Summary of SI2510 Statistical Mechanics

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Abstract

This is a summary of SI2510 Statistical Mechanics.

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1 Basic Concepts

Phase Transitions Landau introduced the concept that phase transitions are defined by spontaneous symmetry breaking.

Order Parameters An order parameter describes spontaneous symmetry breaking. It is zero in one phase and non-zero in another.

Density Matrices The probability distribution is of the form

$$p_n = \frac{1}{\sum_{m} P_m} P_n = \frac{1}{Z} P_n,$$

where the summation is performed over some set of states. We now introduce the density matrix

$$\rho = \frac{1}{Z} \sum_{n} P_n |n\rangle\langle n|,$$

vielding

$$\langle O \rangle = \sum_{n} p_{n} O_{nn} = \sum_{n} \frac{1}{Z} P_{n} \langle n | O | n \rangle = \frac{1}{Z} \sum_{n} \sum_{m} P_{n} \langle n | m \rangle \langle m | O | n \rangle = \frac{1}{Z} \sum_{n} \sum_{m} \langle n | \rho | m \rangle \langle m | O | n \rangle = \operatorname{tr}(O\rho).$$

As a side note, ρ takes the form

$$\rho = \frac{1}{Z}e^{-\beta K},$$

where K is the Hamiltonian in the canonical ensemble and $H - \mu N$ in the grand canonical ensemble. In these cases, the partition function Z may be computed according to

$$Z = \sum_{m} P_m = \sum_{m} e^{-\beta K_m} = \sum_{m} \langle m | e^{-\beta K} | m \rangle = \operatorname{tr}\left(e^{-\beta K}\right).$$

The Ising Model The Ising model is a simple model of magnets. In this model, a magnet is a collection of interacting spins on a lattice under the influence of an external field. Its generalized coordinates are σ_i , which may take the values ± 1 , signifying a particular spin pointing up or down. The Hamiltonian is

$$\mathcal{H} = -J \sum_{i} \sum_{j=\text{nn}(i)} \sigma_i \sigma_j - h \sum_{i} \sigma_i.$$

The inner summation is carried out over the nearest neighbours of site i in the Ising model, but is generally a sum over the whole lattice. The order parameter defining its phase transition is $m = \langle \sigma_i \rangle$.

This model will be used to demonstrate core concepts in the course.

Exact Solution in One Dimension To solve the Ising model in one dimension we will impose periodic boundary conditions $\sigma_N = \sigma_0$. In the absence of an external magnetic field the Hamiltonian is

$$\mathcal{H} = -J \sum_{i=0}^{N-1} \sigma_i \sigma_{i+1} - h \sum_{i=0}^{N-1} \sigma_i.$$

This yields

$$e^{-\beta \mathcal{H}} = \prod_{i=0}^{N-1} e^{\beta(J\sigma_i \sigma_{i+1} + h\sigma_i)}.$$

Consider one particular factor $T_{\sigma_i\sigma_{i+1}} = e^{\beta J\sigma_i\sigma_{i+1}}$. If we could compute the trace of any one of these, that would directly give us the partition function. However, this rewriting does not decouple the Hamiltonian,

making the trace hard to compute. To do that, let us now treat $T_{\sigma_i\sigma_{i+1}}$ as an operator $T_{\sigma_{i+1}}$ working solely on σ_i and fix σ_{i+1} . The matrix elements of $\sigma_i\sigma_{i+1}$ are

$$\langle i|\sigma_i\sigma_{i+1}|j\rangle = ij\sigma_{i+1}.$$

The redefined transfer matrix may thus be written as

$$T_{\sigma_{i+1}} = \begin{bmatrix} e^{\beta J \sigma_{i+1} + h} & e^{-\beta J \sigma_{i+1} - h} \\ e^{\beta J \sigma_{i+1} + h} & e^{-\beta J \sigma_{i+1} - h} \end{bmatrix}$$

Its eigenvalues are the solution to

$$\left(\lambda - e^{\beta J \sigma_{i+1} + h}\right) \left(\lambda - e^{-\beta J \sigma_{i+1} - h}\right) - 1 = 0.$$

