7.10: Appendix II- Additional Examples

Blume-Capel model

The Blume-Capel model provides a simple and convenient way to model systems with vacancies. The simplest version of the model is written

$$\hat{H}=-\frac{1}{2}\sum_{i,j} J_{ij}\,S_i\,S_j+\Delta\sum_i S_i^2\ . \tag{7.10.1}$$

The spin variables S_i range over the values $\{-1\,,\,0\,,\,+1\}$, so this is an extension of the $S=1$ Ising model. We explicitly separate out the diagonal terms, writing $J_{ii}\equiv 0$, and placing them in the second term on the RHS above. We say that site i is occupied if $S_i=\pm 1$ and vacant if $S_i=0$, and we identify $-\Delta$ as the vacancy creation energy, which may be positive or negative, depending on whether vacancies are disfavored or favored in our system.

We make the mean field *Ansatz*, writing $S_i=m+\delta S_i$. This results in the mean field Hamiltonian,

\HH\ns_\ssr{MF}=\half N \jhz\, m^2 - \jhz\, m \sum_i S\ns_i + \RDelta\sum_i S^2_i\ .

Once again, we adimensionalize, writing $f\equiv F/N\hat{J}(0)$, $\theta=k_BT/\hat{J}(0)$, and $\delta=\Delta/\hat{J}(0)$. We assume $\hat{J}(0)>0$. The free energy per site is then

$$f(\theta,\delta,m)=\frac{1}{2}m^2-\theta\ln\Big(1+2e^{-\delta/\theta}\,\cosh(m/\theta)\Big)\ . \tag{7.10.2}$$

Extremizing with respect to m, we obtain the mean field equation,

$$m=\frac{2\sinh(m/\theta)}{\exp(\delta/\theta)+2\cosh(m/\theta)}\ . \tag{7.10.3}$$

Note that $m=0$ is always a solution. Finding the slope of the RHS at $m=0$ and setting it to unity gives us the critical temperature:

$$\theta_c=\frac{2}{\exp(\delta/\theta_c)+2}\ . \tag{7.10.4}$$

This is an implicit equation for θ_c in terms of the vacancy energy δ.

[blume] Mean field phase diagram for the Blume-Capel model. The black dot signifies a tricritical point, where the coefficients of m^2 and m^4 in the Landau free energy expansion both vanish. The dashed curve denotes a first order transition, and the solid curve a second order transition. The thin dotted line is the continuation of the $\theta_c(\delta)$ relation to zero temperature.

Let's now expand the free energy in terms of the magnetization m. We find, to fourth order,

$$\begin{aligned} f\ &=-\theta\ln\left(1+2e^{-\delta/\theta}\right)+\frac{1}{2\theta}\left(\theta-\frac{2}{2+\exp(\delta/\theta)}\right)m^2\\ &\qquad+\frac{1}{12\left(2+\exp(\delta/\theta)\right)\theta^3}\left(\frac{6}{2+\exp(\delta/\theta)}-1\right)m^4+\ldots\ . \end{aligned}$$

Note that setting the coefficient of the m^2 term to zero yields the equation for θ_c. However, upon further examination, we see that the coefficient of the m^4 term can also vanish. As we have seen, when both the coefficients of the m^2 and the m^4 terms vanish, we have a tricritical point[22]. Setting both coefficients to zero, we obtain

$$\theta_t=\frac{1}{3}\quad,\quad\delta_t=\frac{2}{3}\ln 2\ . \tag{7.10.5}$$

At $\theta=0$, it is easy to see we have a first order transition, simply by comparing the energies of the paramagnetic ($S_i=0$) and ferromagnetic ($S_i=+1$ or $S_i=-1$) states. We have

{E\ns_\ssr{MF}\over N\jhz}=\begin{cases} 0 & {if}\ m=0 \\ \half-\RDelta & {if}\ m=\pm 1\ . \end{cases}

These results are in fact exact, and not only valid for the mean field theory. Mean field theory is approximate because it neglects fluctuations, but at zero temperature, there are no fluctuations to neglect!

The phase diagram is shown in Figure [blume]. Note that for δ large and negative, vacancies are strongly disfavored, hence the only allowed states on each site have $S_i=\pm 1$, which is our old friend the two-state Ising model. Accordingly, the phase boundary there approaches the vertical line $\theta_c=1$, which is the mean field transition temperature for the two-state Ising model.

Ising antiferromagnet in an external field

Consider the following model:

$$\hat{H}=J\sum_{\langle ij\rangle}\sigma_i\,\sigma_j-H\sum_i\sigma_i\ , \tag{7.10.6}$$

with $J>0$ and $\sigma_i=\pm 1$. We've solved for the mean field phase diagram of the Ising ferromagnet; what happens if the interactions are antiferromagnetic?

