Thermodynamics of Phase Transitions III [tsc8]

This module begins by picking up a thread from part II: the discussion of the mean-field ferromagnet.

Ginzburg-Landau theory of second-order phase transitions:

Essential features of a continuous order-disorder transition (2^{nd}-order) such as realized in the mean-field model of [tln48] are encoded in the Helmholtz free energy expanded in powers of the order parameter (in scaled units):

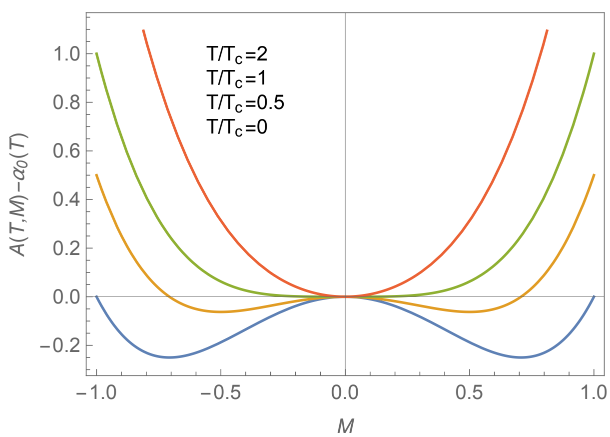
$$A(T,M) = T\left[\frac{1+M}{2}\ln\frac{1+M}{2} + \frac{1-M}{2}\ln\frac{1-M}{2}\right] - \frac{1}{2}T_{\mathrm{c}}M^2$$
$$= -T\ln 2 + \frac{1}{2}(T-T_{\mathrm{c}})M^2 + \frac{T}{12}M^4 + \ldots$$

A theory primarily concerned with the thermodynamics near continuous transitions of systems with specific order parameters can employ the Ginzburg-Landau template for the Helmholtz free energy:

$$A(T,M) = \alpha_0(T) + \alpha_2(T)M^2 + \alpha_4(T)M^4.$$

The expansion coefficients must satisfy two conditions:

$$\alpha_2(T) = \beta_2(T-T_{\mathrm{c}}), \quad \alpha_4(T) > 0.$$



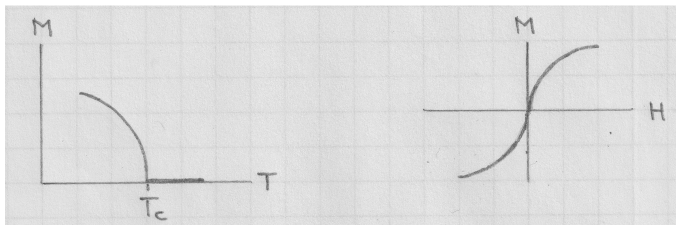
▷ Spontaneous magnetization $M(T,H=0)$:

$$H = \left(\frac{\partial A}{\partial M}\right)_T = 2\alpha_2(T)M + 4\alpha_4(T)M^3 = 0$$

$$\Rightarrow \; M(T,0) = \begin{cases} 0 & : \; T \geq T_{\mathrm{c}}, \\ \sqrt{\dfrac{\beta_2}{2\alpha_4}}(T_{\mathrm{c}}-T)^{1/2} & : \; T \leq T_{\mathrm{c}}. \end{cases}$$

▷ Critical isotherm $M(T = T_\mathrm{c}, H)$:

$$H = 2\underbrace{\alpha_2(T_\mathrm{c})}_{0}M + 4\alpha_4(T_\mathrm{c})M^3 \quad \Rightarrow \quad M(T_\mathrm{c}, H) = \left(\frac{H}{4\alpha_4(T_\mathrm{c})}\right)^{1/3}.$$