This sucks

Alternatively, we may write the partition function as

$$Z = \sum_{\sigma_0 = \pm 1} \cdots \sum_{\sigma_{N-1} = \pm 1} e^{\left(\beta J \sum_{i=0}^{N-1} \sigma_i \sigma_{i+1} + \frac{1}{2} h \sum_{i=0}^{N-1} \sigma_i + \sigma_{i+1}\right)}.$$

Introducing $t_{\sigma\sigma'} = e^{\beta J\sigma\sigma' + \frac{1}{2}h(\sigma + \sigma')}$ we have

$$Z = \sum_{\sigma_0 = \pm 1} \cdots \sum_{\sigma_{N-1} = \pm 1} \prod_{i=0}^{N-1} t_{\sigma_i \sigma_{i+1}}.$$

Now consider some particular spin and perform the summation over this one first. We obtain

$$\sum_{\sigma_{j}=\pm 1} t_{\sigma_{j-1}\sigma_{j}} t_{\sigma_{j}\sigma_{j+1}} = t_{\sigma_{j-1}\sigma_{j+1}}^{2}.$$

This process is repeated until you obtain

$$Z = \operatorname{tr}(t^N).$$

The matrix representation of the transfer matrix is

$$t = \begin{bmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{bmatrix}.$$

Its eigenvalues are the solutions to

$$\left(\lambda - e^{\beta(J+h)}\right)\left(\lambda - e^{\beta(J-h)}\right) - e^{-2\beta J} = 0,$$

and are given by

$$\begin{split} \lambda^2 - 2e^{\beta J}\cosh(\beta h)\lambda + 2\sinh(2\beta J) &= 0, \\ \lambda_\pm &= e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}\cosh^2(\beta h) - 2\sinh(2\beta J)} \\ &= e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}}. \end{split}$$

Now that we have the eigenvalues, we identify the partition function as

$$Z = \lambda_+^N + \lambda_-^N.$$

This can be further simplified to

$$Z = \lambda_+^N \left(1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right) \approx \lambda_+^N.$$

Next, the free energy is given by

$$G = -k_{\rm B}T \left(N \ln(\lambda_+) + \ln\left(1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right) \right).$$

The magnetization is given by

$$\begin{split} m &= -\frac{1}{N} \left(\frac{\partial G}{\partial \beta h} \right)_T \\ &\approx \frac{e^{\beta J} \sinh(\beta h) + \frac{e^{2\beta J} \sinh(\beta h) \cosh(\beta h)}{\sqrt{e^{2\beta J} \sinh^2(\beta h) + e^{-2\beta J}}}}{e^{\beta J} \cosh(\beta h) + \sqrt{e^{2\beta J} \sinh^2(\beta h) + e^{-2\beta J}}} \\ &= \sinh(\beta h) \frac{1 + \frac{\cosh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}}{\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}} \\ &= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}. \end{split}$$

If h = 0 there is no spontaneous magnetization. However, at low temperatures a very small field will produce saturation magnetization. This corresponds to a phase transition at T = 0.

Next consider the pair distribution function

$$g(j) = \langle \sigma_0 \sigma_i \rangle$$
.

The error introduced by assuming uncorrelated spins, as will be done later, is

$$\Gamma(j) = \langle \sigma_i \sigma_{i+j} \rangle - \langle \sigma_i \rangle \langle \sigma_{i+j} \rangle.$$

In a general case with different couplings between spins and without an external field we have

$$\langle \sigma_{i}\sigma_{i+j}\rangle = \frac{1}{Z} \sum_{\sigma_{i}\sigma_{i+j}} \sigma_{i} \sigma_{i+j} e^{\beta \sum_{i=0}^{N-1} J_{i}\sigma_{i}\sigma_{i+1}}$$

$$= \frac{1}{Z} \sum_{\sigma_{i}\sigma_{i+1}\sigma_{i+1}\sigma_{i+2}\dots\sigma_{i+j-1}\sigma_{i+j}} e^{\beta \sum_{i=0}^{N-1} J_{i}\sigma_{i}\sigma_{i+1}}$$

$$= \frac{1}{Z} \frac{\partial}{\partial \beta J_{i}} \dots \frac{\partial}{\partial \beta J_{i+j}} Z.$$

