II. Phase transitions

1. Phases and phase boundaries

Consider a system in a volume V, the free energy is size extensive.
For a large system we can write

$$F = V \cdot f_b(V) + S f_s(S) + O(L^{d-2})$$

f_b: bulk free energy per unit volume
f_s: surface free energy per unit area

For $V \to \infty$ we have (if limit exists)

$$f_b = \lim_{V\to\infty} \frac{F}{V} \quad \text{resp} \quad f_b = \lim_{N\to\infty} \frac{F}{N}$$

(for lattice systems)

$$f_s = \lim_{S\to\infty} \frac{F - f_b V}{S}$$

This limit is called <u>thermodynamic limit</u>. Note that the limit $V\to\infty$ is taken in such a way that the particle density remains constant

$$\lim_{V\to\infty,\ n=\frac{N}{V}\to \text{const}}$$

Let the Hamiltonian βH of the system depend on n couplings K_i and the corresponding combination of dynamical degrees of freedom,

$$-\beta H[K] = \sum_n K_n \Theta_n$$

$\beta = \frac{1}{k_B T}$ ← note that right hand side depends on T

<u>example</u>: Ising model, spins on a lattice Hamiltonian takes form

$$H = -\sum_i B_i S_i - \sum_{ij} J_{ij} S_i S_j - \sum_{ijk} K_{ijk} S_i S_j S_k + \dots$$

B_i: external magnetic field; J_{ij}: two-spin interaction; K_{ijk}: three-spin interaction

$$\begin{matrix} \uparrow & \downarrow & \downarrow & \uparrow \\ \downarrow & \downarrow & \downarrow & \uparrow \\ \uparrow & \uparrow & \uparrow & \uparrow \end{matrix}$$

$$\Rightarrow \{K\} = [T, B_i, J_{ij}, K_{ijk}]$$

Then the bulk free energy per unit volume $f_b = f_b[\{k\}]$

Phases are defined based on the analytical properties of $f_b[\{k\}]$:

- Phases are regions of analyticity of f_b
- Phase boundaries are points, lines, planes, ... of non-analyticities of $f_b[k]$, i.e. derivatives $\frac{\partial f}{\partial k_i}$, $\frac{\partial^2 f}{\partial k_i^2}$ exhibit discontinuities/singularities

Let the dimension of $\{k\}$ be D (for example for Ising model [if $B_i = B$, $J_{ij} = J$, $k_{ijk} = k$]

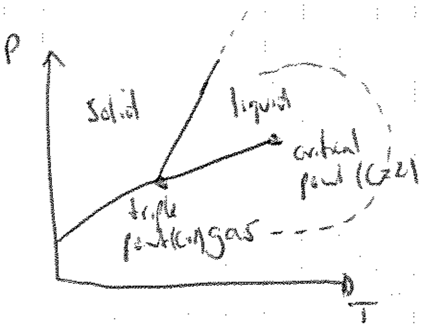
$$D = 4 \quad \{B, J, k, T\}$$

Dimensionality of the singular manifolds D_s needs to be

$$C = D - D_s = 1$$

for a phase boundary. $\searrow$ codimension

Consider room analogy: - room has three dimensions, in order to separate room by a wall, wall needs to have two dimensions, a one-dimensional stick cannot separate room.



- what about a wall that does not reach the ceiling? Then it is possible to get from one "phase" to the other without ever passing a nonanalytic region → liquid-gas trans.

classification of phase transitions (Ehrenfest)

(1) $\frac{\partial f_b[k]}{\partial k_i}$ is discontinuous across a phase boundary ⇒ first order phase tr.
$\searrow$ one or more

(2) all $\frac{\partial f_b[k]}{\partial k_i}$ are continuous across phase boundary
⇒ continuous phase transition (a.k.a. second-order ph. tr.)

remark: it can be shown that f_b is always continuous.

Why do phase boundaries ~~occur~~ occur in the first place?

$$e^{-\beta F} = \mathrm{Tr}\, e^{-\beta H}$$

Tr: sum of terms

$e^{-\beta H}$: analytic function (if H is analytic)

How can f_b develop non-analyticities?

