Seminar: Statistical Physics - Phase Transitions and Critical Phenomena

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1 Reminder on thermodynamics

In order to describe phase transitions and critical phenomena it is important to have a basic understanding of thermodynamics and it's quantities. We will showcase all relevant quantities for a fluid and magnetic system.
First off, we remind ourselves of the thermodynamic potentials:

Thermodynamic state functions	fluid system	magnetic system
Inner energy $U(S,V)$	$dU = TdS - PdV$	$dU = TdS + HdM$
Enthalpy $E(S,P)$	$dE = TdS + VdP$	$dE = TdS - MdH$
Gibbs potential $G(T,P)$	$dG = -SdT + VdP$	$dG = -SdT - MdH$
Helmholtz potential $A(T,V)$	$dA = -SdT - PdV$	$dA = -SdT + HdM$

All these thermodynamical potentials are related to each other by Legendre transformations.
Starting from the state functions we are able to derive the response functions. There are only three independent response functions [9].

- **Specific heat** at constant x (measuring heat absorption from heat stimulus):

$$C_x := \left(\frac{dQ}{dT}\right)_x = T\left(\frac{\partial S}{\partial T}\right)_x, \ x = P, V, M, H \tag{1.1}$$

For fluid systems:

- **Compressibility** at constant x (measuring response of the volume to a pressure stimulus):

$$\kappa_x := -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_x = \frac{1}{\rho}\left(\frac{\partial S}{\partial \rho}\right)_x, \ x = S, T \tag{1.2}$$

- **Coefficient of thermal expansion**:

$$\alpha_P := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{1.3}$$

For the magnetic system we have the following:

- **Susceptibility** at constant x:

$$\chi_x := \left(\frac{\partial M}{\partial H}\right)_x, \; x = S, T \tag{1.4}$$

- **Coefficient of thermal expansion**:

$$\alpha_H := \left(\frac{\partial M}{\partial T}\right)_H. \tag{1.5}$$

Another very useful relation is to express the response functions in terms of second derivatives of the thermodynamic potential (this will become relevant for phase transitions):

$$C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V \qquad C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P \tag{1.6}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T \qquad \kappa_S = -\frac{1}{V}\left(\frac{\partial^2 E}{\partial P^2}\right)_S \tag{1.7}$$

$$\chi_T = -\left(\frac{\partial^2 G}{\partial H^2}\right)_T \qquad \chi_S = -\left(\frac{\partial^2 E}{\partial H^2}\right)_S \tag{1.8}$$

Utilising the relations between the state functions and the response functions, one can find that the responses are not independent of each other and actually fulfill the following relations [1]:

$$\kappa_T(C_P - C_V) = TV\alpha_P^2, \tag{1.9}$$

$$C_P(\kappa_T - \kappa_S) = TV\alpha_P^2, \tag{1.10}$$

$$C_P/C_V = \kappa_T/\kappa_S. \tag{1.11}$$

If we now demand to have stability (thermal and mechanical stability in case of a fluid system) and Le Chatelier's principle (any spontaneous change in the parameters of a system that is in stable equilibrium will give rise to processes that tend to restore the system to equilibrium) it is necessary that the specific heat and the compressibility are positive for all values of the temperature. Therefore,

$$C_P \geq C_V, \tag{1.12}$$

$$\kappa_T \geq \kappa_S \tag{1.13}$$

for all T. We find similar relations for the case of a magnetic system.

With all these relations we have collected so far we are now able to make statements about convexity properties of the thermodynamic potentials (this will become important for critical exponents). First of all, for a fluid system we have that $G(T, P)$ is concave w.r.t to both T and P while $A(T, V)$ is concave w.r.t to T but convex w.r.t V [1]. Unfortunately we cannot make such claims for a magnetic system since we cannot guarantee that χ and C are non-negative. Nonetheless, if we have a Hamiltonian of the form

$$\mathscr{H} = \mathscr{H}_0 - H\mathscr{M} \tag{1.14}$$

we get some convexity relations (Griffiths 1964). Assuming that our system obeys this Hamiltonian we get that $G(T, H)$ is concave w.r.t T and H while $A(T, M)$ is concave w.r.t. T and convex w.r.t. M.

2 Phase Transitions

Substances that have a fixed chemical composition (water being a prominent example) can exist in homogeneous forms. We are able to differentiate between those forms due to their different properties (e.g. gas, solid, liquid), we call those states. More generally one finds that for the same solid or liquid there are multiple arrangements of the molecules or atoms that again have different properties, these will constitute the so-called phases (e.g. 20 phases in ice have been found so far [10]). Phase transitions (in short PT) are in other words property changes of the materials that are induced by acting from the outside to modify an intensive thermodynamic variable (e.g. temperature, pressure, magnetic/electric field). Most commonly one can define critical quantities for phase transitions, such as a critical temperature. In general, we differentiate between phase transitions with and without latent heat. As an example, you can see the phase diagram of water in fig. 2.1 with the phases of ice showcased as Roman numerals (I_h representing the phase of ice that one finds commonly in nature) and the values for the crtical point and phase transition points at atmospheric pressure.

