PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #6 SOLUTIONS

(1) Consider the equation of state

$$p\sqrt{v^2 - b^2} = RT\,\exp\left(-\frac{a}{RTv^2}\right).$$

(a) Find the critical point (v_c, T_c, p_c).

(b) Defining $\bar{p} = p/p_c$, $\bar{v} = v/v_c$, and $\bar{T} = T/T_c$, write the equation of state in dimensionless form $\bar{p} = \bar{p}(\bar{v}, \bar{T})$.

(c) Expanding $\bar{p} = 1 + \pi$, $\bar{v} = 1 + \epsilon$, and $\bar{T} = 1 + t$, find $\epsilon_{liq}(t)$ and $\epsilon_{gas}(t)$ for $-1 \ll t < 0$.

Solution :

(a) We write

$$p(T,v) = \frac{RT}{\sqrt{v^2 - b^2}}\,e^{-a/RTv^2} \qquad \Rightarrow \qquad \left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{2a}{RTv^3} - \frac{v}{v^2 - b^2}\right) p\,.$$

Thus, setting $\left(\frac{\partial p}{\partial v}\right)_T = 0$ yields the equation

$$\frac{2a}{b^2 RT} = \frac{u^4}{u^2 - 1} \equiv \varphi(u)\,,$$

where $u \equiv v/b$. Differentiating $\varphi(u)$, we find it has a unique minimum at $u^* = \sqrt{2}$, where $\varphi(u^*) = 4$. Thus,

$$T_c = \frac{a}{2b^2 R} \quad , \quad v_c = \sqrt{2}\,b \quad , \quad p_c = \frac{a}{2eb^2}\,.$$

(b) In terms of $\bar{p}$, $\bar{v}$, and $\bar{T}$, we have the universal equation of state

$$\bar{p} = \frac{\bar{T}}{\sqrt{2\bar{v}^2 - 1}}\,\exp\left(1 - \frac{1}{\bar{T}\bar{v}^2}\right).$$

(c) With $\bar{p} = 1 + \pi$, $\bar{v} = 1 + \epsilon$, and $\bar{T} = 1 + t$, we have from Eq. 7.32 of the Lecture Notes,

$$\epsilon_{L,G} = \mp\left(\frac{6\,\pi_{\epsilon t}}{\pi_{\epsilon\epsilon\epsilon}}\right)^{1/2}(-t)^{1/2} + \mathcal{O}(t)\,.$$

From `Mathematica` we find $\pi_{\epsilon t} = -2$ and $\pi_{\epsilon\epsilon\epsilon} = -16$, hence

$$\epsilon_{L,G} = \mp\tfrac{\sqrt{3}}{2}\,(-t)^{1/2} + \mathcal{O}(t)\,.$$

(2) You are invited to contemplate the model

$$\hat{H} = -J \sum_{\langle ij \rangle} \hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{n}}_j$$

on a regular lattice of coordination number z, where each local moment $\hat{\boldsymbol{n}}_i$ can take on one of $2n$ possible values: $\hat{\boldsymbol{n}}_i \in \{\pm\, \hat{\boldsymbol{e}}_1, \ldots, \pm\hat{\boldsymbol{e}}_n\}$, where $\hat{\boldsymbol{e}}_i \cdot \hat{\boldsymbol{e}}_j = \delta_{ij}$. You may assume $J > 0$.

(a) Making the mean field *Ansatz* $\boldsymbol{m} = \langle \hat{\boldsymbol{n}}_i \rangle$, find the dimensionless free energy density $f(m, \theta)$, where $\theta = k_{\rm B}T/zJ$ and $f = F/NzJ$.

(b) Consider two possible orientations for the moment: $\boldsymbol{m}_{\rm A} = m\,(1, 0, \ldots, 0)$, in which the moment lies along one of the $\hat{\boldsymbol{e}}_i$ directions, and $\boldsymbol{m}_{\rm B} = m\,\big(\frac{1}{\sqrt{n}}, \ldots, \frac{1}{\sqrt{n}}\big)$, in which the moment makes an angle $\cos^{-1}\big(\frac{1}{\sqrt{n}}\big)$ with each of the $\hat{\boldsymbol{e}}_i$. Which configuration will have the lower free energy?

