Theory of Phase Transitions

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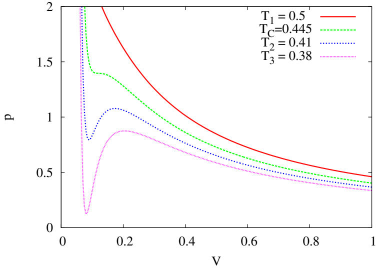
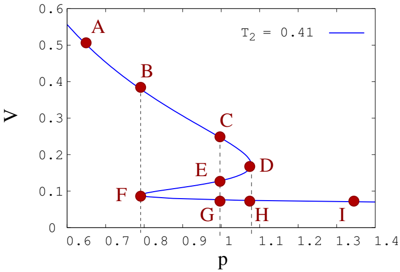
Content

- Phase transitions (e.g. van der Waals)
- Macroscopic/microscopic description
- Symmetry breaking and Phase transitions
- Mean-Field theory for the Ising model
- (Ginzburg-)Landau approach
  - Second order
  - weakly first order
  - coupled orer parameters
- Limitations of mean-field theory
- Excitations
- Quantum Phase transitions and order without symmetry breaking

Reminder: van-der-Waals gas





- $p(V) = \frac{T}{V-b} - \frac{a}{V^2}$
- three V for one p: Can't be! (or: $(\partial V/\partial p)_{T,N} > 0$ must not be)
- Phase transition gas - liquid

van-der-Waals gas

- ideal gas has no transition
- van-der-Waals includes (rudementary) interaction between particles: Can't be in the same spot.
- Phase transitions have to do with interactions!
- Here: same symmetry in both phases
- Different densities
- free enthalpy $G = \mu(p)$ has kink, $V = (\partial G/\partial p)_{T,N}$ is discontinuous: first-order phase transition
- HERE: Focus on symmetry-breaking transitions, typically second- or weakly first- order

Possible Approaches

- Thermodynamics, need thermodynamic potential
- (Ginzburg-)Landau theory: Free eneergy depending on 'order parameter', based on symmetry considerations
- Starting from microscopic model: Get partition function $Z(T)$
  - Mean-field theory (sometimes valid, reasonable first step)
  - Renormalization group
  - Numerical Simulation
  - Important issue: ground state of finite quantum-mechanical system has symmetries of Hamiltonian $\Rightarrow$ need 'thermodynamic limit'

Guinnea pig: Ising model

$$H = \sum_{i,j} J_{i,j} S_i S_j - \frac{g\mu_B}{2} \vec{B} \sum_i S_i \tag{1}$$

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 $S_{i,j} > 0$, just with alternating order.

Mean-field approximation: microscopic variant

$$S_i S_j \to \langle S_i \rangle S_j + S_i \langle S_j \rangle - \langle S_i \rangle \langle S_j \rangle \quad (2)$$

- 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

$$\Delta S_i \Delta S_j = (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \approx 0 \quad (3)$$

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

Non-interacting Spin in Magnetic Field

$$H = \sum_i H_i, \quad H_i = -\frac{g\mu_B}{2} B S_i \tag{4}$$

- Partition function:

$$Z = \Pi_i Z_i, \quad Z_i = \sum_i \mathrm{e}^{-\beta E_i} = \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)\cdot 1} + \mathrm{e}^{-\beta(-\frac{g\mu_B}{2}B)\cdot(-1)} \tag{5}$$

with $\beta = \frac{1}{k_B T}$

- Expectation value $\langle S_i \rangle$:

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

$$= \tanh \frac{g\mu_B B}{2k_b T} \tag{6}$$

Mean Field for NN Ising FM

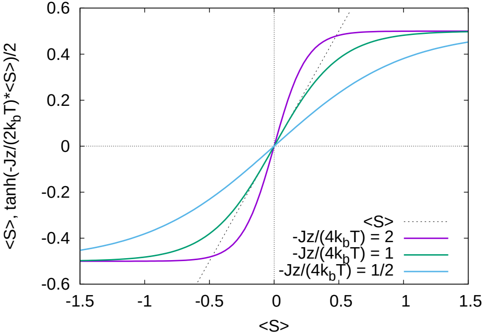
$J_{i,j} = 0$ except for z ('coordination number') nearest neighbors, where $J = -1$. Assume homogeneous FM ground state $\langle S_i \rangle = \langle S \rangle$.