▷ Isothermal susceptibility $\chi_T(T, H = 0)$:

$$\chi_T^{-1} = \left(\frac{\partial^2 A}{\partial M^2}\right)_T = 2\alpha_2 + 12\alpha_4 M^2 = \begin{cases} 2\beta_2(T - T_\mathrm{c}) & : \ T \geq T_\mathrm{c}, \\ 4\beta_2(T_\mathrm{c} - T) & : \ T \leq T_\mathrm{c}. \end{cases}$$

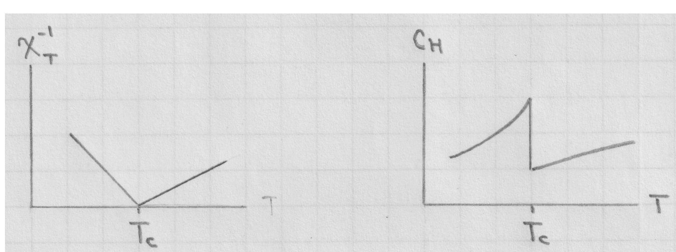
where we have used $\alpha_2 = \beta_2(T - T_\mathrm{c})$, $\quad M^2 = \dfrac{\beta_2}{2\alpha_4}(T_\mathrm{c} - T)\theta(T_\mathrm{c} - T)$.

▷ Heat capacity $C_H(T, H = 0) = -T\left(\dfrac{\partial^2 G}{\partial T^2}\right)_{H=0}$:

For the critical singularity of C_H use the expression,

$$\begin{aligned} G(T, H = 0) = A(T, M) &= \alpha_0 + \alpha_2 M^2 + \dots \\ &= \alpha_0 - \frac{\beta_2^2}{2\alpha_4}(T_\mathrm{c} - T)^2\theta(T_\mathrm{c} - T) + \dots \end{aligned}$$

Discontinuity at T_c: $\Delta C_H = C_H(T_\mathrm{c}^-) - C_H(T_\mathrm{c}^+) = T_\mathrm{c}\dfrac{\beta_2^2}{\alpha_4}$.

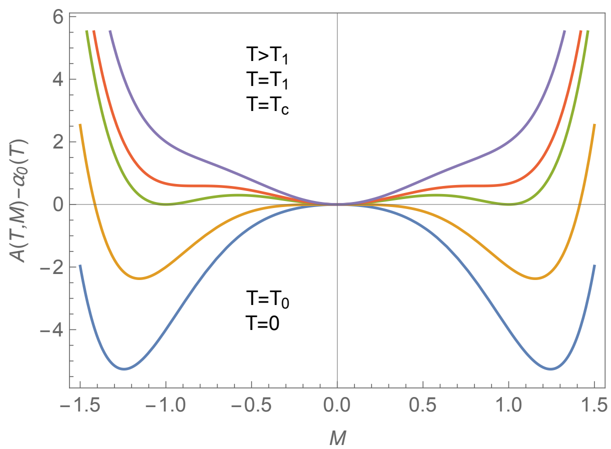


Ginzburg-Landau-theory of first-order phase transitions:

With two modifications, the expression for the Helmholtz free energy describes a discontinuous order-disorder transition (1^{st}-order):

$$A(T, M) = \alpha_0(T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 + \alpha_6(T)M^6,$$

$$\alpha_2(T) = \beta_2(T - T_0), \quad \alpha_4(T) < 0, \quad \alpha_6(T) > 0.$$



Notice the different development of the curves $A(T, M)$ versus order parameter M in situations that characterize 2^{nd}-order and 1^{st}-order transitions:[1]

– Continuous transition: Each curve has either a single minimum at $M = 0$ or a degenerate pair of minima at $\pm M \neq 0$. With T decreasing, the minimum (continuously) shifts from $M = 0$ to $M \neq 0$.
– Discontinuous transition: There is a range of T where the curve has coexisting minima at $M = 0$ and at $M \neq 0$. With T decreasing, the lower minimum (discontinuously) jumps from $M = 0$ to $M \neq 0$.

