**Unit 4-5: The Maxwell Construction and the Gibbs Free Energy Density**

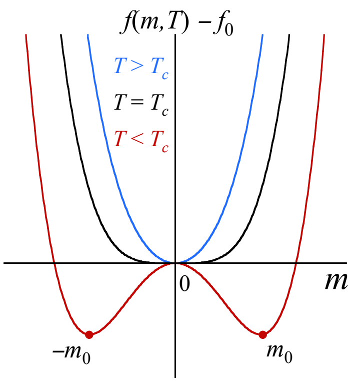
Here we will continue to explore some of the consequences of the mean-field solution for the Ising model. We will work with the Landau form of the free energy,

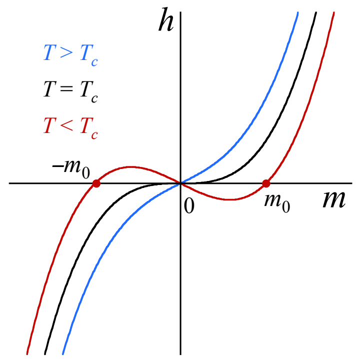
$$f(m,T) = f_0 + am^2 + bm^4 \qquad \text{with } a = a_0(T - T_c) \tag{4.5.1}$$

From $h = \left(\dfrac{\partial f}{\partial m}\right)_T$ we have,

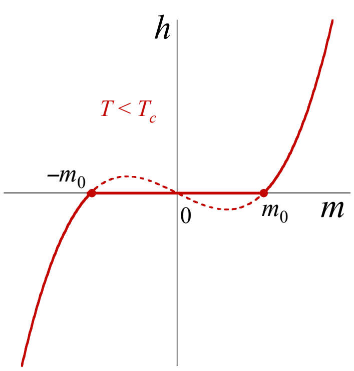
$$h = 2am + 4bm^3 \tag{4.5.2}$$

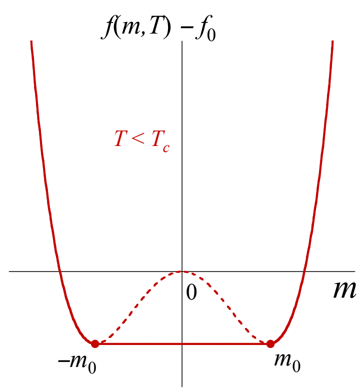
which we plot in the sketch below on the right.




For $T < T_c$ we know that the above $h(m)$ curve cannot be valid for $-m_0 \leq m \leq +m_0$. This is the coexistence region where we should have $h = 0$. For $T < T_c$ the correct $h(m)$ curve should look like the sketch below on the left, where we replace the non-monotonic part of the curve (the dashed line) with a horizontal segment at $h = 0$.




Such a "correction", based on our physical understanding, is called the "Maxwell construction" (originally done in connection with Van der Waals theory of the liquid to gas phase transition).

If we use the "corrected" $h(m)$ for $T < T_c$ to compute $f(m,T) = \int dm\, h(m)$, and adjust the constant of integration so that $f(m_0) - f_0$ remains the same as before, then instead of the double-well form we saw previously, we now get as in the sketch above on the right, where the non-monotonic part of the curve (the dashed line) is replaced with a flat horizontal segment.

Note: this can be thought of as if we took the original, double-well curve and replaced it by it *convex envelop*. The original double-well curve cannot be physically correct since $f(m,T)$ must be convex in $m$. The "corrected" curve is convex as desired.

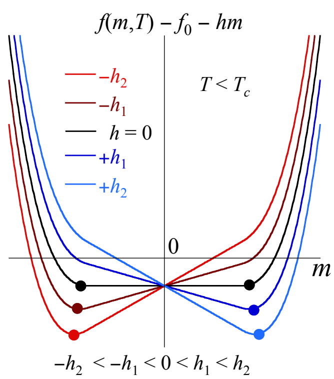
Using the "corrected" form for $f(m,T)$ we can then compute the Gibbs free energy density (note, here we compute

