## Problems & Solutions

1. *The binary alloy:*   A binary alloy (as in β brass) consists of N_A atoms of type A, and N_B atoms of type B. The atoms form a simple cubic lattice, each interacting only with its six nearest neighbors. Assume an attractive energy of $-J$ $(J > 0)$ between like neighbors $A - A$ and $B - B$, but a repulsive energy of $+J$ for an $A - B$ pair.

(a) What is the minimum energy configuration, or the state of the system at zero temperature?

• The minimum energy configuration has as little A-B bonds as possible. Thus, at zero temperature atoms A and B *phase separate*, e.g. as indicated below.
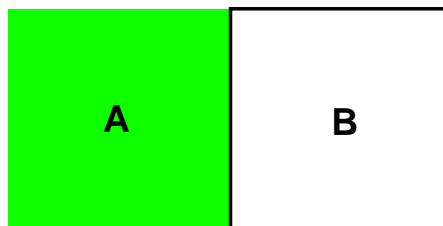
(b) Estimate the total interaction energy assuming that the atoms are randomly distributed among the N sites; i.e. each site is occupied independently with probabilities $p_A = N_A/N$ and $p_B = N_B/N$.

• In a mixed state, the average energy is obtained from

$$E = (\text{number of bonds}) \times (\text{average bond energy})$$
$$= 3N \cdot \left(-Jp_A^2 - Jp_B^2 + 2Jp_Ap_B\right)$$
$$= -3JN \left(\frac{N_A - N_B}{N}\right)^2.$$

(c) Estimate the mixing entropy of the alloy with the same approximation. Assume $N_A, N_B \gg 1$.

• From the number of ways of randomly mixing N_A and N_B particles, we obtain the mixing entropy of

$$S = k_B \ln \left(\frac{N!}{N_A!N_B!}\right).$$

Using Stirling's approximation for large N $(\ln N! \approx N \ln N - N)$, the above expression can be written as

$$S \approx k_B \left(N \ln N - N_A \ln N_A - N_B \ln N_B\right) = -Nk_B \left(p_A \ln p_A + p_B \ln p_B\right).$$

(d) Using the above, obtain a free energy function $F(x)$, where $x = (N_A - N_B)/N$. Expand $F(x)$ to the fourth order in x, and show that the requirement of convexity of F breaks down below a critical temperature T_c. For the remainder of this problem use the expansion obtained in (d) in place of the full function $F(x)$.

• In terms of $x = p_A - p_B$, the free energy can be written as

$$F = E - TS$$

$$= -3JNx^2 + Nk_BT \left\{ \left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right\}.$$

Expanding about $x = 0$ to fourth order, gives

$$F \simeq -Nk_BT \ln 2 + N \left(\frac{k_BT}{2} - 3J \right) x^2 + \frac{Nk_BT}{12} x^4.$$

Clearly, the second derivative of F,

$$\frac{\partial^2 F}{\partial x^2} = N \left(k_BT - 6J \right) + Nk_BTx^2,$$

becomes negative for T small enough. Upon decreasing the temperature, F becomes concave first at $x = 0$, at a critical temperature $T_c = 6J/k_B$.

(e) Sketch $F(x)$ for $T > T_c$, $T = T_c$, and $T < T_c$. For $T < T_c$ there is a range of compositions $x < |x_{sp}(T)|$ where $F(x)$ is not convex and hence the composition is locally unstable. Find $x_{sp}(T)$.

• The function $F(x)$ is concave if $\partial^2 F/\partial x^2 < 0$, i.e. if

$$x^2 < \left(\frac{6J}{k_BT} - 1 \right).$$

This occurs for $T < T_c$, at the spinodal line given by

$$x_{sp}(T) = \sqrt{\frac{6J}{k_BT} - 1},$$

as indicated by the dashed line in the figure below.

(f) The alloy globally minimizes its free energy by separating into A rich and B rich phases of compositions $\pm x_{eq}(T)$, where $x_{eq}(T)$ minimizes the function $F(x)$. Find $x_{eq}(T)$.

• Setting the first derivative of $dF(x)/dx = Nx \left\{ (k_BT - 6J) + k_BTx^2/3 \right\}$, to zero yields the equilibrium value of

$$x_{eq}(T) = \begin{cases} \pm\sqrt{3}\sqrt{\dfrac{6J}{k_BT} - 1} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases}.$$

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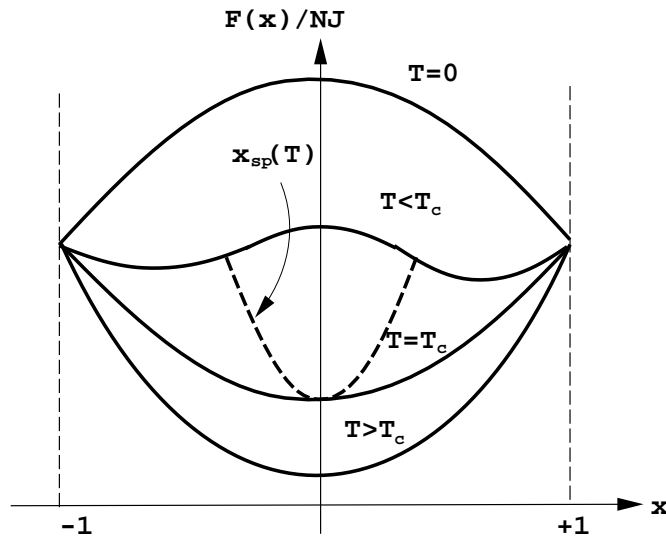
(g) In the (T, x) plane sketch the phase separation boundary $\pm x_{eq}(T)$; and the so called spinodal line $\pm x_{sp}(T)$. (The spinodal line indicates onset of metastability and hysteresis effects.)

• The spinodal and equilibrium curves are indicated in the figure above. In the interval between the two curves, the system is locally stable, but globally unstable. The formation of ordered regions in this regime requires nucleation, and is very slow. The dashed area is locally unstable, and the system easily phase separates to regions rich in A and B.