In both cases the degeneracy of the minima at $\pm M \neq 0$ are indicative of the fact that the spontaneous magnetic ordering is symmetry breaking.

Conditions for T_c in the discontinuous transition: Minima of $A(T, M)$ at $M = 0$ and at $M = \pm M_c \neq 0$ are degenerate.

$$\Rightarrow \; A(T_c, M) - \alpha_0 = 0, \quad \frac{\partial}{\partial M} A(T_c, M)\Big|_{M_c} = 0.$$

[1] In general, when expanding the free energy as a power series of the order parameter, only those terms are included which are compatible with the symmetry of the Hamiltonian.

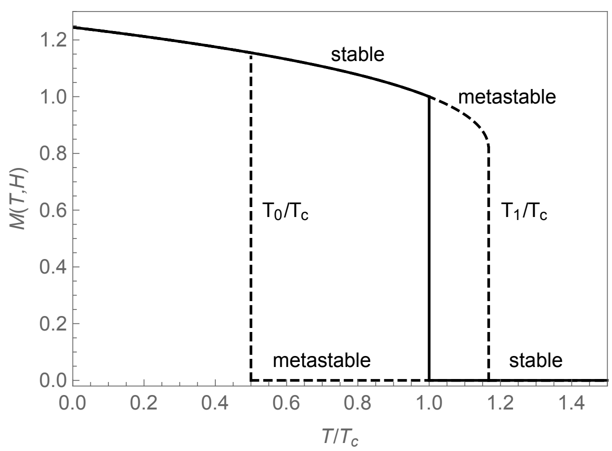
Extraction of M_c and T_c from the degeneracy condition [tex174]:

$$M_{\rm c}^2 = -\frac{\alpha_4}{2\alpha_6}, \quad T_{\rm c} = T_0 + \frac{\alpha_4^2}{4\beta_2\alpha_6}.$$

Find local extrema M_s of free-energy curves [tex174]:

▷ $M_{\rm s} = 0$ is a local minimum for $T > T_0$.

▷ $M_{\rm s}^2 = \frac{|\alpha_4|}{3\alpha_6}\left[1 + \sqrt{1 - \frac{3\alpha_2\alpha_6}{\alpha_4^2}}\right]$ is a local minimum at $T < T_1$, where $T_1 = T_0 + \frac{\alpha_4^2}{3\beta_2\alpha_6}$.



Interpretation of T-dependence of M_s:

- At least on solution exists for any T. For $T_0 < T < T_1$ both exist. The one with the lower free energy energy is stable, the other is metastable.
- Upon cooling from high T, the macrostate with $M_{\rm s} = 0$ will prevail down to T_c and may survive down to T_0.
- The system may switch to the macrostate with $M_{\rm s} = neq0$ with increasing probability between T_c and T_0. It must switch at T_0.
- Upon heating up from low T, the macrostate with $M_{\rm s} \neq 0$ will prevail up to T_c and may survive up to T_1.
- The system may switch to the macrostate with $M_{\rm s} = 0$ with increasing probability between T_c and T_1. It must switch at T_1.
- Quasi-static processes will undergo a reversible transition at T_c. Faster processes will be subject to effects of hysteresis.

Ornstein-Zernike theory for correlations:

The Ginzburg-Landau order parameter is extended into a scalar field $m(\mathbf{r})$.

Free-energy is attributed to the order-parameter field and the rate of its spatial variation. The quadratic Ginzburg-Landau term is generalized into

$$A - \alpha_0 = \tilde{b}_2 t \left[\int d^D r \big[m(\mathbf{r})\big]^2 + g \int d^D r [\nabla m(\mathbf{r})]^2 \right], \quad t \doteq \frac{|T - T_\mathrm{c}|}{T_\mathrm{c}}.$$

