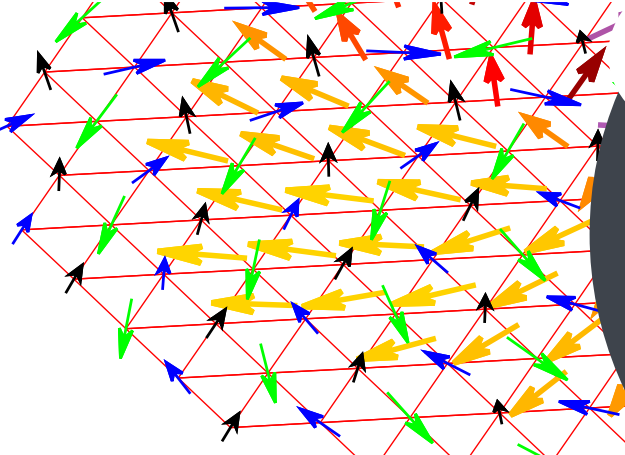
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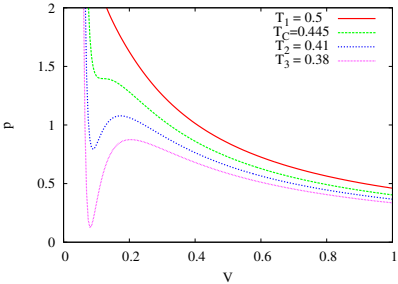
Maria
Daghofer

Phase Transitions

Content

- first example: condensation
  - Macroscopic/microscopic description
  - relevance of interactions
  - classical/quantum
- second example: symmetry breaking
  - mean-field theroy for the Ising model
  - (Ginzburg-)Landau approach
- Limitations of mean-field theory
- Excitations

Reminder: van-der-Waals gas



$$p + \frac{a}{V^2} = \frac{T}{V - b} \qquad (1)$$

We learned in school:

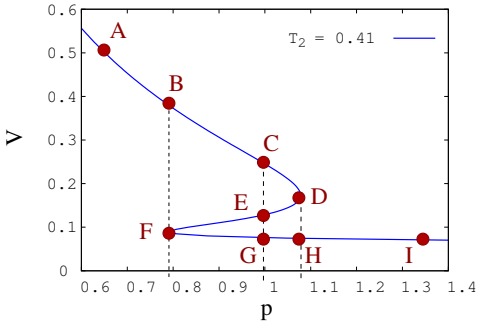
- Three V for one p can't be! (or: $(\partial V/\partial p)_{T,N} > 0$ must not be)
- Phase transition gas - liquid:
  - Coming from large V, p grows.
  - At some point, p remains constant and V shrinks by condesation
  - Finally, p grows again.

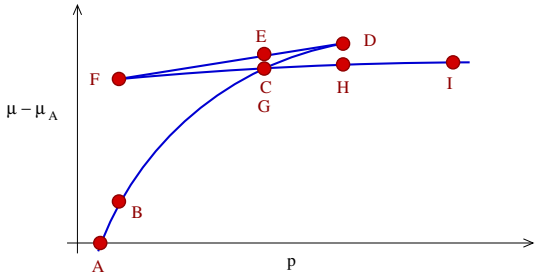
Thermodynamics

Useful principles for equilibrium:

- 'intensive' quantities (temperature T, pressure p, chemical potential μ) constant throughout system
- 'thermodynamic potentials' (energy, enthalpy ..., entropy) extremal
- here useful: chemical potential falls into both categories, free enthalpy $G = \mu N$
  - energy $U(S, V, N) = TS - pV + \mu N$
  - Legendre transforms: $G(T, p, N) = U - TS + pV = \mu N$
  - Gibbs-Duhem: $\mathrm{d}\mu = -\frac{S}{N} \underbrace{\mathrm{d}T}_{=0} + \frac{1}{N} V(p)\,\mathrm{d}p$ along isothermal
- $\Rightarrow \mu(p)$ grows with rate $V(p)$