$$\frac{g\mu_B}{2} B_{\text{eff}} = \frac{g\mu_B}{2} B - zJ\langle S \rangle \quad \text{and} \tag{7}$$

$$\langle S \rangle = \tanh \frac{g\mu_B B_{\text{eff}}}{2k_B T} = \tanh \frac{g\mu_B B - 2zJ\langle S \rangle}{2k_B T}\,. \tag{8}$$

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

Graphical solution for $B = 0$



(plot for $S_i = \pm\frac{1}{2}$) Criterion for more solutions:

$$1 \lessgtr \frac{-2zJ}{2k_BT} = \frac{z|J|}{k_BT} \quad \Rightarrow \quad T_C = \frac{z|J|}{k_B} \tag{9}$$

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!

Large T

$$\chi = \frac{\partial M}{\partial B} = \frac{g\mu_B}{2}\frac{\partial\langle S\rangle}{\partial B} = \frac{g\mu_B}{2}\frac{\partial}{\partial B}\tanh\frac{g\mu_B B - 2zJ\langle S\rangle}{2k_b T} \,. \tag{10}$$

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

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

$$\chi \approx \frac{C}{T - T_C} \,. \tag{11}$$

Curie's law, quite good.

How good is Mean-Field Theory here?

- $d > 2$: 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....)

Heisenberg Spins: continuous Symmtry

$S_i \pm 1$ becomes $\vec{S}_i$ that can point anywhere

- Mean-Field theory essentially unchanged (see exercise in tutorial)
- $\vec{B}$ serves to formally create 'special' direction, but $\vec{B} \to 0$ can be done: breaking of continuous symmetry
- Instead of two equivalent minima, there is a 'Mexican hat', one direction is chosen.
- However, actual physics is different!

What changes for a continuous symmety?

Excitations!

Ising: smallest excitatation is spin flip, only dangerous in $d = 1$

Heisenberg:

- Smallest excitation is sloooooow canting of spin.
- Locally, one is almost FM.
- Different directions, but always in valley of Mexican hat.
- Energy $\to 0$ for wavelength $\to \infty$.
- Impact on long-range order depends on
  - dispersion of excitation (linear vs. quadratic)
  - their density of states (dimensionality)
- Results:
  - $3d$: long-range order stable, $T_C > 0$
  - $2d$: no true long-range order at any $T > 0$
  - $1d$: AF ground state not alternating pattern

Mermin-Wagner Theorem

In $d = 2$, breaking of a continuous symmetry cannot lead to true long-range order.

Why use Mean-Field theory, if it is so wrong?

- Both 'strictly $2d$' and 'continuous symmetry' are a bit academic.
- With exceptions ($1d$ AF), mean-field gives good ground state.
- Even there, it is reasonable starting point.
- There can be 'quasi' long-range order (Berezinskii-Kosterlitz-Thouless transition).

Ginzburg-Landau Theory

Needs:

- Symmetry information
- Idea about plausible order paratmer (scalar, vector, tensor, real/complex $dots$)
- No microscopic model/Hamiltonian

One can learn a lot without a microscopic model!

Is a mean-field theory.

Landau Approach

Assumptions made here:

- Homogeneous system
- Scalar real order parameter η (e.g. $\langle S^z \rangle$)
- $\eta = 0$ at high T
- $\eta \neq 0$ possibly at low $T < T_C$
- $|\eta|$ small for $T \lesssim T_C$

Free energy expansion:

$$\begin{aligned}\Phi(\eta, T, p, \dots) = \Phi_0(T, p, \dots) + \alpha(T, p, \dots)\eta + A(T, p, \dots)\eta^2 + \\ + C(T, p, \dots)\eta^3 + B(T, p, \dots)\eta^4 + \\ + F(T, p, \dots)\eta^5 + D(T, p, \dots)\eta^6 + \dots \qquad (12)\end{aligned}$$

Surviving Terms

- $\eta = 0$ at $T > T_C \quad \Rightarrow \quad \alpha = 0$
- If $\eta > 0$ and $\eta < 0$ are equivalent (inversion symmetry): only even powers of η.

