Phase transitions and critical phenomena

Summary week 1-5

1 Classification of phase transitions

1.1 Discontinous (1st order) transitions

1st derivatives of thermodynamic potentials jump discontinously, e.g. $(\partial F/\partial T) = -S$. This implies a nonzero latent heat. The order parameter also jumps discontinously. Examples are the liquid-solid (melting) or liquid-gas transition, normal to superconducting transition in external field, and paramagnetic to ferromagnetic in external field.

1.2 Continuous (2nd order) transitions

1st derivatives of thermodynamic potentials are continuous, but 2nd derivatives such as the specific heat and compressibility (response functions) have a singular behavior at a *critical point*. Examples are the paramagnetic to ferromagnetic transition, the liquid-gas transition at the critical point, the normal to superfluid transition and the normal to superconductor in zero field.

In order to observe critical behavior, external parameters (temperature, density, external field) must be tuned. It is convenient to define the reduced temperature $t = (T - T_c)/T_c$. The singular behavior is described by a set of *critical exponents*:

- specific heat $C \sim |t|^{-\alpha}$
- order parameter (in zero field) $m \sim |t|^{\beta}$ for $T < T_c$
- order parameter along critical isotherm: $m \sim h^{1/\delta}$
- susceptibility $\chi \sim |t|^{-\gamma}$

Near the critical point, the system becomes strongly correlated and fluctuations occur on all length scales. The only relevant length scale is the *correlation length* ξ, which diverges at the critical point:

$$\xi \sim |t|^{-\nu}.$$

In most cases, the connected correlation function decays exponentially to zero on scales $|\mathbf{r}| > \xi$,

$$G_c(|\mathbf{r}|) = \langle m(\mathbf{r})m(0)\rangle - \langle m\rangle^2 \sim \exp(-|\mathbf{r}|/\xi)$$

The values of the exponents do not depend on the microscopic details, but only on symmetry and dimensionality. This is the phenomenon of *universality*. Additionally, the exponents are not independent, but are constrained by several *scaling laws*. A calculation of the critical exponents can be achieved within the *renormalization group*, which is a scheme for treating fluctuations on all scales.

2 Microscopic models for magnets and fluids

2.1 Ising model

The Ising model is a minimal model for a ferromagnet and considers classical spins $\{\sigma_i = \pm 1\}$. The Hamiltonian for nearest-neighbor interactions in an external field h reads

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \tag{1}$$

The thermodynamic behavior is governed by the free energy

$$F = k_B T \ln Z = -k_B T \ln \operatorname{Tr} e^{-\beta H},$$

where Tr denotes summation over all possible spin configurations.

A useful qualitative estimate of the phase behavior can be made using the *energy-entropy argument*. Since $F = E - TS$, the low T ordered phase is dominated by the energy E, where the high T disordered phase is dominated by entropy S. A phase transition occurs in between.

2.1.1 1D-Ising model

Using the above argument, once can see immediately that the one-dimensional Ising model only has an ordered phase at $T = 0$. For any finite temperature $T > 0$, fluctuations destroy long range order. The free energy per spin can be computed exactly using the transfer matrix method,

$$F/N = -J - k_B T \ln \left[\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{(-4\beta J)}} \right].$$

The thermodynamic behavior follows:

- Magnetization $m = -\frac{\partial (F/N)}{\partial h} = \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-8\beta J}}} \sim \exp(2\beta J)\beta h.$
- Specific heat $c = -T \frac{\partial^2 (F/N)}{\partial T^2} = \frac{J^2}{k_B T^2} \operatorname{sech}^2(\beta J)$ (peaks near $J \sim k_B T$: Schottky anomaly).
- Susceptibility $\chi_T = \frac{\partial m}{\partial h} \sim 1/k_B T$ (Curie's law).