It turns out that under certain circumstances, the ferromagnet and the antiferromagnet behave exactly the same in terms of their phase diagram, response functions, This occurs when $H=0$, and when the interactions are between nearest neighbors on a *bipartite lattice*. A bipartite lattice is one which can be divided into two sublattices, which we call A and B, such that an A site has only B neighbors, and a B site has only A neighbors. The square, honeycomb, and body centered cubic (BCC) lattices are bipartite. The triangular and face centered cubic lattices are non-bipartite. Now if the lattice is bipartite and the interaction matrix J_{ij} is nonzero only when i and j are from different sublattices (they needn't be nearest neighbors only), then we can simply redefine the spin variables such that

$$\sigma'_j=\begin{cases}+\sigma_j & if\ j\in A\\ -\sigma_j & if\ j\in B\ .\end{cases} \tag{7.10.7}$$

Then $\sigma'_i\sigma'_j=-\sigma_i\,\sigma_j$, and in terms of the new spin variables the exchange constant has reversed. The thermodynamic properties are invariant under such a redefinition of the spin variables.

We can see why this trick doesn't work in the presence of a magnetic field, because the field H would have to be reversed on the B sublattice. In other words, the thermodynamics of an Ising ferromagnet on a bipartite lattice in a uniform applied field is identical to that of the Ising antiferromagnet, with the same exchange constant (in magnitude), in the presence of a *staggered field* H\ns_\ssr{A}=+H and H\ns_\ssr{B}=-H.

We treat this problem using the variational density matrix method, using two independent variational parameters \msa and \msb for the two sublattices:

\begin{split} \vrh_\ssr{A}(\sigma)&={1+\msa\over 2} \> \delta\ns_{\sigma,1} + {1-\msa\over 2} \> \delta\ns_{\sigma,-1}\\ \vrh_\ssr{B}(\sigma)&={1+\msb\over 2} \> \delta\ns_{\sigma,1} + {1-\msb\over 2} \> \delta\ns_{

With the usual adimensionalization, $f=F/NzJ$, $\theta=k_BT/zJ$, and $h=H/zJ$, we have the free energy

f(\msa,\msb)=\half\msa\msb-\half\, h\, (\msa+\msb) -\half\,\theta \, s(\msa) -\half\,\theta\,s(\msb)\ ,

where the entropy function is

$$s(m)=-\left[\frac{1+m}{2}\,\ln\!\left(\frac{1+m}{2}\right)+\frac{1-m}{2}\,\ln\!\left(\frac{1-m}{2}\right)\right]\,. \tag{7.10.8}$$

Note that

$$\frac{ds}{dm}=-\frac{1}{2}\ln\!\left(\frac{1+m}{1-m}\right) \qquad , \qquad \frac{d^2s}{dm^2}=-\frac{1}{1-m^2}\,. \tag{7.10.9}$$

[affgraph] Graphical solution to the mean field equations for the Ising antiferromagnet in an external field, here for $\theta=0.6$. Clockwise from upper left: (a) $h=0.1$, (b) $h=0.5$, (c) $h=1.1$, (d) $h=1.4$.

Differentiating f(\msa,\msb) with respect to the variational parameters, we obtain two coupled mean field equations:

\begin{split} {\pz f\over\pz\msa}&=0 \quad \Longrightarrow\quad \msb=h-{\theta\over 2}\ln\!\bigg({1+\msa\over 1-\msa}\bigg) \\ {\pz f\over\pz\msb}&=0 \quad \Longrightarrow\quad \msa=h-{\theta\over 2}\ln\!\bigg({1+\

Recognizing $\tanh^{-1}(x)=\frac{1}{2}\ln\Big[(1+x)/(1-x)\Big]$, we may write these equations in an equivalent but perhaps more suggestive form:

\msa=\tanh\bigg({h-\msb\over\theta}\bigg)\qquad,\qquad \msb=\tanh\bigg({h-\msa\over\theta}\bigg)\ .

In other words, the A sublattice sites see an internal field H\ns_{\ssr{A},{int}}=-zJ\msb from their B neighbors, and the B sublattice sites see an internal field H\ns_{\ssr{B},{int}}=-zJ\msa from their A neighbors.

We can solve these equations graphically, as in Figure [affgraph]. Note that there is always a paramagnetic solution with \msa=\msb=m, where

$$m=h-\frac{\theta}{2}\,\ln\!\left(\frac{1+m}{1-m}\right) \qquad \Longleftrightarrow \qquad m=\tanh\left(\frac{h-m}{\theta}\right)\,. \tag{7.10.10}$$

However, we can see from the figure that there will be *three* solutions to the mean field equations provided that {\pz \msa\over\pz \msb}<-1 at the point of the solution where \msa=\msb=m. This gives us two equations with which to eliminate \msa and \msb, resulting in the curve

$$h^*(\theta)=m+\frac{\theta}{2}\,\ln\!\left(\frac{1+m}{1-m}\right) \qquad with\ \ m=\sqrt{1-\theta}\,. \tag{7.10.11}$$

Thus, for $\theta<1$ and $|h|<h^*(\theta)$ there are three solutions to the mean field equations. It is *usually* the case, the broken symmetry solutions, which mean those for which \msa\ne\msb in our case, are of lower energy than the symmetric solution(s). We show the curve $h^*(\theta)$ in Figure [affpd].