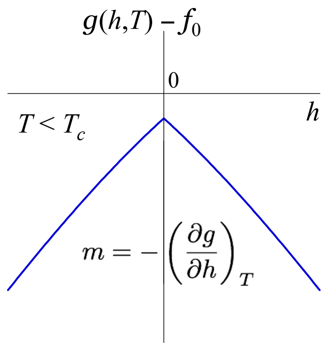
$g(h,T)$ at finite $h$, not just $h=0$ as we did before),

$$g(h,T) = \min_m \left[f(m,T) - hm\right] \tag{4.5.3}$$

Below on the left we plot $f(m,T) - f_0 - mh$ vs $m$, at several values of $h$, for $T < T_c$, denoting the minimum of each curve with a dot. The location of this minimum on the horizontal axis at $m^*$ gives the value of the magnetization $m$ in the equilibrium state at the given $h$, while the location $f(m^*,T) - f_0 - hm^*$ on the vertical axis gives the value of $g(h,T) - f_0$. Note, unlike the "uncorrected" double-well curve which would have two local minima and one local maximum at each $h$, here each curve has a unique minima and no local maximum (except for the case of $h=0$ which has an extended flat minimum for the interval $-m_0 \le m \le +m_0$).

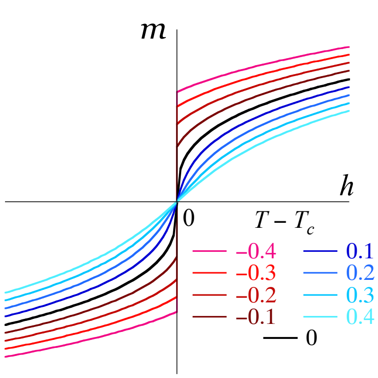
We see that as $h$ increases from negative values to positive, the minimum $m^*$ starts at a negative value, increases slowly (becomes less negative), and then, as one crosses $h=0$, jumps discontinuously to a positive value, and then increases slowly. This discontinuous jump in $m^*$ is just the discontinuity in the magnetization, jumping from $-m_0$ to $+m_0$ as one increases the magnetic field at fixed $T$ to cross the first order coexistence line in the $H-T$ plane.

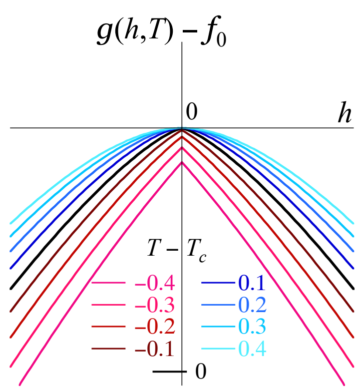



In the figure above to the right we plot the value of the minimum on the vertical axis, $g(h,T) - f_0 = f(m^*,T) - f_0 - hm^*$ vs $h$, to show the Gibbs free energy density. We see that $g(h,T)$ is continuous, but with a finite cusp at $h=0$. Since $m = -(\partial g/\partial h)_T$, we see that the slope of the curve $g(h,T)$ vs $h$ approaches $-(-m_0) = m_0$ as $h \to 0^-$ from below, while the slope approaches $-(m_0)$ as $h \to 0^+$ from above. This is the explanation for the cusp. The discontinuity in the slope of $g(h,T)$ at $h=0$ is thus $2m_0$. As $T \to T_c^-$ from below, and so $m_0 \to 0$, the magnitude of this cusp decreases and then vanishes at $T_c$.

Solving Eq. (4.5.2) numerically for the equilibrium magnetization $m$ at a fixed magnetic field $h$, we plot $m$ vs $h$ for both $T \le T_c$ and $T > T_c$ in the figure below to the left. Using that value of $m$ in $g(h,T) = f(m,T) - hm$, we plot the Gibbs free energy density $g(h,T) - f_0$ vs $h$ in the figure below to the right, again for both $T \le T_c$ and $T > T_c$.