Fourier transform in D-dimensional space:

$$\tilde{m}(\mathbf{q}) = \int d^D r\, m(\mathbf{r})\, e^{\imath \mathbf{q}\cdot\mathbf{r}} \quad \Leftrightarrow \quad m(\mathbf{r}) = \int \frac{d^D q}{(2\pi)^D} \tilde{m}(\mathbf{q})\, e^{-\imath \mathbf{q}\cdot\mathbf{r}}.$$

$$\Rightarrow \; A - \alpha_0 = \int \frac{d^D q}{(2\pi)^D} \big|\tilde{m}(\mathbf{q})\big|^2 \Big[\tilde{b}_2 t + g q^2\Big].$$

The quadratic dependence of A on $\tilde{m}(\mathbf{q})$ is used to justify equipartition:

$$\big|\tilde{m}(\mathbf{q})\big|^2 \Big[\tilde{b}_2 t + g q^2\Big] = k_\mathrm{B} T.$$

Order-parameter correlation function:

$$\Gamma(\mathbf{r}) \doteq \langle m(\mathbf{r}) m(0)\rangle - \langle m(\mathbf{r})\rangle\langle m(0)\rangle.$$

Structure factor (via Fourier transform):

$$\tilde{\Gamma}(\mathbf{q}) = \big|\tilde{m}(\mathbf{q})\big|^2 = \frac{k_\mathrm{B} T}{\tilde{b}_2 t + g q^2}.$$

Ornstein-Zernike correlations: $\Gamma(\mathbf{r}) \sim \begin{cases} \dfrac{e^{-r/\xi}}{r^{D-2}} & : \; T \neq T_\mathrm{c}, \\ \dfrac{1}{r^{D-2}} & : \; T = T_\mathrm{c}. \end{cases}$

Correlation length: $\xi = \sqrt{\dfrac{g T_\mathrm{c}}{\tilde{b}_2 |T - T_\mathrm{c}|}}$.

Low-dimensional systems ($D \leq 2$) are known to be strongly fluctuating. For them the Ornstein-Zernike theory is not applicable.

Critical-point exponents:

Thermodynamic systems at critical points are highly sensitive to specific perturbations and exhibit an enhanced level of fluctuations.

Response functions tend to diverge at critical points and thermodynamic functions tend to have cusp singularities.

Basic types of singularities:

(a) power-law divergence: $f(\epsilon) = A_{\pm}|\epsilon|^{\lambda} + \ldots \qquad (\lambda < 0)$

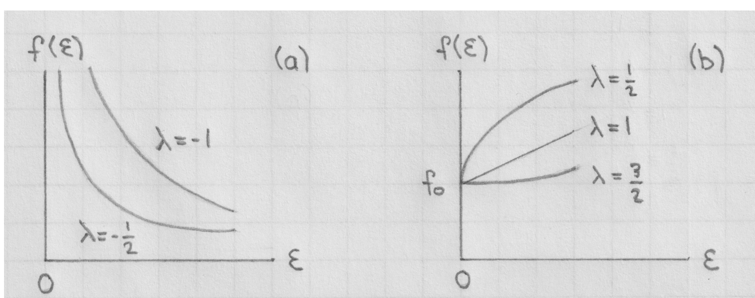
(b) power-law cusp: $f(\epsilon) = f_0 + A_{\pm}|\epsilon|^{\lambda} + \ldots \qquad (\lambda > 0)$

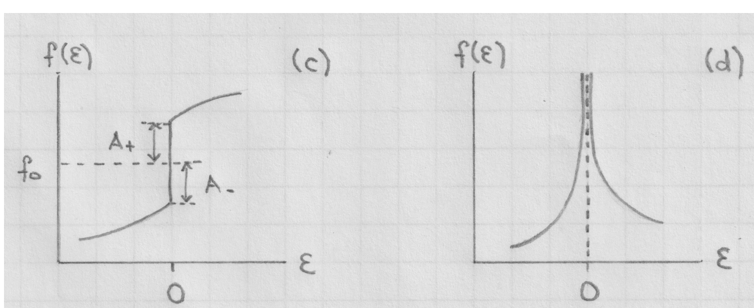
(c) discontinuity: $f(\epsilon) = f_0 + \lim_{\lambda \to 0} A_{\pm}|\epsilon|^{\lambda} + \ldots$