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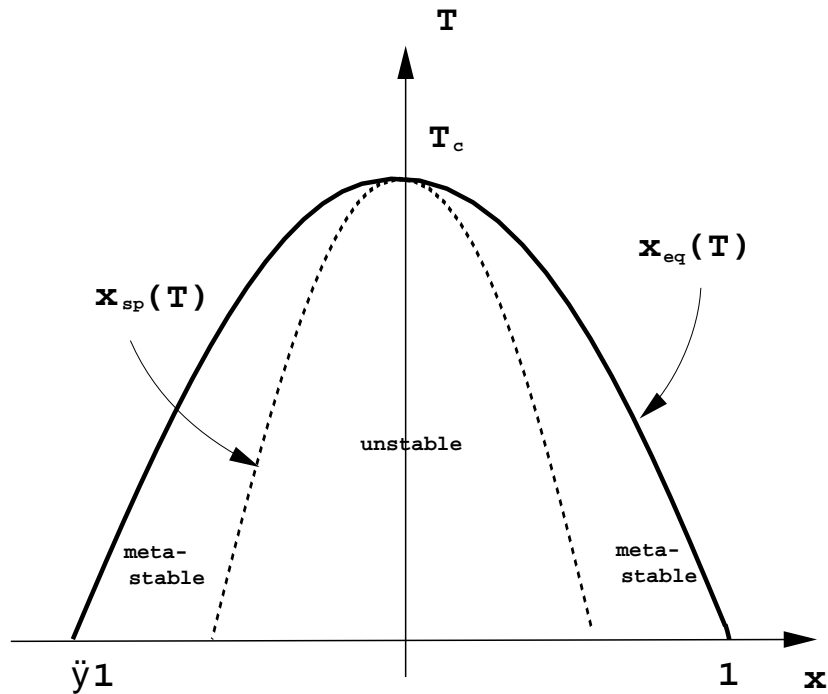
2. *The Ising model of magnetism:* The local environment of an electron in a crystal sometimes forces its spin to stay parallel or anti-parallel to a given lattice direction. As a model of magnetism in such materials we denote the direction of the spin by a single variable $\sigma_i = \pm 1$ (an Ising spin). The energy of a configuration $\{\sigma_i\}$ of spins is then given by

$$\mathcal{H} = \frac{1}{2} \sum_{i,j=1}^{N} J_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i \quad ;$$

where h is an external magnetic field, and J_{ij} is the interaction energy between spins at sites i and j.

(a) For N spins we make the drastic *approximation* that the interaction between all spins is the same, and $J_{ij} = -J/N$ (the equivalent neighbor model). Show that the energy can now be written as $E(M, h) = -N[Jm^2/2 + hm]$, with a magnetization $m = \sum_{i=1}^{N} \sigma_i/N = M/N$.

• For $J_{ij} = -J/N$, the energy of each configuration is only a function of $m = \sum_i \sigma_i/N$, given by

$$E(M, h) = -\frac{J}{2N} \sum_{i,j=1}^{N} \sigma_i \sigma_j - h \sum_{i=1}^{N} \sigma_i$$

$$= -N\frac{J}{2} \left(\sum_{i=1}^{N} \sigma_i/N \right) \left(\sum_{j=1}^{N} \sigma_j/N \right) - Nh \left(\sum_{i=1}^{N} \sigma_i/N \right)$$

$$= -N \left(\frac{J}{2} m^2 + hm \right).$$

(b) Show that the partition function $Z(h, T) = \sum_{\{\sigma_i\}} \exp(-\beta \mathcal{H})$ can be re-written as $Z = \sum_M \exp[-\beta F(m, h)]$; with $F(m, h)$ easily calculated by analogy to problem (1). For the remainder of the problem work only with $F(m, h)$ expanded to 4th order in m.

• Since the energy depends only on the *number* of up spins N_+, and not on their config-

uration, we have

$$Z(h, T) = \sum_{\{\sigma_i\}} \exp(-\beta \mathcal{H})$$

$$= \sum_{N_+=0}^{N} (\text{number of configurations with } N_+ \text{ fixed}) \cdot \exp[-\beta E(M, h)]$$

$$= \sum_{N_+=0}^{N} \left[\frac{N!}{N_+! (N - N_+)!} \right] \exp[-\beta E(M, h)]$$

$$= \sum_{N_+=0}^{N} \exp\left\{ -\beta \left[E(M, h) - k_B T \ln\left(\frac{N!}{N_+! (N - N_+)!} \right) \right] \right\}$$

$$= \sum_{M} \exp[-\beta F(m, h)].$$

By analogy to the previous problem ($N_+ \leftrightarrow N_A$, $m \leftrightarrow x$, $J/2 \leftrightarrow 3J$),

$$\frac{F(m, h)}{N} = -k_B T \ln 2 - hm + \frac{1}{2}(k_B T - J) m^2 + \frac{k_B T}{12} m^4 + \mathcal{O}(m^5).$$

(c) By saddle point integration show that the actual free energy $F(h, T) = -kT \ln Z(h, T)$ is given by $F(h, T) = \min[F(m, h)]_m$. When is the saddle point method valid? Note that $F(m, h)$ is an analytic function but not convex for $T < T_c$, while the true free energy $F(h, T)$ is convex but becomes non-analytic due to the minimization.

• Let $m^*(h, T)$ minimize $F(m, h)$, *i.e.* $\min[F(m, h)]_m = F(m^*, h)$. Since there are N terms in the sum for Z, we have the bounds

$$\exp(-\beta F(m^*, h)) \leq Z \leq N \exp(-\beta F(m^*, h)),$$

or, taking the logarithm and dividing by $-\beta N$,

$$\frac{F(m^*, h)}{N} \geq \frac{F(h, T)}{N} \geq \frac{F(m^*, h)}{N} + \frac{\ln N}{N}.$$

Since F is extensive, we have therefore

$$\frac{F(m^*, h)}{N} = \frac{F(h, T)}{N}$$

in the $N \to \infty$ limit.