Using the fact that

$$Z = 2 \prod_{i=1}^{N} 2 \cosh(\beta J_i)$$

we obtain

$$\langle \sigma_i \sigma_{i+j} \rangle = \prod_{k=i}^{i+j} \tanh(\beta J_k).$$

In one dimension there is no magnetization. In the case where all couplings are the same we obtain

$$\Gamma(j) = \tanh^j(\beta J) = e^{-\frac{j}{\xi}},$$

where we have introduced the correlation length

$$\xi = -\frac{1}{\ln(\tanh(\beta J))}.$$

2 Mean-Field Theory

Mean-Field Theory of the Ising Model Consider the effect of flipping some particular spin i from 1 to -1 while leaving the others unchanged. The change in the Hamiltonian is given by

$$\Delta \mathcal{H} = 2h + 2J \sum_{j=\text{nn}(i)} \sigma_j = -\left(h + J \sum_{j=\text{nn}(i)} \sigma_j\right) \Delta \sigma_i.$$

This is the same as would be obtained for a set of non-interacting spins in a magnetic field

$$h' = h + J \sum_{j=\text{nn}(i)} \sigma_j.$$

The difficulties in solving the Ising model arise due to the fact that the nearest neighbours themselves fluctuate, making the endeavour to solve this with previously developed methods impossible. Instead, we proceed by reducing the interactions to their mean value, the core idea of mean-field theory. The effective field is thus

$$h' = h + J \sum_{j=\text{nn}(i)} \langle \sigma_j \rangle.$$

Using previously developed methods we obtain

$$Z = \sum e^{-\beta \mathcal{H}} = \sum e^{\beta h' \sum_{i} \sigma_{i}} = \left(\sum_{\sigma = \pm 1} e^{\beta h' \sigma}\right)^{N} = 2^{N} \cosh^{N}(\beta h'),$$
$$\langle \sigma_{i} \rangle = \frac{1}{Z} \sum \sigma_{i} e^{\beta h' \sum_{j} \sigma_{j}} = \frac{\mathrm{d}}{\mathrm{d}\beta h'} \ln(2 \cosh(\beta h')) = \tanh(\beta h').$$

Note that this implies that all spins are expected to point in the same direction. Baked into the process there is a specific idea of the structure of the solution, and it is therefore important to make such a guess. We proceed with the ferromagnetic case, where the implication holds true, and introduce $m = \langle \sigma_i \rangle$ to obtain

$$m = \tanh\left(\beta\left(h + J\sum_{j=\text{nn}(i)} m\right)\right).$$

Introducing the coordination number z of a lattice site we obtain

$$m = \tanh(\beta (h + zJm)).$$

This equation can be solved graphically to yield the magnetization, but we will discuss it qualitatively here. Depending on the parameters, the number of solutions is between one and three. In the case where h = 0, one solution is m = 0, and two other solutions may be found at $m = \pm m_0$. At low temperatures the right-hand side approaches \pm , yielding $m_0 = 1$. As the temperature approaches the critical temperature, above which no spontaneous magnetism is found, m_0 is small and we obtain

$$m_0 \approx \beta z J m_0 - \frac{1}{3} (\beta z J m_0)^3,$$

$$(\beta z J)^3 m_0^2 = 3(\beta z J - 1),$$

$$m_0 = \frac{1}{(\beta z J)^{\frac{3}{2}}} \sqrt{3} \sqrt{\beta z J - 1}$$

$$= \sqrt{3} \left(\frac{k_{\rm B} T}{z J}\right)^{\frac{3}{2}} \sqrt{\frac{z J}{k_{\rm B} T} - 1}.$$

We can now identify the temperature such that this is zero, namely

$$T_{\rm C} = \frac{zJ}{k_{\rm B}}$$

to write

$$m_0 = \sqrt{3} \left(\frac{T}{T_{\rm C}}\right)^{\frac{3}{2}} \sqrt{\frac{T_{\rm C}}{T} - 1}.$$

While the existence of solutions to $m = \tanh(\beta z J m)$ would have sufficed to identify the critical temperature, we have now characterized the behaviour of the magnetization close to the phase transition as well. One of the uses of mean-field theory is exactly this qualitative description of the phase diagram.