Go along minimal free enthalpy $N\mu$





A $\rightarrow$ D: $V(p) > 0 \Rightarrow \mu(p)$ resp. $G(p)$ grows

D: dp becomes < 0

D $\rightarrow$ F: μ shrinks, but rate $|V|$ smaller than before

- $\Rightarrow$ remains above previous curve

F: dp becomes > 0 again

F $\rightarrow$ I: μ grows, but rate $|V|$ even smaller

- $\Rightarrow$ crosses path A $\rightarrow$ F

$\Rightarrow$ actual path (minimal μ) jumps from C $\rightarrow$ G

van-der-Waals gas

- ideal gas has no transition
- van-der-Waals includes (rudementary) interaction between particles: Can't be in the same spot.
- Does this generalize? (pretty much)
- free enthalpy $G = \mu(p)$ has kink, $V = (\partial G/\partial p)_{T,N}$ is discontinuous: first-order phase transition
- Here: same symmetry in both phases (will also look at symmetry breaking)
- used thermodynamics: few macroscopic parameters
- alternative statistical physics: microscopic model

Microscopic vs. macroscopic approach

Statistical mechanics starting from microscopic model

- extremely powerful
- lots of approaches
  - Mean-field theory (sometimes valid, reasonable first step)
  - Renormalization group
  - Numerical Simulation
  - Important issue: 'thermodynamic limit'

Thermodynamics expressed in terms of macroscopic quantities

- One knows almost nothing,but can still calculate a lot.
- similar (Ginzburg-)Landau theory:
  - Free eneergy depending on 'order parameter'
  - based on symmetry considerations and not much else
  - can be refined
  - also extremely powerful

Bosonic mode(s)

- one bosonic mode with energy $E_n = \hbar\omega(n + \frac{1}{2})$
- zero-point energy does not change anything here $\Rightarrow$ leave it off

$$H = \hbar\omega \cdot n = \epsilon b^\dagger b \tag{2}$$

- partition function

$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{-\frac{E_n}{k_B T}} = \sum_{n=0}^{\infty} \mathrm{e}^{-\frac{n\epsilon}{k_B T}} = \sum_{n=0}^{\infty} \left(\mathrm{e}^{-\frac{\epsilon}{k_B T}}\right)^n = \frac{1}{1 - \mathrm{e}^{-\frac{\epsilon}{k_B T}}} \,. \tag{3}$$

- many non-interacting modes:

$$H = \sum_k \hbar\omega_k \cdot n_k = \sum_k \epsilon_k b_k^\dagger b_k \tag{4}$$

- Z factorizes, with $\beta = \frac{1}{k_B T}$:

$$Z = \sum_{\{n_k\}} \mathrm{e}^{-\beta(\sum_k \epsilon_k n_k)} = \sum_{n_1} \mathrm{e}^{-\beta\epsilon_1 n_1} \sum_{n_2} \mathrm{e}^{-\beta\epsilon_2 n_2} \cdots \sum_{n_i} \mathrm{e}^{-\beta\epsilon_i n_i} \cdots = \prod_k Z_k \tag{5}$$

Bosonic quantum statistics

- average energy, one mode:

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \frac{1}{Z}\sum_{n=0}^{\infty}\epsilon n \mathrm{e}^{-\beta\epsilon n} = \epsilon\langle n\rangle \tag{6}$$

- OTOH

$$\langle E\rangle = \frac{-1}{Z}\frac{\partial}{\partial\beta}\frac{1}{1-\mathrm{e}^{-\beta\epsilon}} = \frac{1}{Z}\frac{\epsilon\mathrm{e}^{-\beta\epsilon}}{(1-\mathrm{e}^{-\beta\epsilon})^2} = \epsilon\underbrace{\frac{1}{\mathrm{e}^{\beta\epsilon}-1}}_{=\langle n\rangle}, \tag{7}$$

- $\Rightarrow$ Bose-Einstein statistics

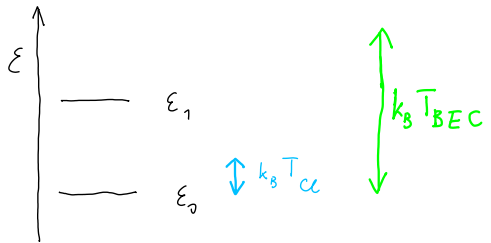
$$\langle n\rangle = \frac{1}{\mathrm{e}^{\beta\epsilon}-1}\,. \tag{8}$$

- classical Boltzmann particles would have

$$\langle n_{\mathrm{cl.}}\rangle = \frac{1}{\mathrm{e}^{\beta\epsilon}} = \mathrm{e}^{-\beta\epsilon}\,. \tag{9}$$