(d) logarithmic singularity: $f(\epsilon) = \lim_{\lambda \to 0} \frac{A_{\pm}}{\lambda}\left[|\epsilon|^{\lambda} - 1\right] = A_{\pm}\big|\ln|\epsilon|\big|$

Here ϵ stands for a deviation of a thermodynamic variable from its critical-point value. In some cases, only positive or only negative ϵ are realized.

The critical amplitudes A_+ and A_- for $\epsilon > 0$ and $\epsilon < 0$, respectively, or often not the same. The critical-point exponent λ may be different for $\epsilon > 0$ and $\epsilon < 0$ as well, but that is rarely the case.





Critical singularities of magnetic system:

The control variables are T (temperature) and H (magnetic field).

The order parameter is the spontaneous magnetization M.

Scaled temperature: $\tau \doteq \dfrac{T - T_c}{T_c}$.

Heat capacity: $C_H \sim \begin{cases} A|\tau|^{-\alpha} & : \ \tau > 0, \\ A'|\tau|^{-\alpha'} & : \ \tau < 0, \end{cases} \qquad H = 0.$

Order parameter: $M \sim B|\tau|^{\beta}, \quad T < T_c, \quad H = 0.$

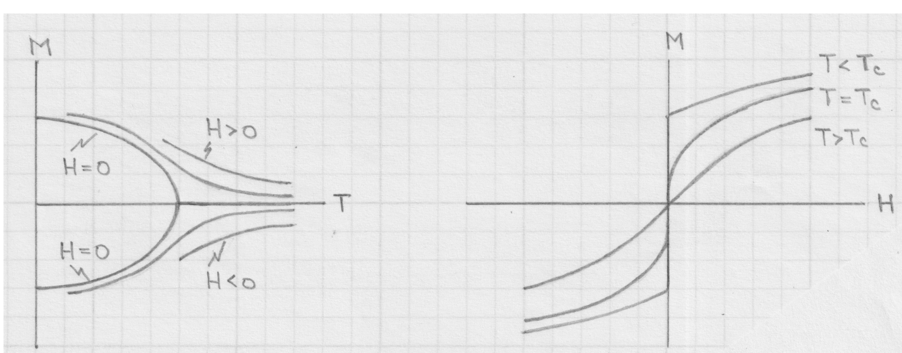
Susceptibility: $\chi_T \sim \begin{cases} C|\tau|^{-\gamma} & : \ \tau > 0, \\ C'|\tau|^{-\gamma'} & : \ \tau < 0, \end{cases} \qquad H = 0.$

Critical isotherm: $M \sim DH^{1/\delta}, \quad T = T_c.$

Correlation function: $\Gamma(r) \sim \begin{cases} \dfrac{e^{-r/\xi}}{r^{D-2}} & : \ T \neq T_c, \\ \dfrac{1}{r^{D-2+\eta}} & : \ T = T_c \quad H = 0. \end{cases}$

Correlation length: $\xi \sim |\tau|^{-\nu}$.

Emergent singularities characterized by exponents β and δ:



Critical singularities of fluid system:

The control variables are T (temperature) and p (pressure).

The order parameter is the scaled density difference: $\dfrac{\rho_\mathrm{l}-\rho_\mathrm{g}}{\rho_\mathrm{c}}$.

Scaled temperature: $\tau \doteq \dfrac{T-T_\mathrm{c}}{T_\mathrm{c}}$.