2.2 Mean field theory for $d > 1$

In higher dimensions $d > 1$, the Ising model exhibits a 2nd order phase transition at finite temperature T_c. It is not possible to solve eq. (1) exactly except for $d = 2$. A first starting point is therefore the *mean field (MF) approximation*, where the exact interaction between spins is replaced by an interaction with a uniform mean field that has to be determined self-consistently. MF theory (sometimes also called Weiss MF theory) therefore ignores all fluctuations. Denoting the mean field by

$$m = \frac{1}{N} \sum_i \langle \sigma_i \rangle,$$

the mean-field Hamiltonian can be written as

$$H_{MF} = \frac{qJ}{2} N m^2 + (Jqm + h) \sum_i \sigma_i, \tag{2}$$

where q is the coordination number of each lattice site. Every spin therefore interacts with an effective field that is the sum of the external field and the mean field, while the fluctutation term $(\sigma_i - m)(\sigma_j - m)$ has been ignored. The trace over the spin variables can now be performed easily to yield

$$m = \tanh(\beta(Jqm + h)).$$

This equation of state has only one solution, $m = 0$, for $\beta Jq < 1$ corresponding to the disordered phase, and two nonzero solutions for $\beta Jq > 1$, corresponding to the ordered phase. The critical temperature is $T_c = qJ/k_B$. The mean field exponents that can be derived from the equation of state or free energy are

$$\alpha = 0,\ \beta = 1/2,\ \gamma = 1,\ \delta = 3.$$

The specific heat is not singular, but jumps from zero in the disordered phase to a finite value in the ordered phase.

2.3 van der Waals gas

The van der Waals equation

$$p + \frac{aN^2}{V^2} = \frac{Nk_BT}{V - Nb}$$

is a generalization of the ideal gas and incorporates short range attraction between molecules and a finite molecular volume. a and b are constants. It therefore has the minimal ingredients to predict a phase transition. For a liquid gas system a suitable order parameter is the difference in specific volume of liquid and gas phase $v_g - v_l$, which vanishes at the critical point. The response function is the compressibility $\kappa = -(\partial V/\partial p)/V$. The van der Waals gas is already a mean field model. The critical exponents are identical to those found above for the MF-Ising model.

3 Ginzburg-Landau Theory

3.1 Field theory via coarse graining

The presence of long correlations and the universal nature of critical phenomena suggest that the microscopic physics is not important. Only long wavelength excitations are relevant, which can be more easily studied on mesoscopic scales. We introduce a coarse-grained order parameter field $m(\mathbf{r})$ obtained through averaging over microscopic regions of size $\Lambda^{-1} \gg a$, where a is a microscopic length scale. The partition function is preserved in this process and can be expressed as a functional integral,

$$Z = \int \mathcal{D}m(\mathbf{r}) \exp(-\beta H[m(\mathbf{r})]),$$

where the symbol $\mathcal{D}m(\mathbf{r})$ denotes integration over all possible configurations of $m(\mathbf{r})$. $\beta H[m(\mathbf{r})]$ is called the *effective Hamiltonian* or *effective action*. The effective Hamiltonian must reflect the symmetries of the underlying microscopic system. For a uniform material with rotational symmetry one is led to the *Landau-Ginzburg* (GL) Hamiltonian

$$\beta H = \int d^d r \left[\frac{t}{2} m^2(\mathbf{r}) + u m^4(\mathbf{r}) + \frac{K}{2} (\nabla m)^2 + ... - \beta h m(\mathbf{r}) \right]. \tag{3}$$

Higher order gradient terms can be added if nonlocal interactions are important. Note that βH contains a set of temperature-dependent phenomenological parameters $\{t, u, K\}$, and individual terms are no longer proportional to β. The GL Hamiltonian serves as a sort of meta-model that will be studied exclusively from here onward.

