Variational Density Matrix

Let $\hat{\rho} = \sum_\gamma P_\gamma |\gamma\rangle\langle\gamma|$ where $|\gamma\rangle$ denotes a configuration of a given system. For N spins, take $\gamma = \vec{\sigma} = \{\sigma_1, \ldots, \sigma_N\}$. The free energy is

$$F = E - TS = Tr(\hat{\rho}\hat{H}) + k_B T \, Tr(\hat{\rho}\log\hat{\rho})$$
$$= \sum_\gamma P_\gamma E_\gamma + k_B T \sum_\gamma P_\gamma \log P_\gamma$$

In equilibrium, F achieves a minimum at fixed (T, V, N). Since $Tr\,\hat{\rho} = \sum_\gamma P_\gamma = 1$ (normalization), we extremize F using Lagrange's method of undetermined multipliers:

← extended function   multiplier ↓

$$F^*(\{P_\gamma\}, \lambda) = \sum_\gamma \left(E_\gamma P_\gamma + k_B T P_\gamma \log P_\gamma\right) + \lambda\left(\sum_\gamma P_\gamma - 1\right)$$

If there are Ω total states γ, this results in $\Omega + 1$ equations in $\Omega + 1$ unknowns $\{P_1, \ldots, P_\Omega, \lambda\}$:

- $$\frac{\partial F}{\partial P_\gamma} = E_\gamma + k_B T \log P_\gamma + k_B T + \lambda = 0$$

- $$\frac{\partial F}{\partial \lambda} = \sum_\gamma P_\gamma - 1 = 0$$

Note that setting $\partial F/\partial\lambda = 0$ yields the constraint equation. The solution is the Boltzmann dist$^{\underline{n}}$:

$$P_\gamma^{eq} = \frac{1}{Z} e^{-E_\gamma/k_B T} = \text{Boltzmann weight}$$

$$Z = \sum_\gamma e^{-E_\gamma/k_B T} = \text{partition function}$$

Here, $Z = \exp\left(1 + \frac{\lambda}{k_B T}\right)$.

We conclude that any dist$^{\underline{n}}$ other than P_γ^{eq} must yield a greater value of F than that at the true thermodynamic equilibrium. The disadvantage with the exact dist^{n} P_γ^{eq} is that it is difficult to calculate with.

But we can construct an approximation to P_γ^{eq} which involves a set of variational parameters.

Consider the Ising model,

$$\hat{H} = -\frac{1}{2}\sum_{i,j}^{N} J_{ij}\,\sigma_i\sigma_j - H\sum_{i=1}^{N}\sigma_i$$

and the variational density matrix

$$\rho_{var}(\vec{\sigma}) = \prod_{i=1}^{N} \rho(\sigma_i)$$

NB normalized

with $\rho(\sigma) = \frac{1}{2}(1+m)\,\delta_{\sigma,+1} + \frac{1}{2}(1-m)\,\delta_{\sigma,-1}$

Then $\langle\sigma_i\rangle = \sum_{\sigma=\pm1} \sigma\rho(\sigma) = \frac{1+m}{2} - \frac{1-m}{2} = m$

$$E = \mathrm{Tr}\left(\rho_{var}\hat{H}\right) = -\frac{1}{2}N\hat{J}(0)\,m^2 - NHm$$

with $\hat{J}(0) = \sum_{\vec{R}} J(\vec{R})$ and $J_{ij} = J(|\vec{R}_i - \vec{R}_j|)$.

The entropy is $S = -k_B \mathrm{Tr}\,\rho_{var}\log\rho_{var} = Ns$

$$s = -k_B \mathrm{Tr}\,\rho\log\rho = -k_B\sum_{\sigma}\rho(\sigma)\log\rho(\sigma)$$

$$= -k_B\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right)\right]$$

Thus with $\theta = k_B T / \hat{J}(0)$, $h = H/\hat{J}(0)$, $f = F/N\hat{J}(0)$ we have