One more thing should be mentioned, namely the assertion that there actually is spontaneous magnetization. After all, if three solutions are possible, who is to say that one of the non-zero ones are found? To do this, we consider the entropy of an ideal paramagnet, which can be shown to be

$$S = -Nk_{\rm B}\left(\frac{1-m}{2}\ln\left(\frac{1-m}{2}\right) + \frac{1+m}{2}\ln\left(\frac{1+m}{2}\right)\right).$$

We see that the non-zero solutions maximize entropy - a relief.

Critical Behaviour Using the mean-field result, we may now study other quantities close to the phase transition. The susceptibility is given by

$$\chi = \left(\frac{\partial m}{\partial h}\right)_T.$$

The implicit equation for the magnetization yields

$$\chi = \frac{1}{\cosh^2(\beta(qJm+h))}(\beta qJ\chi + \beta),$$

$$\chi = \frac{\beta}{\cosh^2(\beta(qJm+h)) - \beta qJ} = \frac{1}{k_{\rm B}\left(T\cosh^2(\beta(qJm+h)) - \frac{qJ}{k_{\rm B}}\right)}.$$

Introducing the critical temperature, we write this as

$$\chi = \frac{1}{k_{\rm B} \left(T \cosh^2(\beta (qJm + h)) - Tc \right)}.$$

In particular, for h = 0 and temperatures above T_c , where there is no magnetization, we obtain

$$\chi = \frac{1}{k_{\rm B} \left(T - T c \right)}.$$

When approaching the phase transition from below for h = 0, we use the asymptotic expression for the magnetization to obtain

$$\chi = \frac{1}{k_{\rm B} \left(T \cosh^2 \left(\beta q J \sqrt{3} \left(\frac{T}{T_{\rm C}} \right)^{\frac{3}{2}} \sqrt{\frac{T_{\rm c}}{T} - 1} \right) - Tc \right)} \\
= \frac{1}{k_{\rm B} \left(T \cosh^2 \left(\sqrt{3} \sqrt{1 - \frac{T}{T_{\rm c}}} \right) - Tc \right)} \\
= \frac{1}{k_{\rm B} \left(T \left(1 + 3 \left(1 - \frac{T}{T_{\rm c}} \right) \right) - Tc \right)} \\
= \frac{1}{k_{\rm B} T_{\rm c} \left(\frac{T}{T_{\rm c}} \left(1 + 3 \left(1 - \frac{T}{T_{\rm c}} \right) \right) - 1 \right)} \\
= \frac{1}{k_{\rm B} T_{\rm c} \left(\frac{T}{T_{\rm c}} + 3 \left(1 - \frac{T}{T_{\rm c}} \right) - 1 \right)} \\
= \frac{1}{2k_{\rm B} (T - Tc)}.$$

I hate this.

The Bragg-Williams Approximation The Bragg-Williams approximation to mean-field theory starts with constructing the availability in terms of the order parameter. In the case of the Ising model, we introduce the numbers N_{\pm} of spins with values ± 1 . Furthermore, we introduce the numbers $N_{\pm\pm}$ of spin pairs of any kind. The Hamiltonian is thus

$$\mathcal{H} = -J(N_{++} + N_{--} - N_{+-}) - h(N_{+} - N_{-}).$$

Treating the spins as independent allows us to write

$$S = -k_{\rm B} \left(N_+ \ln(N_+) + N_- \ln(N_-) \right).$$

The number of pairs is given by

$$N_{\pm\pm} = \frac{qN_{\pm}^2}{2N}, \ N_{+-} = \frac{qN_{+}N_{-}}{N}.$$

To proceed, we re-express the spin numbers in terms of the order parameter by using $N=N_++N_-$ and $\sigma=N_+-N_-$ to obtain

