Thermodynamic relations for magnetic materials

(adopted from Landau & Lifshitz, "Electrodynamics of Continuous Media")

1. \( B \) and \( H \)
   - \( B(\mathbf{r}, t) \) = magnetic induction. This is the value of magnetic field averaged over a small volume surrounding a given point \( \mathbf{r} \) and a small time interval around a given time \( t \).
   - \( H(\mathbf{r}, t) \) = magnetic moment per unit volume of the medium obtained by the same averaging procedure. Also termed magnetization.
   - \( \mathbf{H} \equiv \mathbf{B} - 4\pi \mathbf{M} \). This quantity is referred to as magnetic field; however, the true average magnetic field is \( \mathbf{B} \), not \( \mathbf{H} \). The usefulness of \( \mathbf{H} \) comes through the Maxwell equation \( \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} \), \( \mathbf{j} \) = external current.

2. Change of energy due to change in magnetic field

Magnetic field by itself does not exert work but changes in \( \mathbf{B} \) result in creation of an electric field \( \mathbf{E} \), \( \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \), that does. Suppose that \( \mathbf{B} \) is generated by external current \( \mathbf{j}(\mathbf{r}) \). The work exerted on the currents during time \( \Delta t \) is \( \Delta t \int \mathbf{E} \cdot \mathbf{j} \, dV \).

The work done on the system by the current source differs by the sign:

\[
\Delta W = - \Delta t \int \mathbf{E} \cdot \mathbf{j} \, dV = - \Delta t \int \mathbf{E} \cdot \frac{c}{4\pi} [\nabla \times \mathbf{H}] \, dV = \Delta t \frac{c}{4\pi} \int \text{div} \left( \mathbf{E} \times \mathbf{H} \right) \, dV
\]

\[
- \Delta t \frac{c}{4\pi} \int \mathbf{H} \cdot \nabla \mathbf{E} \, dV = \frac{1}{4\pi} \int \mathbf{H} \cdot d\mathbf{B}
\]

This implies the following for the differential change in the free and internal energies:

\[
dF = -S \, dT + \ldots + \frac{1}{4\pi} \mathbf{H} \cdot d\mathbf{B},
\]

\[
dU = T \, dS + \ldots + \frac{1}{4\pi} \mathbf{H} \cdot d\mathbf{B}.
\]
(3) Thermodynamic potential for $H = \text{const}$

The quantity that reaches its minimum under the condition of a given fixed $H$ (and a given fixed temperature) is not $F$ but

$$\tilde{F} \equiv F - \frac{1}{4\pi} H \cdot \vec{B},$$

Clearly,

$$d\tilde{F} = -SdT + \ldots - \frac{1}{4\pi} \vec{B} \cdot dH. \hspace{1cm} (1)$$

To put it another way, the work done on the system at fixed sources (currents $j$) is equal to the change of $\int \tilde{F} dV$, not $\int F dV$.

Let $\vec{H}_{\text{ext}}$ be the magnetic field that would exist if the current source $j(r)$ was in vacuum. Then $\vec{H} = \vec{B} = \vec{H}_{\text{ext}}$ and $\tilde{F} = -\frac{1}{8\pi} \vec{H}_{\text{ext}}^2$. Let's therefore define "total" thermodynamic potential by

$$\tilde{F} \equiv \int (\tilde{F} - \tilde{F}_{\text{vac}}) dV = \int \left( \tilde{F} + \frac{1}{8\pi} \vec{H}_{\text{ext}}^2 \right) dV.$$

Note that the integration volume includes both inside and outside of the sample. Since the sample generally changes the field around itself, the integrand is nonzero everywhere. This is of course very inconvenient. Remarkably, using the relations $\nabla \times \vec{H} = \nabla \times \vec{H}_{\text{ext}} = \frac{4\pi}{c} \vec{j}$ one can show that

$$\delta \tilde{F} = -\int M \cdot \delta \vec{H}_{\text{ext}} dV. \hspace{1cm} (2)$$

Another useful expression is

$$\tilde{F} = \int (\tilde{F} + \frac{\vec{H} \cdot \vec{B}}{8\pi} - \frac{1}{2} \vec{M} \cdot \vec{H}_{\text{ext}}) dV. \hspace{1cm} (3)$$

A nice property of these formulas is that the integrand does vanish outside of the sample.
The case of a weakly magnetic material