For the definition of phases the limit processes $V \to \infty$, $N \to \infty$ play a central role. Phases are in general only well-defined in this limit!

<u>Central question:</u> How can the phase diagram be computed as a function of the external parameters K_i (including critical exponents, ~~scaling relations~~ and understanding of universality)

2. Phase transitions at zero temperature and the Ising model

Consider an Ising model with a <u>constant external</u> magnetic field B and a constant two-spin interaction J that couples <u>nearest neighbors</u>

$$H = -B \cdot \sum_{i=1}^{N} S_i - J \sum_{\langle i,j \rangle} S_i S_j$$

free energy: $F(T, B, J) = -k_B T \log \mathrm{Tr}\, e^{-\beta H}$

$$\hookrightarrow \mathrm{Tr} = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} = \sum_{\{S_i=\pm 1\}}$$

<u>For example:</u> the ~~average~~ magnetization ~~per lattice site~~ is given by

$$M = -\frac{\partial F}{\partial B} = +k_B T \frac{1}{\mathrm{Tr}\, e^{-\beta H}} \mathrm{Tr} \frac{S_i}{k_B T} e^{-\beta H}$$

$$= \mathrm{Tr}\, \rho S_i = \langle S_i \rangle$$

At zero temperature the magnetization can be determined by simple inspection (assume $J>0$)

$-J\sum_{\langle ij\rangle} S_i S_j$ can be minimized for $J>0$ for $S_i = S_j$

$-B\sum_i S_i$ can be minimized by $S_i = \begin{cases} +1 & B>0 \\ -1 & B<0 \end{cases}$

$\Rightarrow$ ground state configuration:

$$S_i = \begin{cases} +1, & B>0,\ J>0 \\ -1, & B<0,\ J>0 \end{cases} \quad \Rightarrow \quad m = \frac{1}{N}\sum_i \langle S_i\rangle = \begin{cases} +1 & B>0 \\ -1 & B<0 \end{cases}$$

$\rightarrow$ $m = -\dfrac{\partial f}{\partial B} = -\dfrac{1}{N}\dfrac{\partial F}{\partial B}$ is discontinuous at $B=0$, phase transition

Note that in present case transition happens at finite N, no thermodynamic limit needed, non-analytic behavior results from $\beta\to\infty$, not $N\to\infty$ in

$$e^{-\beta F} = \mathrm{Tr}\, e^{-\beta H}$$

3. Phase transitions at $T>0$ in one dimension (short-range interactions)

consider a spin chain in 1 dimension at $T>0$, $B=0$

- ground state at $T=0$ looks like $\ldots\uparrow\uparrow\uparrow\uparrow\ldots$ or $\ldots\downarrow\downarrow\downarrow\downarrow\ldots$ (see above). The energy of ground state is $E=-NJ$, $F=E-TS=-NJ$
- raising temp leads to brownian motion and random spin flips

<u>Question</u>: Do these spin flips destroy the long-range order?

To answer this consider system at $T>0$ with <u>two</u> domains:

$$\ldots\uparrow\uparrow\uparrow\,|\,\downarrow\downarrow\downarrow\downarrow\ldots$$

the energy is now $E = -(N-1)J + J$
$= -NJ + 2J$

for free energy we need the entropy contribution TS

For determination of entropy note that domain boundary can be at any of the N lattice sites

⇒ $S = k_B \cdot \log N$

hence difference of free energy between two- and one-domain state is

$$F^{two} - \underset{S^{one}=0}{\underset{\downarrow}{F^{one}}} = 2J - k_B \cdot T \cdot \log N$$

⇒ For $N \to \infty$ we can lower the free energy by creating a domain wall, i.e. energy can be lowered further by creating additional domain walls

→ argument can be repeated until all long-range order is destroyed

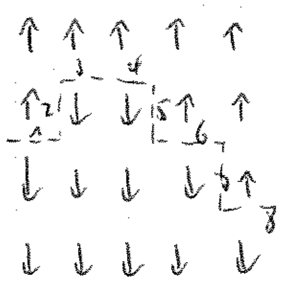
⇒ long-range order is unstable against thermal fluctuations at $T > 0$

