7 Mean Field Theory of Phase Transitions: Summary

• van der Waals system: The van der Waals equation of state may be written \( p = \frac{RT}{v-b} - \frac{a}{v^2} \), where \( v \) is the molar volume. Comparing with the ideal gas law \( p = RT/v \), the vdW equation accounts for (i) an excluded volume effect due to finite molecular size, and (ii) a long-distance attraction between molecules. The energy per mole is \( \varepsilon(T,v) = \frac{1}{2} fRT - a v^2 \), where \( f \) is the number of independent quadratic terms in the individual molecular Hamiltonian.

At fixed \( T \), \( p(v) \) is monotonic and decreasing for \( T > T_c = \frac{8a}{27bR} \). For \( T < T_c \), the pressure is no longer monotonic, and \( p'(v) \) vanishes at two points \( v_\pm(T) \). For \( v \in [v_-, v_+] \), the isothermal compressibility \( \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T \) is negative, indicating an absolute thermodynamic instability. From \( p(v,T) \) and \( \varepsilon(v,T) \), one can derive the molar free energy

\[
\hat{f}(T,v) = -RT \ln \left( \frac{Tf(v-b)}{2} \right) - a v - Ts_0
\]

where \( s_0 \) is a constant. Analyzing \( \hat{f}(T,v) \), one finds an even wider range of instability applies, with \( v_\ell < v_- < v_+ < v_g \), where the extremal liquid and gas volumes are determined by the coupled equations

\[
p(T,v_\ell) = p(T,v_g) \quad ; \quad \int_{v_\ell}^{v_g} dv p(T,v) = (v_g - v_\ell) p(T,v_\ell) .
\]

The Maxwell construction extends \( f(T,v) \) by a straight line connecting \( f(T,v_\ell) \) and \( f(T,v_g) \), resulting in the isotherms in Fig. 1. This corresponds to a two phase region in which the homogeneous phase is unstable, either to nucleation, which requires surmounting an energy barrier, or spinodal composition, which is a spontaneous process.

• Lattice gas model: For interactions consisting of a hard core and a weakly attractive tail, such as the Lennard-Jones potential, one can imagine discretizing space into unit cells on the scale of the core size \( a \). Each cell \( i \) can then accommodate either zero or one particle. The resulting Hamiltonian is an Ising ferromagnet,

\[
\hat{H} = -\sum_{i<j} J_{ij} \sigma_i \sigma_j - H \sum_i \sigma_i ,
\]

with \( \sigma_i = \pm 1 \), \( J_{ij} = -\frac{1}{4} V(R_i - R_j) \), and \( H = \frac{1}{2} k_B T \ln \left( \frac{e^{\mu/k_BT}}{\lambda_d^d} \right) \). The correspondences between the ferromagnet and the liquid-gas system are then \( v \) (or \( n \)) \( \leftrightarrow \) \( m \), with \( m = M/N \) the magnetization per site, and \( p \) (or \( \mu \)) \( \leftrightarrow \) \( H \). The isothermal compressibility \( \kappa_T \) is analogous to the isothermal magnetic susceptibility \( \chi_T = \left( \frac{\partial m}{\partial H} \right)_T \). At the critical point, \( \kappa_T(T_c,p_c) = \infty \leftrightarrow \chi_T(T_c,H_c) = \infty \). See Fig. 2.
• **Mean field theory:** Consider the Ising model, \( H = -J \sum_{ij} \sigma_i \sigma_j - H \sum_i \sigma_i \). On each site \( i \), write \( \sigma_i = m + \delta \sigma_i \), where \( m = \langle \sigma_i \rangle \). Then \( \sigma_i \sigma_j = -m^2 + m(\sigma_i + \sigma_j) + \delta \sigma_i \delta \sigma_j \), and neglecting the term quadratic in the fluctuations, we arrive at the mean field Hamiltonian,

\[
\hat{H}_{MF} = \frac{1}{2} N z J m^2 - (H + z J m) \sum_i \sigma_i ,
\]

where \( z \) is the lattice coordination number.