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

Now we extremize wrt the variational parameter m:

$$\frac{\partial f}{\partial m} = -m - h + \tfrac{1}{2}\theta \log\left(\frac{1+m}{1-m}\right) = 0 \Rightarrow$$

$$m = \tanh\left(\frac{m+h}{\theta}\right)$$

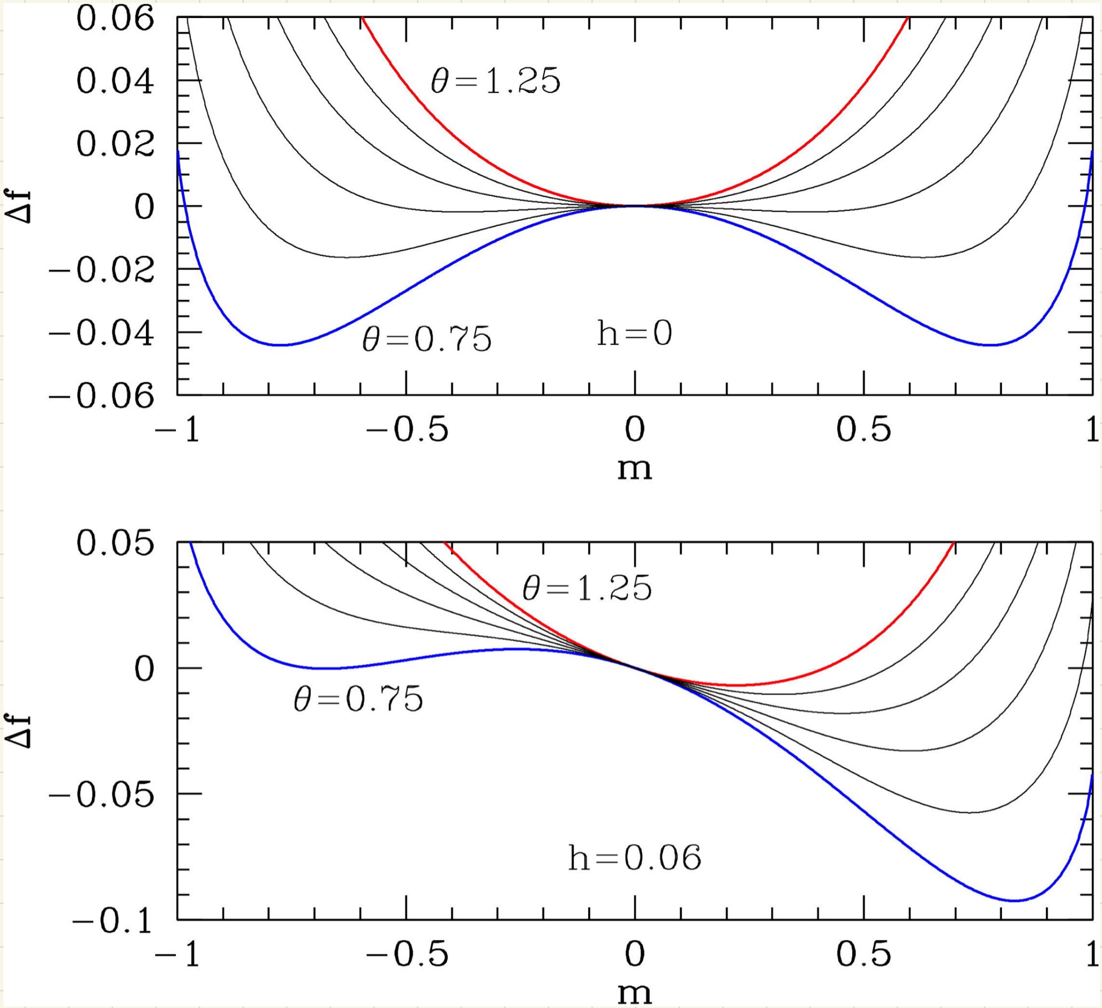
Thus we recover the same MF theory as we derived using the neglect of fluctuations method. A Landau expansion yields

$$f(m,\theta,h) = -\theta\log 2 - hm - \tfrac{1}{2}(\theta-1)m^2 + \frac{\theta}{12}m^4 + \frac{\theta}{30}m^6 + \ldots$$