$M(B=0) = 0$ for $T > 0$ → valid for all interactions for $J_{ij} = \frac{J}{|r_i - r_j|^\sigma}$ $\sigma > 2$ (for $1 \leq \sigma \leq 2$ long-range order might persist for $0 < T < T_c$)

4. Phase transitions in two dimensions

now we extend the arguments of the previous section to two dimensions, this discussion highlights the significance and key role of dimensionality of systems for phase transitions

in 2d ground state at $T=0$ is state with energy $E = -N \cdot J$ and zero entropy, consider state consisting of two domains, border may contains n bonds



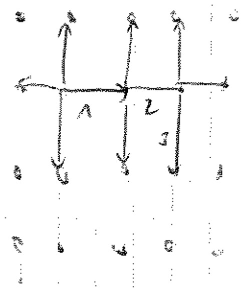
here, $n = 8$ bonds energy difference $\Delta E = 2Jn$

now we need to determine the entropy of the two-domain state, determine upper estimate:

~~choose a point on the boundary~~

How many ways are there to form a boundary with n bonds? Choose a ~~upper~~ lattice point, if we choose a square lattice there are 4 possible adjacent lattice points, we need to take n steps to next lattice points to form a domain boundary with n bonds. In order to avoid backtracking we ~~do~~ effectively only have 3 choices at each lattice point. Hence as an upper limit

$$S_{upper} \sim k_B \log(\underset{\substack{\uparrow \\ N \text{ possible starting points}}}{N} 3^n) \sim k_B n \log 3$$



We are interested in domains that contain a macroscopically large number of spins, hence consider thermodynamic limit $\lim_{n\to\infty}$

$$\Delta F = F^{two} - F^{one} = 2Jn - k_B T n \log 3$$
$$= n(2J - k_B T \log 3)$$

hence for $T > T_c = \frac{2J}{k_B \log 3}$ $\Delta F \to -\infty$ for $n \to \infty$ and the system is unstable against formation of new domain walls (see 1d case)

but for $T < T_c$ long range order is stable and ground state exhibits nonvanishing net magnetization

The results above apply to all Hamiltonians with a <u>discrete symmetry</u> and <u>short range interactions</u>. (see previous section)

5. Spontaneous symmetry breaking and ergodicity breaking

consider the Hamiltonian of the Ising model for $B=0$

$$H = J \sum_{\langle ij \rangle} S_i S_j$$

the Hamiltonian has the symmetry $H(\{S_i\}) = H(\{-S_i\})$.
Despite this invariance, the statistical expectation values are not invariant under this symmetry: $\langle S_i \rangle \neq 0$ for $T < T_c$

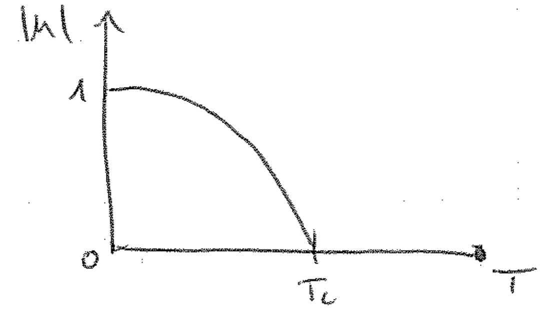
$$M = \lim_{N\to\infty} \frac{1}{N} \sum_i \langle S_i \rangle \neq 0$$

This phenomenon is called spontaneous symmetry breaking. The value of M (i.e. the sign) is determined by the initial conditions of the system before undergoing the phase transition below T_c.
The value of M depends on T: – at $T=0$ $M = \pm 1$, all spins aligned
– at $T>0$ thermal fluctuations lead to a reduction until it vanishes at $T=T_c$