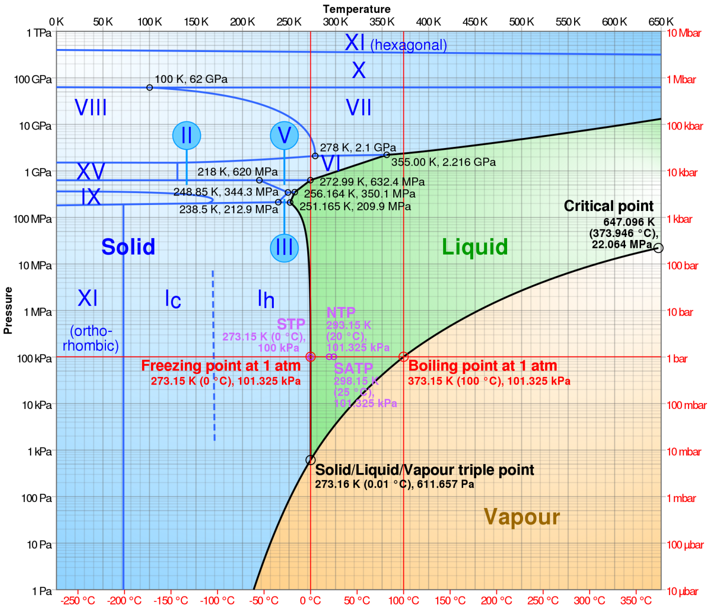


Figure 2.1: Log-lin pressure-temperature phase diagram of water. Roman numerals indicate ice phases. Source:[6]

2.1 Thermodynamic Description

One can categorise phase transitions into those that involve latent heat and those that do not. The physicist P. Ehrenfest in 1933 proposed to classify the phase transitions by the behaviour of the thermodynamic potentials. This was then generalized by Fisher in the definition of the second-order transitions. We define phase transitions in the thermodynamic point of view the following way [6]:

First-order transitions: Ehrenfest spoke of transitions of first order if they involve discontinuities of the first order derivatives of thermodynamic potentials, i.e. quantities such as entropy and volume (latent heat is featured in the discontinuity of the entropy).

Second-order transitions: These kind of transitions are described by continuuous thermodynamic potentials **and** continuous first-order derivatives while the second-order derivatives (w.r.t state variables) are zero or approach asymptotically infinite at the transition point. These second-order derivatives are the response functions such as heat capacity and compressibility.

These two described situations are being depicted in fig. 2.2 and fig. 2.3. If we look at phase diagrams of a fluid/magnetic system, we have those two transition types: the lines corresponding to latent heat transitions and the critical points corresponding to transitions without latent heat (see fig. 2.4).

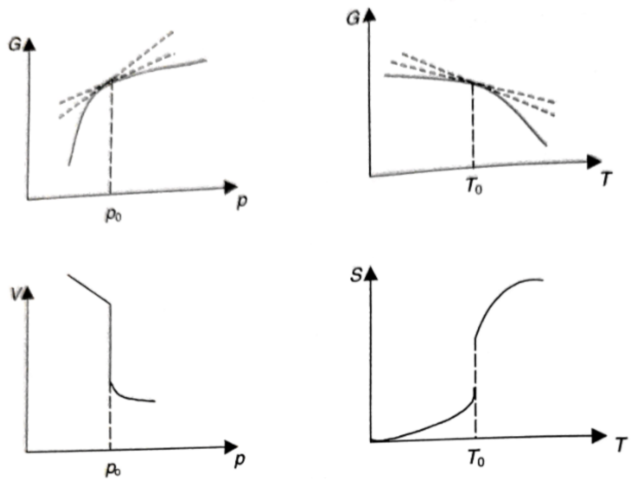


Figure 2.2: First order phase transitions: The thermodynamic potentials are continuous, as seen here in the potential G in the upper two graphs around the transition point. The first derivatives on the other hand are discontinuous, as seen in the lower two graphs. Source:[6]

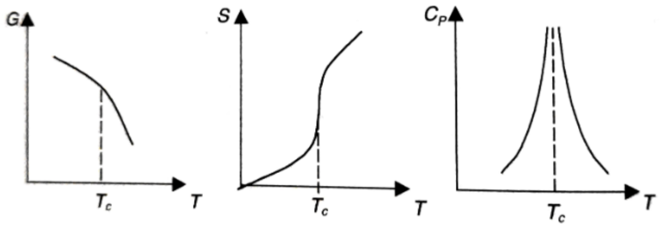
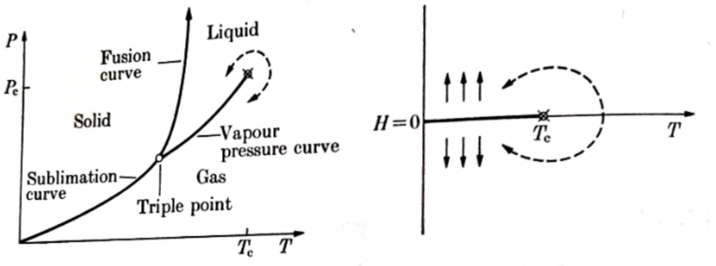