[affpd] Mean field phase diagram for the Ising antiferromagnet in an external field. The phase diagram is symmetric under reflection in the $h=0$ axis.

We can make additional progress by defining the average and staggered magnetizations m and m_s,

m\equiv \half(\msa+\msb) \qquad,\quad \mss\equiv\half (\msa-\msb)\ .

We expand the free energy in terms of m_s:

$$\begin{aligned} f(m,m_s) &=\frac{1}{2}m^2-\frac{1}{2}m_s^2-h\,m-\frac{1}{2}\,\theta\,s(m+m_s)-\frac{1}{2}\,\theta\,s(m-m_s)\\ &=\frac{1}{2}m^2-h\,m-\theta\,s(m)-\frac{1}{2}\Big(1+\theta\,s''(m)\Big)\,m_s^2-\frac{1}{24}\,\theta\,s''''(m)\,m_s^4+\ldots\,. \end{aligned}$$

The term quadratic in m_s vanishes when $\theta\,s''(m)=-1$, when $m=\sqrt{1-\theta}$. It is easy to obtain

$$\frac{d^3s}{dm^3}=-\frac{2m}{(1-m^2)^2} \qquad , \qquad \frac{d^4s}{dm^4}=-\frac{2\,(1+3m^2)}{(1-m^2)^3}\,, \tag{7.10.12}$$

from which we learn that the coefficient of the quartic term, $-\frac{1}{24}\,\theta\,s''''(m)$, never vanishes. Therefore the transition remains second order down to $\theta=0$, where it finally becomes first order.

We can confirm the $\theta\to 0$ limit directly. The two competing states are the ferromagnet, with \msa=\msb=\pm 1, and the antiferromagnet, with \msa=-\msb=\pm 1. The free energies of these states are

f^\ssr{FM}=\half-h \qquad,\qquad f^\ssr{AFM}=-\half\ .

There is a first order transition when f^\ssr{FM}=f^\ssr{AFM}, which yields $h=1$.

Canted quantum antiferromagnet

Consider the following model for *quantum* $S=\frac{1}{2}$ spins:

$$\hat{H}=\sum_{\langle ij\rangle}\Big[-J\big(\sigma_i^x\sigma_j^x+\sigma_i^y\sigma_j^y\big)+\Delta\,\sigma_i^z\sigma_j^z\Big]+\frac{1}{4}K\sum_{\langle ijkl\rangle}\sigma_i^z\sigma_j^z\sigma_k^z\sigma_l^z\,, \tag{7.10.13}$$

where σ_i is the vector of Pauli matrices on site i. The spins live on a square lattice. The second sum is over all square plaquettes. All the constants J, Δ, and K are positive.

Let's take a look at the Hamiltonian for a moment. The J term clearly wants the spins to align ferromagnetically in the (x, y) plane (in internal spin space). The Δ term prefers antiferromagnetic alignment along the $\hat{\mathbf{z}}$ axis. The K term discourages any kind of moment along $\hat{\mathbf{z}}$ and works against the Δ term. We'd like our mean field theory to capture the physics behind this competition.

Accordingly, we break up the square lattice into two interpenetrating $\sqrt{2} \times \sqrt{2}$ square sublattices (each rotated by 45° with respect to the original), in order to be able to describe an antiferromagnetic state. In addition, we include a parameter α which describes the *canting angle* that the spins on these sublattices make with respect to the $\hat{\mathbf{x}}$-axis. That is, we write

\begin{split} \vrh\ns_\ssr{A}&=\half + \half m\,\big(\sin\alpha\>\sigma^x +\cos\alpha\>\sigma^z)\\ \vrh\ns_\ssr{B}&=\half + \half m\,\big(\sin\alpha\>\sigma^x - \cos\alpha\>\sigma^z)\ .\vph \end{split}

Note that \Tra\vrh\ns_\ssr{A}=\Tra\vrh\ns_\ssr{B}=1 so these density matrices are normalized. Note also that the mean direction for a spin on the A and B sublattices is given by

\Bm\ns_\ssr{A,B}=\Tra(\vrh\ns_\ssr{A,B}\,\Bsigma)=\pm\, m\cos\alpha\,\HBz + m\sin\alpha\>\HBx\ .