(d) For $h = 0$ find the critical temperature T_c below which spontaneous magnetization appears; and calculate the magnetization $\overline{m}(T)$ in the low temperature phase.

- From the definition of the *actual* free energy, the magnetization is given by

$$\overline{m} = -\frac{1}{N}\frac{\partial F(h,T)}{\partial h},$$

i.e.

$$\overline{m} = -\frac{1}{N}\frac{dF(m,h)}{dh} = -\frac{1}{N}\left\{\frac{\partial F(m,h)}{\partial h} + \frac{\partial F(m,h)}{\partial m}\frac{\partial m}{\partial h}\right\}.$$

Thus, if m^* minimizes $F(m,h)$, *i.e.* if $\partial F(m,h)/\partial m|_{m^*} = 0$, then

$$\overline{m} = -\frac{1}{N}\frac{\partial F(m,h)}{\partial h}\bigg|_{m^*} = m^*.$$

For $h = 0$,

$$m^{*2} = \frac{3(J - k_B T)}{k_B T},$$

yielding

$$T_c = \frac{J}{k_B},$$

and

$$\overline{m} = \begin{cases} \pm\sqrt{\dfrac{3(J - k_B T)}{k_B T}} & \text{if } T < T_c \\ 0 & \text{if } T > T_c \end{cases}.$$

(e) Calculate the singular (non-analytic) behavior of the response functions

$$C = \frac{\partial E}{\partial T}\bigg|_{h=0}, \quad \text{and} \quad \chi = \frac{\partial \overline{m}}{\partial h}\bigg|_{h=0}.$$

- The hear capacity is given by

$$C = \frac{\partial E}{\partial T}\bigg|_{h=0,m=m^*} = -\frac{NJ}{2}\frac{\partial m^{*2}}{\partial T} = \begin{cases} \dfrac{3NJT_c}{2T^2} & \text{if } T < T_c \\ 0 & \text{if } T > T_c \end{cases},$$

i.e. $\alpha = 0$, indicating a discontinuity. To calculate the susceptibility, we use

$$h = (k_B T - J)\overline{m} + \frac{k_B T}{3}\overline{m}^3.$$

Taking a derivative with respect to h,

$$1 = \left(k_B T - J + k_B T\overline{m}^2\right)\frac{\partial \overline{m}}{\partial h},$$

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which gives

$$\chi = \left.\frac{\partial \overline{m}}{\partial h}\right|_{h=0} = \begin{cases} \dfrac{1}{2k_B\,(T_c - T)} & \text{if } T < T_c \\[2mm] \dfrac{1}{k_B\,(T - T_c)} & \text{if } T > T_c \end{cases}.$$

From the above expression we obtain $\gamma_\pm = 1$, and $A_+/A_- = 2$.

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3. *The lattice–gas model:* Consider a gas of particles subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i{}^2}{2m} + \frac{1}{2}\sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j), \quad \text{in a volume } V.$$

(a) Show that the grand partition function Ξ can be written as

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N \int \prod_{i=1}^{N} d^3\vec{r}_i \exp\left[-\frac{\beta}{2}\sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j)\right].$$

- The grand partition function is calculated as

$$\begin{aligned}
\Xi &= \sum_{N=0}^{\infty} \frac{e^{N\beta\mu}}{N!} Z_N \\
&= \sum_{N=0}^{\infty} \frac{e^{N\beta\mu}}{N!} \int \prod_{i=1}^{N} \frac{d^3p_i\, d^3r_i}{h^3} e^{-\beta\mathcal{H}} \\
&= \sum_{N=0}^{\infty} \frac{e^{N\beta\mu}}{N!} \left(\prod_{i=1}^{N} \int \frac{d^3p_i}{h^3} e^{-\beta p_i^2/2m}\right) \int \prod_{i=1}^{N} d^3r_i \exp\left(-\frac{\beta}{2}\sum_{i,j} \mathcal{V}_{ij}\right) \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{N\beta}}{\lambda^3}\right)^N \int \prod_{i=1}^{N} d^3r_i \exp\left(-\frac{\beta}{2}\sum_{i,j} \mathcal{V}_{ij}\right),
\end{aligned}$$

where $\lambda^{-1} = \sqrt{2\pi m k_B T}/h$.

(b) The volume V is now subdivided into $\mathcal{N} = V/a^3$ cells of volume a^3, with the spacing a chosen small enough so that each cell α is either empty or occupied by one particle; i.e. the cell occupation number n_α is restricted to 0 or 1 ($\alpha = 1, 2, \cdots, \mathcal{N}$). After approximating the integrals $\int d^3\vec{r}$ by sums $a^3 \sum_{\alpha=1}^{\mathcal{N}}$, show that

$$\Xi \approx \sum_{\{n_\alpha = 0,1\}} \left(\frac{e^{\beta\mu} a^3}{\lambda^3}\right)^{\sum_\alpha n_\alpha} \exp\left[-\frac{\beta}{2}\sum_{\alpha,\beta=1}^{\mathcal{N}} n_\alpha n_\beta \mathcal{V}(\vec{r}_\alpha - \vec{r}_\beta)\right].$$

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- Since

$$\int \prod_{i=1}^{N} d^3 r_i \exp\left(-\frac{\beta}{2}\sum_{i,j}\mathcal{V}_{ij}\right) \approx a^{3N}\sideset{}{'}\sum \exp\left\{-\frac{\beta}{2}\sum_{\alpha,\beta=1}^{\mathcal{N}} n_\alpha n_\beta \mathcal{V}\left(\vec{r}_\alpha - \vec{r}_\beta\right)\right\} \cdot N!,$$

where the primed sum is over the configurations $\{n_\alpha = 0, 1\}$ with fixed N, and

$$N = \sum_{\alpha=1}^{\mathcal{N}} n_\alpha,$$

we have

$$\Xi \approx \sum_{\{n_\alpha=0,1\}} \left(\frac{e^{\beta\mu} a^3}{\lambda^3}\right)^{\sum_\alpha n_\alpha} \exp\left\{-\frac{\beta}{2}\sum_{\alpha,\beta=1}^{\mathcal{N}} n_\alpha n_\beta \mathcal{V}\left(\vec{r}_\alpha - \vec{r}_\beta\right)\right\}.$$

(c) By setting $n_\alpha = (1+\sigma_\alpha)/2$ and approximating the potential by $\mathcal{V}(\vec{r}_\alpha - \vec{r}_\beta) = -J/\mathcal{N}$, show that this model is identical to the one studied in problem (2). What does this imply about the behavior of this imperfect gas?