Figure 2.3: Second order phase transitions: The thermodynamic potentials as well as the first derivative are continuous, as seen here in the potential G and the entropy S around the transition point. The second derivatives on the other hand are discontinuous, as seen in the specific heat graph. Source:[6]

2.2 Symmetry description

The thermodynamic point of view of looking at phase transitions already helped immensely to distinguish but also to see similarities between different kinds of phase transition phenomenas such as superconductivity, ferroelecricity, magnetism etc. Nonetheless, there is still another way to classify phase transitions which was firstly noted by L.D. Landau in 1937. Landau classified phase transitions without latent heat by a symmetry change, e.g. permanent magnetization only below the Curie point (ferromagnetic). One can even talk of a symmetry break during a transition, e.g. below the Curie point . He introduced the notion of an order parameter (e.g. magnetisation) that takes a null value



(a) Fluid

(b) Magnet

Figure 2.4: Left: PT-plane projection of a fluid system. The three regions divided by the lines correspond to three phases. The lines correspond to coexistence curves of two phases (or equilibrium lines between phases) with the intersection point of the lines corresponding to a so-called triple point in which all three phases coexist. At the end of the vapour-pressure curve we reach a critical point at which we observe second-order transitions. Right: HT-plane projection of a magnetic system. There we also see a coexistence line ending in a critical point. Source:[1]

in the disordered phase and a non-zero value in the ordered phase. We define the phase transitions in the symmetry description the following way [6]:

Phase transitions with no order parameter: Symmetry groups of the two phases are strictly not included in each other. These kind of phase transitions are always first-order (i.e. with latent heat) in Ehrenfest's sense.

Phase transitions with an order parameter: One can define an order parameter and the symmetry group of the ordered (least symmetric) phase is a subgroup of the disordered (most symmetric) phase. We can speak of a first-order transitions in Ehrenfest's sense in case of a discontinuous order parameter at the transitions and of a second-order transition in case of a continuity at the transition.

2.3 Correlation length description and Ornstein-Zernike approximation

Phase transitions can also be associated with the divergence of the correlation length. In order to describe this analytically we introduce the pair correlation function which is an integral part in the discussion of critical phenomena. It is expressed in dependence of the order parameter m,

$$G(\boldsymbol{r}, \boldsymbol{r'}) \equiv \langle (m(\boldsymbol{r}) - \langle m(\boldsymbol{r}) \rangle)(m(\boldsymbol{r'}) - \langle m(\boldsymbol{r'}) \rangle) \rangle \tag{2.1}$$

This quantity measures the correlations of the fluctuations of the order parameter from its average value. For fluid systems the parameter is the particle density, for magnetic systems it is the spin. Assuming a spatially uniform system (including translational invariance) we write the correlation function as

$$G(\boldsymbol{r}-\boldsymbol{r'}) = \langle m(\boldsymbol{r})m(\boldsymbol{r'})\rangle - \langle m\rangle^2 \tag{2.2}$$

due to $G(\boldsymbol{r},\boldsymbol{r'}) \to G(\boldsymbol{r}-\boldsymbol{r'})$ and $m(\boldsymbol{r}) = m(\boldsymbol{r'})$. Further we notice that for $|\boldsymbol{r}-\boldsymbol{r'}| \to \infty$ the probability of finding a particle at $\boldsymbol{r'}$ becomes independent of what is at $\boldsymbol{r}$.

$$\Longrightarrow \langle m(\boldsymbol{r})m(\boldsymbol{r'})\rangle \to \langle m(\boldsymbol{r})\rangle\langle m(\boldsymbol{r'})\rangle = m^2 \text{ for } |\boldsymbol{r}-\boldsymbol{r'}| \to \infty \tag{2.3}$$

$$\Longrightarrow G(\boldsymbol{r}-\boldsymbol{r'}) \to 0 \text{ for } |\boldsymbol{r}-\boldsymbol{r'}| \to \infty \tag{2.4}$$

For a fluid system we have $m(\boldsymbol{r}) = n(\boldsymbol{r}) \equiv \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r_i})$. Inserting this into the correlation function we get

$$G(\boldsymbol{r}-\boldsymbol{r'}) = \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r_i})\delta(\boldsymbol{r'}-\boldsymbol{r_j}) \right\rangle - n^2 \tag{2.5}$$

where $i = j$ is not excluded, therefore correlations with itself is included. This motivates the partition of the correlation function into the following 2 terms (correlations with itself on the left and corellations between different particles on the right):

$$G(\boldsymbol{r}-\boldsymbol{r'}) \equiv n\delta(\boldsymbol{r}-\boldsymbol{r'}) + n^2\Gamma(\boldsymbol{r}-\boldsymbol{r'}) \tag{2.6}$$