3.2 Saddle point (mean field) approximation

The field theoretic functional integral is not easier to treat than the original microscopic partition function. The simplest possible approximation consists of considering only the most probable field configuration, which must be a uniform everywhere in space and obeys

$$\frac{\delta \beta H}{\delta m(\mathbf{r})} = 0.$$

The integral is therefore governed by the saddle point, and the free energy in this approximation reads

$$\beta F_{SP} = -\ln Z_{SP} = V \min \left[\frac{t}{2} m^2 + u m^4 - h m \right].$$

The phase behavior can be inferred by inspecting the free energy. For $t > 0$ and $h = 0$, βF is minimized by $\bar{m} = 0$ and the system is in the disordered phase, but for $t < 0$ βF is minimized by a finite value of the order parameter, i.e.

$$\bar{m} = \begin{cases} 0 & \text{for } t > 0, \\ \sqrt{\frac{-t}{4u}} & \text{for } t < 0. \end{cases}$$

This result shows also that in the saddle point approximation $\beta = 1/2$. Similarly for $t = 0$ one obtains $\bar{m} = (h/4u)^{1/3}$, giving $\delta = 3$. The behavior of the response functions is

$$\bar{\chi}^{-1} = \left. \frac{\partial h}{\partial \bar{m}} \right|_{h=0} = \begin{cases} t & \text{for } t > 0, \\ -2t & \text{for } t < 0 \end{cases}$$

and

$$C = -T \left(\frac{\partial^2 F}{\partial T^2} \right) \approx \begin{cases} 0 & \text{for } t > 0, \\ \frac{1}{8u} & \text{for } t < 0 \end{cases}$$

which implies $\nu = 1$ and $\alpha = 0$.

3.3 Correlations

Correlation functions may be obtained through functional differntiation wrt. an external potential $h(\mathbf{r})$ in the Hamiltonian, $H = H_0 - \int d^d r h(\mathbf{r}) m(\mathbf{r})$:

$$\langle m(\mathbf{r}) \rangle = \frac{1}{\beta Z} \frac{\delta Z}{\delta h(\mathbf{r})} = -\frac{\delta F}{\delta h(\mathbf{r})}$$

$$\langle m(\mathbf{r}) m(\mathbf{r}') \rangle = \frac{1}{\beta^2 Z} \frac{\delta^2 Z}{\delta h(\mathbf{r}) \delta h(\mathbf{r}')}$$

$$G_c(\mathbf{r}, \mathbf{r}') = \langle m(\mathbf{r}) m(\mathbf{r}') \rangle_c = \frac{\delta^2 \ln Z}{\beta^2 \delta h(\mathbf{r}) \delta h(\mathbf{r}')} = \frac{\delta \langle m(\mathbf{r}) \rangle}{\beta \delta h(\mathbf{r}')} = \chi(\mathbf{r}, \mathbf{r}')/\beta$$

The latter relationship between correlation and response is an instance of the *fluctuation dissipation theorem.* To compute $G_c(\mathbf{r}-\mathbf{r}')$ within the saddle-point approximation, compute $\langle m(\mathbf{r})\rangle$ from the stationarity condition and differentiate wrt $h(\mathbf{r}')$. The result is

$$(-\nabla^2 + \xi_\pm^{-2})G_c(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')/K,$$

with the correlation length

$$\xi_\pm^2 = \begin{cases} K/t & \text{for } t > 0, \\ -K/2t & \text{for } t < 0. \end{cases}$$

In both cases we find that the correlation length exponent $\nu = 1/2$. The solution to above differential equation for $G_c(\mathbf{r}-\mathbf{r}')$ in Fourier space reads

$$\tilde{G}(\mathbf{q}) = \frac{1}{K(\mathbf{q}^2 + \xi_\pm^{-2})}.$$

A scattering experiment would therefore see a Lorentzian form of the structure factor

$$S(\mathbf{q}) \propto \frac{1}{\mathbf{q}^{(2-\eta)} + \xi_\pm^{-2}}.$$

Near T_c small deviations from $1/q^2$ scaling are found and described by the exponent η. The correlation function in real space reads

$$G_c(r) \propto \begin{cases} 1/r^{d-2+\eta} & \text{for } r \ll \xi, \\ \frac{\xi^{(3-d)/2}}{r^{(d-1)/2}} \exp(-r/\xi) & \text{for } r \gg \xi. \end{cases}$$

At distances $r \ll \xi$ the correlation function decays algebraically, which implies a scaling property that will be used in the renormalization group.