$$N_{+} = \frac{1}{2}N(1+m), \ N_{-} = \frac{1}{2}N(1-m).$$

The Hamiltonian is now given by

$$\mathcal{H} = -\frac{qJ}{2N}(N_+^2 + N_-^2 - 2N_+N_-) - Nhm$$

$$= -\frac{qJN}{8}((1+m)^2 + (1-m)^2 - 2(1+m)(1-m)) - Nhm$$

$$= -\frac{qJN}{2}m^2 - Nhm,$$

and the free energy is somehow

$$G(h,T) = \mathcal{H} - TS$$

$$= -\frac{qJN}{2}m^2 - Nhm + \frac{1}{2}Nk_BT\left((1+m)\ln\left(\frac{1}{2}N(1+m)\right) + (1-m)\ln\left(\frac{1}{2}N(1-m)\right)\right).$$

Minimizing it with respect to the order parameter yields

$$-qJNm - Nh + \frac{1}{2}Nk_{\rm B}T\left(\ln\left(\frac{1}{2}N(1+m)\right) + 1 - \ln\left(\frac{1}{2}N(1-m)\right) - 1\right) = 0,$$

$$-qJm - h + \frac{1}{2}k_{\rm B}T\ln\left(\frac{1+m}{1-m}\right) = 0.$$

Its solution is

$$\begin{split} \frac{1+m}{1-m} &= e^{2\beta(qJm+h)},\\ 1+m &= (1-m)e^{2\beta(qJm+h)},\\ m(1+e^{2\beta(qJm+h)}) &= e^{2\beta(qJm+h)}-1,\\ m &= \tanh(\beta(qJm+h)), \end{split}$$

as expected.

Inaccuracies of Mean-Field Theories The mean-field arguments predict the existence of a phase transition, but this cannot be the case in one dimension. To see this, consider a chain in its ground state and the set of excitations that flips all spins to the right of some spin k. The change in energy is 2J, and the number of possible states corresponding to this energy is N-1, hence the free energy changes by $2J-k_{\rm B}\ln(N-1)$. For large N such states are thus always preferable. Their removal of translation invariance implies that there is no magnetization, in contradiction of the mean-field results.

A slightly better result is obtained for a $N \times N$ lattice in two dimensions. The set of excitations now consists of excitations that split the system in two distinct magnetic domains. Any particular excitation is

described by a chain running through the bonds. Each segment crosses one bond, and the energy change due to the excitation is 2LJ, where L is the number of segments. The typical length is 2N. The next segment may always be placed in at least two sites, neglecting the boundaries. Including the N possible starting points, the multiplicity of the chain is $N2^L$, and the free energy change of the excitation is

$$\Delta G = 4NJ - k_{\rm B}T \ln(2^{2N}N).$$

The phase transition occurs when this energy change is negative, i.e. when

$$k_{\rm B}T\ln(2^{2N}N) > 4NJ, \ k_{\rm B}T(2N\ln(2) + \ln(N)) > 4NJ, \ T < T_{\rm c} \approx \frac{2J}{k_{\rm B}\ln(2)},$$

which is decently close to the analytically obtained results.

Antiferromagnetism

3 Landau Theory

Things Close to the phase transition temperature the free energy may be expanded as

$$G(m,T) = a_0(T) + \sum_{i} \frac{1}{2i} a_i(T) m^{2i}.$$

At T=0 you will have $|\mathbf{m}|=1$. The free energy may only depend on the length of the free energy, hence we have

$$G(\mathbf{m}, T) = a_0(T) + \sum_{i} \frac{1}{2i} a_{2i}(T) m^{2i}.$$

In order for the free energy to be bounded, the highest-order coefficient must be positive.