Next, we introduce the direct correlation function by it's Fourier transform

$$C(\boldsymbol{q}) \equiv \frac{\Gamma(\boldsymbol{q})}{1+n\Gamma(\boldsymbol{q})} \tag{2.7}$$

with $\Gamma(\boldsymbol{q})$ being the Fourier transform of $\Gamma(\boldsymbol{r})$. We notice that when $T \to T_c$ we have $\Gamma(\boldsymbol{q}=0) \to \infty$ since the correlation length becomes infinite at the critical temperature. This leads to $C(\boldsymbol{q}=0) \sim n^{-1}$.
With that quantity we can calculate the structure factor (the spatial Fourier transform of the correlation function)

$$\frac{S(q)}{n} = 1 + n\Gamma(q) = \frac{\Gamma(q)}{C(q)} = \frac{1}{1-nC(q)} \tag{2.8}$$

$$\tag{2.9}$$

We now Taylor-expand $C(q)$ about $q = 0$ for all T up to T_c:

$$C(q) = C(0) + \sum_{l=0}^{\infty} c_l(n,T)q^l \tag{2.10}$$

with the coefficients $c_l(n,T)$ given by Maclaurin's expansion [1],

$$c_l(n,T) = \frac{1}{l!}\left\{\frac{\partial^l}{\partial q^l}C(q)\right\}_{q=0} \propto \frac{i^l}{l!}\int_{-1}^{1}\mu^l d\mu \int_0^{\infty} r^{l+2}C(r)dr. \tag{2.11}$$

We assume for the further steps that all of the moments of $C(r)$ are integrable at T_c. This expansion leads now to

$$\frac{n}{S(q)} = 1 - nC(q) = 1 - n\left\{C(0) + c_2(n,T) + \mathscr{O}(q^4)\right\} \tag{2.12}$$

$$= c_2(n,T)\left\{\frac{1-nC(0)}{c_2(n,T)} - nq^2 + \mathscr{O}(q^4)\right\} \tag{2.13}$$

$$= R^2\left\{\kappa_1^2 + q^2 + \mathscr{O}(q^4)\right\} \tag{2.14}$$

with $\kappa_1^2 \equiv \frac{1-nC(0)}{R^2}$ related to the zeroth moment of $C(r)$ and $R^2 \equiv -nc_2(n,T)$ related to the second moment. The so-called Ornstein-Zernike approximation now simply involves truncating all terms of order q^4 and higher. Inverse Fourier transforming the expression will yield us the asymptotic form of the correlation function for large r [1]:

$$G(r) \sim \frac{e^{-\kappa_1 r}}{r^{d-2}} \tag{2.15}$$

whereby d denotes the dimension. For $d = 2$ the approximation yields a logarithmic dependence [1], which is an unphysical result. Relabeling κ_1 to the inverse correlation length ξ^{-1} which is motivated by the fact that $\kappa_1^2 \to 0$ for $T \to T_c$ since $C(0) \to n^{-1}$, our final correlator looks like the following:

$$G(r) \sim \frac{e^{-\frac{r}{\xi}}}{r^{d-2}} \tag{2.16}$$

In other words the correlation length is diverging at T_c leading to scale invariance and in this case also to an universal property.

3 Critical Phenomena

3.1 Critical-point exponent

Having established the basics of thermodynamics and phase transitions, we are now able to head into critical phenomena that emerge in those studies. We will firstly define a set of numbers or indices, the so-called critical-point exponents, that help us to describe the behaviour near the critical point of the quantities we have looked at so far. For this we define a dimensionless variable based on the temperature difference to the critical temperature:

$$t \equiv \frac{T - T_c}{T_c}. \tag{3.1}$$

Taking a general function $f(t)$ which is positive and continuous for small, positive values of t, we can define the exponent by

$$\lambda \equiv \lim_{t \to 0} \frac{\ln f(t)}{\ln t} \text{ with the relation } f(t) \sim t^{\lambda}. \tag{3.2}$$

We also note here that we do not mean a direct proportionality for the function $f(t)$ but rather that there might be also corrections terms and it could be expressed as $f(t) = At^x(1 + Bt^y + ...)$. One must also distinguish whether we approach the critical point from below or above. Analogous to above one can define the exponent (marked by a dash) for approaching from below:

$$\lambda' \equiv \lim_{t \to 0} \frac{\ln |f(-t)|}{\ln |t|} \text{ with the relation } f(t) \sim (-t)^{\lambda'}. \tag{3.3}$$

In fig. 3.1 and fig. 3.2 below we see three different cases of values that λ can take. Fig. 3.1 shows that $f(t)$ diverges to infinity for negative values of λ while approaching zero for positive values. Another thing to note is that the absolute value also determines how steep or "sharp" the curve becomes. An additional interesting case arises when looking at $\lambda = 0$. The logarithmic divergence on the left graph and cusp-like divergence on the right graph of fig. 3.2 show that depending on the analytic form of the function, we get a different behaviour around the critical point. Another case, not showcased here, is that the function doesn't show any anomalous behaviour (up to a jump discontinuity). In order to differ the cases showcased in fig. 3.2 we introduce yet another exponent

$$\lambda_s := j + \lim_{t \to 0} \frac{\ln |f^{(j)}(t)|}{\ln t}, \;\; j = \min_{n \in \mathbb{N}} \{n | f^{(n)}(t) \to \infty \text{ for } t \to 0\}. \tag{3.4}$$