Using the neglect of fluct^s method,

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

$$= -\theta\log 2 - \frac{hm}{\theta} + \tfrac{1}{2}(1-\theta^{-1})m^2 + \frac{m^4}{12\theta^3} - \frac{m^6}{45\theta^5} + \ldots$$



q-state Potts Model

Hamiltonian: $\hat{H} = -\frac{1}{2}\sum_{i,j} J_{ij}\,\delta_{\sigma_i,\sigma_j} - H\sum_i \delta_{\sigma_i,1}$
where $\sigma_i \in \{1,\ldots,q\}$. When $H=0$ the model has a S_q-symmetry, where S_q is the symmetric group, i.e. permutations of $\{1,2,\ldots,q\}$. For the single site variational density matrix,

take $\rho(\sigma) = x\,\delta_{\sigma,1} + \frac{1-x}{q-1}\left(1-\delta_{\sigma,1}\right)$ and

$$\rho_{var}(\vec{\sigma}) = \prod_{i=1}^{N} \rho(\sigma_i)$$

Thus $\mathrm{Prob}[\sigma=1] = x$ and $\mathrm{Prob}[\sigma=2] = \ldots \mathrm{Prob}[\sigma=N] = \frac{1-x}{q-1}$

Note $\sum_{\sigma=1}^{q} = 1$ so the dist^{n} is normalized. Now

$$E = \mathrm{Tr}\left(\rho_{var} \hat{H}\right) = -\frac{1}{2} N \hat{J}(0) \left\{ x^2 + \frac{(1-x)^2}{q-1} \right\} - NHx$$

$$S = -k_B \mathrm{Tr}\left(\rho_{var} \log \rho_{var}\right) = -Nk_B \left\{ x \log x + (1-x) \log\left(\frac{1-x}{q-1}\right) \right\}$$

Rescaling as before,

$$f(x,\theta,h) = -\frac{1}{2}\left\{ x^2 + \frac{(1-x)^2}{q-1} \right\} + \theta \left\{ x \log x + (1-x) \log\left(\frac{1-x}{q-1}\right) \right\} - hx$$

The MF eq^{n} is

$$0 = \frac{\partial f}{\partial x} = -x + \frac{1-x}{q-1} + \theta \log x - \theta \log\left(\frac{1-x}{q-1}\right) - h\,x$$

The order parameter is $u = x - q^{-1}$. This vanishes in the symmetric (high temperature) phase when $h = 0$ (i.e. no symmetry-breaking field).

A Landau expansion yields

$$f(x,\theta,h) = f_0 + \frac{1}{2}au^2 - \frac{1}{3}yu^3 + \frac{1}{4}bu^4 + \dots$$

with coefficients

$$a = \frac{q(q\theta-1)}{q-1}, \quad y = \frac{(q-2)q^3\theta}{2(q-1)^2}, \quad b = \frac{q^3\theta}{3}\left[1+(q-1)^{-3}\right]$$

Note that $y=0$ when $q=2$. This is because the 2-state Potts model is equivalent to the 2-state Ising model, for which the transition at $h=0$ is second order. For $q>2$ there is a cubic term in the Landau expansion, which suggests that the transition is first order (i.e. discontinuous). If we truncate the Landau expansion at fourth order in u, the transition occurs when $y^2 = \frac{9}{2}ab$, which gives

$$\theta_c = \frac{6(q^2-3q+3)}{(5q^2-14q+14)q}, \quad u(\theta_c^-) = \left(\frac{2a(\theta_c)}{b(\theta_c)}\right)^{1/2}$$