critical exponent

$$|M| \sim |T-T_c|^\beta$$

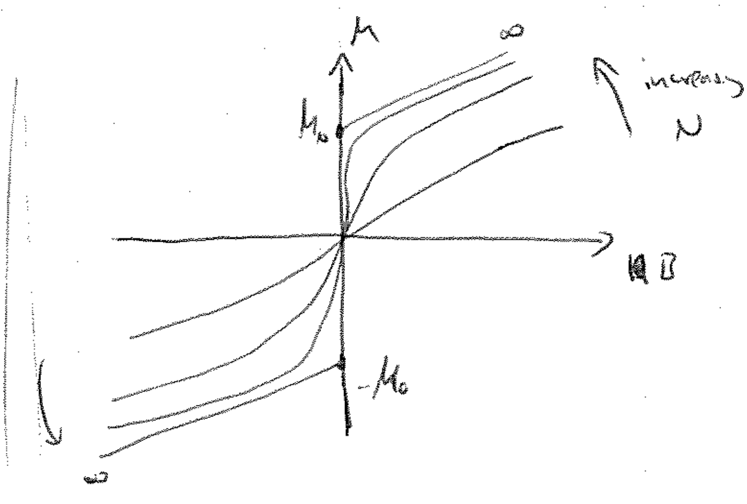
M is order parameter



consider the role of the limits $B\to 0$, $N\to\infty$, at $T>0$: there is no discontinuity for finite N

$$M_0 = \lim_{B\to 0^+} \lim_{N\to\infty} \left(-\frac{\partial f}{\partial B}\right)$$

$$-M_0 = \lim_{B\to 0^-} \lim_{N\to\infty} \left(-\frac{\partial f}{\partial B}\right)$$



Note that the limits $N \to \infty$, $B \to 0$ do <u>NOT</u> commute

$$\lim_{N \to \infty} \lim_{B \to 0} \frac{\partial f}{\partial B} = 0 \quad \text{but} \quad \lim_{B \to 0} \lim_{N \to \infty} \frac{\partial f}{\partial B} \neq 0$$

The use of the limit $B \to 0^+$ plus thermodynamic limit is equivalent to setting $B = 0$, but using a <u>restricted ensemble</u>, which only includes states contributing to $+M$. Hence the probability distribution for a system <u>after</u> the thermodynamic limit has been taken is <u>identically</u> zero for all states with negative magnetization.
System is trapped in a subregion of phase space

$\Rightarrow$ <u>ergodicity breaking</u>

- however, ergodicity breaking does <u>not</u> imply symmetry breaking (for example consider liquid-gas transition, phase space fragments into two parts, which do <u>not</u> differ in terms of symmetries)

6. Continuous symmetries

Consider a spin system with a continuous symmetry, for example the Heisenberg model for ferromagnets

$$H(\{\vec{S}_i\}) = -\sum_{\langle ij \rangle} J_{ij}\, \vec{S}_i \cdot \vec{S}_j - \sum_i \vec{B}_i \cdot \vec{S}_i$$

with $\vec{S}_i = (S_i^x, S_i^y, S_i^z)$. This model has the symmetry

$$H(\{R(\Omega)\vec{S}_i\}) = H(\{\vec{S}_i\}) \qquad (O(3) \text{ symmetry})$$

How do the arguments regarding the presence of long-range order change at $T > 0$ compared to discrete symmetry $H(\{S_i\}) = H(\{-S_i\})$?

- ~~for continuous~~ it is easier for thermal fluctuations to destroy long-range order for a continuous symmetry, since ~~fluctuation~~ spins can rotate by small ~~...~~ angles
- again we need $\Delta F = F^{2\,\text{domains}} - F^{1\,\text{domain}} \overset{!}{>} 0$; energy E can be increased by increasing dimensionality of lattice $\Rightarrow$ can be shown that for <u>$d \le 2$</u> long range order
- for continuous symmetries <u>Goldstone excitations</u> (more later!)