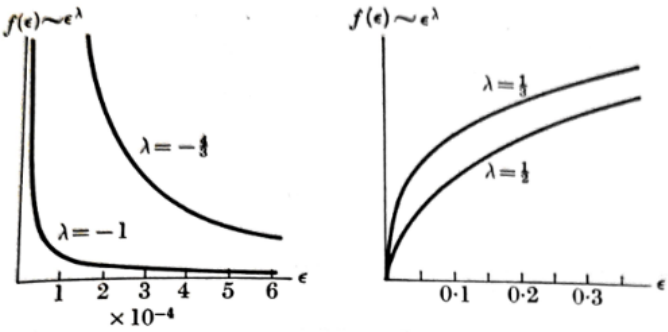


Figure 3.1: $\epsilon \equiv t$. Left: $\lambda < 0$, divergence to ∞ at $\epsilon = 0$. Right: $\lambda > 0$, approaching 0 at $\epsilon = 0$. Source:[1]

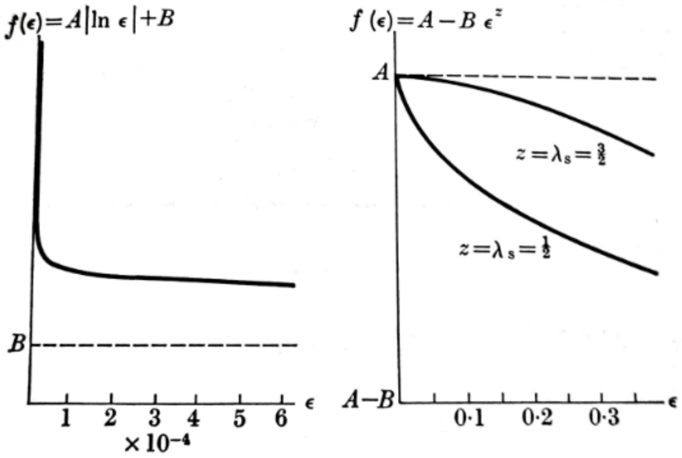


Figure 3.2: $\epsilon \equiv t$. Two different anomalous cases for $\lambda = 0$. Left: logarithmic divergence. Right: cusp-like divergence. Source:[1]

Now we are able to introduce the common exponents used to describe the critical behaviour of the thermodynamic quantities. We will only list the common exponents for the fluid system here since they are analogously defined for the magnetic system (see [1]).

Exponent	Definitions	Quantity
α	$C_V \sim t^{-\alpha}$	specific heat at V_c
α'	$C_V \sim (-t)^{-\alpha'}$	specific heat at V_c
β	$\rho_L - \rho_G \sim (-t)^{\beta}$	liquid-gas density difference (in general an order parameter)
γ	$\kappa_T \sim t^{-\gamma}$	isothermal compressibility
γ'	$\kappa_T \sim (-t)^{-\gamma'}$	isothermal compressibility
ν	$\xi \sim t^{-\nu}$	correlation length
ν'	$\xi \sim (-t)^{-\nu'}$	correlation length
η	$G(r) \sim \lvert r\rvert^{-(d-2+\eta)}$	pair correlation function (d = dimensionality)

3.2 The Scaling Hypothesis

Widom, Domb and Hunter (1965) looked into ways to simplify the form of the thermodynamic functions that will describe the critical phenomena near T_c. They concluded that they need to approach the problem by making assumptions about the form of the thermodynamic potential, which will be called the static scaling law or homogeneous function approach. For this we divide the thermodynamic potential into a singular part (which we denote with the subscript S) and a non-singular part. The Scaling Hypothesis now assumes that the singular part is a homogeneous function:

$$G_S(\lambda^r t, \lambda^k H) = \lambda G_S(t, H). \tag{3.5}$$

Note that we did not specify the values for the scaling parameter r and k, nonetheless, one can relate those parameters to the critical-point exponents.

3.3 Universality

Different mathematical models as well as various experiments have shown that phase transition of different materials or systems share the same critical exponents. We call this property universality and we can divide this into classes of systems that share the same critical behaviour. The liquid-gas transition for the fluids Xenon and Carbondioxide have been shown to be in a universality class with the 3D Ising-model (Hocken and Moldover, 1976). Universality is also a prediction of the renormalization group theory for phase transitions, where we only have dependences on the dimension and the degree of isotropy of the system [2]. Here we speak of classes of Hamiltionians whose critical exponents and characertistics of the scaling functions are completely independent on the "details" of the Hamiltonian, i.e. only dimensions and symmetries play a role. The renormalization group approach is not an approximation but can be followed through exactly but it is actually harder to follow through than to calculate the partiton function for almost all models with the exception of very simple models. Another thing to note is that universality and the scaling law are separate aspects that are not necessarily fulfilled at the same time for every system (e.g. universality fails but scaling is fulfilled for the eight-vertex model [3]).