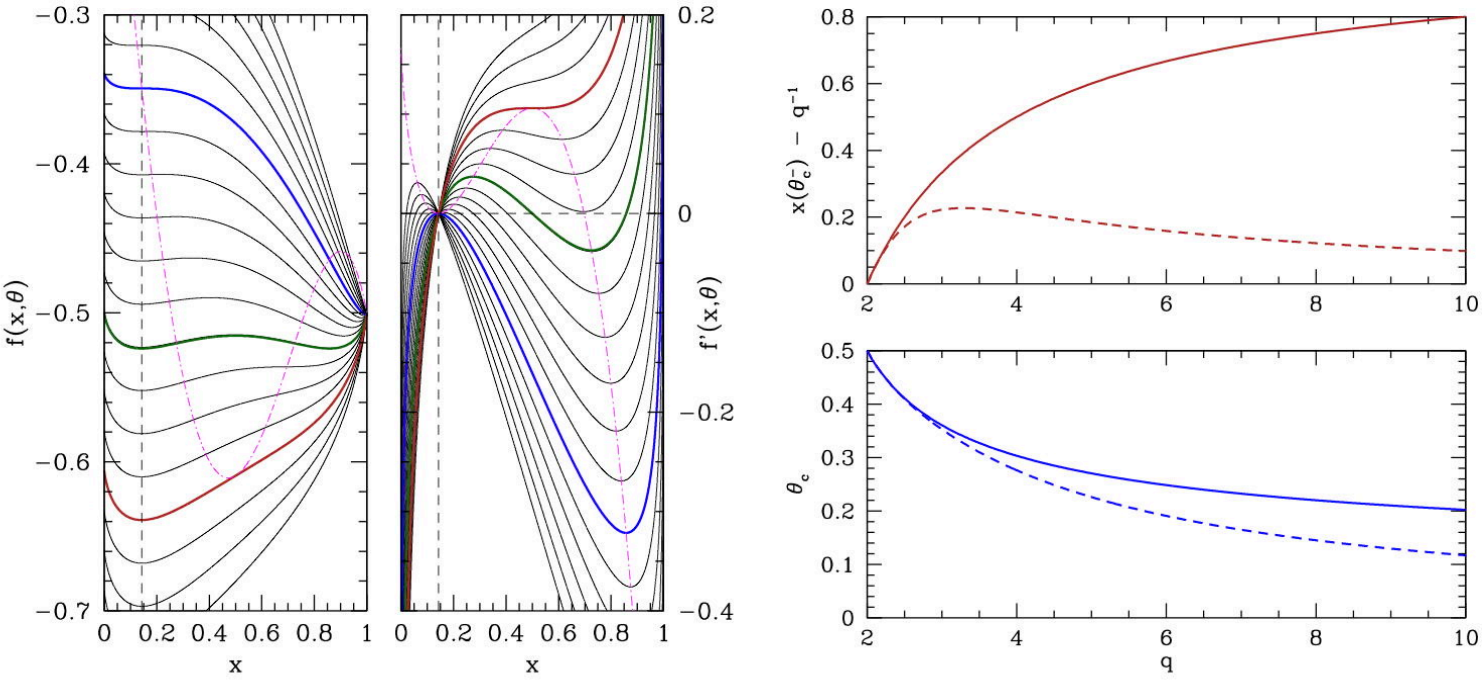


Figure 7.20: The left panels show the variational free energy $f(x,\theta)$ of the $q = 7$ state Potts model and its $x-$derivative $f'(x,\theta)$ *versus* the variational parameter x, for a set of equally spaced temperatures. The vertical dashed black line is at $x = q^{-1} = \frac{1}{7}$. The dot-dash magenta curve in both cases is the locus of points for which the second derivative $f''(x,\theta)$ with respect to x vanishes. Three characteristic temperatures are marked: (i) $\theta = q^{-1}$ (blue), where the coefficient of the quadratic term in the Landau expansion changes sign, (ii) $\theta = \theta_0$ (red), where there is a saddle-node bifurcation and above which the free energy has only one minimum at $x = q^{-1}$ (symmetric phase), and (iii) $\theta = \theta_c$ (green), where the first order transition occurs. The right panels show comparisons of the order parameter jump at θ_c (top) and critical temperature θ_c (bottom) *versus* q for untruncated (solid lines) and truncated (dashed lines) expansions of the mean field free energy. Note the agreement as $q \to 2$, where the jump is small and a truncated expansion is then valid.

But if we do not truncate and solve for the exact MF results for the transition, we find

$$\theta_c^{MF} = \frac{q-2}{2(q-1)\log(q-1)} \quad , \quad x(\theta_c^-) = \frac{q-2}{q}$$