(c) Analyze the mean field theory and show that for $n \leq 3$ there is a second order transition. Find the critical temperature $\theta_{\rm c}(n)$.

(d) Show that for $n > 3$ the transition is first order. Numerically obtain $\theta_{\rm c}(n)$ for $n = 4, 5, 6$.

Hint: The case $n = 3$ is examined in example problem 7.16.

Solution :

(a) The effective mean field is $\boldsymbol{H}_{\rm eff} = zJ\boldsymbol{m}$, where $\boldsymbol{m} = \langle \hat{\boldsymbol{n}}_i \rangle$. The mean field Hamiltonian is found to be

$$\hat{H}^{\rm MF} = \tfrac{1}{2} NzJ\boldsymbol{m}^2 - \boldsymbol{H}_{\rm eff} \cdot \sum_i \hat{\boldsymbol{n}}_i \;.$$

With $\theta = k_{\rm B}T/zJ$ and $f = F/zJN$, we then have

$$\begin{aligned} f(\theta\,,\boldsymbol{m}) &= -\frac{k_{\rm B}T}{NzJ} \ln \mathsf{Tr}\, e^{-\hat{H}_{\rm eff}/k_{\rm B}T} \\ &= \tfrac{1}{2}\boldsymbol{m}^2 - \theta\, \ln\!\left[2 \sum_{j=1}^{n} \cosh\!\Big(\frac{m_j}{\theta}\Big)\right] \;, \end{aligned}$$

where $m_j = \boldsymbol{m} \cdot \hat{\boldsymbol{e}}_j$ is the component of $\boldsymbol{m}$ along $\hat{\boldsymbol{e}}_j$.

(b) The free energies for the A and B orientations are

$$f_{\rm A}(\theta, m) = \tfrac{1}{2}m^2 - \theta \ln\!\left(1 + \frac{\cosh(m/\theta) - 1}{n}\right) - \theta \ln(2n)$$

$$f_{\rm B}(\theta, m) = \tfrac{1}{2}m^2 - \theta \ln \cosh\big(m/\sqrt{n}\,\theta\big) - \theta \ln(2n) \quad .$$

Define $u = m/\theta$. Note that

$$1 + \frac{\cosh u - 1}{n} = 1 + \frac{u^2}{2!\,n} + \frac{u^4}{4!\,n} + \frac{u^6}{6!\,n} + \ldots$$
$$\cosh\left(\frac{u}{\sqrt{n}}\right) = 1 + \frac{u^2}{2!\,n} + \frac{u^4}{4!\,n^2} + \frac{u^6}{6!\,n^3} + \ldots \quad .$$

Note that the first two terms of these expansions are identical, but for terms of order u^4 and above, the upper expression is larger than the lower one, for any nonzero value of u. Taking the logarithm of each, we have shown $f_{\rm A}(\theta, m) \le f_{\rm B}(\theta, m)$, with equality holding only for $m/\theta = 0$. Thus, configuration B is never preferred.