Thus, when $\alpha = 0$, the system is an antiferromagnet with its staggered moment lying along the $\hat{\mathbf{z}}$ axis. When $\alpha = \frac{1}{2}\pi$, the system is a ferromagnet with its moment lying along the $\hat{\mathbf{x}}$ axis.

Finally, the eigenvalues of \vrh\ns_\ssr{A,B} are still $\lambda_\pm = \frac{1}{2}(1 \pm m)$, hence

\begin{split} s(m)&\equiv-\Tra (\vrh\ns_\ssr{A}\ln\vrh\ns_\ssr{A})=-\Tra (\vrh\ns_\ssr{B}\ln\vrh\ns_\ssr{B})\\ &=-\Bigg[{1+m\over 2}\>\ln\!\bigg({1+m\over 2}\bigg) +{1-m\over 2}\> \ln\!\bigg({1-m\over 2}\bigg) \Bigg

Note that we have taken m\ns_\ssr{A}=m\ns_\ssr{B}=m, unlike the case of the antiferromagnet in a uniform field. The reason is that there remains in our model a symmetry between A and B sublattices.

The free energy is now easily calculated:

$$\begin{aligned} F &= \mathsf{Tr}\,(\varrho \hat{H}) + k_B T\, \mathsf{Tr}\,(\varrho \ln \varrho) \\ &= -2N\Big(J\,\sin^2\!\alpha + \Delta\,\cos^2\!\alpha\Big)\, m^2 + \frac{1}{4} N K m^4 \cos^4\!\alpha - N k_B T\, s(m) \end{aligned}$$

We can adimensionalize by defining $\delta \equiv \Delta/J$, $\kappa \equiv K/4J$, and $\theta \equiv k_B T/4J$. Then the free energy per site is $f \equiv F/4NJ$ is

$$f(m,\alpha) = -\frac{1}{2} m^2 + \frac{1}{2}\big(1-\delta\big)\, m^2 \cos^2\!\alpha + \frac{1}{4}\kappa\, m^4 \cos^4\!\alpha - \theta\, s(m)\ . \tag{7.10.14}$$

There are two variational parameters: m and θ. We thus obtain two coupled mean field equations,

$$\begin{aligned} \frac{\partial f}{\partial m} &= 0 = -m + \big(1-\delta\big)\, m\,\cos^2\!\alpha + \kappa\, m^3 \cos^4\!\alpha + \frac{1}{2}\theta\,\ln\!\bigg(\frac{1+m}{1-m}\bigg) \\ \frac{\partial f}{\partial \alpha} &= 0 = \Big(1 - \delta + \kappa\, m^2 \cos^2\!\alpha\Big)\, m^2 \sin\alpha\, \cos\alpha\ . \end{aligned}$$

Let's start with the second of the mean field equations. Assuming $m \neq 0$, it is clear from Equation [cantedferg] that

$$\cos^2\!\alpha = \begin{cases} 0 & if\ \ \delta < 1 \\ (\delta - 1)/\kappa m^2 & if\ \ 1 \le \delta \le 1 + \kappa\, m^2 \\ 1 & if\ \ \delta \ge 1 + \kappa\, m^2\ . \end{cases} \tag{7.10.15}$$

Suppose $\delta < 1$. Then we have $\cos\alpha = 0$ and the first mean field equation yields the familiar result

$$m = \tanh\big(m/\theta\big)\ . \tag{7.10.16}$$

Along the θ axis, then, we have the usual ferromagnet-paramagnet transition at $\theta_c = 1$.

[cantpd] Mean field phase diagram for the model of Equation [cantham] for the case $\kappa = 1$.

For $1 < \delta < 1 + \kappa m^2$ we have canting with an angle \[\alpha=\alpha^*(m)=\cos^{-1}\sqrt

\ .\] Substituting this into the first mean field equation, we once again obtain the relation $m = \tanh\big(m/\theta\big)$. However, eventually, as θ is increased, the magnetization will dip below the value $m_0 \equiv \sqrt{(\delta-1)/\kappa}$. This occurs at a dimensionless temperature \[\theta\ns_0={m\ns_0\over\tanh^{-1}(m\ns_0)} < 1\qquad;\qquad m\ns_0=\sqrt\ .\] For $\theta > \theta_0$, we have $\delta > 1 + \kappa m^2$, and we must take $\cos^2\!\alpha = 1$. The first mean field equation then becomes

$$\delta m - \kappa m^3 = \frac{\theta}{2}\,\ln\!\bigg(\frac{1+m}{1-m}\bigg)\ , \tag{7.10.17}$$

or, equivalently, $m = \tanh\big((\delta m - \kappa m^3)/\theta\big)$. A simple graphical analysis shows that a nontrivial solution exists provided $\theta < \delta$. Since $\cos\alpha = \pm 1$, this solution describes an antiferromagnet, with \Bm\ns_\ssr{A}=\pm m\zhat and \Bm\ns_\ssr{B}=\mp m\zhat. The resulting mean field phase diagram is then as depicted in Figure [cantpd].