This corresponds to independent spins in an effective field \( H_{eff} = H + z J m \). For non-interacting spins in an external field, we have \( m = \tanh(H_{eff}/k_B T) \), i.e.

\[
m = \tanh \left( \frac{H + z J m}{k_B T} \right) ,
\]

which is a self-consistent equation for \( m(T, H) \). This equation also follows from extremizing the mean field free energy, given by \( F = -k_B T \ln \text{Tr} e^{-\hat{H}_{MF}/k_B T} \). It is convenient to dimensionalize by writing \( f = F/zJN, h = H/zJ, \) and \( \theta = k_B T/zJ \). Then

\[
f(m, T, h) = \frac{1}{2} m^2 - \theta \ln \cosh \left( \frac{m + h}{\theta} \right) - \theta \ln 2
\]

\[
= f_0 + \frac{1}{4} (\theta - 1) m^2 + \frac{1}{12} m^4 - hm + \ldots ,
\]

where the second line is an expansion for small \( m \) and \( h \). The dimensionless mean field equation is \( m = \tanh ((m + h)/\theta) \). When \( h = 0 \), we have \( m = \tanh(m/\theta) \), and for \( \theta > \theta_c \), where \( \theta_c = 1 \) (i.e. \( T_c = z J/k_B \)), there is only one solution at \( m = 0 \). For \( \theta < \theta_c \), there are two additional broken symmetry solutions at \( m = \pm m_0 \), and one can check that they correspond to minima in the free energy, whereas \( m = 0 \) is a local maximum. Just below \( \theta_c \), one finds \( m(\theta) = \sqrt{3(1-\theta)} \propto (\theta_c - \theta)^{\beta} \), where \( \beta = \frac{1}{2} \) is the mean field order parameter exponent.

An order parameter is a quantity which vanishes throughout a disordered phase, usually at high temperature, but which spontaneously breaks a global symmetry to take a finite value in the ordered phase. For the Ising ferromagnet, the order parameter is \( m \), the local magnetization. The global symmetry of the Ising model in zero external field is the \( \mathbb{Z}_2 \) symmetry associated with flipping all the spins: \( \sigma_i \rightarrow -\sigma_i \) for all \( i \). An external field explicitly breaks this symmetry. For a given system, there may be several distinct ordered phases and a cascade of symmetry-breaking transitions as temperature is lowered.

Again setting \( h = 0 \), we see that \( f(\theta > \theta_c) = f_0 \), while \( f(\theta < \theta_c) = f_0 - \frac{3}{4} (\theta_c - \theta)^2 \) just below the transition. Thus, there is a jump in the specific heat \( c = -\theta \frac{\partial^2 f}{\partial \theta^2} \) at the transition,
Figure 3: Phase diagram for the Ising ferromagnet. In the hatched blue region, the mean field equations have three solutions. Along the boundary dashed green line, where is a saddle-node bifurcation so that there is a unique solution to the MF equations in the white region. The thermodynamic properties are singular, with discontinuous magnetization, along the solid black line, which terminates in the critical point at \((\theta, h) = (1, 0)\).

with \(\Delta c = -\frac{3}{2}\). Very close to the transition, we therefore have \(c(T) \propto |\theta - \theta_c|^{-\alpha}\), where the mean field value of the exponent is \(\alpha = 0\).

As we increase \(|h|\) from zero, two of the solutions merge and eventually annihilate at \(h^*(\theta)\), leaving a unique solution for \(h > h^*(\theta)\), as depicted in Fig. 3. For small \(m\) and \(h\), setting \(\frac{\partial f}{\partial m} = 0\), we obtain \(\frac{1}{3}m^3 + (\theta - 1)m - h = 0\). Thus, when \(\theta\) is just above \(\theta_c = 1\), we have \(m = h/(\theta - 1)\), hence the susceptibility is \(\chi = \frac{\partial m}{\partial h} \propto |\theta - \theta_c|^{-\gamma}\), where \(\gamma = 1\) is the mean field susceptibility exponent. The same power law behavior is found for \(\theta < \theta_c\); one finds \(m(\theta) = m_0(\theta) + \frac{h}{2(1-\theta)}\). Finally, if we fix \(\theta = \theta_c\), we have \(m(\theta_c, h) \propto h^{1/\delta}\) with \(\delta = 3\). The quantities \(\alpha, \beta, \gamma,\) and \(\delta\) are critical exponents for the Ising transition. Mean field theory becomes exact when the number of neighbors is infinite, which arises in two hypothetical settings: (i) infinite range interactions, or (ii) infinite spatial dimension.