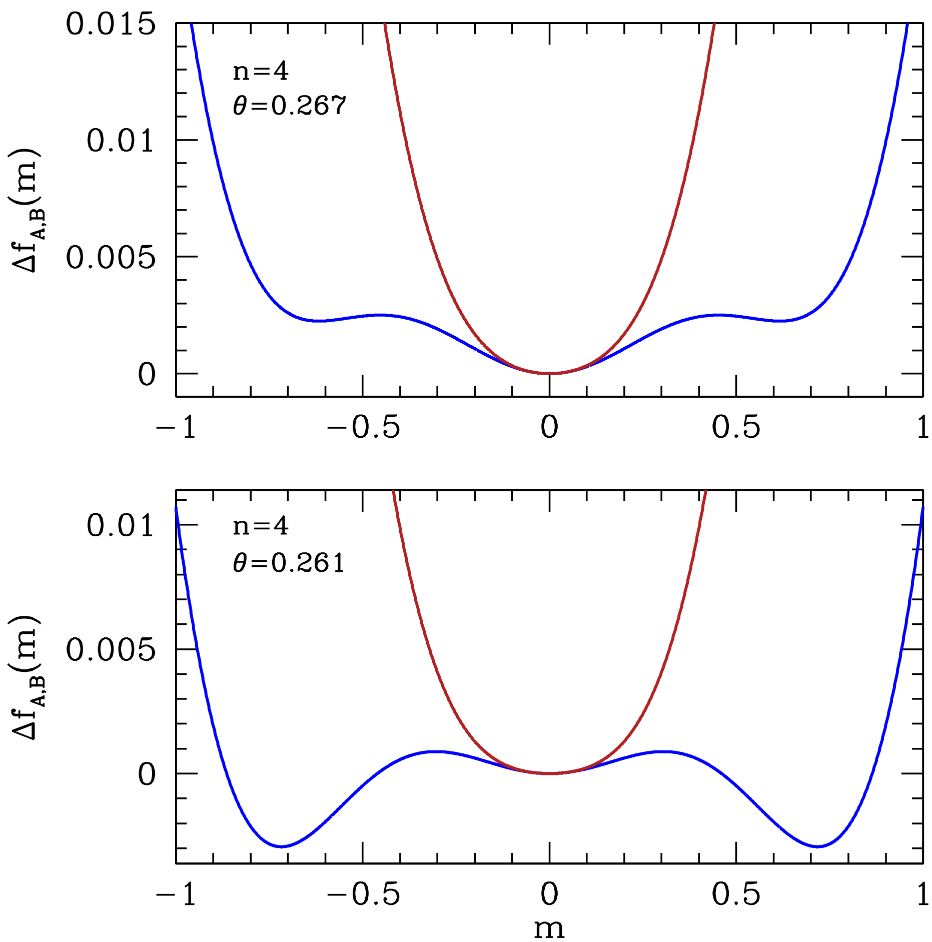

Figure 1: Free energies $\Delta f_{\rm A,B}(m) = f_{\rm A,B}(m) - f_{\rm A,B}(0)$ for A (blue) and B (dark red) configurations for $n = 4$. Upper panel has $\theta = 0.267$ and lower panel $\theta = 0.261$. A first order phase transition sets in at $\theta_{\rm c} = 0.264187$.

(c) Expanding the free energy $f_A(m,\theta)$ in powers of m, we obtain

$$f_A = -\theta \ln(2n) + \tfrac{1}{2}\left(1 - \frac{1}{n\theta}\right) m^2 + \frac{3-n}{24n\theta^3}\, m^4 - \frac{n^2 - 15n + 30}{720 n^3 \theta^5}\, m^6 + \mathcal{O}(m^8) \quad .$$

The quadratic term changes sign at $\theta = n^{-1}$. For $n < 3$, the sign of the quartic term is positive, so the transition is second order. For $n = 3$ the transition is also second order because the sextic term is positive. For $n > 3$, the quartic term switches sign, allowing for a first order transition.. Thus for $n \le 3$, the mean field critical temperature is $\theta_c = n^{-1}$.

