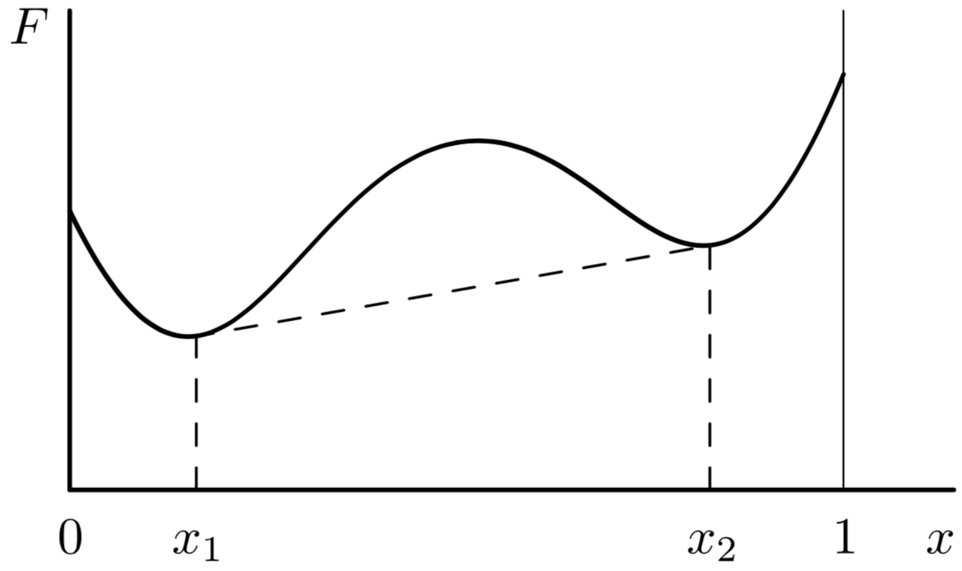
4.7.7 Phase separation curve — the binodal

- The concentrations x_1 and x_2 of the two separated phases are determined from the *double tangent construction*.

- Must solve the simultaneous equations

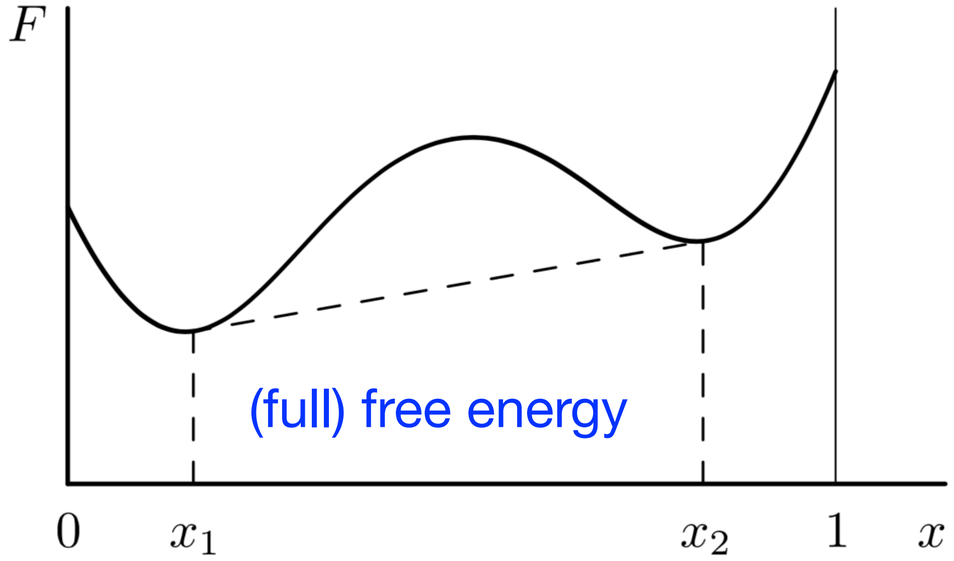
$$\left.\frac{\mathrm{d}F(x)}{\mathrm{d}x}\right|_{x_1} = \left.\frac{\mathrm{d}F(x)}{\mathrm{d}x}\right|_{x_2}$$