3.4 Relations among critical exponents

Utilising the scaling law, as well as properties and relations of the thermodynamic variables we have discussed so far (see also Rushbrooke 1963, Griffith 1965, Widom 1965, Fisher 1967, Kadanoff 1967), we are able to make strong statements about the relations between the critical-point exponents [1]:

$$\alpha = \alpha' \tag{3.6}$$
$$\gamma = \gamma' \tag{3.7}$$
$$\nu = \nu' \tag{3.8}$$
$$2 = \alpha + 2\beta + \gamma \tag{3.9}$$
$$2 = \alpha + \beta(\delta + 1) \tag{3.10}$$
$$\gamma = \beta(\delta - 1) \tag{3.11}$$
$$\gamma = (2 - \eta)\nu \tag{3.12}$$
$$d\nu = 2 - \alpha \tag{3.13}$$

with d denoting the dimension.

These relations are not independent of each other and because of that it suffices to know two exponents to determine the rest. Utilising the Renormalization Group theory (Wilson 1971), Fisher showed [2] that the critical exponents can now simply be expressed by the dimension of the model/system d and by the degree of isotropy n. In fig. 3.3 you can see the series expansion of the critical point exponents calculated by renormalization group methods.

3.5 Ising model in the mean field approach

We start from a nearest-neighbour Ising model of N spins (arguing that the N+1 spin is the first spin again, i.e. periodic boundary conditions). The dimensionless Hamiltonian of this model reads [9]

$$\mathscr{H} = -K \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i \tag{3.14}$$

with the coupling constant K, external field H and $\sigma_i \in \{+1, -1\}$ the spin on site i. We will see that for dimension $d > 1$ the model yields two phases: a paramagnetic phase

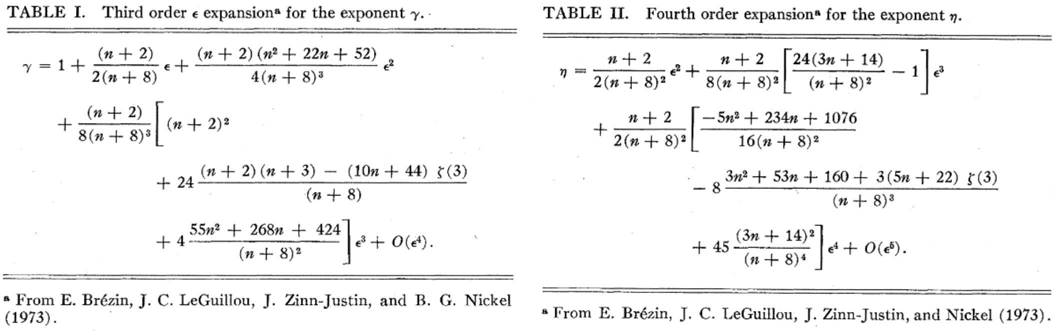


TABLE I. Third order ϵ expansion[a] for the exponent γ.

$$\gamma = 1 + \frac{(n+2)}{2(n+8)}\epsilon + \frac{(n+2)(n^2+22n+52)}{4(n+8)^3}\epsilon^2 + \frac{(n+2)}{8(n+8)^3}\left[(n+2)^2 + 24\frac{(n+2)(n+3) - (10n+44)\ \zeta(3)}{(n+8)} + 4\frac{55n^2+268n+424}{(n+8)^2}\right]\epsilon^3 + O(\epsilon^4).$$

[a] From E. Brézin, J. C. LeGuillou, J. Zinn-Justin, and B. G. Nickel (1973).

TABLE II. Fourth order expansion[a] for the exponent η.

$$\eta = \frac{n+2}{2(n+8)^2}\epsilon^2 + \frac{n+2}{8(n+8)^2}\left[\frac{24(3n+14)}{(n+8)^2} - 1\right]\epsilon^3 + \frac{n+2}{2(n+8)^2}\left[\frac{-5n^2+234n+1076}{16(n+8)^2} - 8\frac{3n^2+53n+160+3(5n+22)\ \zeta(3)}{(n+8)^3} + 45\frac{(3n+14)^2}{(n+8)^4}\right]\epsilon^4 + O(\epsilon^5).$$

[a] From E. Brézin, J. C. LeGuillou, J. Zinn-Justin, and Nickel (1973).

Figure 3.3: Third order expansion of the critical point exponents in terms of $\epsilon \equiv 4 - d$ with d denoting the dimension. Source:[2]

(spin disorder due to thermal fluctuations) and a ferromagnetic phase (spin alignment). They are separated by a critical temperature T_c.
We furthermore define the magnetisation

$$m \equiv \frac{1}{N}\sum_{i=1}^{N}\langle\sigma_i\rangle, \quad \langle\sigma_i\rangle = \frac{1}{Z}\,\mathrm{Tr}(\sigma_i e^{-\beta\mathscr{H}}). \tag{3.15}$$

With $Z = \mathrm{Tr}(e^{-\beta\mathscr{H}})$ being the partition function, $\beta = \frac{1}{k_B T}$ and the trace representing the sum over all possible configurations. You will see shortly that $m = 0$ will correspond to the paramagnetic while $m \neq 0$ to the ferromagnetic phase.
Our next step is to decouple this Hamiltonian using a mean field approach, we do this by expressing the spins in the form

$$\sigma_i = \langle\sigma_i\rangle + \delta\sigma_i, \quad \delta\sigma_i \equiv \sigma_i - \langle\sigma_i\rangle \tag{3.16}$$

with $\delta\sigma_i$ denoting the fluctuations about the mean value. Neglecting quadratic fluctuations, this turns the quadratic term in our Hamiltonian into

$$\sigma_i\sigma_j \approx \langle\sigma_i\rangle\sigma_j + \langle\sigma_j\rangle\sigma_i - \langle\sigma_i\rangle\langle\sigma_j\rangle. \tag{3.17}$$