Coupled order parameters

Consider the Landau free energy

$$f(m,\phi) = \frac{1}{2}\, a_m\, m^2 + \frac{1}{4}\, b_m\, m^4 + \frac{1}{2}\, a_\phi\, \phi^2 + \frac{1}{4}\, b_\phi\, \phi^4 + \frac{1}{2}\Lambda\, m^2\, \phi^2\ . \tag{7.10.18}$$

We write

$$a_m \equiv \alpha_m\, \theta_m \qquad , \qquad a_\phi = \alpha_\phi\, \theta_\phi\ , \tag{7.10.19}$$

where

$$\theta_m = \frac{T - T_{c,m}}{T_0} \qquad , \qquad \theta_\phi = \frac{T - T_{c,\phi}}{T_0}\ , \tag{7.10.20}$$

where T_0 is some temperature scale. We assume without loss of generality that $T_{c,m} > T_{c,\phi}$. We begin by rescaling:

$$m \equiv \left(\frac{\alpha_m}{b_m}\right)^{1/2} \widetilde{m} \qquad , \qquad \phi \equiv \left(\frac{\alpha_m}{b_m}\right)^{1/2} \widetilde{\phi}\,. \tag{7.10.21}$$

We then have

$$f = \varepsilon_0 \left\{ r\left(\frac{1}{2}\theta_m\, \widetilde{m}^2 + \frac{1}{4}\,\widetilde{m}^4\right) + r^{-1}\left(\frac{1}{2}\,\theta_\phi\, \widetilde{\phi}^2 + \frac{1}{4}\,\widetilde{\phi}^4\right) + \frac{1}{2}\,\lambda\, \widetilde{m}^2 \widetilde{\phi}^2 \right\}, \tag{7.10.22}$$

where

$$\varepsilon_0 = \frac{\alpha_m\, \alpha_\phi}{(b_m\, b_\phi)^{1/2}} \qquad , \qquad r = \frac{\alpha_m}{\alpha_\phi}\left(\frac{b_\phi}{b_m}\right)^{1/2} \qquad , \qquad \lambda = \frac{\Lambda}{(b_m\, b_\phi)^{1/2}}\,. \tag{7.10.23}$$

It proves convenient to perform one last rescaling, writing

$$\tilde{m} \equiv r^{-1/4}\, \mathsf{m} \quad , \quad \tilde{\phi} \equiv r^{1/4}\, \varphi\,. \tag{7.10.24}$$

Then

$$f = \varepsilon_0 \left\{ \frac{1}{2} q\, \theta_m\, \mathsf{m}^2 + \frac{1}{4}\, \mathsf{m}^4 + \frac{1}{2} q^{-1}\, \theta_\phi\, \varphi^2 + \frac{1}{4}\, \varphi^4 + \frac{1}{2}\,\lambda\, \mathsf{m}^2\, \varphi^2 \right\}, \tag{7.10.25}$$

where

$$q = \sqrt{r} = \left(\frac{\alpha_m}{\alpha_\phi}\right)^{1/2} \left(\frac{b_\phi}{b_m}\right)^{1/4}. \tag{7.10.26}$$

Note that we may write

$$f(\mathsf{m},\varphi) = \frac{\varepsilon_0}{4} \begin{pmatrix} \mathsf{m}^2 & \varphi^2 \end{pmatrix} \begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \mathsf{m}^2 \\ \varphi^2 \end{pmatrix} + \frac{\varepsilon_0}{2} \begin{pmatrix} \mathsf{m}^2 & \varphi^2 \end{pmatrix} \begin{pmatrix} q\, \theta_m \\ q^{-1}\, \theta_\phi \end{pmatrix}\,. \tag{7.10.27}$$

The eigenvalues of the above 2×2 matrix are $1 \pm \lambda$, with corresponding eigenvectors $\left(\begin{smallmatrix} 1 \\ \pm 1 \end{smallmatrix}\right)$. Since $\varphi^2 > 0$, we are only interested in the first eigenvector $\left(\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right)$, corresponding to the eigenvalue $1 + \lambda$. Clearly when $\lambda < 1$ the free energy is unbounded from below, which is unphysical.

We now set

$$\frac{\partial f}{\partial \mathsf{m}} = 0 \qquad , \qquad \frac{\partial f}{\partial \varphi} = 0\,, \tag{7.10.28}$$

and identify four possible phases:

- Phase I : $\mathsf{m} = 0$, $\varphi = 0$. The free energy is f\ns_\ssr{I}=0.
- Phase II : $\mathsf{m} \neq 0$ with $\varphi = 0$. The free energy is

$$f = \frac{\varepsilon_0}{2}\left(q\, \theta_m\, \mathsf{m}^2 + \frac{1}{2}\, \mathsf{m}^4\right), \tag{7.10.29}$$

  hence we require $\theta_m < 0$ in this phase, in which case

  \Sm\ns_\ssr{II}=\sqrt{-q\,\thm}\qquad,\qquad f\ns_\ssr{II}=-{\ve\ns_0\over 4}\,q^2\,\theta_m^2\ .