(similar for $\epsilon \gg k_B T$)

N classical particles in two levels



Boltzmann statistics:

$$\frac{\langle n_1 \rangle}{\langle n_0 \rangle} = \frac{\mathrm{e}^{-\beta\epsilon_1}}{\mathrm{e}^{-\beta\epsilon_0}} = \mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)} \qquad (10)$$

$\Rightarrow$ favors particles to be in ϵ_0 for $k_B T_{\mathrm{Cl}} \ll \epsilon_1 - \epsilon_0$

N Boltzmann particles:

- each can be in ϵ_0 or ϵ_1
- $\Rightarrow Z_{\mathrm{Cl.},N} = (Z_1)^N$ with $Z_1 = \mathrm{e}^{-\beta\epsilon_0} + \mathrm{e}^{-\beta\epsilon_1}$
- $\Rightarrow Z$ factorizes

$$\langle N_0 \rangle = -\frac{1}{\beta}\frac{\partial}{\partial_{\epsilon_0}} \ln Z_{\mathrm{Cl},N} = -\frac{N}{\beta}\frac{\partial}{\partial_{\epsilon_0}} \ln\left(\mathrm{e}^{-\beta\epsilon_0} + \mathrm{e}^{-\beta\epsilon_1}\right) = -\frac{N}{\beta}\frac{-\beta\mathrm{e}^{-\beta\epsilon_0}}{\mathrm{e}^{-\beta\epsilon_0} + \mathrm{e}^{-\beta\epsilon_1}}$$

$$\Rightarrow \frac{\langle N_0 \rangle}{N} = \frac{1}{1 + \mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)}} \,. \qquad (11)$$

- $\Rightarrow$ temperature scale $\epsilon_1 - \epsilon_0$

N bosons in two levels

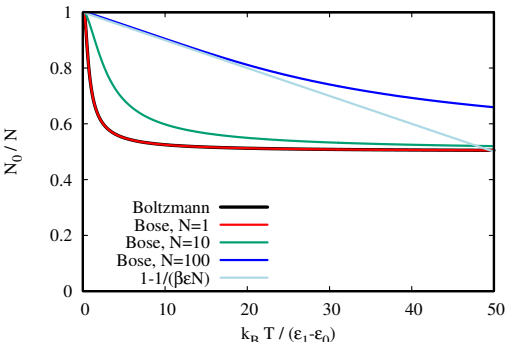
- indistinguishable
- $\Rightarrow$ 'first particle in ϵ_0 and second particle in ϵ_1' is the same state as 'first particle in ϵ_1 and second particle in ϵ_0'
  - one state with N in ϵ_0
  - one state with $N-1$ in ϵ_0 and 1 in ϵ_1
  - one state with $N-2$ in ϵ_0 and 1 in ϵ_2
  - $\vdots$
  - one state with N in ϵ_1
- geometric series again:

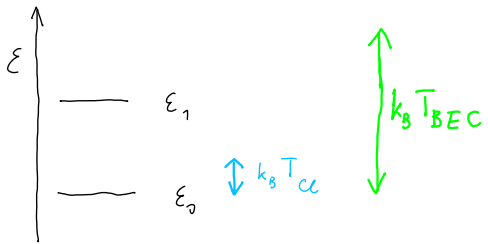
$$
\begin{aligned}
Z_B &= \mathrm{e}^{-\beta N\epsilon_0} + \mathrm{e}^{-\beta[(N-1)\epsilon_0+\epsilon_1]} + \cdots + \mathrm{e}^{-\beta N\epsilon_1} = \\
&= \mathrm{e}^{-\beta N\epsilon_0}\left(1 + \mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)} + \mathrm{e}^{-2\beta(\epsilon_1-\epsilon_0)} + \cdots + \mathrm{e}^{-\beta N(\epsilon_1-\epsilon_0)}\right) = \\
&= \mathrm{e}^{-\beta N\epsilon_0}\,\frac{1-\mathrm{e}^{-(N+1)\beta(\epsilon_1-\epsilon_0)}}{1-\mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)}} \qquad (12)
\end{aligned}
$$

