Critical phenomena

In a second order phase transition the system normally goes from a higher temperature phase to a lower temperature phase with less symmetry. We say that a *symmetry is broken spontaneously.* For example, ferromagnetic material will get polarized below a certain critical temperature. The spin rotation symmetry is broken. The amount of the symmetry break is described by an *order parameter*, which is usually assigned to the expectation value of some observable of the system. In the ferromagnetic system a suitable order parameter is the magnetization $\boldsymbol{m}$. In the symmetric phase $\boldsymbol{m} = 0$ and in the ordered, i.e. symmetry breaking phase $\boldsymbol{m} \neq 0$.
Let the order parameter be m and h the external field coupling to the corresponding observable. We consider the system close to the critical point $T = T_c$. When we denote

$$\tau = T - T_c,$$

the critical point is at origin of the (τ, h)-plane.
Since the critical point is a singular point of thermodynamic potentials we divide them into regular and singular parts. For example, we write

$$\begin{aligned} F(T,m) &= F_0(T,m) + F_s(T,m) \\ G(T,h) &= G_0(T,h) + G_s(T,h) = F - hm, \end{aligned}$$

where the functions F_0 and G_0 are regular at the vicinity of the point $(\tau = 0, h = 0)$ whereas the functions F_s and G_s are singular there. Their differentials are

$$\begin{aligned} dF(T,m) &= -S\,dT + h\,dm \\ dG(T,h) &= -S\,dT - m\,dh. \end{aligned}$$

Critical exponents

Close to the critical point the singular parts are (with great accuracy) proprtional to some powers of the thermodynamical quantities τ and h. The *critical exponents* or the *critical indeces* are defined as follows:

- α, α' determine the singular part of the specific heat so that

  $$\begin{aligned} C_h &= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_h \\ &= \begin{cases} K\,\tau^{-\alpha}, & \text{when } T > T_c \\ K'\,(-\tau)^{-\alpha'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

  In practice we have $\alpha' = \alpha$.

- β tells how the order parameter behaves:

  $$m(T) = \begin{cases} 0, & \text{when } T > T_c \\ K\,(-\tau)^{\beta}, & \text{when } T < T_c. \end{cases}$$

- γ, γ' are related with the susceptivity:

  $$\begin{aligned} \chi &= \left(\frac{\partial m}{\partial h}\right)_T = -\left(\frac{\partial^2 G}{\partial h^2}\right)_T \\ &= \begin{cases} K\,\tau^{-\gamma}, & \text{when } T > T_c \\ K'\,(-\tau)^{-\gamma'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

  Within the experimental accuracy $\gamma' = \gamma$.

- δ tells how the order parameter depends on the external field h at the critical temperature $T = T_c$:

  $$m(T_c, h) = K\,h^{1/\delta}.$$

- ν determines the dependence of the correlation length on the temperature,

  $$\xi = K\,|\tau|^{-\nu}.$$

  The index ν is not actually a thermodynamic quantity since it is related with the microscopical parameter ξ.

Scaling theory

A *scalable* equation is such that it remains invariant under the scale transformations if the units of measurements are selected by scaling them properly. As an example we consider *Navier-Stokes'* equation of flow:

$$\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v}\cdot\nabla)\boldsymbol{v} = \boldsymbol{f} - \frac{1}{m\rho}\nabla p + \nu\nabla^2\boldsymbol{v},$$

where $\boldsymbol{v}$ is the velocity, ρ the density, p the pressure and $\boldsymbol{f}$ the force. The coefficient

$$\nu = \frac{\eta}{m\rho}$$

is the kinematic viscosity and η the viscosity. Let T, L, V and M be the dimensional units of the time, length, velocity and mass. With the help of the corresponding measures t', $\boldsymbol{r}'$, $\boldsymbol{v}'$ and m' (for example the mass is $m = m'M$) the Navier-Stokes equation takes the form

$$\frac{\partial \boldsymbol{v}'}{\partial t'} + (\boldsymbol{v}'\cdot\nabla')\boldsymbol{v}' = \boldsymbol{f}' - \frac{1}{m'\rho'}\nabla' p' + \frac{1}{R}\nabla'^2\boldsymbol{v}'.$$