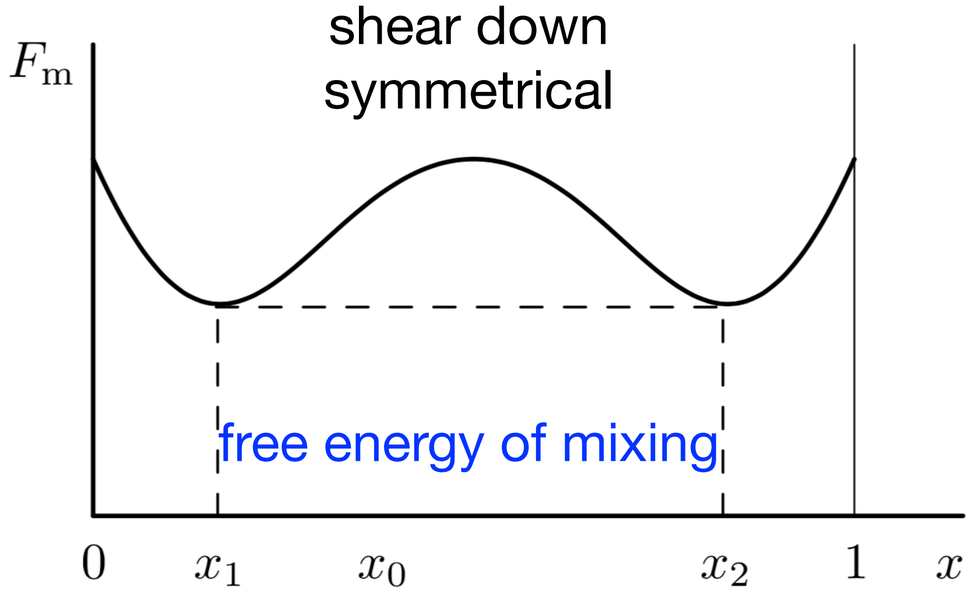
$$F(x_2) = F(x_1) + (x_2 - x_1)\left.\frac{\mathrm{d}F(x)}{\mathrm{d}x}\right|_{x_1,x_2}$$



- This is horrible and messy. So let's be clever . . .Think . . .

$$F = \frac{Ns}{2}\underbrace{\left[x\varepsilon_{\mathrm{aa}} + (1-x)\varepsilon_{\mathrm{bb}}\right]}_{\text{vertical shear}} + \underbrace{2x(1-x)\varepsilon}_{\text{energy of mixing}} + NkT\left[x\ln x + (1-x)\ln(1-x)\right]$$





So work with free energy of mixing — now simply require $\mathrm{d}F_{\mathrm{m}}/\mathrm{d}x = 0$.

- $$F_{\mathrm{m}} = Nsx(1-x)\varepsilon + NkT\left[x\ln x + (1-x)\ln(1-x)\right].$$

- Concentration x_1 and x_2 of separated phases determined from

$$\frac{\mathrm{d}F_m(x)}{\mathrm{d}x} = 0$$

so differentiate

$$\frac{\mathrm{d}F_m(x)}{\mathrm{d}x} = Ns\varepsilon(1-2x) - NkT\ln\frac{1-x}{x} = 0.$$

- Would like to solve this for $x(T)$, giving two solutions x_1 and x_2.

- But can't do it!

- We can't solve

$$Ns\varepsilon(1-2x) - NkT\ln\frac{1-x}{x} = 0$$

for $x(T)$, but we can solve for $T(x)$. Familiar?

- This gives the transition temperature as a function of x:

$$T_{\mathrm{ps}} = \frac{s\varepsilon(1-2x)}{k\ln\left[(1-x)/x\right]}.$$

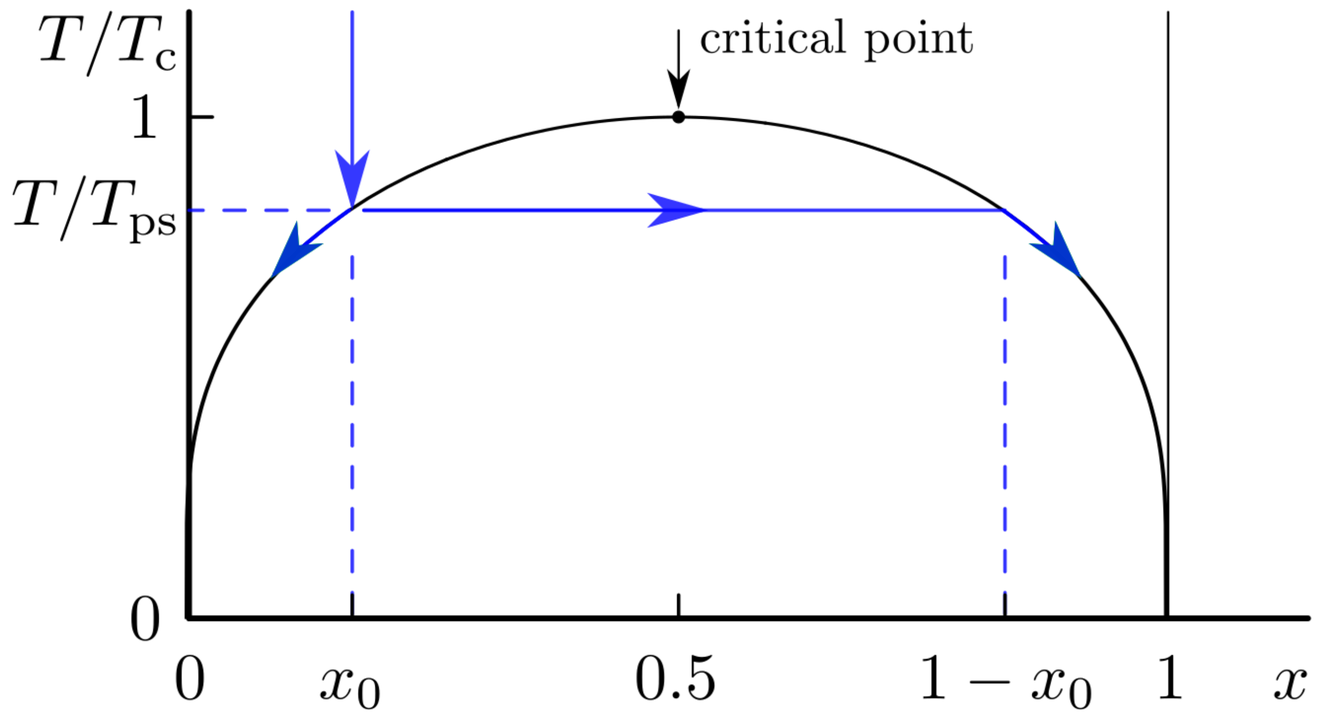
- The *critical temperature* T_{c} corresponds to the maximum T_{ps}, occuring at $x = \frac{1}{2}$ by symmetry. So $T_{\mathrm{c}} = \frac{s\varepsilon}{2k}$.

•

$$T_{\mathrm{ps}} = \frac{2(1-2x)}{\ln\left[(1-x)/x\right]} T_{\mathrm{c}}$$

- Path of a transition

phase transition curve / binodal



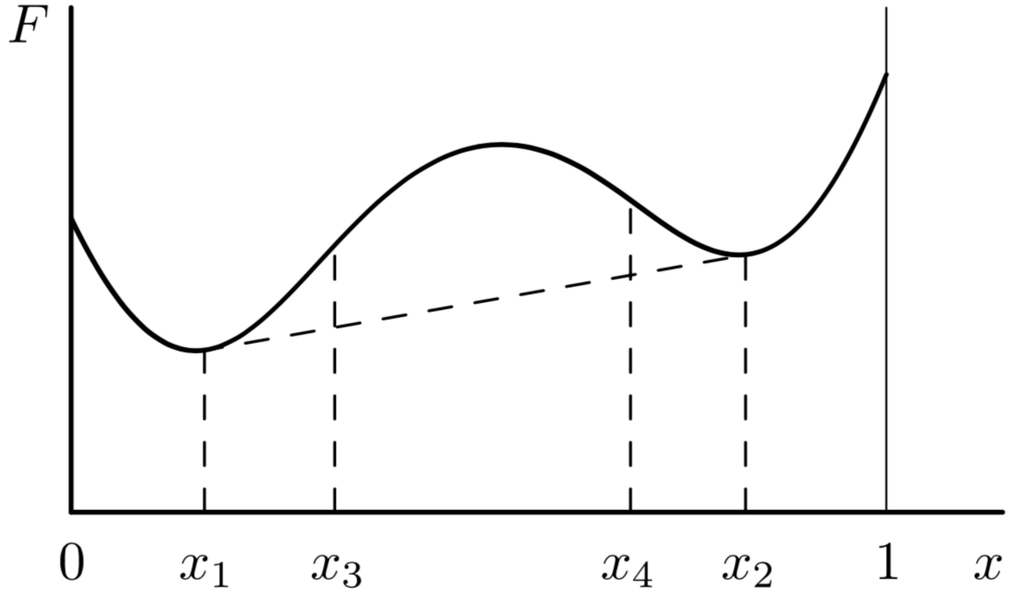
Strictly regular solution.