- Phase III : $m = 0$ with $\varphi \neq 0$. The free energy is

$$f = \frac{\varepsilon_0}{2}\left(q^{-1}\, \theta_\phi\, \varphi^2 + \frac{1}{2}\, \varphi^4\right), \tag{7.10.30}$$

  hence we require $\theta_\phi < 0$ in this phase, in which case

  \vphi\ns_\ssr{III}=\sqrt{-q^{-1}\,\thp}\qquad,\qquad f\ns_\ssr{III}=-{\ve\ns_0\over 4}\,q^{-2}\,\theta_\phi^2\ .

- Phase IV : $\mathsf{m} \neq 0$ and $\varphi \neq 0$. Varying f yields

$$\begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \mathsf{m}^2 \\ \varphi^2 \end{pmatrix} = -\begin{pmatrix} q\, \theta_m \\ q^{-1}\, \theta_\phi \end{pmatrix}, \tag{7.10.31}$$

  with solution

$$\mathsf{m}^2 = \frac{q\, \theta_m - q^{-1}\, \theta_\phi\, \lambda}{\lambda^2 - 1}$$

$$\varphi^2 = \frac{q^{-1}\, \theta_\phi - q\, \theta_m\, \lambda}{\lambda^2 - 1}\,.$$

  Since m^2 and φ^2 must each be nonnegative, phase IV exists only over a yet-to-be-determined subset of the entire parameter space. The free energy is

  f\ns_\ssr{IV}={q^2\,\theta_m^2 + q^{-2}\,\theta_\phi^2 - 2\lambda\,\thm\,\thp\over 4(\lambda^2-1)}\ .

We now define $\theta \equiv \theta_m$ and $\tau \equiv \theta_\phi - \theta_m = (T_{c,m} - T_{c,\phi)}/T_0$. Note that $\tau > 0$. There are three possible temperature ranges to consider.

- $\theta_\phi > \theta_m > 0$. The only possible phases are I and IV. For phase IV, we must impose the conditions $m^2 > 0$ and $\phi^2 > 0$. If $\lambda^2 > 1$, then the numerators in eqns. [IVab] must each be positive:

$$\lambda < \frac{q^2\, \theta_m}{\theta_\phi} \quad , \quad \lambda < \frac{\theta_\phi}{q^2\, \theta_m} \quad \Rightarrow \quad \lambda < min\left(\frac{q^2\, \theta_m}{\theta_\phi}\,, \frac{\theta_\phi}{q^2 \theta_m}\right). \tag{7.10.32}$$

  But since either $q^2\theta_m/\theta_\phi$ or its inverse must be less than or equal to unity, this requires $\lambda < -1$, which is unphysical.

  If on the other hand we assume $\lambda^2 < 1$, the non-negativeness of m^2 and φ^2 requires

$$\lambda > \frac{q^2\, \theta_m}{\theta_\phi} \quad , \quad \lambda > \frac{\theta_\phi}{q^2\, \theta_m} \quad \Rightarrow \quad \lambda > max\left(\frac{q^2\, \theta_m}{\theta_\phi}\,, \frac{\theta_\phi}{q^2 \theta_m}\right) > 1\,. \tag{7.10.33}$$

  Thus, $\lambda > 1$ and we have a contradiction.

  Therefore, the only allowed phase for $\theta > 0$ is phase I.

- $\theta_\phi > 0 > \theta_m$. Now the possible phases are I, II, and IV. We can immediately rule out phase I because f\ns_\ssr{II} < f\ns_\ssr{I}. To compare phases II and IV, we compute

  \RDelta f = f\ns_\ssr{IV}-f\ns_\ssr{II}={(q\,\lambda\,\thm - q^{-1}\,\thp)^2\over 4(\lambda^2-1)}\ .