A phenomenological model for magnetization dynamics takes \(\frac{\partial m}{\partial t} = -\frac{\partial f}{\partial m}\), so \(m\) is dissipatively driven to a local minimum of the free energy. This is a simple dynamical system with control parameters \((\theta, h)\). For \(h = 0\), the point \(\theta = \theta_c\) corresponds to a supercritical pitch-fork bifurcation, and more generally there is a imperfect bifurcation everywhere along the curve \(h = h^*(\theta)\), defined by the simultaneous vanishing of both \(\partial f/\partial m\) and \(\partial^2 f/\partial m^2\), corresponding to the dashed green curve in Fig. 3. This leads to the phenomenon of hysteresis: a protocol in which the control parameters cross both branches of this curve is irreversible.

Variational density matrix: The free energy is given by \(F = \text{Tr}(\rho \hat{H}) + k_B T \text{Tr}(\rho \ln \rho)\). Extremizing \(F\) with respect to \(\rho\) subject to the normalization condition \(\text{Tr} \rho = 1\) yields the equilibrium Gibbs distribution \(\rho = Z^{-1} e^{-\beta \hat{H}}\). Any distribution other than that of Gibbs will yield a larger value of \(F\). Therefore, we can construct a variational Ansatz for \(\rho\) and minimize \(F\) with respect to its variational parameters. For example, in the case of the Ising model \(\hat{H} = -\sum_{i<j} J_{ij} \sigma_i \sigma_j - H \sum_i \sigma_i\), then assuming translational invariance \(J_{ij} = J(|R_i - R_j|)\), we write \(\rho_{\text{var}}(\sigma_1, \ldots, \sigma_N) = \prod_{i=1}^N \tilde{\rho}(\sigma_i)\), with

\[
\tilde{\rho}(\sigma) = \frac{1 + m}{2} \delta_{\sigma,1} + \frac{1 - m}{2} \delta_{\sigma,-1}.
\]
Adimensionalizing by writing $\theta = k_B T/J(0)$ and $h = H/J(0)$ with $J(0) = \sum_j J_{ij}$, one finds the variational free energy is

$$f(m, \theta, h) = -\frac{1}{2} m^2 - hm + \theta \left\{ \left(\frac{1+m}{2}\right) \ln \left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right) \ln \left(\frac{1-m}{2}\right) \right\}$$

$$= -\theta \ln 2 - hm + \frac{1}{2} (\theta - 1) m^2 + \frac{\theta}{12} m^4 + \frac{\theta}{30} m^6 + \ldots$$

Extremizing with respect to $m$ yields the same equation as before: $m = \tanh ((m + h)/\theta)$. One can prove that this variational density matrix formulation of mean field theory yields identical results to the "neglect of fluctuations" method described above.

- **Landau theory of phase transitions**: The basic idea is to write a phenomenological expansion of the free energy in powers of the order parameter(s) of a system, with coefficients depending on quantities such as temperature and field, and keeping terms only up to some low order. On then analyzes how the minima of the resulting finite degree polynomial behave as a function of these coefficients. The simplest case is that of a model with Ising symmetry, where the order parameter is a real scalar quantity $m$. One writes

$$f = f_0 + \frac{1}{2}a m^2 + \frac{1}{4} b m^4 - hm,$$

with $b > 0$ for stability. Extremizing with respect to $m$ yields $am + bm^3 - h = 0$. For $a > 0$ there is a unique solution to this equation for $m(h)$, but for $a < 0$ there are three roots when $|h| < h^*(a)$, with $h^*(a) = \frac{2}{3\sqrt{3}} b^{-1/2} (-a)^{3/2}$. For $h = 0$, one has $m(a > 0) = 0$ and $m(a < 0) = \pm \sqrt{-a/b}$. Thus, $a_c = 0$ is the critical point in zero field.