4.7.8 The spinodal curve

- The spinodal curve traces out the region of *instability* in the $T - x$ plane.

- Negative $\mathrm{d}^2F/\mathrm{d}x^2 < 0$; between points x_3 and x_4.

- These boundary points correspond to $\mathrm{d}^2F/\mathrm{d}x^2 = 0$. (can use F_m)



- We found $\mathrm{d}F/\mathrm{d}x$. So differentiate again

$$\frac{\mathrm{d}^2F_\mathrm{m}}{\mathrm{d}x^2} = -2Ns\varepsilon + NkT\left(\frac{1}{1-x} + \frac{1}{x}\right) = 0.$$

- Solution of

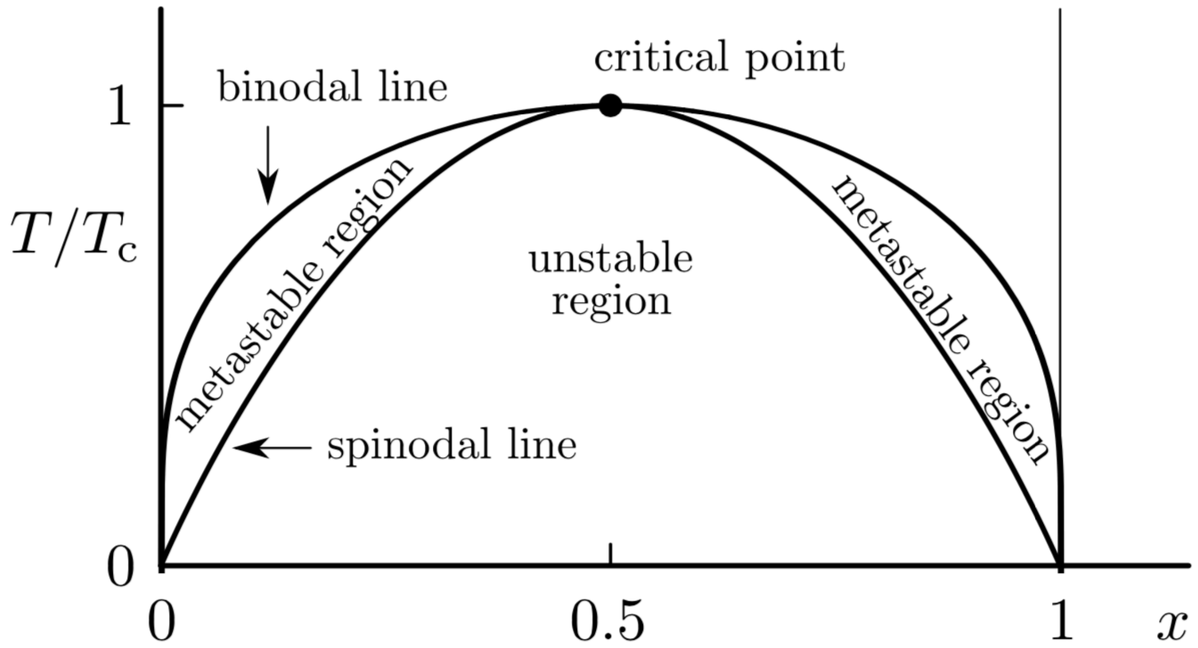
$$-2Ns\varepsilon + NkT\left(\frac{1}{1-x} + \frac{1}{x}\right) = 0$$

gives $T_{\mathrm{sp}}(x)$:

$$T_{\mathrm{sp}}(x) = \frac{2s\varepsilon}{k}x(1-x)$$

or, in terms of T_{c}:

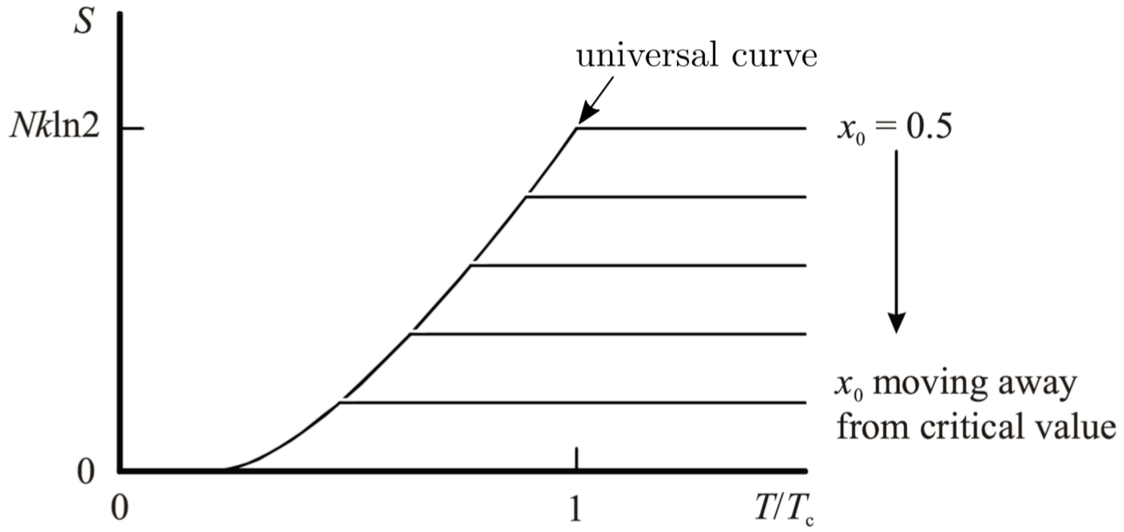
$$T_{\mathrm{sp}} = 4x(1-x)T_{\mathrm{c}}$$

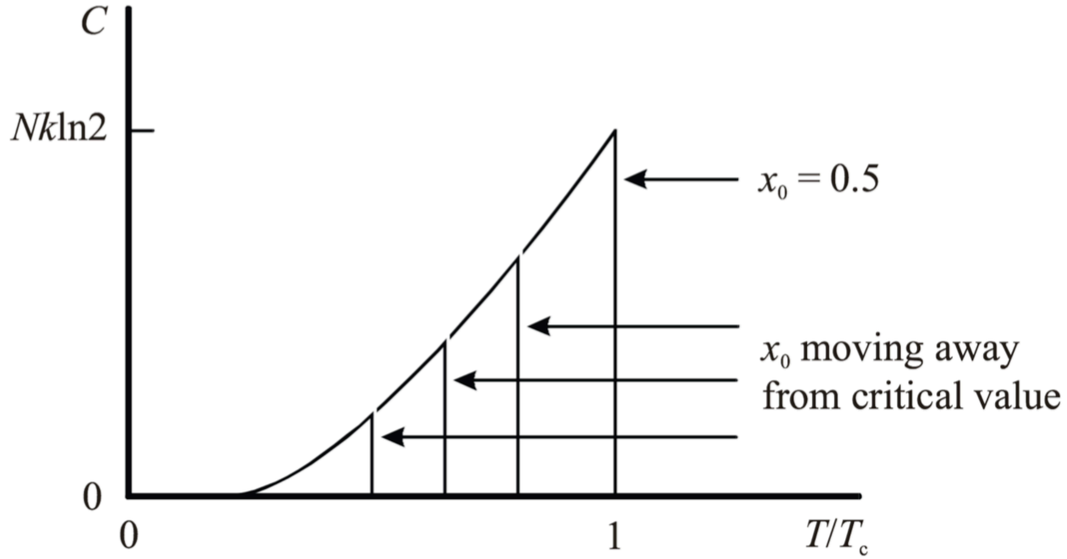


- Spinodal and binodal lines meet at the critical point.