  Thus, phase II has the lower energy if $\lambda^2 > 1$. For $\lambda^2 < 1$, phase IV has the lower energy, but the conditions $\mathsf{m}^2 > 0$ and $\varphi^2 > 0$ then entail

  $$\frac{q^2\theta_m}{\theta_\phi} < \lambda < \frac{\theta_\phi}{q^2\theta_m} \quad\Rightarrow\quad q^2|\theta_m| > \theta_\phi > 0\ . \tag{7.10.34}$$

  Thus, λ is restricted to the range

  $$\lambda \in \left[-1\,,\,-\frac{\theta_\phi}{q^2|\theta_m|}\right]\ . \tag{7.10.35}$$

  With $\theta_m \equiv \theta < 0$ and $\theta_\phi \equiv \theta + \tau > 0$, the condition $q^2|\theta_m| > \theta_\phi$ is found to be

  $$-\tau < \theta < -\frac{\tau}{q^2+1}\ . \tag{7.10.36}$$

  Thus, phase IV exists and has lower energy when

  $$-\tau < \theta < -\frac{\tau}{r+1} \quad and \quad -1 < \lambda < -\frac{\theta+\tau}{r\theta}\ , \tag{7.10.37}$$

  where $r = q^2$.
- $0 > \theta_\phi > \theta_m$. In this regime, any phase is possible, however once again phase I can be ruled out since phases II and III are of lower free energy. The condition that phase II have lower free energy than phase III is

  f\ns_\ssr{II} - f\ns_\ssr{III} = {\ve\ns_0\over 4}\big(q^{-2}\theta_\phi^2-q^2\theta_m^2\big) < 0\ ,

  $|\theta_\phi| < r|\theta_m|$, which means $r|\theta| > |\theta| - \tau$. If $r > 1$ this is true for all $\theta < 0$, while if $r < 1$ phase II is lower in energy only for $|\theta| < \tau/(1-r)$.

[FcoupledLandau] Phase diagram for $\tau = 0.5$, $r = 1.5$ (top) and $\tau = 0.5$, $r = 0.25$ (bottom). The hatched purple region is unphysical, with a free energy unbounded from below. The blue lines denote second order transitions. The thick red line separating phases II and III is a first order line.

We next need to test whether phase IV has an even lower energy than the lower of phases II and III. We have

\begin{split} f\ns_\ssr{IV}-f\ns_\ssr{II}&={(q\,\lambda\,\thm - q^{-1}\,\thp)^2\over 4(\lambda^2-1)}\vph\\ f\ns_\ssr{IV}-f\ns_\ssr{III}&={(q\,\thm - q^{-1}\,\lambda\,\thp)^2\over 4(\lambda^2-1)}\ . \end{split}

In both cases, phase IV can only be the true thermodynamic phase if $\lambda^2 < 1$. We then require $\mathsf{m}^2 > 0$ and $\varphi^2 > 0$, which fixes

$$\lambda \in \left[-1\,,\,min\bigg(\frac{q^2\,\theta_m}{\theta_\phi}\,,\,\frac{\theta_\phi}{q^2\theta_m}\bigg)\right]\ . \tag{7.10.38}$$

The upper limit will be the first term inside the rounded brackets if $q^2|\theta_m| < \theta_\phi$, if $r|\theta| < |\theta| - \tau$. This is impossible if $r > 1$, hence the upper limit is given by the second term in the rounded brackets:

$$r > 1\ :\ \lambda \in \left[-1\,,\,\frac{\theta+\tau}{r\,\theta}\right] \qquad \text{(condition for phase IV)}\ . \tag{7.10.39}$$

If $r < 1$, then the upper limit will be $q^2\theta_m/\theta_\phi = r\theta/(\theta+\tau)$ if $|\theta| > \tau/(1-r)$, and will be $\theta_\phi/q^2\theta_m = (\theta+\tau)/r\theta$ if $|\theta| < \tau/(1-r)$.

$$r < 1\ ,\ -\frac{\tau}{1-r} < \theta < -\tau \quad :\ \lambda \in \left[-1\,,\,\frac{\theta+\tau}{r\theta}\right] \qquad \text{(phase IV)}$$

$$r < 1\ ,\ \theta < -\frac{\tau}{1-r} \quad :\ \lambda \in \left[-1\,,\,\frac{r\theta}{\theta+\tau}\right] \qquad \text{(phase IV)}\ .$$

Representative phase diagrams for the cases $r > 1$ and $r < 1$ are shown in Figure [FcoupledLandau].