The parameter R is the dimensionless *Reynolds number*

$$R = \frac{L^2}{T\nu} = \frac{VL}{\nu} = \frac{m\rho VL}{\eta},$$

which characterizes the flow: if $R \lesssim 10\ldots100$, the flow is usually laminar and if $R \gtrsim 10\ldots100$, it's turbulent.
Looking at the Navier-Stokes equation written using the measurement numbers we see that the behaviour of the system is dictated by the Reynolds number. If one can go from a system S to a system S_1 by scaling the measuring units so that the Reynolds number remains fixed, the equation describing the system as well as its solution remain also invariant. We say that the systems S ja S_1 are *similar.*
As a concrete example we consider two systems which are composed of same material, i.e.

$$\rho = \rho_1 \text{ ja } \nu = \nu_1.$$

We scale the linear measure by the factor s i.e.

$$L_1 = sL.$$

If we want the systems to be similar the Reynolds number must stay invarinat. For example

$$R = \frac{L^2}{T\nu} = \frac{L_1^2}{T_1\nu_1} = \frac{s^2L^2}{s_T T\nu},$$

so the scaling factor of the time s_T must be

$$s_T = s^2.$$

Let A and A_1 be some dimensional units of measure corresponding to similar systems S and S_1. It turns out that all scaling laws are of the form

$$A_1 = s^{-d_a} A,$$

where is d_a is a rational number.

Scaling hypothesis
In dense matter (liquid, solid, ...)

- the microscopical length scale is determined by the distance between atoms or molecules.
- when macroscopic properties are considered the microscopic structure is invisible.
- the only macroscopically essential parameter related to microscopical properties is the correlation length ξ, because in the vicinity of the critical point it grows macroscopically large.

We can thus assume that when we approach the critical point the classical similarity will hold:

- Consider two systems of same material with correlation lengths ξ and ξ_1.
- The correlation length tells the scale of the fluctuations, i.e. the scale of structure of the matter (provided that we cannot observe the atomic structure).
- When the systems are observed using such magnifications that ξ and ξ_1 seem to be of equal length (and possibly adjusting sampling frequencies) no differences between the systems can be found.

Since the correlation length at the critical point is infinite all sizes of fluctuations related to the order parameter are present. Except the atomic scale, there is no natural measure of length in the system. Thus the system looks similar no matter what scale is used, the system is *self similar*. The self similarity assumption is formulated mathematically as the *scaling hypothesis*:

- The singular parts of all thermodynamic potentials scale as exponential functions of the correlation length ξ only.
- The quantity A behaves in the vicinity of the critical point like
$$A \propto \xi^{-d_A},$$
where d_A is the *scaling dimension* of A.

The scaling dimension of the correlation length is then obviously $d_\xi = -1$. Further, we see that the scaling dimension of the quatity $A^x B^y \cdots$ is

$$d_{(A^x B^y \ldots)} = x d_A + y d_B + \cdots.$$

Because the critical index ν was defined so that

$$\xi \propto |\tau|^{-\nu},$$

the scaling dimension of the temperature is

$$d_\tau = \nu^{-1}.$$

The scaling dimensions of the most important quantities are

- *Correlation length ξ:* We saw above that
$$d_\xi = -1.$$
- *Temperature τ:* We had
$$d_\tau = \frac{1}{\nu}.$$
- *Length ℓ:* Since the correlation length determines the length scale of the system ℓ scales like ξ i.e.
$$d_\ell = -1.$$
- *Wave vector q:* The wave vector is inversely proportional to the length so
$$d_q = 1.$$
- *Order parameter m:* The index β was defined so that $m \propto (-\tau)^\beta$, so
$$d_m = \beta d_\tau = \frac{\beta}{\nu}.$$
- *Free energy G:* Scale transformation do not affect the free energy of the system, so
$$d_G = 0.$$
- *Free energy per volume element g:* Since $g = G/V$, we have
$$d_g = d_G - d_V = -dd_\ell = d,$$
when d is the spatial dimension.
- *Specific heat c:* Since the specific heat (density) is
$$c \approx -T_c \frac{\partial^2 g}{\partial \tau^2},$$
the scaling dimension d_c satisfies the condition
$$d_c = d_g - 2d_\tau = d - \frac{2}{\nu}.$$
Thus we have for the specific heat
$$c \propto \xi^{(2/\nu)-d} \propto |\tau|^{d\nu-2}$$