For certain systems, such as the liquid-gas transition, there is no true Ising symmetry between the two homogeneous phases. The order parameter, which can taken to be proportional to the density relative to that at the critical point, is again a real scalar. With no $Z_2$ symmetry, we write

$$f = f_0 + \frac{1}{2}a m^2 - \frac{1}{3} y m^3 + \frac{1}{4} b m^4,$$

with $b > 0$ and $y > 0$. Extremizing yields $(a - ym + bm^2) m = 0$, which has three roots, one at $m = 0$ and the other two at $m = m_{\pm} = \frac{y}{2b} \pm \sqrt{\left(\frac{y}{2b}\right)^2 - \frac{a}{b}}$. The situation is as depicted in Fig. 4. For $y^2 > 4ab$ only the $m = 0$ root is real. For $4ab < y^2 < \frac{9}{8}ab$, all three roots are real, but the minimum of $f$ remains at $m = 0$. For $y^2 > \frac{9}{8}ab$, all three roots are real, with a global minimum at $m = m_+$ and a local one at $m = m_-$. Thus, along the curve $y^2 = \frac{9}{8}ab$, there is a discontinuous change in the order parameter, between $m = 0$ and $m = 3a/y$, which is the hallmark of a first order phase transition. Note that this occurs for $a > 0$, before the coefficient of the quadratic term in $f(m)$ has changed sign. One says in this case that the first order transition preempts the second order one.

![Figure 4: Behavior of the quartic free energy](image-url)
• **Mean field theory of fluctuations:** For the Ising model, \( \hat{H} = -\sum_{i<j} J_{ij} \sigma_i \sigma_j - \sum_i H_i \sigma_i \), now with local fields \( H_i \), the local magnetization is \( m_i = \langle \sigma_i \rangle = -\frac{\partial F}{\partial H_i} \). The susceptibility, given by \( \chi_{ij} = \frac{\partial m_i}{\partial m_j} \), is an example of a thermodynamic response function. In equilibrium, it is related to the correlation function,

\[
C_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle,
\]

with \( C_{ij} = k_B T \chi_{ij} \). Within mean field theory, this relation no longer applies, and it is the response functions which are more accurately represented: the usual MF description treats each site as independent, hence \( C_{ij}^{MF} = 0 \) (!) To compute \( \chi_{ij}^{MF} \), take a variational density matrix which is a product of single-site ones, as above, where the local magnetization is \( m_i \). Extremizing the resulting free energy with respect to each \( m_i \) yields a set of coupled nonlinear equations,

\[
m_i = \tanh \left( \frac{\sum_j J_{ij} m_j + H_i}{k_B T} \right).
\]

Expanding for small fields and magnetizations, one obtains \( \sum_j (k_B T \delta_{ij} - J_{ij}) m_j = H_i \), hence \( \chi_{ij} = \frac{\partial m_i}{\partial m_j} = (k_B T \cdot \mathbb{I} - \mathbb{J})^{-1} \). For translationally invariant systems, the eigenvectors of the matrix \( J_{ij} \) are plane waves \( \psi_{q,i} = e^{iq \cdot R} \), and one has

\[
\hat{m}(q) = \frac{\hat{H}(q)}{k_B T - J(q)} \quad \Rightarrow \quad \hat{\chi}(q) = \frac{\partial \hat{m}(q)}{\partial \hat{H}(q)} = \frac{1}{k_B T - J(q)},
\]

where \( \hat{J}(q) = \sum_R J(R) e^{-iq \cdot R} \). The mean field value of \( T_c \) is then \( \hat{J}(Q) \), where \( q = Q \) is the ordering wavevector which maximizes \( \hat{J}(q) \). For a ferromagnet, which is dominated by positive values of \( J_{ij} \), one has \( Q = 0 \), and expanding about this point one may write \( \hat{J}(q) = k_B T_c - Cq^2 + \ldots \), in which case \( \chi(q) \propto (\xi^{-2} + q^2)^{-1} \) at long wavelengths, which is of the Ornstein-Zernike (OZ) form.