Entropy and heat capacity — no details

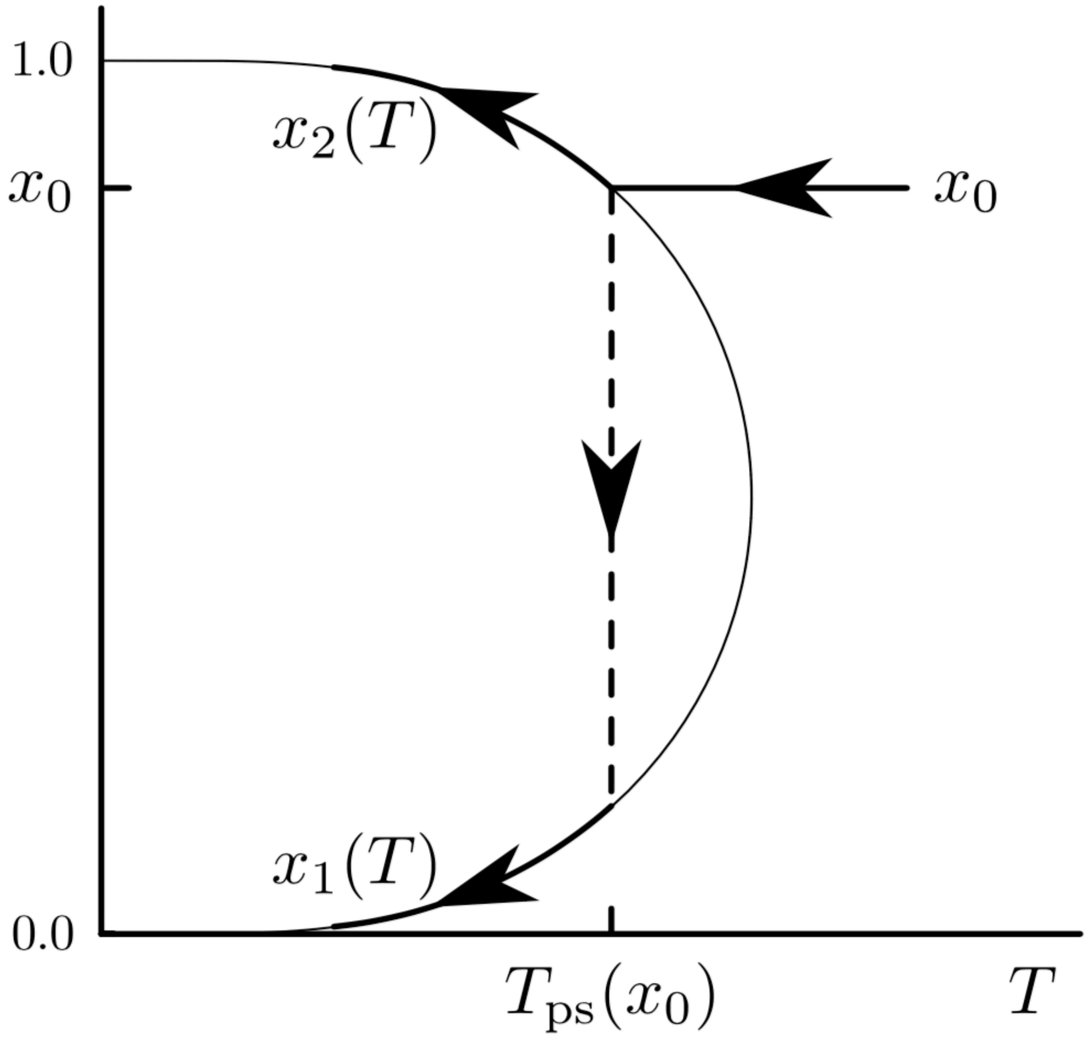
- Look in book for further details





The entropy is continuous at the transition and there is a simple discontinuity in the heat capacity. This means that there is *no latent heat* even though the transition is first order!!! (Because V is constant rather than p.)

4.7.11. Order of the transition and the critical point

- 

Discontinuity in x at the transition

$\Longrightarrow$ First order transition.