- With $n_\alpha = (1+\sigma_\alpha)/2$, and $\mathcal{V}\left(\vec{r}_\alpha - \vec{r}_\beta\right) = -J/\mathcal{N}$,

$$\Xi = \sum_{\{n_\alpha=0,1\}} \exp\left\{\left(\beta\mu + 3\ln\frac{a}{\lambda}\right)\sum_{\alpha=1}^{\mathcal{N}}\left(\frac{1+\sigma_\alpha}{2}\right) + \frac{\beta J}{2\mathcal{N}}\sum_{\alpha,\beta=1}^{\mathcal{N}}\left(\frac{1+\sigma_\alpha}{2}\right)\left(\frac{1+\sigma_\beta}{2}\right)\right\}.$$

Setting $m \equiv \sum_\alpha \sigma_\alpha/\mathcal{N}$, $h' = \frac{1}{2}\left(\mu + \frac{3}{\beta}\ln\frac{a}{\lambda} + \frac{J}{2}\right)$, and $J' = J/4$, the grand partition function is written

$$\Xi = \text{const.} \sum_{\{n_\alpha=0,1\}} \exp\left\{\mathcal{N}\beta\left(J'm^2/2 + h'm\right)\right\}.$$

The phase diagram of the lattice-gas can thus be mapped onto the phase diagram of the Ising model of problem 2. In particular, at a chemical potential μ such that $h' = 0$, there is a continuous "condensation" transition at a critical temperature $T_c = J/4k_B$. (Note that

$$m = \sum_\alpha \sigma_\alpha/\mathcal{N} = \sum_\alpha \left(2n_\alpha - 1\right)/\mathcal{N} = 2a^3\rho - 1,$$

where $\rho = N/V$ is the density of the gas.)

- The manifest equivalence between these three systems is a straightforward consequence of their mapping onto the same (Ising) Hamiltonian. However, there is a more subtle equivalence relating the critical behavior of systems that cannot be so easily mapped onto each other due to the Universality Principle.

4. *Cubic invariants:* When the order parameter m, goes to zero discontinuously, the phase transition is said to be first order (discontinuous). A common example occurs in systems where symmetry considerations do not exclude a cubic term in the Landau free energy, as in

$$\beta\mathcal{H} = \int d^d\mathbf{x} \left[\frac{K}{2}(\nabla m)^2 + \frac{t}{2}m^2 + cm^3 + um^4 \right] \qquad (K, c, u > 0).$$

(a) By plotting the energy density $\Psi(m)$, for uniform m at various values of t, show that as t is reduced there is a discontinuous jump to $\overline{m} \neq 0$ for a positive $\overline{t}$ in the saddle–point approximation.

• To simplify the algebra, let us rewrite the energy density $\Psi(m)$, for uniform m, in terms of the rescaled quantity

$$m_r = \frac{u}{c}m.$$

In this way, we can eliminate the constant parameters c, and u, to get the expression of the energy density as

$$\Psi_r(m_r) = \frac{1}{2}t_r m_r^2 + m_r^3 + m_r^4,$$

where we have defined

$$\Psi_r = \left(\frac{c^4}{u^3}\right)\Psi, \qquad \text{and} \qquad t_r = \left(\frac{u}{c^2}\right)t.$$

To obtain the extrema of Ψ_r, we set the first derivative with respect to m_r to zero, i.e.

$$\frac{d\Psi_r(m_r)}{dm_r} = m_r\left(t_r + 3m_r + 4m_r^2\right) = 0.$$

The trivial solution of this equation is $m_r^* = 0$. But if $t_r \leq 9/16$, the derivative vanishes also at $m_r^* = (-3 \pm \sqrt{9 - 16t_r})/8$. Provided that $t_r > 0$, $m_r^* = 0$ is a minimum of the function $\Psi_r(m_r)$. In addition, if $t_r < 9/16$, $\Psi_r(m_r)$ has another minimum at

$$m_r^* = -\frac{3 + \sqrt{9 - 16t_r}}{8},$$

and a maximum, located in between the two minima, at

$$m_r^* = \frac{-3 + \sqrt{9 - 16t_r}}{8}.$$

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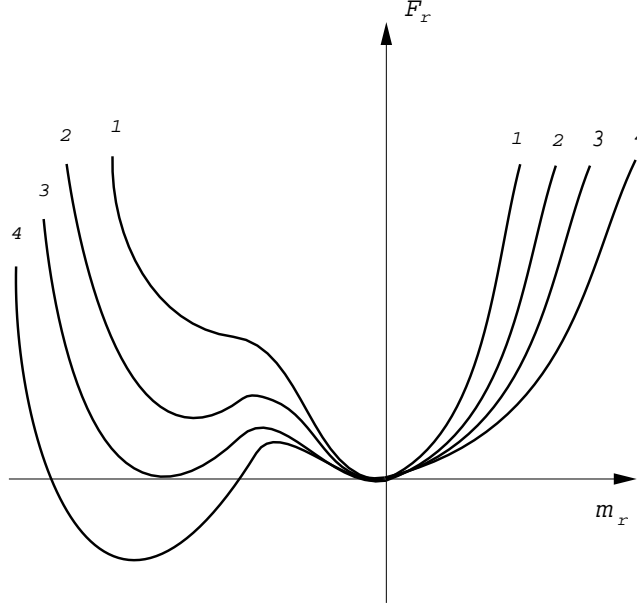
The accompanying figure depicts the behavior of $\Psi_r(m_r)$ for different values of t_r.