If we now utilise the translational invariance of our system then the mean value of the spin at site i becomes independent of which site it is located at. Therefore we can say that $m = \langle\sigma_i\rangle$ which in turn simplifies our quadratic term to

$$\sigma_i\sigma_j = m[(\sigma_i + \sigma_j) - m]. \tag{3.18}$$

This turns our Hamiltonian into it's mean field form

$$\mathscr{H}_{MF} = -mK\sum_{\langle ij\rangle}(2\sigma_i - m) - H\sum_{i=1}^{N}\sigma_i. \tag{3.19}$$

We can simplify this even further by noticing that

$$\sum_{\langle ij\rangle} \rightarrow \frac{1}{2}\sum_{i=1}^{N}\sum_{j\in n.n.(i)} \tag{3.20}$$

with $n.n.(i)$ denoting the nearest neighbours of site i and the factor of $\frac{1}{2}$ to avoid double counting. Since we also have no explicit j dependence in our Hamiltonian anymore, we can express $\sum_{j\in n.n.(i)} = q$, whereby q is the number of neighbours for site i. Our Hamiltonian thus can be written as

$$\mathscr{H}_{\text{MF}} = \frac{NqKm^2}{2} - H_{\text{eff}} \sum_{i=1}^{N} \sigma_i \tag{3.21}$$

with $H_{\text{eff}} \equiv (H + qKm)$. In order to calculate the the magnetisation we first of all need to compute the partition function:

$$\begin{aligned}
Z_{\text{MF}} &= \text{Tr}(e^{-\beta\mathscr{H}_{\text{MF}}}) && (3.22)\\
&= \prod_{i=1}^{N} \left(\sum_{\sigma_i=\pm 1} \right) e^{-\beta\mathscr{H}_{\text{MF}}} && (3.23)\\
&= \prod_{i=1}^{N} \left(\sum_{\sigma_i=\pm 1} \right) e^{-\beta N m^2 qK/2} e^{\beta H_{\text{eff}} \sum_{j=1}^{N} \sigma_j} && (3.24)\\
&= e^{-\beta N m^2 qK/2} \prod_{i=1}^{N} \left(\sum_{\sigma_i=\pm 1} e^{\beta H_{\text{eff}} \sigma_i} \right) && (3.25)\\
&= e^{-\beta N m^2 qK/2} \prod_{i=1}^{N} \left(e^{-\beta H_{\text{eff}}} + e^{\beta H_{\text{eff}}} \right) && (3.26)\\
&= e^{-\beta N m^2 qK/2} [2\cosh(\beta H_{\text{eff}})]^N && (3.27)
\end{aligned}$$

Using the fact that

$$\begin{aligned}
m &= \frac{1}{N} \sum_{i=1}^{N} \frac{\text{Tr}\left(\sigma_i e^{-\beta\mathscr{H}_{\text{MF}}}\right)}{Z_{\text{MF}}} && (3.28)\\
&= \frac{1}{N Z_{\text{MF}}} \text{Tr} \left(\sum_{i=1}^{N} \sigma_i e^{-\beta\mathscr{H}_{\text{MF}}} \right) && (3.29)\\
&= \frac{1}{N\beta} \frac{1}{Z_{\text{MF}}} \frac{\partial Z_{\text{MF}}}{\partial H_{\text{eff}}} && (3.30)\\
&= \frac{1}{N\beta} \frac{\partial (\ln Z_{\text{MF}})}{\partial H_{\text{eff}}}. && (3.31)
\end{aligned}$$

we are able to get a self-consistency equation for the magnetisation m:

$$m = \tanh[\beta(H + qKm)]. \tag{3.32}$$

Being interested in the transition at the critical point, we set $H = 0$. Solving this equation, for example graphically, one finds:

$\beta Kq \leq 1$: only one solution at $m = 0 \rightarrow$ paramagnetic state for $T \geq T_c$

$\beta Kq > 1$: three solutions, each located at $m = 0$ (unstable solution) and $m = \pm m_0$ with $m_0 \leq 1 \rightarrow$ ferromagnetic state for $T < T_c$

$$\Longrightarrow T_c = qK/k_B. \tag{3.33}$$

Knowing T_c we can express the magnetisation in terms of the dimensionless variable t and expand in terms of m,

$$m = (1+t)\,\mathrm{arctanh}\,m \approx (1+t)(m + m^3/3) \tag{3.34}$$

which we then can solve after m,

$$\Longrightarrow 1 = (1+t)(1+m^2/3) = 1 + m^2/3 + t + t/3m^2 \tag{3.35}$$

$$\Longrightarrow m^2/3(1+t) = -t \tag{3.36}$$

$$\Longrightarrow m = (-3t)^{\frac{1}{2}} \left(\frac{1}{1+t}\right)^{\frac{1}{2}} = (-3t)^{\frac{1}{2}}\{1 + \mathscr{O}(t)\}, \tag{3.37}$$