But — at the critical point the Discontinuity vanishes

$\Longrightarrow$ Transition goes second order

4.7.12 Around the critical point

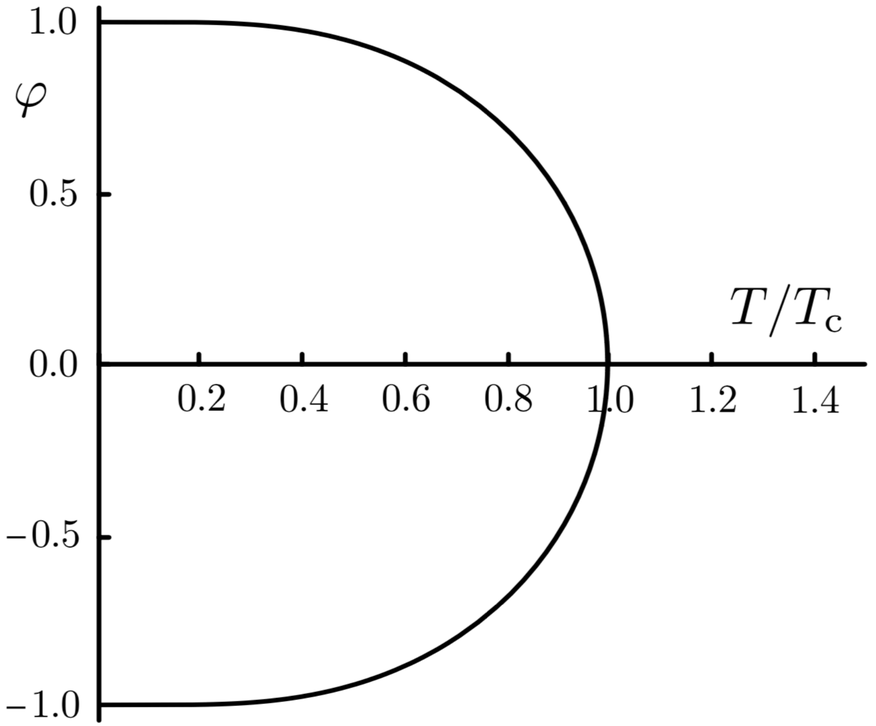
- Define $\varphi = 2x - 1$. So

$$\varphi \to 0 \quad \text{as } T \to T_c$$

$$\varphi \to \pm 1 \text{ as } T \to 0$$

$$\frac{T}{T_c} = \frac{2\varphi}{\ln\left[(1+\varphi)/(1-\varphi)\right]}$$

Identical to Weiss ferromagnet!!



Critical exponent β

- $$\frac{T}{T_c} = \frac{2\varphi}{\ln\left[(1+\varphi)/(1-\varphi)\right]}$$

- Expand $1 - T/T_c$ in powers of φ: $\frac{T}{T_c} = 1 - \frac{1}{3}\varphi^2 - \frac{4}{45}\varphi^4 + \ldots$

  and invert the series:

$$\varphi = \sqrt{3}\left(1 - \frac{T}{T_c}\right)^{1/2} - \frac{2\sqrt{3}}{5}\left(1 - \frac{T}{T_c}\right)^{3/2} + \ldots$$

giving $\beta = \frac{1}{2}$ and $b = \sqrt{3}$.

Difference between cop and n-cop

- The diagram above, showing the critical point may be similar in both cases, but the interpretation is different.

  — For a non-conserved order parameter when the critical point is approached there is a *bifurcation* and the system breaks symmetry by choosing one rather than the other branch.

  — For a conserved order parameter *both* branches are chosen; we have coexisting fractions determined by the lever rule.

- The two are connected by Lagrange multiplier / Legendre transformation.