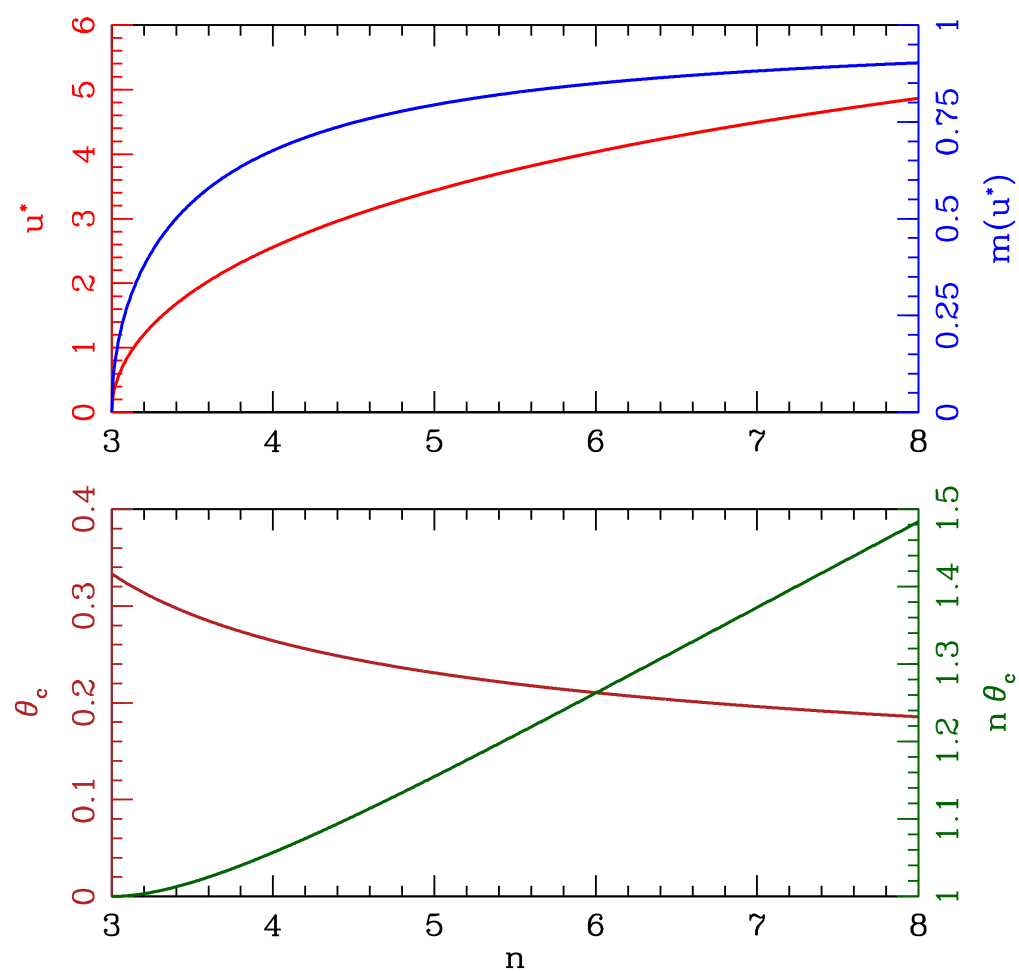

Figure 2: Location of first order transitions for $n \in [3,8]$. Upper panel shows solutions for $u = m/\theta$ (red, left scale) and m (blue, right scale) for $\theta = \theta_c^-$. Lower panel shows θ_c (dark red, left scale) and $n * \theta_c$ (green, right scale). Note that $\theta_c > n^{-1}$ for all $n > 3$. For $n \le 3$ there is a second order transition at $\theta_c = n^{-1}$.

(d) The mean field equation $\partial f_{\rm A}/\partial m = 0$ yields

$$m = \frac{\sinh(m/\theta)}{n-1+\cosh(m/\theta)} \quad .$$

For a first order transition, we also demand $f_{\rm A}(m) = f_{\rm A}(0)$, which signals the moment, as the temperature θ is lowered, when a local minimum at $m \neq 0$ becomes the global minimum. This is the condition for a first order transition. (In the case of a second order transition, the minimum evolves smoothly from $m = 0$ for $\theta < \theta_{\rm c}$.) Since $f_{\rm A}(\theta, m=0) = -\ln(2n)$, we obtain the condition

$$\phi(u) \equiv \tfrac{1}{2} u\, m(u) - \ln\!\left(1 + \frac{\cosh u - 1}{n}\right) \quad ,$$

where

$$m(u) = \frac{\sinh u}{n-1+\cosh u} \quad .$$

Note that $u = m/\theta$ here. If the equation $\phi(u) = 0$ has a (unique) solution $u = u^* \neq 0$, the corresponding value of m where the magnetized solution achieves a minimizing free energy is $m(u^*)$, and the first order transition temperature is $\theta_{\rm c} = m(u^*)/u^*$. Numerical results are shown in Figs. 1 and 2. Note that $n\,\theta_{\rm c} > 1$, *i.e.* $\theta_{\rm c} > n^{-1}$, which is the temperature where the coefficient of the quadratic term in the Landau expansion of $f_{\rm A}(m)$ changes sign. Thus, the first order transition preempts the second order transition.

(3) A *ferrimagnet* is a magnetic structure in which there are different types of spins present. Consider a sodium chloride structure in which the A sublattice spins have magnitude $S_{\rm A}$ and the B sublattice spins have magnitude $S_{\rm B}$ with $S_{\rm B} < S_{\rm A}$ (*e.g.* $S = 1$ for the A sublattice but $S = \frac{1}{2}$ for the B sublattice). The Hamiltonian is

$$\hat{H} = J \sum_{\langle ij \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + g_{\rm A} \mu_0 H \sum_{i \in {\rm A}} S_i^z + g_{\rm B} \mu_0 H \sum_{j \in {\rm B}} S_j^z$$

where $J > 0$, so the interactions are antiferromagnetic.