• **Global symmetries:** A global symmetry is an operation carried out equally at every point in space (continuous systems) or in every unit cell of the lattice (discrete systems) such that the Hamiltonian is left invariant. The symmetry operations comprise a group \( G \). In the absence of a symmetry-breaking external field, Ising systems have symmetry group \( \mathbb{Z}_2 \). The \( p \)-state clock model has symmetry group \( \mathbb{Z}_p \). The \( q \)-state Potts model has symmetry group \( S_q \) (the permutation group on \( q \) elements). In each of these cases, the group \( G \) is discrete. Examples of models with continuous symmetries include the \( XY \) model \( (G = \mathbb{O}(2)) \), the Heisenberg model \( (G = \mathbb{O}(3) \text{ or } \mathbb{O}(n)) \), the Standard Model of particle physics \( (G = SU(3) \times SU(2) \times U(1)) \), etc. Depending on whether \( G \) is discrete or continuous, and on the dimension of space, there may be no ordered phase possible. The lower critical dimension \( d_c \) of a model is the dimension at or below which there is no spontaneous symmetry breaking at any finite temperature. For systems with discrete global symmetries, \( d_c = 1 \). For systems with continuous global symmetries, \( d_c = 2 \). The upper critical dimension \( d_u \) is the dimension above which mean field exponents are exact. This depends on structure of the model itself, and not all models have a finite upper critical dimension.
• **Random systems**: A system with quenched randomness orders in a different way than a pure one. Typically the randomness may be modeled as a weak symmetry breaking field that is spatially varying, but averages to zero on large scales. Imry and Ma (1975) reasoned that such a system could try to lower its energy by forming domains in which the order parameter takes advantage of local fluctuations in the random field. If the size of these domains is $L_d$, then the rms fluctuations of the random field integrated over a single domain are proportional to $L_d^{d/2}$, where $d$ is the dimension of space. By aligning the order parameter in each domain with the direction of the average field there in, one lowers the energy by

$$E_{\text{bulk}} \approx -H_{\text{rms}} \left( \frac{L_d}{a} \right)^{d/2} \text{ per domain},$$

where $a$ is a microscopic length. The surface energy of a single domain is

$$E_{\text{surf}} \approx J \left( \frac{L_d}{a} \right)^{d-\sigma},$$

where $\sigma = 1$ if the global symmetry is discrete and $\sigma = 2$ if it is continuous. This follows from a simple calculation of the associated domain wall energy. Dividing by the number of atoms (or unit cells) in a domain $(L_d/a)^d$, one obtains the energy density,

$$f \approx J \left( \frac{a}{L_d} \right)^{\sigma} - H_{\text{rms}} \left( \frac{a}{L_d} \right)^{d/2}.$$

For $d < 2\sigma$ the surface term $(\propto J)$ dominates for small $L_d$ and the bulk term for large $L_d$. The energy has a minimum at $L_d \approx a (2\sigma J/dH_{\text{rms}})^{2/(2\sigma-d)}$. Thus, for $d < 2\sigma$ the ordered state is always unstable to domain formation in the presence of a random field. For $d > 2\sigma$, the relevant dominance of the two terms is reversed, and the minimum becomes a maximum. There are then two possibilities, depending on the relative size of $J$ and $H_{\text{rms}}$. The smallest allowed value for $L_d$ is the lattice scale $a$, in which case $f(L_d = a) \approx J - H_{\text{rms}}$. Comparing with $f(L_d = \infty) = 0$, we see that if the random field is weak, so $J > H_{\text{rms}}$, the minimum energy state occurs for $L_d = \infty$, i.e. the system has an ordered ground state. We then expect a finite critical temperature $T_c > 0$ for a transition to a high $T$ disordered state. If on the other hand the random field is strong and $J < H_{\text{rms}}$, then the energy is minimized for $L_d = a$, meaning the ground state of the system is disordered down to the scale of the lattice spacing. In this case there is no longer any finite temperature phase transition, because there is no ordered phase.