4.9 Restrospective

4.9.1 The existence of order

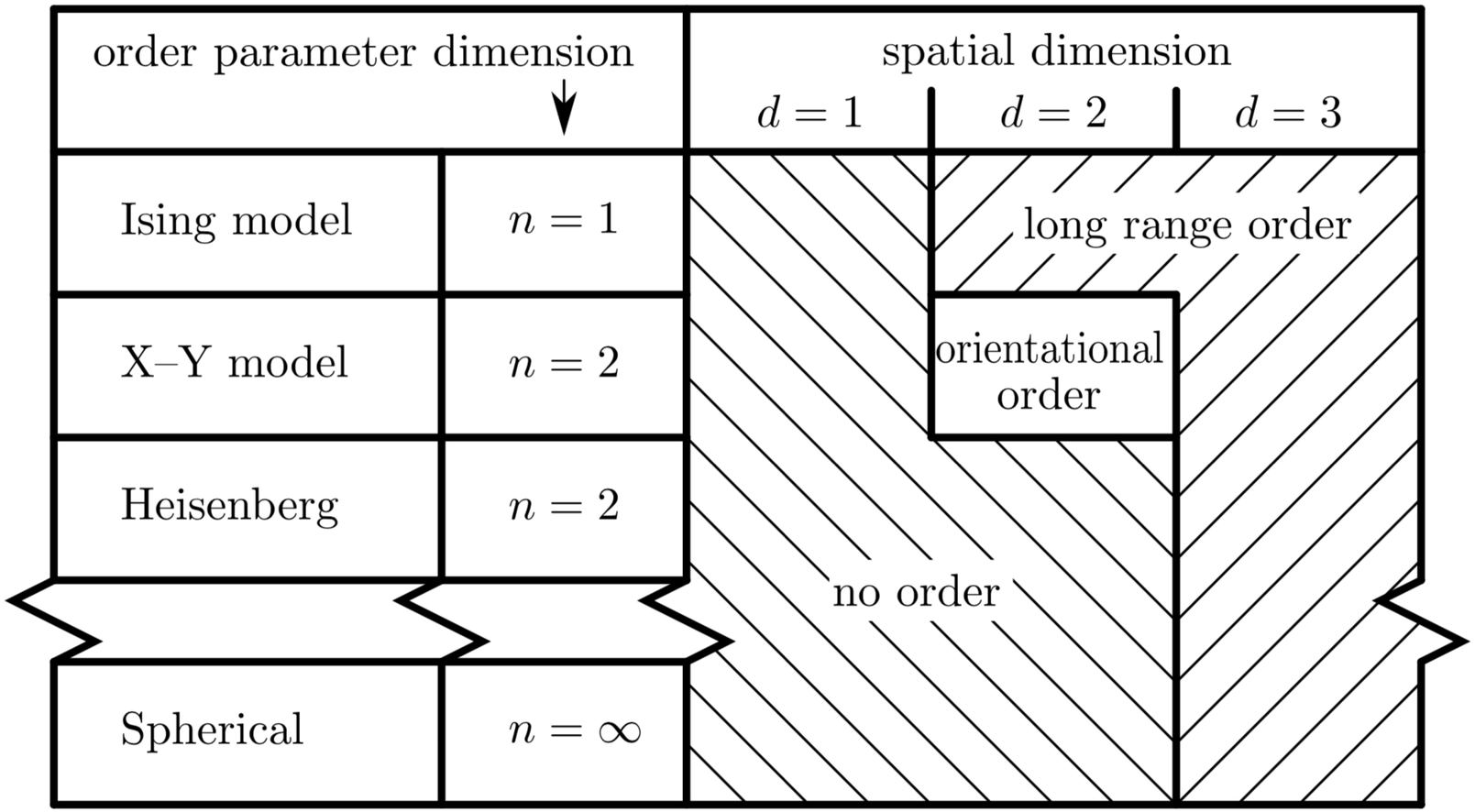
- Ising model ($n = 1$): no transition in $d = 1$, but a transition in $d \geq 2$.
- Heisenberg model ($n = 3$): no transition in $d = 1$ or 2, but a transition in $d \geq 3$. (Mermin-Wagner theorem — fluctuations kill order in 1 and 2 d.)
- Spherical model ($n = \infty$): no transition in $d = 1$ or 2; $\exists$ a transition in $d \geq 3$.
- XY model ($n = 2$): no transition in $d = 1$. $\exists$ transition in $d \geq 3$. $d = 2$?????

d is dimension of space, n is dimension of order parameter “vector”

- $n = 2, d = 2$ case is *marginal*. There is a special order: *orientational* order. Transition called a Kosterlitz-Thouless transition. Nobel 2016.

Could tabulate

$kT_c = x\hbar J$???



Universality classes

	d	n	α	β	γ	δ	ν	η
Mean field	any	any	0	½	1	3	½	0
2d Ising	2	1	0	⅛	¾	15	1	¼
3d Ising	3	1	0.11	0.33	1.24	4.79	0.63	0.04
3d XY	3	2	−0.01	0.35	1.32	4.78	0.67	0.04
3d Heisenberg	3	3	−0.12	0.37	1.40	4.8	0.71	0.04
3d spherical	3	∞	−1	½	2	5	1	0

The liquid-gas transition (Section 4.2), for which $d = 3,\ n = 1$, has critical exponents corresponding to those of the 3d Ising model, as expected.

But in, general, n is not sufficient to specify the order parameter (may not be a vector).

4.9.2 Validity of mean field theory

- For short range interactions mean field is exact for $d = 4$ (and higher).
- It's all about connectivity: greater d, $\Longrightarrow$ larger the number of neighbours.
- But some (3d) systems *seem* to be mean field — e.g. superconductivity.
  — have to be very close to T_c to observe breakdown of mean field.
- Mean field is killed by fluctuations — anomalous broadening of free energy.
- The Ginzburg criterion tells you how close.

4.9.3 Features of different Phase Transition Models

	first order		**second order**	**symmetry broken**
conserved order parameter	liquid–gas (but ∃ critical point)	$\longrightarrow$	liquid–gas along critical isochore	none
	binary alloy (but ∃ critical point)	$\longrightarrow$	binary alloy at critical concentration	none
	solid–fluid: no critical point	$\longrightarrow$	– – – – –	translational invariance
non-conserved order parameter	– – – – –	$\longrightarrow$	ferromagnet	rotational invariance
	ferroelectric at high pressure	tricritical $\leftarrow$ point $\rightarrow$	ferroelectric at low pressure	inversion symmetry