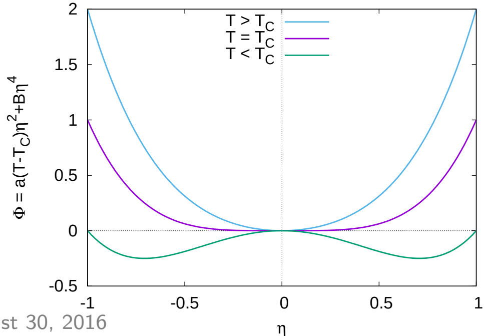
Simplest case:

$$\Phi(\eta, T, p, \dots) = \Phi_0(T, p, \dots) + A(T, p, \dots)\eta^2 + B(T, p, \dots)\eta^4 \tag{13}$$

with $B(T, p, \dots) > 0$. Equilibrium for $\eta \cdot \left(A(T) + 2B(T)\eta^2\right) = 0$.

Equilibrium

- $\eta = 0$ always solution
- $\eta = \pm\sqrt{-\frac{A(T)}{2B(T)}} = \pm\sqrt{\frac{|A(T)|}{2B(T)}}$ solution for $A < 0$
- $A(T, p, \dots)$ must change sign at T_C.
- Simplest case: $A(T) = a(T - T_C)$
- $\eta = \pm\sqrt{\frac{a\cdot(T_C - T)}{2B}}$



Second order

$$\Phi_{\text{min}} = \Phi_0 + A\eta_{\text{min}}^2 + \cdots = \Phi_0 \begin{cases} +\ 0 & \text{for } \eta_{\text{min}}^2 = 0 \text{ at } T > \\ -\frac{a^2}{2B}(T - T_C)^2 + \ldots & \text{for } \eta_{\text{min}}^2 = \frac{a\cdot(T - T_C)}{2B} \end{cases} \tag{14}$$

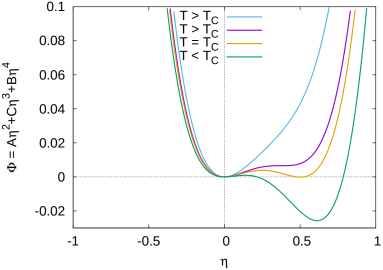
entropy

$$S = -\frac{\partial \Phi}{\partial T} = \underbrace{-\frac{\partial \Phi_0}{\partial T}}_{=S_0} + \begin{cases} 0 & \text{for } T > T_C, \\ \frac{a^2}{B}(T - T_C) + \ldots & \text{for at } T \leq T_C \end{cases}, \tag{15}$$

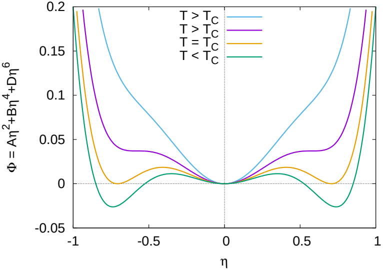
specific heat

$$c_p = T\frac{\partial S}{\partial T} = T\frac{\partial S_0}{\partial T} + \begin{cases} 0 & \text{for } T > T_C, \\ T \cdot \frac{a^2}{B} + \ldots & \text{for at } T \leq T_C \end{cases}, \tag{16}$$

Weakly first order



$C\eta^3$



$B < 0, D\eta^6$

$$\Phi(\eta, T, p, \dots) = \Phi_0(T, p, \dots) + A(T, p, \dots)\eta^2 + \\ + C(T, p, \dots)\eta^3 + B(T, p, \dots)\eta^4 + \\ + F(T, p, \dots)\eta^5 + D(T, p, \dots)\eta^6 + \dots \quad (17)$$