Heat capacity: $C_p \sim \begin{cases} A|\tau|^{-\alpha} & : \tau > 0, \\ A'|\tau|^{-\alpha'} & : \tau < 0, \end{cases} \qquad p = p_\mathrm{c}.$

Order parameter: $\dfrac{\rho_\mathrm{l}-\rho_\mathrm{g}}{\rho_\mathrm{c}} \sim B|\tau|^\beta, \quad T < T_\mathrm{c}, \quad p = p_\mathrm{c}.$

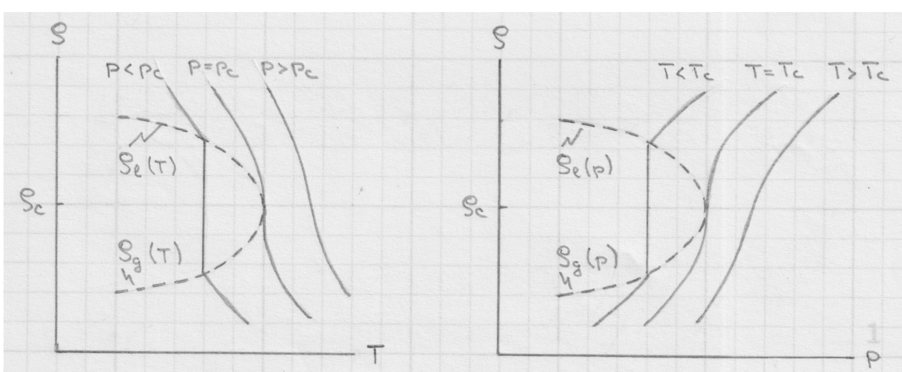
Compressibility: $\kappa_T \sim \begin{cases} C|\tau|^{-\gamma} & : \tau > 0, \\ C'|\tau|^{-\gamma'} & : \tau < 0, \end{cases} \qquad p = p_\mathrm{c}.$

Critical isotherm: $\left|\dfrac{\rho-\rho_\mathrm{c}}{\rho_\mathrm{c}}\right| \sim D\left|\dfrac{p-p_\mathrm{c}}{p_\mathrm{c}}\right|^{1/\delta}, \quad T = T_\mathrm{c}.$

Correlation function: $\Gamma(r) \sim \begin{cases} \dfrac{e^{-r/\xi}}{r^{D-2}} & : T \neq T_\mathrm{c}, \\ \dfrac{1}{r^{D-2+\eta}} & : T = T_\mathrm{c} \quad p = p_\mathrm{c}. \end{cases}$

Correlation length: $\xi \sim |\tau|^{-\nu}$.

Emergent singularities characterized by exponents β and δ:



Inequalities for critical-point exponents:

The exponents identified identified above for critical-point singularities cannot assume just any values. They are constrained in a number of different ways, which includes thermal equilibrium and stability conditions.

These constraints manifest themselves as inequalities that must be satisfied two or three exponents. For the sake of simplicity (with only a minor sacrifice of rigor) we do not distinguish between primed and unprimed exponents here.

The five must important inequalities are the following:

- ▷ $\alpha + 2\beta + \gamma \geq 2$
- ▷ $\alpha + \beta(\delta + 1) \geq 2$
- ▷ $\gamma \geq \beta(\delta - 1)$
- ▷ $\gamma \leq (2 - \eta)\nu$
- ▷ $D\nu \geq 2 - \alpha$ (D is the dimensionality of the space)[2]

The derivation of the first inequality is outlined here as an example:

– Use a well-established thermodynamic relation:

$$C_H - C_M = \frac{T\alpha_H^2}{\chi_T}, \quad \alpha_H \doteq -\left(\frac{\partial M}{\partial T}\right)_H .$$

– Use a thermal stability condition: $C_M \geq 0 \quad \Rightarrow \ C_H \geq \dfrac{T\alpha_H^2}{\chi_T}$.