BEC in two-level system

$$\langle N_0 \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_0} \ln Z_B = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_0}\left(-\beta N \epsilon_0 + \ln(1 - \mathrm{e}^{-(N+1)\beta(\epsilon_1-\epsilon_0)}) - \ln(1 - \mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)})\right) =$$

$$= \cdots = \frac{N+1}{1 - \mathrm{e}^{-(N+1)\beta(\epsilon_1-\epsilon_0)}} - \frac{1}{1 - \mathrm{e}^{-\beta(\epsilon_1-\epsilon_0)}} \qquad (13)$$





Thermodynamic limit for box

- free particles in bix with $V = L \times L \times L$) with periodic boundary conditions
- $\epsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m}$, with discrete (k_x, k_y, k_z)
- classical particles mostly in ground state for

$$k_B T_{\mathrm{Cl}} \lesssim \frac{\hbar^2 \vec{k}^2_{\mathrm{min}}}{2m} \propto \frac{1}{L} \quad \text{with} \quad \vec{k}_{\mathrm{min}} = \left(\frac{2\pi}{L}, 0, 0\right) \tag{14}$$

- N_0 negligible for $T > T_{\mathrm{Cl}}$
- for any fixed T, N_0 drops when system becomes bigger
- $\Rightarrow$ classical Boltzmann particles do not show macroscopic ground-state occupation in thermodynamic limit

Chemical potential

- want fixed number of bosons (e.g. cold atoms)
- many available states:

$$Z = \sum_{n_1} \mathrm{e}^{-\beta\epsilon_1 n_1} \sum_{n_2} \mathrm{e}^{-\beta\epsilon_2 n_2} \cdots \sum_{n_i} \mathrm{e}^{-\beta\epsilon_i n_i} \ldots \delta(n - \sum_j n_j) \tag{15}$$

  δ spoils factorization!
- $\Rightarrow$ do grand canonical instead: $\epsilon_k \to \epsilon_k - \mu$
- adjust μ so that

$$N = \sum_j \langle n_j \rangle = \sum_j \frac{1}{\mathrm{e}^{\beta(\epsilon_j - \mu)} - 1} \tag{16}$$

- Clearly, μ must not be larger than smallest ϵ_j

Thermodynamic limit: sum $\rightarrow$ integral

- total particle number to fix μ:

$$\langle \hat{N} \rangle = \sum_{\vec{k}} \frac{1}{\mathrm{e}^{\beta(\epsilon(\vec{k})-\mu)} - 1} \quad \rightarrow \quad \frac{\langle \hat{N} \rangle}{V} = \int \mathrm{d}^3 k \frac{1}{\mathrm{e}^{\beta(\epsilon(\vec{k})-\mu)} - 1} \,, \tag{17}$$

- isotropic box

$$\frac{\langle \hat{N} \rangle}{V} = 4\pi \int \mathrm{d}k k^2 \frac{1}{\mathrm{e}^{\beta(\frac{\hbar^2 k^2}{2m}-\mu)} - 1} = 4\pi \int \mathrm{d}k k^2 \frac{1}{\mathrm{e}^{\beta \frac{\hbar^2 k^2}{2m}} \mathrm{e}^{-\beta\mu} - 1} = 2\pi \sqrt{\frac{2m}{\hbar^2 \beta}}^3 \underbrace{\int \mathrm{d}\omega \frac{\sqrt{\omega}}{\mathrm{e}^{\omega} \mathrm{e}^{-\beta\mu} - 1}}_{\lesssim 2.3} \tag{18}$$

- final integral only depends on T via $\mu \leq 0$
- mximal value ≈ 2.3 for $\mu = 0 = \epsilon_0$

Contradiction for low T

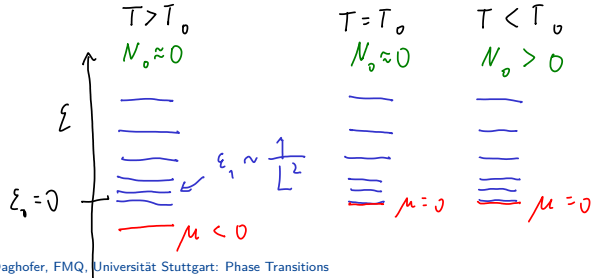
$$\underbrace{\frac{N}{V}}_{\text{does not depend on } T} = \frac{\langle \hat{N} \rangle}{V} \lesssim \frac{2.3 \cdot 4\sqrt{2}\pi\sqrt{m}^3}{\hbar^3} \underbrace{\sqrt{k_B T}^3}_{\to 0 \text{ for } T \to 0} \tag{19}$$