• **Ginzburg-Landau theory**: Allow the order parameter to vary in space. The free energy is then a functional of $m(x)$:

$$F[m(x), h(x)] = \int dx \left\{ f_0 + \frac{1}{2}a m^2 + \frac{1}{4}b m^4 - h m + \frac{1}{2}\kappa (\nabla m)^2 + \ldots \right\}.$$ 

Extremize $F$ by setting the functional derivative $\delta F/\delta m(x)$ to zero, resulting in

$$am + bm^3 - hm - \kappa \nabla^2 m = 0.$$ 

---

Figure 5: Left panel: Imry-Ma domains for an O(2) model. The arrows point in the direction of the local order parameter field $\langle \Omega(r) \rangle$. Right panel: free energy density as a function of domain size $L_d$. Note $L_d > a$ always.
For $a > 0$ and small $h$ (take $b,c > 0$) then $m$ is small, and one has $(a - \kappa \nabla^2) m = h$, hence $\tilde{m}(q) = \hat{h}(q)/(a + \kappa q^2)$, which is of the OZ form. If $a < 0$, write $m(x) = m_0 + \delta m(x)$, and for small $|a|$ find $m_0^2 = -a/3b$ and $\tilde{m}(q) = \hat{h}(q)/(-2a + \kappa q^2)$. Deeper in the ordered ($a < 0$) phase, and for $h = 0$, one can envisage a situation where $m(x)$ interpolates between the two degenerate values $\pm m_0$. Assuming the variation occurs only along one direction, one can solve $am + bm^3 - \kappa d^2 m/dx^2 = 0$ to obtain $m(x) = m_0 \tanh(x/\sqrt{2}\xi)$, where the \textit{coherence length} is $\xi = (\kappa/|a|)^{1/2}$.

- \textit{Ginzburg criterion}: The actual Helmholtz free energy, which we will here call $A(T,H,V,N)$, is obtained by performing a functional integral over the order parameter field. The partition function is $Z = e^{-\beta A} = \int Dm e^{-\beta F|m(x)|}$. Near $T_c$, we are licensed to keep only up to quadratic terms in $m$ and its gradients in $F[m]$, resulting in

$$A = \frac{1}{2} k_B T \sum_q \ln \left( \frac{a + \kappa q^2}{\pi k_B T} \right).$$

Let $a(t) = \alpha t$ with $t \equiv (T - T_c)/T_c$, and let $\Lambda^{-1}$ be the microscopic (lattice) cutoff. The specific heat is then (for $t > 0$):

$$c = -\frac{1}{V A^d} \frac{\partial^2 A}{\partial T^2} = \frac{\alpha^2 \Lambda^{-d}}{2\kappa^2} \int \frac{d^d q}{(2\pi)^d} \frac{1}{(\xi^{-2} + q^2)^2} \sim \begin{cases} \text{const.} & \text{if } d > 4 \\ -\ln t & \text{if } d = 4 \\ t^{d-2} & \text{if } d < 4, \end{cases}$$

with $\xi = (\kappa/\alpha |t|)^{1/2} \propto |t|^{-1/2}$.

The upper critical dimension is $d_u = 4$. For $d > 4$, mean field theory is qualitatively accurate, with finite corrections. In dimensions $d \leq 4$, the mean field result is overwhelmed by fluctuation contributions as $t \to 0^+$ (i.e. as $T \to T_c^+$). We see that MFT is sensible provided the fluctuation contributions are small, i.e. provided

$$R^{-4} a^d \xi^{4-d} \ll 1,$$

with $R = (\kappa/\alpha)^{1/2}$, which entails $t \gg t_c$, where

$$t_c = (\frac{a}{R})^{\frac{4-d}{d}}.$$

is the \textit{Ginzburg reduced temperature}. The criterion for the sufficiency of mean field theory, namely $t \gg t_c$, is known as the \textit{Ginzburg criterion}. The region $|t| < t_c$ is known as the \textit{critical region}. In a lattice ferromagnet, $R \sim a$ is on the scale of the lattice spacing itself, hence $t_c \sim 1$ and the critical regime is very large. Mean field theory then fails quickly as $T \to T_c$. In a (conventional) three-dimensional superconductor, $R$ is on the order of the Cooper pair size, and $R/a \sim 10^2 - 10^3$, hence $t_c = (a/R)^6 \sim 10^{-18} - 10^{-12}$ is negligibly narrow. The mean field theory of the superconducting transition – BCS theory – is then valid essentially all the way to $T = T_c$. 

7