and, according to the definition of the critical index α,

$$c \propto |\tau|^{-\alpha}.$$

Hence the critical indeces are related via the *scaling law*

$$\alpha = 2 - \nu d.$$

- *Field h:* In an equilibrium the order parameter m is

$$m = -\frac{\partial g}{\partial h},$$

so

$$d_m = d - d_h.$$

For the field h we thus have

$$d_h = d - d_m = d - \frac{\beta}{\nu}.$$

The suceptivity obeys according to the definition of the index γ the relation

$$\chi = \frac{\partial m}{\partial h} \propto |\tau|^{-\gamma},$$

so

$$d_m - d_h = -\gamma d_\tau.$$

Comparing the dimension obtained from this for d_h with our earlier result we end up with the scaling law

$$\gamma = \nu d - 2\beta.$$

Further, the index δ was defined so that at the critical temperature

$$m \propto h^{1/\delta}.$$

Then we have

$$d_m = \frac{d_h}{\delta},$$

from which, using our earlier result, we get the scaling law

$$\delta = \frac{\nu d}{\beta} - 1.$$

The hard to measure index ν, which is related to the microscopical correlation length, can be eliminated from the three scaling laws derived above. We are left with scaling laws relating thermodynamic indeces:

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma. \end{aligned}$$

Note Although the scaling laws derived above are based on phenomenological arguments they are valid within experimental accuracy.

Widom scaling

We consider the Gibbs function per primitive cell (or particle)

$$g(\tau, h) = g_0(\tau, h) + g_s(\tau, h),$$

where we have again separated the regular and singular parts from eachother at the singular point ($\tau = 0, h = 0$). Its differential is

$$dg = -s\, d\tau - m\, dh,$$

when $s = S/N$ is the entropy per primitive cell (or particle). Since the order parameter m is zero at temperatures above the critical point the critical exponents related to it must come from the singular function g_s.
The functio f is a *generalized homogenous function* if it satisfies the condition

$$f(\lambda^{\alpha_1} x_1, \lambda^{\alpha_2} x_2, \ldots) = \lambda f(x_1, x_2, \ldots).$$

According to *Widom's hypothesis* the function g_s behaves in the vicinity of the critical point like a generalized homogenous function, i.e. it *scales* like

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

when $\lambda > 0$ and p and q are system independent exponents.
Because the scaling equation holds for all positive values of λ it holds when $\lambda = h^{-1/q}$, in which case $\lambda^q h = 1$. Thus we can write the scaling hypothesis as

$$\begin{aligned} g_s(\tau, h) &= h^{1/q} g_s\left(\frac{\tau}{h^{p/q}}, 1\right) \\ &= h^{1/q} \phi\left(\frac{\tau}{h^{p/q}}\right). \end{aligned}$$

Here we have defined

$$\phi(x) = g_s(x, 1).$$

The critical indeces can be obtained as follows

- β. Take the derivative of the scaling equation

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

with respect to the field h and recall that the order parameter is

$$m(\tau, h) = -\frac{\partial g_s(\tau, h)}{\partial h},$$

so we have the scaling condition

$$\lambda^q m(\lambda^p \tau, \lambda^q h) = \lambda m(\tau, h). \qquad (*)$$

Since the order parameter is supposed to be $m \neq 0$, we have $\tau < 0$. Then we can choose λ so that $\lambda^p \tau = -1$. Setting $h = 0$ we get

$$m(\tau, 0) = (-\tau)^{(1-q)/p} m(-1, 0).$$

According to the definition we have

$$m(\tau, 0) \propto (-\tau)^\beta,$$

so

$$\beta = \frac{1-q}{p}.$$

- δ. We set in the equation $(*)$ $\tau = 0$ and $\lambda^q = 1/h$, so
$$m(0,h) = h^{1/q-1} m(0,1).$$
According to the definition $m(0,h) \propto h^{1/\delta}$, so
$$\delta = \frac{q}{1-q}.$$

- γ, γ'. According to the definition the susceptivity is
$$\chi(\tau,h) = \frac{\partial m(\tau,h)}{\partial h},$$
which close to the critical point behaves like
$$\chi \propto \begin{cases} \tau^{-\gamma}, & \text{when } \tau > 0 \\ (-\tau)^{-\gamma'}, & \text{when } \tau < 0. \end{cases}$$
Differentiating $(*)$ with respect to the field h we get
$$\lambda^{2q}\chi(\lambda^p\tau, \lambda^q h) = \lambda\chi(\tau,h).$$
Setting $h = 0$ and $\lambda^p\tau = \pm 1$ we have
$$\chi(\tau,0) = |\tau|^{-(2q-1)/p}\chi(\pm 1, 0).$$
From this we can read for γ and γ'
$$\gamma = \gamma' = \frac{2q-1}{p}.$$