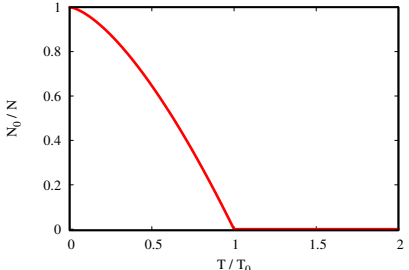
- below some T_{wrong}, r.h.s. will be smaller than $\frac{N}{V}$
- but l.h.s. just stays the same
- no problem with too large r.h.s. at high T: just make μ more negative to reduce r.h.s.
- but μ cannot be made larger than 0 at low T

Pay attention to ground state

- integral (instead of sum) kicks out ground state
- density of states $N(\omega) \propto \sqrt{\omega}$ (vanishes at $\omega = 0$)
- usually not a problem: just one state and others lie just above
- Here: need to includ it to 'catch' missing particles

$$\frac{N}{V} = \frac{N_0}{V} + \underbrace{\frac{2.3 \cdot 4\sqrt{2}\pi\sqrt{m}^3}{\hbar^3}}_{=\frac{N}{V}\frac{1}{\sqrt{k_B T_0}^3}} \sqrt{k_B T}^3 \quad \text{resp.} \quad \frac{N_0}{N} = 1 - \sqrt{\frac{T}{T_0}}^3 \quad \text{for } T < T_0 \,. \tag{20}$$





Summary BEC

- two-level system: Bosons mostly in ground state at higher T then Boltzmann particles
- system larger $\Rightarrow$ energy spacing $\epsilon_1 - \epsilon_0$ typically shrinks,
- Temperature where classical particles predominantly go into the ground state, thus vanishes.
- In contrast, it remains finite for bosons.
- Key aspect: 'macroscopic' ground-state occupancy:
  - Chemical potential can only be raised up to $\epsilon_0 = 0$.
  - $\Rightarrow$ maximal total particle number (with $\mu = \epsilon_0$) that becomes smaller than the actual number of bosons for low T.
  - The solution is to explcitly include the fraction of particles in the ground state.

remarks:

- Non-interacting bosons, 'interaction' is just Bose statistics!
- Lack of interactions makes exact treatment much easier.

Summary Condensation

- van-der-Waals gas
  - interactions allow condensation
  - used classical thermodynamics
- Bose-Einstein condsation
  - used statistical physics
  - both Boltzmann and Bose particles in ground state at $T = 0$
  - appreciable fraction in ground state
    - Boltzmann particles: $k_B T_{\mathrm{Cl}} \ll \epsilon_1 - \epsilon_0$
    - much larger T for Bose particles!
    - transition temperature for Boltzmann particles tends to 0 for large systems
    - condensation survives thermodynamic limit for bosons
  - quantum statistics allows phase transition for bosons

Guinnea pig: Ising model

$$H = \sum_{i,j} J_{i,j} S_i S_j - \frac{g\mu_B}{2} \vec{B} \sum_i S_i \tag{21}$$

with $S_1 = \pm 1$.

Suppose $B = 0$ and $J_{i,j} < 0$:

- ground state should be FM
- entropy wants mixture at high T
- Phase transition?

Similar for NN $J_{i,j} > 0$, just with alternating order.

Mean-field approximation: microscopic variant

$$S_i S_j \to \langle S_i \rangle S_j + S_i \langle S_j \rangle - \langle S_i \rangle \langle S_j \rangle \tag{22}$$

- S_i sees effective magnetic field $-\frac{g\mu_B}{2} B + \sum_j J_{i,j} \langle S_j \rangle$
- S_i contributes to effecive field for other spins
- neglects correlations between deviations from average

$$\Delta S_i \Delta S_j = (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \approx 0 \tag{23}$$

- good, when:
  - $|J_{i,j}| \ll |B|$ (here boring, 'small interaction')
  - ΔS_i small (relevant criterion)
  - ΔS_i and Δ_j uncorrelated
  - e.g. many neighbours: $\sum_j J_{i,j} \Delta_j \approx 0$ due to cancellation $\Rightarrow$ better in higher dimension