giving us our first value for a critical-point exponent: $\beta = \frac{1}{2}$. Since we only need 2 critical exponents to get the rest, we simply differentiate the magnetisation with respect to H and hold T constant in order to get the susceptibility

$$\chi_T = \frac{\beta}{\cosh^2(\beta qKm) - \beta qK}. \tag{3.38}$$

Approaching the critical point ($H \rightarrow 0$, for $T \rightarrow T_c^+$: $m \rightarrow 0$),

$$\chi_T = \frac{1}{k_B(T - T_c)} \propto (t)^{-1} \tag{3.39}$$

and therefore $\gamma = 1$.
From our equality relations we have established before we get $\alpha = 0$ and $\delta = 3$. Onsager calculated these exponents exactly and got $\alpha = 0$, $\beta = \frac{1}{8}$, $\nu = 1$, $\delta = 15$ and $\gamma = \frac{7}{4}$ (ABRAHAM 1973). We see that mean field approximations might yield a good qualitative look into critical phenomena and also far away from the critical temperature but fails quantitatively at T_c. This arises from the fact that such approximations usually neglect long range correlations which become prevalent at T_c.

4 Conclusion and outlook

There are still some unsolved problems in the study of phase transitions and critical phenomena, the most prominent examples being the analytical solutions of the 2D Ising problem **with** a non-vanishing external field (the vanishing case was solved by Lars Onsager [1944]) and the 3D Ising problem. A good overview is given in fig. 4.1. Another unsolved problem arised when people found out about the discrepancy between experimental and theoretical results of the heat capacity critical exponent in the superfluid transition of helium-4 with the experimental value of $\alpha = -0.0127(3)$ [5].

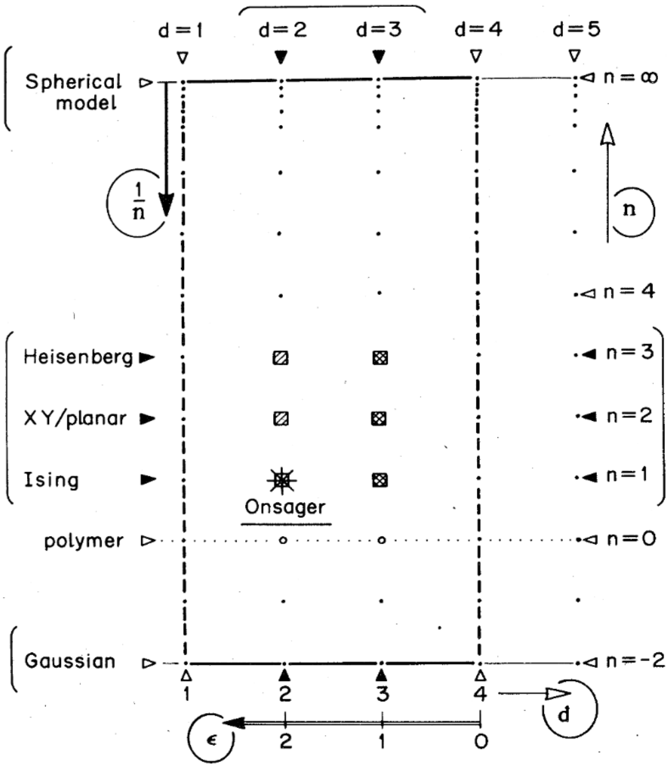


Figure 4.1: (d, n)-plane diagram showcasing various theoretical models and the fact that there is only one analytical solution by Onsager thus far, marked by a star and his name. The rest is still unsolved. Source:[2]

While analytical solutions have not been found so far, people have nonetheless found numerical approaches or approximation methods and approximate solutions for these analytically unsolvable problem [3]. There are some general approximation schemes.

The cell or cluster approximation in which the system is extrapolated from a few parts inside of chosen clusters whereby the approximations are made for the interaction of the cluster with the rest of the system. For example, the mean-field approach is this type of approximation.
There is also the approximate integral equations for the correlation functions or computer calculations on large systems on a microscopic scale. But also series expansions the corresponding functions and their variables.
Another approach, which is not an approximation but exact, is the renormalization group method for phase transitions which was introduce by M.E. Fisher in 1974 [2]. The method itself was introduced by Kadanoff (1966) and Wilson (1971). Nonetheless, it's hard to calculate this through exactly, one therefore needs to use some additional approximation method.

But there also has been developments of some "newer" theoretical methods of determining critcal exponents such as the so-called conformal bootstrap which is based on conformal field theory. This theory operates with scaling dimensions of local operators of this field theory for phase transitions and relates or expresses the critical exponents in terms of these scaling dimensions. This method of calculating the critical exponents has been shown to be even more accurate than older techniques [8].

Important to mention is that the theory of phase transitions and critical phenomena is not only applicable to statistical physics or condensed matter physics but also in other fields of physics such as cosmology or in biological systems. Examples being the phase transitions the universe went through [4] or the proposal of a critical point description for neural networks [7].

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