(a) Work out the mean field theory for this model. Assume that the spins on the A and B sublattices fluctuate about the mean values

$$\langle \boldsymbol{S}_{\rm A} \rangle = m_{\rm A}\, \hat{\boldsymbol{z}} \qquad , \qquad \langle \boldsymbol{S}_{\rm B} \rangle = m_{\rm B}\, \hat{\boldsymbol{z}}$$

and derive a set of coupled mean field equations of the form

$$\begin{aligned} m_{\rm A} &= F_{\rm A}(\beta g_{\rm A} \mu_0 H + \beta J z m_{\rm B}) \\ m_{\rm B} &= F_{\rm B}(\beta g_{\rm B} \mu_0 H + \beta J z m_{\rm A}) \end{aligned}$$

where z is the lattice coordination number ($z = 6$ for NaCl) and $F_{\rm A}(x)$ and $F_{\rm B}(x)$ are related to Brillouin functions.

(b) Show graphically that a solution exists, and find the criterion for broken symmetry solutions to exist when $H = 0$, *i.e.* find T_c. Then linearize, expanding for small m_A, m_B, and H, and solve for $m_A(T)$ and $m_B(T)$ and the susceptibility

$$\chi(T) = -\frac{1}{2}\frac{\partial}{\partial H}(g_A\mu_0 m_A + g_B\mu_0 m_B)$$

in the region $T > T_c$. Does your T_c depend on the sign of J? Why or why not?

Solution :

(a) We apply the mean field *Ansatz* $\langle \boldsymbol{S}_i\rangle = \boldsymbol{m}_{A,B}$ and obtain the mean field Hamiltonian

$$\hat{H}^{MF} = -\tfrac{1}{2}NJz\boldsymbol{m}_A \cdot \boldsymbol{m}_B + \sum_{i\in A}\big(g_A\mu_0\boldsymbol{H} + zJ\boldsymbol{m}_B\big)\cdot \boldsymbol{S}_i + \sum_{j\in B}\big(g_B\mu_0\boldsymbol{H} + zJ\boldsymbol{m}_A\big)\cdot \boldsymbol{S}_j \ .$$

Assuming the sublattice magnetizations are collinear, this leads to two coupled mean field equations:

$$m_A(x) = F_{S_A}\big(\beta g_A\mu_0 H + \beta Jzm_B\big)$$
$$m_B(x) = F_{S_B}\big(\beta g_B\mu_0 H + \beta Jzm_A\big) \ ,$$

where

$$F_S(x) = -S\,B_S(Sx) \ ,$$

and $B_S(x)$ is the Brillouin function,

$$B_S(x) = \big(1 + \tfrac{1}{2S}\big)\,\mathrm{ctnh}\,\big(1 + \tfrac{1}{2S}\big)x - \tfrac{1}{2S}\,\mathrm{ctnh}\,\tfrac{x}{2S} \ .$$

(b) The mean field equations may be solved graphically, as depicted in fig. 3.

Expanding $F_S(x) = -\frac{1}{3}S(S+1)x + \mathcal{O}(x^3)$ for small x, and defining the temperatures $k_B T_{A,B} \equiv \frac{1}{3}S_{A,B}(S_{A,B}+1)\,zJ$, we obtain the linear equations,

$$m_A - \frac{T_A}{T}\,m_B = -\frac{g_A\mu_0}{zJ}\,H$$
$$m_B - \frac{T_B}{T}\,m_A = -\frac{g_B\mu_0}{zJ}\,H \ ,$$

with solution

$$m_A = -\frac{g_A T_A T - g_B T_A T_B}{T^2 - T_A T_B}\,\frac{\mu_0 H}{zJ}$$
$$m_B = -\frac{g_B T_B T - g_A T_A T_B}{T^2 - T_A T_B}\,\frac{\mu_0 H}{zJ} \ .$$