1. For $t_r > 9/16$, there is only one minimum $m_r^* = 0$.
2. For $0 < \bar{t}_r < t_r < 9/16$, there are two minima, but $\Psi_r(m_r^*) > \Psi_r(0) = 0$.
3. For $0 < t_r = \bar{t}_r$, $\Psi_r(m_r^*) = \Psi_r(0) = 0$.
4. For $0 < t_r < \bar{t}_r$, $\Psi_r(m_r^*) < \Psi_r(0) = 0$.

The discontinuous transition occurs when the local minimum at $m_r^* < 0$ becomes the absolute minimum. There is a corresponding jump of m_r, from $m_r^* = 0$ to $m_r^* = \overline{m}_r$, where $\overline{m}_r = m_r^*(t_r = \bar{t}_r)$.

(b) By writing down the two conditions that $\overline{m}$ and $\bar{t}$ must satisfy at the transition, solve for $\overline{m}$ and $\bar{t}$.

• To determine $\overline{m}_r$ and $\bar{t}_r$, we have to simultaneously solve the equations
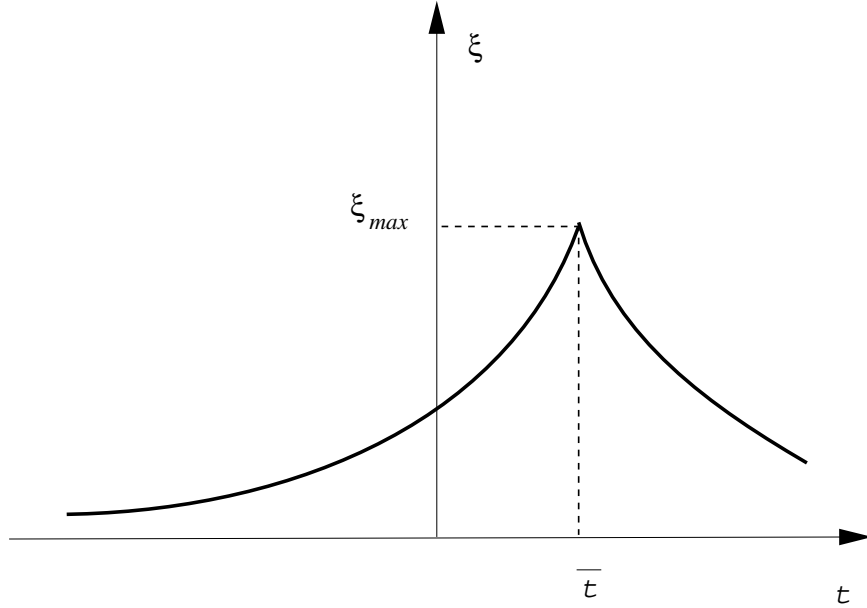
$$\frac{d\Psi_r(m_r)}{dm_r} = 0, \qquad \text{and} \qquad \Psi_r(m_r) = \Psi_r(0) = 0.$$

Excluding the trivial solution $m_r^* = 0$, from

$$\begin{cases} t_r + 3m_r + 4m_r^2 = 0 \\ \dfrac{t_r}{2} + m_r + m_r^2 = 0 \end{cases},$$

we obtain $\bar{t}_r = -\overline{m}_r = 1/2$, or in the original units,

$$\bar{t} = \frac{c^2}{2u}, \qquad \text{and} \qquad \overline{m} = -\frac{c}{2u}.$$

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(c) Recall that the correlation length ξ is related to the curvature of $\Psi(m)$ at its minimum by $K\xi^{-2} = \partial^2\Psi/\partial m^2|_{eq.}$. Plot ξ as a function of t.

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Likewise, the equilibrium value of $m = m_{eq}$ in the original units equals to

$$
m_{eq} = \begin{cases} 0 & \text{for} \quad t > \bar{t} = \dfrac{c^2}{2u}, \\[2ex] -\left(\dfrac{c}{u}\right)\dfrac{3 + \sqrt{9 - 16ut/c^2}}{8} & \text{for} \quad t < \bar{t}. \end{cases}
$$

The correlation length ξ, is related to the curvature of $\Psi(m)$ at its equilibrium minimum by

$$
K\xi^{-2} = \left.\frac{\partial^2\Psi}{\partial m^2}\right|_{m_{eq}} = t + 6cm_{eq} + 12um_{eq}^2,
$$

which is equal to

$$
\xi = \begin{cases} \left(\dfrac{K}{t}\right)^{1/2} & \text{if} \quad t > \bar{t}, \\[3ex] \left(-\dfrac{K}{2t + 3cm_{eq}}\right)^{1/2} & \text{if} \quad t < \bar{t}. \end{cases}
$$

(To arrive to the last expression, we have used $d\Psi(m)/dm|_{m=m_{eq}} = 0$.)

$$
\xi_{max} = \xi(\bar{t}) = \frac{\sqrt{2Ku}}{c}.
$$

A plot of ξ as a function of t is presented here. Note that the correlation length ξ, is finite at the discontinuous phase transition, attaining a maximum value of

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5. *Tricritical point:* By tuning an additional parameter, a second order transition can be made first order. The special point separating the two types of transitions is known as a tricritical point, and can be studied by examining the Landau–Ginzburg Hamiltonian

$$\beta\mathcal{H} = \int d^d\mathbf{x} \left[\frac{K}{2}(\nabla m)^2 + \frac{t}{2}m^2 + um^4 + vm^6 - hm \right],$$

where u can be positive or negative. For $u < 0$, a positive v is necessary to ensure stability.

(a) By sketching the energy density $\Psi(m)$, for various t, show that in the saddle–point approximation there is a first-order transition for $u < 0$ and $h = 0$.