– Set $H = 0$, take the limit $T \to T_c^-$, and identify the singularities:

$$C_H \sim |\tau|^{-\alpha}, \quad \chi_T \sim |\tau|^{-\gamma}, \quad M \sim |\tau|^{\beta} \quad \Rightarrow \ \alpha_H \sim |\tau|^{\beta-1}.$$

– Invoke lemma: if $f_1(x) \sim x^{\lambda_1}$, $f_2(x) \sim x^{\lambda_2}$ and $f_1(x) \leq f_2(x)$, it follows that $\lambda_1 \geq \lambda_2$.

– Immediate consequence: $-\alpha - \gamma \leq 2(\beta - 1)$.

– Resulting exponent inequality: $\alpha + 2\beta + \gamma \geq 2$.

The *scaling hypothesis* assumes that thermodynamic quantities near criticality can be accurately represented by generalized homogeneous functions.

The scaling hypothesis upgrades the exponent inequalities to exponent equalities named *scaling laws*.

[2]See section on marginal dimensionality below.

Test of scaling laws:

The Ginzburg-Landau theory with Ornstein Zernike extension discussed earlier predict the following set of critical-point exponents:

$$\alpha = 0, \quad \beta = \frac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \eta = 0, \quad \nu = \frac{1}{2},$$

where the exponent $\alpha = 0$ is associated with a discontinuity.

The first four of this set of *classical* exponents are also realized in the mean-field model for the ferromagnet discussed previously and in the van der Waals gas as worked out in [tex175].

The classical exponents satisfy the first four scaling laws. The last scaling law is satisfied for the (marginal) dimensionality $D = 4$ only.

One prominent exactly solvable statistical mechanical model that undergoes a second-order phase transition is the Ising model in $D = 2$ dimensions. Its set of critical-point exponents,

$$\alpha = 0, \quad \beta = \frac{1}{8}, \quad \gamma = \frac{7}{4}, \quad \delta = 15, \quad \eta = \frac{1}{4}, \quad \nu = 1,$$

where the exponent $\alpha = 0$ is associated with a logarithmic singularity, satisfies all five scaling laws.

Note of caution: For critical points at $T = 0$, which do exist, some of the scaling laws must be modified due to confluent power-law terms associated with temperature.

Marginal dimensionality:

In studies of critical phenomena, $D = 4$ has been identified as a marginal dimensionality for systems with short-range interactions. It delimits regimes of qualitatively different impact of thermal fluctuations.

Estimate of the contribution ΔA from fluctuations to the Helmholtz free energy near criticality:

- equipartition estimates fluctuation energy: $\Delta\epsilon \sim k_B T$.
- correlation length estimates volume of fluctuation: $\Delta V \sim \xi^D$.
- correlation length diverges at criticality: $\xi \sim |\tau|^{-\nu}$.
- Prediction for free-energy fluctuations: $\Delta A \sim |\tau|^{D\nu}$.
- Heat capacity near criticality: $C_V \sim |\tau|^{-\alpha}$.

– Heat capacity (response function) is second derivative of free energy.

– Prediction for free energy: $A \sim |\tau|^{2-\alpha}$.

– Condition for mean-field validity near criticality: $\Delta A \ll A$,

– Implied exponent inequality: $D\nu > 2 - \alpha$.

– Marginal dimensionality: $D_{\mathrm{marg}} = \dfrac{2-\alpha}{\nu}$.

– Value for short-range interactions: $\alpha_{\mathrm{TM}} = 0,\ \nu_{\mathrm{TM}} = \frac{1}{2} \quad \Rightarrow\ D_{\mathrm{marg}} = 4$.

Longer-range interactions tend to suppress thermal fluctuations, which may lower the value of the marginal dimensionality. Example: $D_{\mathrm{marg}} = 3$ for spontaneous magnetic ordering caused by magnetic dipole interaction.

The theory of phase transitions distinguishes between upper and lower marginal dimensionalities. Only the former has been discussed here.

At the lower marginal dimensionality, fluctuations have become too strong to facilitate spontaneous ordering at any nonzero temperature.