Non-interacting Spin in Magnetic Field

$$H = \sum_i H_i, \quad H_i = -\frac{g\mu_B}{2} B S_i \tag{24}$$

- Partition function:

$$Z = \Pi_i Z_i, \quad Z_i = \sum_i \mathrm{e}^{-\beta E_i} = \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)\cdot 1} + \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)\cdot(-1)} \tag{25}$$

- Expectation value $\langle S_i \rangle$:

$$\langle S_i \rangle = \frac{1}{Z_i}\left(1 \cdot \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)\cdot 1}(-1) \cdot \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)+\cdot(-1)}\right) = \tanh\frac{g\mu_B B}{2k_b T} \tag{26}$$

- susceptibility

$$\Rightarrow \chi \approx \frac{\partial}{\partial B} g^2\mu_B^2 \frac{B}{4k_b T} = \frac{g^2\mu_B^2}{4k_b T} = \frac{C}{T} \quad \text{for} \quad B \ll T \tag{27}$$

Mean Field for NN Ising FM

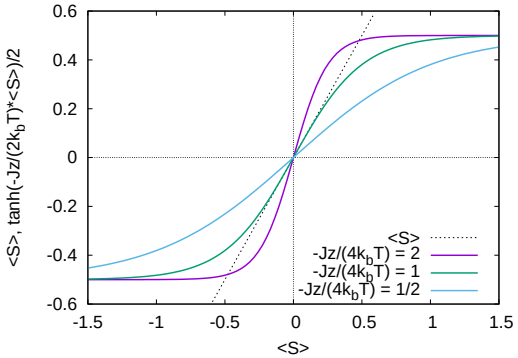
$J_{i,j} = 0$ except for z ('coordination number') nearest neighbors, where $J = -1$. Assume homogeneous FM ground state $\langle S_i \rangle = \langle S \rangle$.

$$\frac{g\mu_B}{2} B_{\text{eff}} = \frac{g\mu_B}{2} B - zJ\langle S \rangle \quad \text{and} \tag{28}$$

$$\langle S \rangle = \tanh \frac{g\mu_B B_{\text{eff}}}{2k_B T} = \tanh \frac{g\mu_B B - 2zJ\langle S \rangle}{2k_B T} \, . \tag{29}$$

- Equation for $\langle S \rangle$. (Not hard to solve numerically.)
- $\langle S \rangle = 0$ always a solution for $B \to 0$.
- Are there others?

Graphical solution for $B = 0$



(plot for $S_i = \pm\frac{1}{2}$)

Criterion for more solutions:

- slope of $\tanh > 1$
- $1 \lessgtr \frac{-2zJ}{2k_BT} = \frac{z|J|}{k_BT}$
- $\Rightarrow \quad T_C = \frac{z|J|}{k_B}$

Large $T \gg T_C$

$$\chi = \frac{\partial M}{\partial B} = \frac{g\mu_B}{2}\frac{\partial \langle S\rangle}{\partial B} = \frac{g\mu_B}{2}\frac{\partial}{\partial B}\tanh\frac{g\mu_B B - 2zJ\langle S\rangle}{2k_bT}\,. \tag{30}$$

For large T, the $\tanh$ almost straight line:

$$\chi \approx \frac{g\mu_B}{2}\frac{\partial}{\partial B}\frac{g\mu_B B - 2zJ\langle S\rangle}{2k_bT} = \frac{g^2\mu_B^2}{4k_bT} + \underbrace{\frac{z|J|}{k_b}}_{=T_C}\frac{1}{T}\underbrace{\frac{g\mu_B}{2}\frac{\partial\langle S\rangle}{\partial B}}_{=\chi}$$

$$\chi \approx \frac{C}{T - T_C}\,. \tag{31}$$

Curie's law, quite good.

lower $T \lesssim T_C$

Ordered State

- Extra solutions at $T < T_C$ have lower free energy than $\langle S \rangle = 0$.
- System chooses one of them.
- Original symmetry between $\langle S \rangle > 0$ and $\langle S \rangle < 0$ 'broken'.
- Finite $\langle S \rangle$ continuously moves away from 0 as T goes below T_C: Not first order! (turns out to be second.)

How good it mean field theory?

- $d > 2$: quite good
- $d = 2$: qualitatively good, but phase transition itself wrong (critical exponent)
- $1d$: wrongly gives $T_C > 0$ (Spin flip costs energy and has low probability, but on an infintie chain....)