Suppose now that as the temperature is lowered, a_2 is the first coefficient to change sign (one coefficient must do this in order for a minimum to exist). Expand it close to the transition temperature as

$$a_2(T) = a_{2,0}(T - T_c).$$

The temperature dependence of the order parameter may now be obtained as

$$a_2m + a_4(T_c)m^3 + \dots = 0.$$

Ignoring higher-order terms we obtain

$$m = \sqrt{\frac{a_{2,0}}{a_4(T_c)}(T_c - T)}.$$

Next we study the heat capacity

$$C = T \left(\frac{\partial S}{\partial T} \right)_h.$$

We have

$$S = -\frac{\partial G}{\partial T} = -\frac{\mathrm{d}a_0}{\mathrm{d}T} - \sum_{i} \frac{1}{2i} \left(\frac{\mathrm{d}a_{2i}}{\mathrm{d}T} m^{2i} + a_{2i} \frac{\mathrm{d}m^{2i}}{\mathrm{d}T} \right).$$

Close to and below the critical temperature we have

$$C = T \left(-\frac{\mathrm{d}^2 a_0}{\mathrm{d}T^2} - \sum_i \frac{1}{2i} \left(\frac{\mathrm{d}^2 a_{2i}}{\mathrm{d}T^2} m^{2i} + \frac{\mathrm{d}a_{2i}}{\mathrm{d}T} \frac{\mathrm{d}m^{2i}}{\mathrm{d}T} + \frac{\mathrm{d}a_{2i}}{\mathrm{d}T} \frac{\mathrm{d}m^{2i}}{\mathrm{d}T} + a_{2i} \frac{\mathrm{d}^2 m^{2i}}{\mathrm{d}T^2} \right) \right)$$

$$= T \left(-\frac{\mathrm{d}^2 a_0}{\mathrm{d}T^2} - \sum_i \frac{1}{2i} \left(\frac{\mathrm{d}^2 a_{2i}}{\mathrm{d}T^2} m^{2i} + 2 \frac{\mathrm{d}a_{2i}}{\mathrm{d}T} \frac{\mathrm{d}m^{2i}}{\mathrm{d}T} + a_{2i} \frac{\mathrm{d}^2 m^{2i}}{\mathrm{d}T^2} \right) \right).$$

We have

$$\begin{split} \frac{\mathrm{d}m^{2i}}{\mathrm{d}T} &= im^{2(i-1)}\frac{\mathrm{d}m^2}{\mathrm{d}T} = -im^{2(i-1)}\frac{a_{2,0}}{a_4(T_\mathrm{c})},\\ \frac{\mathrm{d}^2m^{2i}}{\mathrm{d}T^2} &= i(i-1)m^{2(i-2)}\frac{a_{2,0}^2}{a_4^2(T_\mathrm{c})}, \end{split}$$

and thus

$$\begin{split} C = & T \left(-\frac{\mathrm{d}^2 a_0}{\mathrm{d} T^2} - \sum_{i=1}^\infty \frac{1}{2i} \left(\frac{\mathrm{d}^2 a_{2i}}{\mathrm{d} T^2} m^{2i} - 2i \frac{\mathrm{d} a_{2i}}{\mathrm{d} T} \frac{a_{2,0}}{a_4(T_{\mathrm{c}})} m^{2(i-1)} + a_{2i}i(i-1) m^{2(i-2)} \frac{a_{2,0}^2}{a_4^2(T_{\mathrm{c}})} \right) \right) \\ = & - T \frac{\mathrm{d}^2 a_0}{\mathrm{d} T^2} + T \frac{a_{2,0}^2}{a_4(T_{\mathrm{c}})} - T \sum_{i=2}^\infty \frac{1}{2i} \left(\frac{\mathrm{d}^2 a_{2i}}{\mathrm{d} T^2} m^{2i} - 2i \frac{\mathrm{d} a_{2i}}{\mathrm{d} T} \frac{a_{2,0}}{a_4(T_{\mathrm{c}})} m^{2(i-1)} + a_{2i}i(i-1) m^{2(i-2)} \frac{a_{2,0}^2}{a_4^2(T_{\mathrm{c}})} \right) \\ = & - T \frac{\mathrm{d}^2 a_0}{\mathrm{d} T^2} + T \frac{a_{2,0}^2}{a_4(T_{\mathrm{c}})} - \frac{1}{4} T \left(\frac{\mathrm{d}^2 a_4}{\mathrm{d} T^2} m^4 - 4 \frac{\mathrm{d} a_4}{\mathrm{d} T} \frac{a_{2,0}}{a_4(T_{\mathrm{c}})} m^2 + 2a_4 \frac{a_{2,0}^2}{a_4^2(T_{\mathrm{c}})} \right) \\ & - T \sum_{i=3}^\infty \frac{1}{2i} \left(\frac{\mathrm{d}^2 a_{2i}}{\mathrm{d} T^2} m^{2i} - 2i \frac{\mathrm{d} a_{2i}}{\mathrm{d} T} \frac{a_{2,0}}{a_4(T_{\mathrm{c}})} m^{2(i-1)} + a_{2i}i(i-1) m^{2(i-2)} \frac{a_{2,0}^2}{a_4^2(T_{\mathrm{c}})} \right) \\ & \approx - T \frac{\mathrm{d}^2 a_0}{\mathrm{d} T^2} + T \frac{a_{2,0}^2}{2a_4(T_{\mathrm{c}})}, \end{split}$$