We see that $m$ increases monotonically as $h$ increases. For $T < T_c$, $m$ takes a discontinuous jump from $-m_0$ to $+m_0$ as one crosses $h=0$. As $T \to T_c^-$, we have the spontaneous magnetization $m_0 \to 0$, and this discontinuity vanishes. Exactly at $T = T_c$ we have $|m| \sim |h|^{1/\delta}$ vanishes singularly as $|h| \to 0$. Since the magnetic susceptibility is $\chi = \lim_{h\to 0}(\partial m/\partial h)_T$, we have $\chi \sim \lim_{h\to 0}|h|^{1/\delta-1}$ at $T_c$, and since $1/\delta = 1/3 < 1$ in mean-field theory, we see that $\chi$ diverges at $T_c$, as we saw in the previous Notes 4-4. For $T > T_c$, $m$ varies continuously and analytically, with a finite slope (and hence a finite $\chi$), as the magnetic field crosses $h = 0$. As $T \to T_c^+$ from above, the slope of $m$ vs $h$ at $h = 0$ (this is just $\chi$) steepens and diverges.

The corresponding behavior of $g(h,T)$ is as follows. For $T < T_c$, $g(h,T)$ has a finite cusp at $h = 0$, with a jump $2m_0$ in the slope. This is a reflection of the jump in the spontaneous magnetization $m_0$ as one crosses the coexistence line. The magnitude of the cusp decreases, and vanishes, as $T \to T_c^-$ and $m_0 \to 0$. At $T_c$ one can solve easily for $g(h,T)$. Since $a = a_0(T - T_c) = 0$ as $T = T_c$, Eq. (4.5.2) becomes simply,

$$h = 4bm^3 \quad \Rightarrow \quad m = \left(\frac{h}{4b}\right)^{1/3} \quad \Rightarrow \quad g(h,T) - f_0 = bm^4 - hm = b\left(\frac{h}{4b}\right)^{4/3} - h\left(\frac{h}{4b}\right)^{1/3} = -3b\left(\frac{h}{4b}\right)^{4/3} \tag{4.5.4}$$

So now $m = -(\partial g/\partial h)_T \sim h^{4/3-1} \sim h^{1/3}$, which is continuous as one crosses $h = 0$. The magnetic susceptibility, $\chi = (\partial m/\partial h)_T = -(\partial^2 g/\partial h^2)_T \sim h^{4/3-2} \sim h^{-2/3}$, however, diverges.

For $T > T_c$ one can also easily solve for $g(h,T)$. Above $T_c$ there is no Maxwell construction, and since $m$ is small as we approach $T_c$, to lowest order we can drop the $bm^4$ term and write $f(m,T) = f_0 + am^2$. The equilibrium magnetization is then determined by $(\partial f/\partial m)_T = h = 2am$. We then have,

$$h = 2am \quad \Rightarrow \quad m = \frac{h}{2a} \quad \Rightarrow \quad g(h,T) - f_0 = am^2 - hm = a\left(\frac{h}{2a}\right)^2 - h\left(\frac{h}{2a}\right) = -\frac{h^2}{4a} = \frac{-h^2}{4a_0(T - T_c)} \tag{4.5.5}$$

Thus, unlike $T < T_c$ where $g(h,T)$ has a cusp at $h = 0$, for $T > T_c$ we see that $g(h,T)$ is smooth and parabolic at $h = 0$. The curvature at $h = 0$ is just the magnetic susceptibility, $\chi = -(\partial^2 g/\partial h^2)_T = 1/[2a_0(T - T_c)]$, which diverges as $T \to T_c^+$ from above.

**Summary**

For $T < T_c$, the *Helmholtz free energy* density has a double-welled form; for $h = 0$ the two wells are of equal depth at $\pm m_0$, while for $|h| > 0$ one well is the global minima while the other is a local minima. When one makes the Maxwell construction, these two minima are connected by a straight line so that $f(m,T)$ becomes a convex function of $m$. For $T > T_c$, $f(m,T)$ has a single minimum at $m \propto h$. The curvature of $f(m,T)$ as $h \to 0$ is the inverse magnetic susceptibility $\chi^{-1}$, which vanishes as $T \to T_c^+$.

For $T < T_c$, the *Gibbs free energy* density is a concave function with a sharp cusp at $h = 0$, with a jump in slope equal to $2m_0$. As $T \to T_c^-$ from below, the magnitude of this cusp vanishes as $m_0 \to 0$. For $T > T_c$, $g(h,T)$ has a parabolic maximum at $h = 0$. The curvature of $g(h,T)$ at $h = 0$ is just the magnetic susceptibility $\chi$, which diverges as $T \to T_c^+$ from above.