3.4 Lower and upper critical dimension

In a system with continuous symmetry, the ordered phase spontaneously breaks the symmetry of the underlying Hamiltonian and long range order is established. However, the energy may still be invariant under a global rotation of all spins or a phase change. Corresponding long wavelength excitations are therefore easily excited and are called *Goldstone modes.* A standard example is the two-component order parameter for the superfluid phase $\psi(\mathbf{r}) = |\psi|e^{i\phi(\mathbf{r})}$. The corresponding GL-Hamiltonian for a uniform order parameter has the characteristic wine bottle or Mexican hat potential form. It can be shown that the correlation function

$$\langle \psi(\mathbf{r})\psi^*(0)\rangle = \begin{cases} \bar{\psi}^2 & \text{for } d > 2 \text{ and } x \to \infty, \\ 0 & \text{for } d \leq 2 \text{ and } x \to \infty, \end{cases}$$

where $\bar{\psi}$ is the saddle point value of the order parameter. This indicates that for dimensions less or equal the *lower critical dimension* $d_l = 2$ fluctuations destroy long range order, a result known as the *Mermin-Wagner theorem.*

To determine whether mean-field theory is self-consistent, we can compare the strength of fluctuations to the magnitude of the order parameter in the *correlation volume* ξ^d. Requiring

$$\left| \int_V d^d r\, G_c(\mathbf{r}) \right| \ll \int_V d^d r\, m(\mathbf{r})^2$$

leads to the *Ginzburg criterion*

$$|t|^{(4-d)/2} \gg \frac{k_B}{4\Delta C \xi_0^d},$$

where ΔC is the heat capacity jump between ordered and disordered phase and ξ_0 is a microscopic length scale. This criterion is always satisfied when d exceeds the *upper critical dimension* $d_u = 4$ and mean-field theory becomes exact, but fails for $d < 4$. The Ginzburg criterion is also useful to estimate the size of the critical region, which determines whether fluctuations are important or the transition looks mean-field like as in superconductors. The interesting range of dimensionality is thus $2 < d < 4$.

3.5 The Gaussian approximation

As a first improvement to the saddle-point approximation, one may study the Gaussian model, which consists of neglecting the quartic interaction term in the effective Hamiltonian, so that

$$\beta H = \int d^d r \left[\frac{t}{2} m^2(\mathbf{r}) + \frac{K}{2} (\nabla m)^2 + ... - \beta h m(\mathbf{r}) \right]. \tag{4}$$

This theory is of course unstable in the ordered phase, but can be used to study the region $t > 0$. The effective Hamiltonian can be diagonalized exactly via Fourier transform, so that ($h = 0$):

$$\beta H = \frac{1}{2V} \sum_q |m_q|^2 (t + Kq^2)$$

One finds that the field fluctuates as a Gaussian random variable and the critical exponents $\eta = 0$, $\nu = 1/2$, $\gamma = 1$, i.e. they remain at their mean field values. The only change occurs in the behavior of the heat capacity, which changes from discontinuous to singular for $d < 4$ and the exponent $\alpha = 2 - 2/d$.

Appendix A: Gaussian integrals

$$\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} dx e^{-\frac{K}{2}x^2+yx} = \sqrt{\frac{2\pi}{K}}\, e^{y^2/2K}$$

$$\int_{-\infty}^{\infty} \prod_{i=1}^{N} dx_i \exp\left[-\frac{1}{2}x_i K_{ij} x_j + y_i x_i\right] = \sqrt{\frac{(2\pi)^N}{\det K}} \exp[K^{-1}_{ij} y_i y_j/2]$$

$$\int_{-\infty}^{\infty} \mathcal{D}\phi(\mathbf{r}) \exp\left[-\int d^d\mathbf{r} d^d\mathbf{r}' \frac{1}{2}\phi(\mathbf{r}) K(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}') + \int d^d\mathbf{r} h(\mathbf{r})\phi(\mathbf{r})\right]$$
$$\propto (\det K)^{-1} \exp\left[-\int d^d\mathbf{r} d^d\mathbf{r}' \frac{1}{2} h(\mathbf{r}) K^{-1}(\mathbf{r},\mathbf{r}') h(\mathbf{r}')\right]$$