For most materials, the relation between $M$ and $H$ is linear, $M = \chi H$ and the susceptibility $\chi$ is very small. In this case, $B \approx H \approx H_{\text{ext}}$ and Eq. (2) becomes

$$\delta \mathcal{F} = - \int \chi \mathbf{H} \cdot \delta \mathbf{H}_{\text{ext}} \, dV \approx - \chi \int \mathbf{H}_{\text{ext}} \cdot \delta \mathbf{H}_{\text{ext}} \, dV$$

$$\mathcal{F}(H_{\text{ext}}) = \mathcal{F}(0) - \frac{1}{2} \chi H_{\text{ext}}^2 - V. \quad (4)$$

This formula is written assuming the material is isotropic. The generalization to anisotropic case is straightforward. For example, if $\chi$ takes two different values, $\chi_\parallel$ and $\chi_\perp$ for $\mathbf{H}_{\text{ext}}$ in $\hat{z}$ and in $\hat{x}, \hat{y}$ directions, respectively, then

$$\mathcal{F}(H_{\text{ext}}) = \mathcal{F}(0) - \frac{1}{2} V \left[ \chi_\parallel (H_{\text{ext}}^2) + \chi_\perp (H_{\text{ext}}^2) + \chi_\perp (H_{\text{ext}}^2) \right]$$
Effective thermodynamic potential of a ferromagnet

In a ferromagnet, \( \vec{M} \) is determined primarily by exchange interaction. On the other hand, interaction of \( \vec{M} \) with other fields (e.g., electric fields inside of the crystal) is weak in parameter \( e^2/\hbar c \) (fine structure constant). Thus, it makes sense to build a thermodynamic theory where \( M \) is an independent variable whose actual value is determined eventually by minimization of an appropriate thermodynamic potential \( \tilde{\Phi}(T, M, \ldots) \): \( \tilde{F}(T, H) = \min_M \tilde{\Phi}(T, M, H) \). \( \tilde{\Phi} \) is thus the effective thermodynamic potential.

Similar to \( \tilde{F} \), it must satisfy \( \frac{\partial \tilde{\Phi}}{\partial H} = -\frac{4\pi}{\hbar c} \vec{B} \), which entails

\[
\tilde{\Phi}(T, M, H) = \tilde{\Phi}(T, M, 0) - \vec{M} \cdot \vec{H} - \frac{H^2}{8\pi} . \tag{5}
\]

(formula \( \vec{B} = \vec{H} + 4\pi \vec{M} \) was used)

We must now replace every occurrence of \( \tilde{F} \) by \( \tilde{\Phi} \), in particular, instead of Eq. (3) we have

\[
\tilde{F} = \int \left[ \tilde{\Phi}(T, M, 0) - \vec{M} \cdot \vec{H} - \frac{H^2}{8\pi} + \frac{\vec{H} \cdot \vec{B}}{8\pi} - \frac{1}{2} \vec{M} \cdot (\vec{H} + \text{Hex}) \right] dV
\]

\[
= \int \left[ \tilde{\Phi}(T, M, 0) - \frac{1}{2} \vec{M} \cdot (\vec{H} + \text{Hex}) \right] dV . \tag{6}
\]
Demagnetization energy of a ferromagnetic ellipsoid

If an ellipsoid is magnetized along one of its axes and is placed into a uniform $\mathbf{H}_{ext} \parallel \mathbf{M}$, then inside of the ellipsoid $\mathbf{H}$ is also uniform and is equal to $\mathbf{H} = \mathbf{H}_{ext} - 4\pi N \mathbf{M}$, where $N$ = demag. factor for the given axis.

(for example, $N = \frac{1}{3}$ for a sphere; $N = 1$ for the disk in the direction normal to its plane, etc.)

Note that the magnetic induction $\mathbf{B}$ inside the ellipsoid is

$$\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} = \mathbf{H}_{ext} + 4\pi (1-N) \mathbf{M}.$$

Substituting the formula for $\mathbf{H}$ into Eq. (6), we get

$$\mathcal{F} = \mathcal{F}(M,0) + 2\pi NM^2 V - M \mathbf{H}_{ext} V. \quad (V = \text{volume of the ellipsoid})$$

In particular, if $\mathbf{H}_{ext} = 0$, then

$$\mathcal{F} = \mathcal{F}(M,0) + Edm,$$

$$Edm = 2\pi NM^2 V \quad \text{demagnetization energy}.$$