7. 1-dimensional Ising model - exact solution

the Ising model allows to illustrate many of the formal concepts of the previous sections in practical calculations

in one dimension the nearest neighbor Ising model can be solved exactly

$$H = -B \sum_i S_i - J \sum_{\langle ij \rangle} S_i S_j \qquad J > 0$$

the partition function is given by (using periodic boundary cond $S_{N+1} = S_1$)

$$Z_N(T, B, J) = \mathrm{Tr}\, e^{-\beta H}$$

introducing $\boxed{h = \beta \cdot B}$ and $\boxed{k = \beta J}$

$$\Rightarrow Z_N(h,k) = \mathrm{Tr} \exp\left(h \sum_i S_i + k \sum_i S_i S_{i+1}\right)$$

$$= \sum_{S_1} \sum_{S_2} \dots \sum_{S_N} \left[e^{\frac{h}{2}(S_1+S_2) + k S_1 S_2} \right] \left[e^{\frac{h}{2}(S_2+S_3) + k S_2 S_3} \right] \dots \left[e^{\frac{h}{2}(S_N+S_1) + k S_N S_1} \right]$$

introduce the <u>transfer matrix</u> $\quad T_{S_1 S_2} = e^{\frac{h}{2}(S_1+S_2) + k S_1 S_2}$

i.e. in matrix form $\quad T = \begin{pmatrix} T_{11} & T_{1-1} \\ T_{-11} & T_{-1-1} \end{pmatrix} = \begin{pmatrix} e^{h+k} & e^{-k} \\ e^{-k} & e^{-h+k} \end{pmatrix}$

$$\Rightarrow Z_N(h,k) = \sum_{S_1} \sum_{S_2} \dots \sum_{S_N} \underbrace{T_{S_1 S_2} T_{S_2 S_3} \dots T_{S_N S_1}}_{\text{matrix product}}$$

$$= \sum_{S_1} T^N_{S_1 S_1} = \mathrm{Tr}(T^N)$$

↳ conventional matrix trace, no sum over phase space!

the trace can be evaluated by diagonalizing T: $T' = S^{-1} T S$ and use cyclic invariance of trace $\Rightarrow \mathrm{Tr}(T) = \mathrm{Tr}(T')$

denote eigenvalues of T by λ_1 and λ_2

$$\Rightarrow \mathrm{Tr}(T^N) = \mathrm{Tr}(T'^N) = \lambda_1^N + \lambda_2^N$$

$$\downarrow$$

$$T' = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

if $\lambda_1 \neq \lambda_2$ thermodynamics is governed by largest eigenvalue:

$$Z_N(h,k) = \lambda_1^N \Big(1 + \underbrace{\Big(\frac{\lambda_2}{\lambda_1}\Big)^N}_{\to\, 0 \text{ for } N \to \infty}\Big)$$

$$\Rightarrow \lim_{N\to\infty} \frac{F(h,k,T)}{N} = -k_B T \log \lambda_1$$

diagonalization of T gives $\lambda_{1,2} = e^k \left(\cosh(h) \pm \sqrt{\sinh^2(h) + e^{-4k}}\right)$

the magnetization per lattice site turns out to be:

$$\boxed{M = -\frac{1}{N}\frac{\partial F}{\partial B} = -\frac{1}{N k_B T}\frac{\partial F}{\partial h} = \frac{\sinh(h)}{\sqrt{\sinh^2(h) + e^{-4k}}}}$$

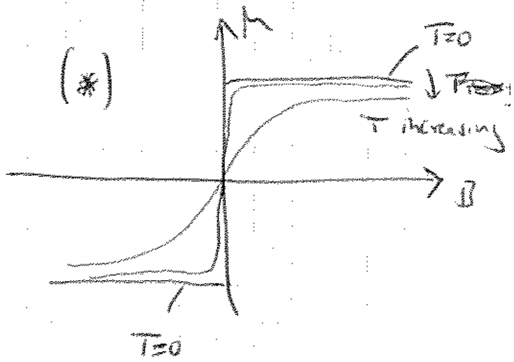
$$\boxed{\begin{aligned} h &= \beta \cdot B \\ k &= \beta \cdot J \end{aligned}}$$

for $T \to 0$ ($k \to \infty$) we obtain $M_{T=0} = \frac{\sinh(h)}{|\sinh(h)|} = \begin{cases} 1 & \text{for } h > 0 \\ -1 & \text{for } h < 0 \end{cases}$

(as above) ~~as above~~

but <u>no phase transition</u> for $T > 0$ (in agreement with arguments of section 3)