• If we consider $h = 0$, the energy density $\Psi(m)$, for uniform m, is

$$\Psi(m) = \frac{t}{2}m^2 + um^4 + vm^6.$$

As in the previous problem, to obtain the extrema of Ψ, let us set the first derivative with respect to m to zero. Again, provided that $t > 0$, $\Psi(m)$ has a minimum at $m^* = 0$. But the derivative also vanishes for other nonzero values of m as long as certain conditions are satisfied. In order to find them, we have to solve the following equation

$$t + 4um^2 + 6vm^4 = 0,$$

from which,

$$m^{*2} = -\frac{u}{3v} \pm \frac{\sqrt{4u^2 - 6tv}}{6v}.$$

Thus, we have real and positive solutions provided that

$$u < 0, \qquad \text{and} \qquad t < \frac{2u^2}{3v}.$$

Under these conditions $\Psi(m)$ has another two minima at

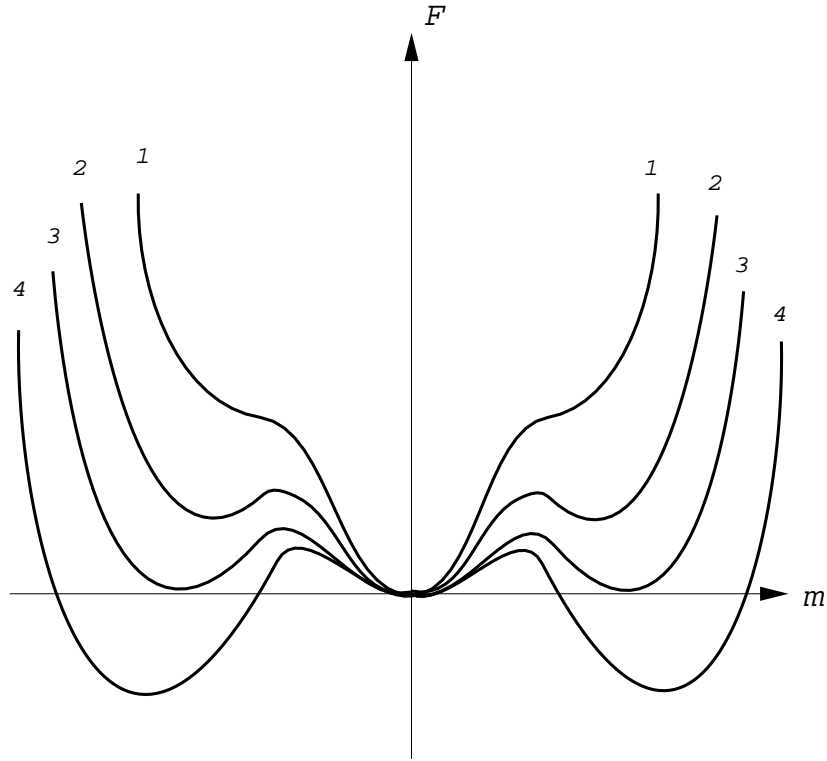$$m^{*2} = \frac{|u|}{3v} + \frac{\sqrt{4u^2 - 6tv}}{6v},$$

and two maxima at

$$m^{*2} = \frac{|u|}{3v} - \frac{\sqrt{4u^2 - 6tv}}{6v},$$

as depicted in the accompanying figure.

The different behaviors of the function $\Psi(m)$ are as follows:

1. For $t > 2u^2/3v$, there is only one minimum $m^* = 0$.
2. For $0 < \bar{t} < t < 2u^2/3v$, there are three minima, but $\Psi(\pm m^*) > \Psi(0) = 0$.

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3. For $0 < t = \bar{t}$, $\Psi(\pm m^*) = \Psi(0) = 0$.

4. For $0 < t < \bar{t}$, $\Psi(\pm m^*) < \Psi(0) = 0$.

There is a thus discontinuous phase transition for $u < 0$, and $t = \bar{t}(u)$.

(b) Calculate $\bar{t}$ and the discontinuity $\overline{m}$ at this transition.

• To determine $\bar{t}$, and $\overline{m} = m^*(t = \bar{t})$, we again have to simultaneously solve the equations

$$\frac{d\Psi(m)}{dm^2} = 0, \qquad \text{and} \qquad \Psi(m^2) = \Psi(0) = 0,$$

or equivalently,

$$\begin{cases} \dfrac{t}{2} + 2um^2 + 3vm^4 = 0 \\[2mm] \dfrac{t}{2} + um^2 + vm^4 = 0 \end{cases},$$

from which we obtain

$$\bar{t} = \frac{u^2}{2v}, \qquad \text{and} \quad \overline{m}^2 = -\frac{u}{2v} = \frac{|u|}{2v}.$$

(c) For $h = 0$ and $v > 0$, plot the phase boundary in the (u, t) plane, identifying the phases, and order of the phase transitions.

• In the (u, t) plane, the line $t = u^2/2v$ for $u < 0$, is a first-order phase transition boundary. In addition, the line $t = 0$ for $u > 0$, defines a second-order phase transition boundary, as indicated in the accompanying figure.