where we have ignored terms containing the magnetization and set all temperatures to be the critical temperature. Above the critical temperature the magnetization is instead identically zero, netting

$$C = -T \frac{\mathrm{d}^2 a_0}{\mathrm{d} T^2}.$$

Suppose instead that a_4 is the first coefficient to change sign. In this case a discontinuous step in the order parameter might occur. To show that such a step exists, we need to show that $a_2(T_c) > 0$. We investigate this by comparing $G(m_0, T_c)$ to $G(0, T_c)$, where m_0 is the magnetization at the minimum. The phase transition occurs when the two are equal, i.e. when

$$G(m_0, T_c) - G(0, T_c) = \sum_{i} \frac{1}{2i} a_{2i}(T_c) m_0^{2i} = 0.$$

The magnetization corresponds to a minimum of G, and thus satisfies

$$\sum_{i} a_{2i}(T_{\rm c}) m_0^{2i-1} = 0.$$

Ignoring terms above order 6 we have

$$a_2(T_c)m_0 + a_4(T_c)m_0^3 + a_6(T_c)m_0^5 = 0, \ \frac{1}{2}a_2(T_c)m_0^2 + \frac{1}{4}a_4(T_c)m_0^4 + \frac{1}{6}a_4(T_c)m_0^6 = 0.$$

The non-trivial value satisfies

$$a_2(T_{\rm c}) + a_4(T_{\rm c})m_0^2 + a_6(T_{\rm c})m_0^4 = 0, \ \frac{1}{2}a_2(T_{\rm c}) + \frac{1}{4}a_4(T_{\rm c})m_0^2 + \frac{1}{6}a_4(T_{\rm c})m_0^4 = 0.$$

Combining the equation nets

$$\begin{split} \frac{1}{2}a_4(T_{\rm c})m_0^2 + \frac{2}{3}a_6(T_{\rm c})m_0^4 &= 0,\\ \frac{1}{2}a_4(T_{\rm c}) + \frac{2}{3}a_6(T_{\rm c})m_0^2 &= 0,\\ m_0^2 &= -\frac{3a_4(T_{\rm c})}{4a_6(T_{\rm c})}. \end{split}$$

For this to work, we must have $a_6(T_c) > 0$ to keep the global minimum at finite magnetization and $a_4(T_c) < 0$ per our assumption of the existence of a local minimum, making the magnetization real. Inserting this into a previous expression yields

$$a_2(T_{\rm c}) - a_4(T_{\rm c}) \frac{3a_4(T_{\rm c})}{4a_6(T_{\rm c})} + a_6(T_{\rm c}) \frac{9a_4^2(T_{\rm c})}{16a_6^2(T_{\rm c})} = a_2(T_{\rm c}) - \frac{3}{4} \frac{a_4^2(T_{\rm c})}{a_6(T_{\rm c})} + \frac{9}{16} \frac{a_4^2(T_{\rm c})}{a_6(T_{\rm c})} = a_2(T_{\rm c}) - \frac{3}{16} \frac{a_4^2(T_{\rm c})}{a_6(T_{\rm c})} = 0,$$

and thus

$$a_2(T_c) = \frac{3}{16} \frac{a_4^2(T_c)}{a_6(T_c)} > 0,$$

as we wanted to show.