Consider F for $h = 0$: $\lambda_1 = e^k(1 + e^{-2k}) = 2\cosh(k)$ (*)



$$\Rightarrow F(h=0,k) = -k_B T \cdot N \left[k + \log(1 + e^{-2k})\right]$$

$$\Rightarrow \frac{F(h=0,k)}{N} = \begin{cases} -J & \text{for } T=0 \ (k \to \infty) \\ -k_B T \log(2) & T \to \infty \ (k \to 0) \end{cases}$$

cf $F = E - TS \to S = k_B \log \underbrace{2^N}_{\text{total disorder } \cdots\uparrow\downarrow\downarrow\uparrow\cdots}$

8. Spatial correlations and correlation length (here for 1d Ising model)

correlations play a key role for phase transitions

to quantify correlations in a many-body system correlation functions are used

the two-point correlation function reads for a spin system:

$$G(i,j) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \rangle$$

For $B=0$ and $T>0$ we have shown that $\langle S_i \rangle = 0$ in 1d Ising model

$$\Rightarrow G(i,j) = \langle S_i S_j \rangle$$

For practical calculation of $\langle S_i S_j \rangle$ start with $\langle S_i S_{i+1} \rangle$ and we first allow for general J_i resp. k_i in the Hamiltonian: $H = -\sum_i J_i S_i S_{i+1}$ $(B=0)$

$$\langle S_i S_{i+1} \rangle = \frac{1}{Z_N} \frac{\partial}{\partial k_i} \operatorname{Tr} e^{k_1 S_1 S_2 + k_2 S_2 S_3 + \dots + k_{N-1} S_{N-1} S_N + k_N S_N S_1}$$

$$= \frac{1}{Z_N} \operatorname{Tr} S_i S_{i+1} e^{-\beta H} = \frac{1}{Z_N} \frac{\partial}{\partial k_i} Z_N = \frac{\partial}{\partial k_i} \log Z_N$$

For Z_N we found $Z_N = \prod_{i=1}^{N} 2\cosh(k_i)$ (see (*) previous page)

$$\Rightarrow \langle S_i S_{i+1} \rangle = \frac{\sinh(k_i)}{\cosh(k_i)} = \tanh(k_i)$$

For calculation of general $\langle S_i S_j \rangle$ note that

$$\frac{1}{Z_N} \frac{\partial}{\partial k_i} \frac{\partial}{\partial k_{i+1}} Z_N = \frac{1}{Z_N} \operatorname{Tr} S_i S_{i+1} S_{i+1} S_{i+2} \, e^{-\beta H}$$

$$= \operatorname{Tr} S_i \underbrace{S_{i+1} S_{i+1}}_{1} S_{i+2} \, \rho$$

$$= \langle S_i S_{i+2} \rangle$$

by induction it follows that

$$G(i, i+j) = \prod_{a=i}^{i+j-1} \tanh k_a \quad \xrightarrow{\text{setting all } k_i = k} \quad \underline{G(i, i+j) = [\tanh(k)]^j}$$

At $T=0$, $K\to\infty$ we have $\tanh(K)\to 1$

$$\Rightarrow G(i,i+j) = 1 \quad \text{for all } j$$

$\Rightarrow$ all spin maximally correlated $\Rightarrow$ long-range order

for $T>0$ we can write

$$G(i,i+j) = [\tanh(K)]^j$$
$$= e^{j\log[\tanh(K)]}$$
$$= e^{-j\log[\coth(K)]}$$

The <u>correlation length</u> ξ is defined via $G(i,i+j) = e^{-j/\xi}$

$$\Rightarrow \text{here } \xi = \frac{1}{\log(\coth(K))}$$

correlation length is a measure over which distance degrees of freedom are correlated with propability $O(1)$.

In present case ξ behaves like $\xi(T) = \frac{1}{2} e^{\frac{J}{k_B T}}$ as $T\to 0$

Usually the correlation length behaves like

$$\xi(T) \sim (T-T_c)^{-\nu}$$

near a continuous transition, i.e. a power law instead of an exponential behaviour.