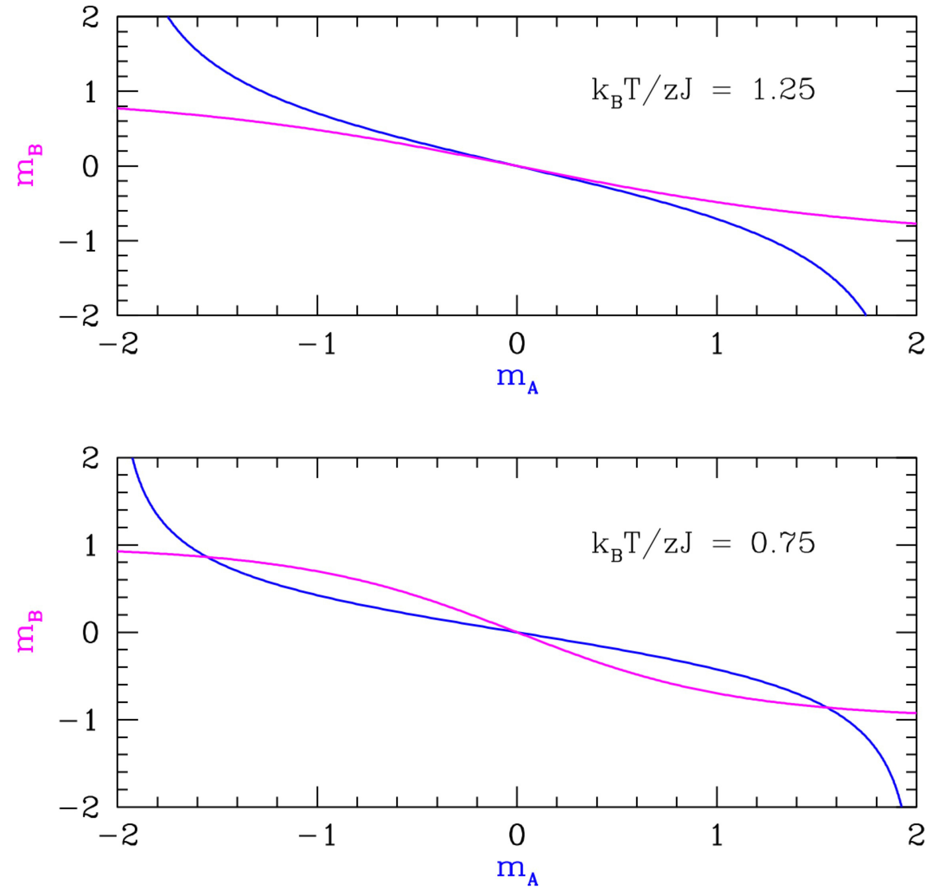

Figure 3: Graphical solution of of mean field equations with $S_{\rm A} = 1$, $S_{\rm B} = 2$, $g_{\rm A} = g_{\rm B} = 1$, $zJ = 1$, and $H = 0$. Top: $T > T_{\rm c}$; bottom: $T < T_{\rm c}$.

The susceptibility is

$$\chi = \frac{1}{N}\frac{\partial M}{\partial H} = -\frac{1}{2}\frac{\partial}{\partial H}\left(g_{\rm A}\mu_0 m_{\rm A} + g_{\rm B}\mu_0 m_{\rm B}\right) = \frac{(g_{\rm A}^2\, T_{\rm A} + g_{\rm B}^2\, T_{\rm B})T - 2g_{\rm A}g_{\rm B}\, T_{\rm A}T_{\rm B}}{T^2 - T_{\rm A}T_{\rm B}}\,\frac{\mu_0^2}{2zJ}\ ,$$

which diverges at

$$T_{\rm c} = \sqrt{T_{\rm A}T_{\rm B}} = \sqrt{S_{\rm A}S_{\rm B}(S_{\rm A}+1)(S_{\rm B}+1)}\,\frac{z|J|}{3k_{\rm B}}\ .$$

Note that $T_{\rm c}$ does not depend on the sign of J. Note also that the signs of $m_{\rm A}$ and $m_{\rm B}$ may vary. For example, let $g_{\rm A} = g_{\rm B} \equiv g$ and suppose $S_{\rm A} > S_{\rm B}$. Then $T_{\rm B} < \sqrt{T_{\rm A}T_{\rm B}} < T_{\rm A}$ and while $m_{\rm A} < 0$ for all $T > T_{\rm c}$, the B sublattice moment changes sign from negative to positive at a temperature $T_{\rm B} > T_{\rm c}$. Finally, note that at high temperatures the susceptibility follows a Curie $\chi \propto T^{-1}$ behavior.