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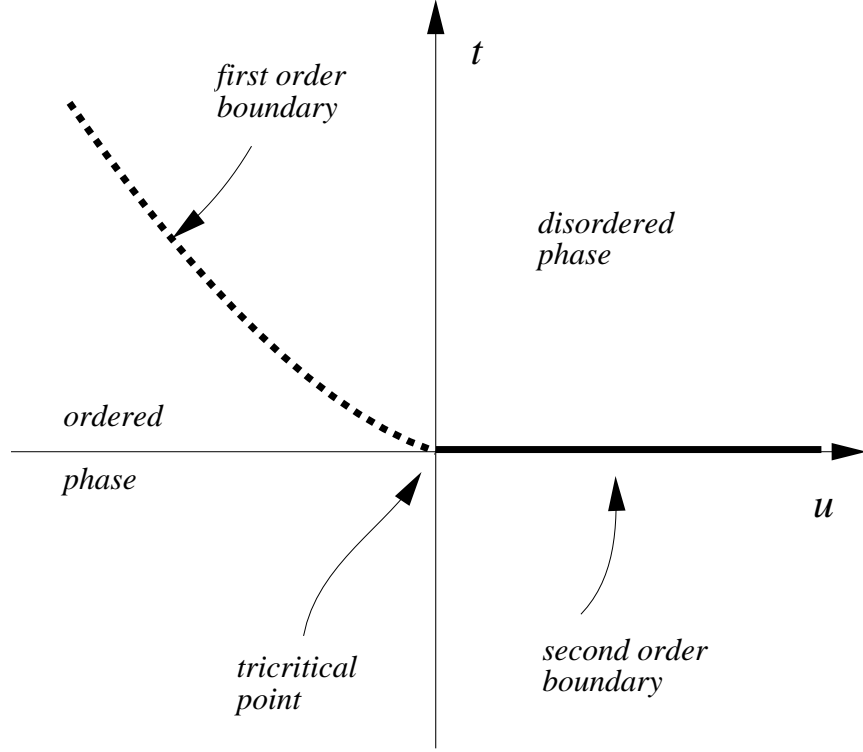
(d) The special point $u = t = 0$, separating first– and second–order phase boundaries, is a *tricritical* point. For $u = 0$, calculate the tricritical exponents β, δ, γ, and α, governing the singularities in magnetization, susceptibility, and heat capacity. (Recall: $C \propto t^{-\alpha}$; $\overline{m}(h = 0) \propto t^{\beta}$; $\chi \propto t^{-\gamma}$; and $\overline{m}(t = 0) \propto h^{1/\delta}$.)

• For $u = 0$, let us calculate the tricritical exponents α, β, γ, and δ. In order to calculate α and β, we set $h = 0$, so that

$$\Psi(m) = \frac{t}{2}m^2 + vm^6.$$

Thus from

$$\left.\frac{\partial \Psi}{\partial m}\right|_{\overline{m}} = \overline{m}\left(t + 6v\overline{m}^4\right) = 0,$$

we obtain,

$$\overline{m} = \begin{cases} 0 & \text{for} \quad t > \overline{t} = 0, \\ \left(-\dfrac{t}{6v}\right)^{1/4} & \text{for} \quad t < 0 \end{cases},$$

resulting in,

$$\overline{m}(h = 0) \propto t^{\beta}, \qquad \text{with} \qquad \beta = \frac{1}{4}.$$

The corresponding free energy density scales as

$$\Psi(\overline{m}) \sim \overline{m}^6 \propto (-t)^{3/2}.$$

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The tricritical exponent α characterizes the non-analytic behavior of the heat capacity $C \sim (\partial^2 \Psi / \partial T^2)|_{h=0,\overline{m}}$, and since $t \propto (T - T_c)$,

$$C \sim \left. \frac{\partial^2 \Psi}{\partial t^2} \right|_{h=0,\overline{m}} \propto t^{-\alpha}, \qquad \text{with} \qquad \alpha = \frac{1}{2}.$$

To calculate the tricritical exponent δ, we set $t = 0$ while keeping $h \neq 0$, so that

$$\Psi(m) = vm^6 - hm.$$

Thus from

$$\left. \frac{\partial \Psi}{\partial m} \right|_{\overline{m}} = 6v\overline{m}^5 - h = 0,$$

we obtain,

$$\overline{m} \propto h^{1/\delta}, \qquad \text{with} \qquad \delta = 5.$$

Finally, for $h \neq 0$ and $t \neq 0$,

$$\left. \frac{\partial \Psi}{\partial m} \right|_{\overline{m}} = t\overline{m} + 6v\overline{m}^5 - h = 0,$$

so that the susceptibility scales as

$$\chi = \left. \frac{\partial \overline{m}}{\partial h} \right|_{h=0} \propto |t|^{-1}, \qquad \text{for both} \qquad t < 0 \qquad \text{and} \qquad t > 0,$$

i.e. with the exponents $\gamma_{\pm} = 1$.

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6. *Transverse susceptibility:* An n–component magnetization field $\vec{m}(\mathbf{x})$ is coupled to an external field $\vec{h}$ through a term $-\int d^d\mathbf{x}\, \vec{h} \cdot \vec{m}(\mathbf{x})$ in the Hamiltonian $\beta \mathcal{H}$. If $\beta \mathcal{H}$ for $\vec{h} = 0$ is invariant under rotations of $\vec{m}(\mathbf{x})$; then the free energy density ($f = -\ln Z / V$) only depends on the absolute value of $\vec{h}$; i.e. $f(\vec{h}) = f(h)$, where $h = |\vec{h}|$.

(a) Show that $m_\alpha = \langle \int d^d\mathbf{x}\, m_\alpha(\mathbf{x}) \rangle / V = -h_\alpha f'(h)/h$.

• The magnetic work is the product of the magnetic field and the magnetization density, and appears as the argument of the exponential weight in the (Gibbs) canonical ensemble. We can thus can "lower" the magnetization $M = \int d^d x\, m_\alpha(\mathbf{x})$ "inside the average" by taking derivatives of the (Gibbs) partition function with respect to h_α, as

$$m_\alpha = \frac{1}{V} \left\langle \int d^d x\, m_\alpha(\mathbf{x}) \right\rangle = \frac{1}{V} \frac{\int \mathcal{D}\mathbf{m}(\mathbf{x}) \left(\int d^d x'\, m_\alpha(\mathbf{x}') \right) e^{-\beta \mathcal{H}}}{\int \mathcal{D}\mathbf{m}(\mathbf{x}) e^{-\beta \mathcal{H}}}$$

$$= \frac{1}{V} \frac{1}{Z} \frac{1}{\beta} \frac{\partial}{\partial h_\alpha} \int \mathcal{D}\mathbf{m}(\mathbf{x}) e^{-\beta \mathcal{H}} = \frac{1}{\beta V} \frac{\partial}{\partial h_\alpha} \ln Z = -\frac{\partial f}{\partial h_\alpha}.$$

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For an otherwise rotationally symmetric system, the (Gibbs) free energy depends only on the magnitude of **h**, and using

$$\frac{\partial h}{\partial h_\alpha} = \frac{\partial \sqrt{h_\beta h_\beta}}{\partial h_\alpha} = \frac{1}{2}\frac{2\delta_{\alpha\beta}h_\beta}{\sqrt{h_\beta h_\beta}} = \frac{h_\alpha}{h},$$

we obtain

$$m_\alpha = -\frac{\partial f}{\partial h_\alpha} = -\frac{df}{dh}\frac{\partial h}{\partial h_\alpha} = -f'\frac{h_\alpha}{h}.$$

(b) Relate the susceptibility tensor $\chi_{\alpha\beta} = \partial m_\alpha/\partial h_\beta$, to $f''(h)$, $\vec{m}$, and $\vec{h}$.