- α, α'. The specific heat is
$$c_h \propto \frac{\partial^2 g}{\partial \tau^2}.$$
Differentiating the scaling equation
$$g_s(\lambda^p\tau, \lambda^q h) = \lambda g_s(\tau,h)$$
twice with respect to τ we get
$$\lambda^{2p} c_h(\lambda^p\tau, \lambda^q h) = \lambda c_h(\tau,h).$$
We set $h = 0$ and $\lambda^p\tau = \pm 1$ and compare the result with the definitions of α and α':
$$c_h \propto \begin{cases} \tau^{-\alpha}, & \text{kun } \tau > 0 \\ (-\tau)^{-\alpha'}, & \text{kun } \tau < 0. \end{cases}$$
We see that
$$\alpha = \alpha' = 2 - \frac{1}{p}.$$

It is easy to verify that the Widom scaling hypothesis leads to the scaling laws
$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma. \end{aligned}$$

Kadanoff scaling theory

Unlike the Widom scaling hypothesis the method developed by Kadanoff (1966) is based on the microscopic properties of matter.
Outlines of Kadanoffs method:

- Combine the original microscopical state variables blockwise to *block variables.*
- Determine the efective interactions between the blocks. This coarsing of the system is called the *block transform.*
- The block transforms form a semigroup, so called *renormalization group.* One can perform transforms sequentially.
- Because in a system at the critical point there is no natural length scale the transformed systems look copies of eachother. Thus the critical point corresponds to a *fixed point* of the transformations.

We apply the method to the d-dimensional Ising spin system.

Block transform
We denote by $i, j, \ldots$ the origininal lattice points and the blocks obtained by combining them by indeces $I, J, \ldots$. The block spin σ'_I of the block I is defined so that
$$\sigma'_I = \sum_{i \in I} \sigma_i.$$
If we end up with the blocks I by scaling the length measure by the factor L, each block has L^d spins. Because in the Ising model each spin can get the values $\sigma_i = \pm 1$ the block spin can get the values
$$\sigma'_I = -L^d, -L^d + 2, \ldots, L^d$$
i.e. alltogether $L^d + 1$ different values.
Let H be the original Hamiltonian. We denote
$$\mathcal{H}[\sigma_i] = \beta H = -K \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i.$$
The state sum is
$$Z = e^{-\mathcal{G}} = \mathrm{Tr}\, e^{-\mathcal{H}[\sigma_i]} = \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]},$$
where $\mathcal{G} = \beta G$, G is the Gibbs function. We divide the trace summation into two parts
$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma'_I\}} \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right) \\ &= \sum_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma'_I]}. \end{aligned}$$
Here we have defined
$$\begin{aligned} e^{-\mathcal{H}[\sigma'_I]} &= \mathrm{Tr}_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right). \end{aligned}$$

As can be seen from the definition

$$\mathcal{H}[\sigma'_I] = \ln \mathrm{Tr}_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]}$$

the *Hamilton block function* $\mathcal{H}[\sigma'_I]$ is actually the *reduced free energy.* Thus it can be written as

$$\mathcal{H}[\sigma'_I] = \overline{\mathcal{H}[\sigma_i]}\Big|_{\{\sigma'_I\}} - TS|_{\{\sigma'_I\}},$$

where $\overline{\mathcal{H}[\sigma_i]}\Big|_{\{\sigma'_I\}}$ is the expectation value of the energy (the internal energy) evaluated in the block configuration $\{\sigma'_I\}$. Hence the Hamiltonian block function contains the internal entropy related to the internal variables of the blocks.

Close to the critical point, due to the scale invariance, we assume the reduced free energy to take approximately the same form as the original Hamiltonian. To achieve this we scale the range of the block spins so that

$$\sigma'_I = z\sigma_I,$$

where $\sigma_I = \pm 1$. Because the maximum of the block spin is L^d we must have $z \le L^d$.