1. There is always a solution to $(\partial p/\partial v)_T = 0$ at $v = \infty$.↩
2. Don't confuse the molar free energy (f) with the number of molecular degrees of freedom (f)!↩
3. Johannes Diderik van der Waals, the eldest of ten children, was the son of a carpenter. As a child he received only a primary school education. He worked for a living until age 25, and was able to enroll in a three-year industrial evening school for working class youth. Afterward he continued his studies independently, in his spare time, working as a teacher. By the time he obtained his PhD, he was 36 years old. He received the Nobel Prize for Physics in 1910.↩
4. See www.nobelprize.org/nobel_prizes/physics/laureates/1910/waals-lecture.pdf↩
5. One could equally well identify the second correspondence as $n \longleftrightarrow m$ between density (rather than specific volume) and magnetization. One might object that H is more properly analogous to μ. However, since $\mu = \mu(p,T)$ it can equally be regarded as analogous to p. Note also that $\beta p = z\lambda_T^{-d}$ for the ideal gas, in which case $\xi = z(a/\lambda_T)^d$ is proportional to p.↩
6. Note the distinction between the number of lattice sites N_S and the number of occupied cells N. According to our definitions, $N = \frac{1}{2}(M + N_\mathsf{S})$.↩
7. In the third of the following exponent equalities, d is the dimension of space and ν is the correlation length exponent.↩
8. A Bravais lattice is one in which any site is equivalent to any other site through an appropriate discrete translation. Examples of Bravais lattices include the linear chain, square, triangular, simple cubic, face-centered cubic, lattices. The honeycomb lattice is not a Bravais lattice, because there are two sets of inequivalent sites – those in the center of a Y and those in the center of an upside down Y.↩
9. To obtain this result, one writes $f = f\big(\theta, m(\theta)\big)$ and then differentiates twice with respect to θ, using the chain rule. Along the way, any naked (undifferentiated) term proportional to $\frac{\partial f}{\partial m}$ may be dropped, since this vanishes at any θ by the mean field equation.↩
10. Pierre Curie was a pioneer in the fields of crystallography, magnetism, and radiation physics. In 1880, Pierre and his older brother Jacques discovered piezoelectricity. He was 21 years old at the time. It was in 1895 that Pierre made the first systematic studies of the effects of temperature on magnetic materials, and he formulated what is known as *Curie's Law*, $\chi = C/T$, where C is a constant. Curie married Marie Sklodowska in the same year. Their research turned toward radiation, recently discovered by Becquerel and Röntgen. In 1898, Pierre and Marie Curie discovered radium. They shared the 1903 Nobel Prize in Physics with Becquerel. Marie went on to win the 1911 Nobel Prize in Chemistry and was the first person ever awarded two Nobel Prizes. Their daughter Irène Joliot Curie shared the 1935 Prize in Chemistry (with her husband), also for work on radioactivity. Pierre Curie met an untimely and unfortunate end in the Spring of 1906. Walking

across the Place Dauphine, he slipped and fell under a heavy horse-drawn wagon carrying military uniforms. His skull was crushed by one of the wagon wheels, killing him instantly. Later on that year, Pierre-Ernest Weiss proposed a modification of Curie's Law to account for ferromagnetism. This became known as the Curie-Weiss law, $\chi = C/(T - T_c)$.↩

11. The self-interaction terms with $i = j$ contribute a constant to $\hat{H}$ and may be either included or excluded. However, this property only pertains to the $\sigma_i = \pm 1$ model. For higher spin versions of the Ising model, say where $S_i \in \{-1, 0, +1\}$, then S_i^2 is not constant and we should explicitly exclude the self-interaction terms.↩
12. The sum in the discrete Fourier transform is over all 'direct Bravais lattice vectors' and the wavevector $\mathbf{q}$ may be restricted to the 'first Brillouin zone'. These terms are familiar from elementary solid state physics.↩
13. How do we take the logarithm of a matrix? The rule is this: $A = \ln B$ if $B = \exp(A)$. The exponential of a matrix may be evaluated via its Taylor expansion.↩
14. The denominator of 2π in the measure is not necessary, and in fact it is even slightly cumbersome. It divides out whenever we take a ratio to compute a thermodynamic average. I introduce this factor to preserve the relation $\mathsf{Tr}\ 1 = 1$. I personally find unnormalized traces to be profoundly unsettling on purely aesthetic grounds.↩
15. Note that the coefficient of the quartic term in ε is negative for $\theta > \frac{2}{3}$. At $\theta = \theta_c = \frac{1}{2}$, the coefficient is positive, but for larger θ one must include higher order terms in the Landau expansion.↩
16. It is always the case that f is bounded from below, on physical grounds. Were b negative, we'd have to consider higher order terms in the Landau expansion.↩
17. We needn't waste our time considering the $m = m_-$ solution, since the cubic term prefers positive m.↩
18. There is a sign difference between the particle susceptibility defined in chapter 6 and the spin susceptibility defined here. The origin of the difference is that the single particle potential v as defined was repulsive for $v > 0$, meaning the local density response δn should be negative, while in the current discussion a positive magnetic field H prefers $m > 0$.↩
19. To evoke a negative eigenvalue on a d-dimensional cubic lattice, set $q_\mu = \frac{\pi}{a}$ for all μ. The eigenvalue is then $-2dK_1$.↩
20. It needn't be an equally spaced sequence, for example.↩
21. The function $\Phi(\sigma)$ may involve one or more adjustable parameters which could correspond, for example, to an external magnetic field h. We suppress these parameters when we write the free energy as $f(\theta)$.↩
22. We should really check that the coefficient of the sixth order term is positive, but that is left as an exercise to the eager student.↩