• The susceptibility tensor is now obtained as

$$\chi_{\alpha\beta} = \frac{\partial m_\alpha}{\partial h_\beta} = \frac{\partial}{\partial h_\beta}\left(-\frac{h_\alpha}{h}f'(h)\right) = -\frac{\partial h_\alpha}{\partial h_\beta}\frac{1}{h}f' - \frac{\partial h^{-1}}{\partial h_\beta}h_\alpha f' - \frac{h_\alpha}{h}\frac{\partial f'}{\partial h_\beta}$$

$$= -\left(\delta_{\alpha\beta} - \frac{h_\alpha h_\beta}{h^2}\right)\frac{f'}{h} - \frac{h_\alpha h_\beta}{h^2}f''.$$

In order to express f' in terms of the magnetization, we take the magnitude of the result of part (a),

$$m = |f'(h)| = -f'(h),$$

from which we obtain

$$\chi_{\alpha\beta} = \left(\delta_{\alpha\beta} - \frac{h_\alpha h_\beta}{h^2}\right)\frac{m}{h} + \frac{h_\alpha h_\beta}{h^2}\frac{dm}{dh}.$$

(c) Show that the transverse and longitudinal susceptibilities are given by $\chi_t = m/h$ and $\chi_\ell = -f''(h)$; where m is the magnitude of $\vec{m}$.

• Since the matrix $\left(\delta_{\alpha\beta} - h_\alpha h_\beta/h^2\right)$ removes the projection of any vector along the magnetic field, we conclude

$$\begin{cases} \chi_\ell = -f''(h) = \dfrac{dm}{dh} \\ \chi_t = \dfrac{m}{h} \end{cases}.$$

Alternatively, we can choose the coordinate system such that $h_i = h\delta_{i1}$ $(i = 1,\ldots,d)$, to get

$$\begin{cases} \chi_\ell = \chi_{11} = \left(\delta_{11} - \dfrac{h_1 h_1}{h^2}\right)\dfrac{m}{h} - \dfrac{h_1 h_1}{h^2}f''(h) = \dfrac{dm}{dh} \\ \chi_t = \chi_{22} = \left(\delta_{22} - \dfrac{h_2 h_2}{h^2}\right)\dfrac{m}{h} - \dfrac{h_2 h_2}{h^2}f''(h) = \dfrac{m}{h} \end{cases}.$$

(d) Conclude that χ_t diverges as $\vec{h} \to 0$, whenever there is a spontaneous magnetization. Is there any similar a priori reason for χ_ℓ to diverge?

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• Provided that $\lim_{h \to 0} m \neq 0$, the transverse susceptibility clearly diverges for $h \to 0$. There is no similar reason, on the other hand, for the longitudinal susceptibility to diverge. In the saddle point approximation of the Landau–Ginzburg model, for example, we have

$$tm + 4um^3 + h = 0,$$

implying (since $4um^2 = -t$ at $h = 0$, for $t < 0$) that

$$\chi_\ell|_{h=0} = \left(\frac{dh}{dm}\right)^{-1}\bigg|_{h=0} = (t - 3t)^{-1}, \qquad i.e. \qquad \chi_\ell = \frac{1}{2\,|t|},$$

at zero magnetic field, in the ordered phase ($t < 0$).

NOTE: Another, more pictorial approach to this problem is as follows. Since the Hamiltonian is invariant under rotations about $\mathbf{h}$, $\mathbf{m}$ must be parallel to $\mathbf{h}$, *i.e.*

$$m_\alpha = \frac{h_\alpha}{h} \varphi(h),$$

where φ is some function of the magnitude of the magnetic field. For simplicity, let $\mathbf{h} = h\mathbf{e}_1$, with $\mathbf{e}_1$ a unit vector, implying that

$$\mathbf{m} = m\mathbf{e}_1 = \varphi(h)\,\mathbf{e}_1.$$

The longitudinal susceptibility is then calculated as

$$\chi_\ell = \frac{\partial m_1}{\partial h_1}\bigg|_{\mathbf{h}=h\mathbf{e}_1} = \frac{dm}{dh} = \varphi'(h).$$

To find the transverse susceptibility, we first note that if the system is perturbed by a small external magnetic field $\delta h\mathbf{e}_2$, the change in m_1 is, by symmetry, the same for $\delta h > 0$ and $\delta h < 0$, implying

$$m_1(h\mathbf{e}_1 + \delta h\mathbf{e}_2) = m_1(h\mathbf{e}_1) + \mathcal{O}\left(\delta h^2\right).$$

Hence

$$\frac{\partial m_1}{\partial h_2}\bigg|_{\mathbf{h}=h\mathbf{e}_1} = 0.$$

Furthermore, since $\mathbf{m}$ and $\mathbf{h}$ are parallel,

$$\frac{m_1(h\mathbf{e}_1 + \delta h\mathbf{e}_2)}{h} = \frac{m_2(h\mathbf{e}_1 + \delta h\mathbf{e}_2)}{\delta h},$$

from which

$$m_2(h\mathbf{e}_1 + \delta h\mathbf{e}_2) = \frac{m_1(h\mathbf{e}_1)}{h}\delta h + \mathcal{O}\left(\delta h^3\right),$$

yielding

$$\chi_t = \frac{\partial m_2}{\partial h_2}\bigg|_{\mathbf{h}=h\mathbf{e}_1} = \frac{m}{h}.$$

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