Critical exponents

According to Kadanoff effectively the most important values of the block variable are $\pm z$. We denote

$$\mathcal{H}_L[\sigma_I] = \mathcal{H}[z\sigma_I].$$

We let the new Hamiltonian $\mathcal{H}_L$ to be of the same form as the original $\mathcal{H}$:

$$\mathcal{H}_L[\sigma_I] = -K_L \sum_{\langle IJ\rangle} \sigma_I\sigma_J - h_L \sum_I \sigma_I.$$

The parameters K_L and h_L depend now on the scale L. Let the values of the parameters at the critical point to be

$$\begin{aligned} K &= K_c \\ h &= h_c = 0. \end{aligned}$$

Since at the critical point nothing changes while scaling we must also have

$$\begin{aligned} K_L &= K_c \\ h_L &= h_c = 0. \end{aligned}$$

We consider the neighbourhood of the critical point. We suppose that $h \neq 0$, so also the corresponding scaled field satisfies $h_L \neq 0$. We write the original coupling constant as

$$K = K_c + \Delta K$$

and the corresponding scaled coupling constant as

$$K_L = K_c + \Delta K_L.$$

We now vary the scale factor L by a (small) amount δL. The relative variation of the scale is then $\delta L/L$. we can assume (as a good approximation) that the relative variations of the scaled parameters are proportional to the relative variation of the scale, i.e.

$$\begin{aligned} \frac{\delta \Delta K_L}{\Delta K_L} &= x\frac{\delta L}{L} \\ \frac{\delta h_L}{h_L} &= y\frac{\delta L}{L}, \end{aligned}$$

where x and y are constants.

When the change in the ratio is infinitesimal we get the differential equations

$$\begin{aligned} x &= \frac{\partial \ln \Delta K_L}{\partial \ln L} \\ y &= \frac{\partial \ln h_L}{\partial \ln L}, \end{aligned}$$

which after integration give

$$\begin{aligned} K_L &= K_c + L^x(K - K_c) \\ h_L &= L^y h. \end{aligned}$$

To obtain the same energy from the original and scaled Hamiltonians the coupling to the external field must satisfy the condition

$$h\sum_{i\in I} \sigma_i = h\sigma'_I = hz\sigma_I = h_L\sigma_I,$$

so the field scales like $h_L = zh$. We see that

$$z = L^y \text{ and } y \le d.$$

The same reasoning allows us to assume that the relative deviation of the temperature from the critical point,

$$\tau = \frac{T - T_c}{T_c},$$

behaves like the relative deviation of the coupling constant K from the critical value, i.e.

$$\tau_L = L^x \tau.$$

Thus the Gibbs function per spin unit scales like

$$g(\tau_L, h_L) = g(L^x\tau, L^y h) = L^d g(\tau, h),$$

where the factor L^d is due to the fact that the new block contains L^d old spins. Writing

$$\begin{aligned} x &= pd \\ y &= qd \end{aligned}$$

we end up with the Widom scaling.

Renormalization group

Let us suppose that the Hamiltonian $\mathcal{H}$ depends on the parameters

$$\mu = (\mu_1, \mu_2, \ldots),$$

For example $\mu = (K, h)$, as above. Block transforms are now mappings in the parameter space

$$\mu \longrightarrow \mu_L.$$

Let $\boldsymbol{R}_L$ be the operator corresponding to the block transform, i.e.

$$\mu \longrightarrow \mu_L = \boldsymbol{R}_L \mu.$$

Since the block transform is a change in the scale we must have

$$\boldsymbol{R}_L \boldsymbol{R}_{L'} = \boldsymbol{R}_{LL'}.$$

Furthermore, it does not matter in which order the scale transforms are performed:

$$\boldsymbol{R}_L \boldsymbol{R}_{L'} = \boldsymbol{R}_{L'} \boldsymbol{R}_L.$$

In the block transform we loose information, for example the detailed knowledge of the values of the original spin variables. Thus it is impossible to return to the original system by scaling: the operation $\boldsymbol{R}_{L'}$ has no inverse transformation among the operations $\{\boldsymbol{R}_L\}$. We see that the operations

$$\mathcal{R} = \{\boldsymbol{R}_L\}$$

form a *commutative semigroup* which is called the *renormalization group.*
A point μ^* which satisfies the condition

$$\mu^* = \boldsymbol{R}\mu^* \quad \forall \boldsymbol{R} \in \mathcal{R},$$

is called a *fixed point.* A system corresponding to the parameter values μ^* is at the critical point since any transformation of that systems results an exactly identical system. The set of those points that after sequential block transforms lead to the fixed point μ^* is called the *critical surface.* If the system is on the critical surface, but not at the critical point, it is at a critical point of the phase transition. However, one can still observe it using the scale where microscopical details are visible.