Magnetic work

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When we discuss the magnetic work in the thermodynamics, we realize that the internal energy is expressed in terms of different forms,

$$dU_R = TdS - MdB\,, \qquad\qquad dU_K = TdS + BdM$$

where the suffixes R and K denote the names of Reif and Kittel, for convenience. There are two gedanken experiments on the magnetic work, (1) Kittel and (ii) Reif. The expression of the internal energy is different, depending on the experiments. First we show such gedanken experiments.

In the quantum mechanics, the mutual energy should be equal to $-MdB$ as is expected from the Zeeman energy. This means that Reif's expression is close to the prediction from the quantum mechanics. Note that the origin of the magnetic energy lies in the quantum mechanics, but not in the classical physics since no work can be done for the Lorentz force.

Here we discuss the validity of the two expressions based on the quantum statistical mechanics. To this end, we use the simple model of spin 1/2 paramagnet. We show that the Reis's expression can be derived from this method.

It is important to stress that the results of the thermodynamic properties based on the Reif notation are the same as those based on the Kittel's notation. The thermodynamics of superconductivity can be discussed mainly in terms of the Kittel's notation.

1. Gedanken experiment on the magnetic work by Kittel (classical method)

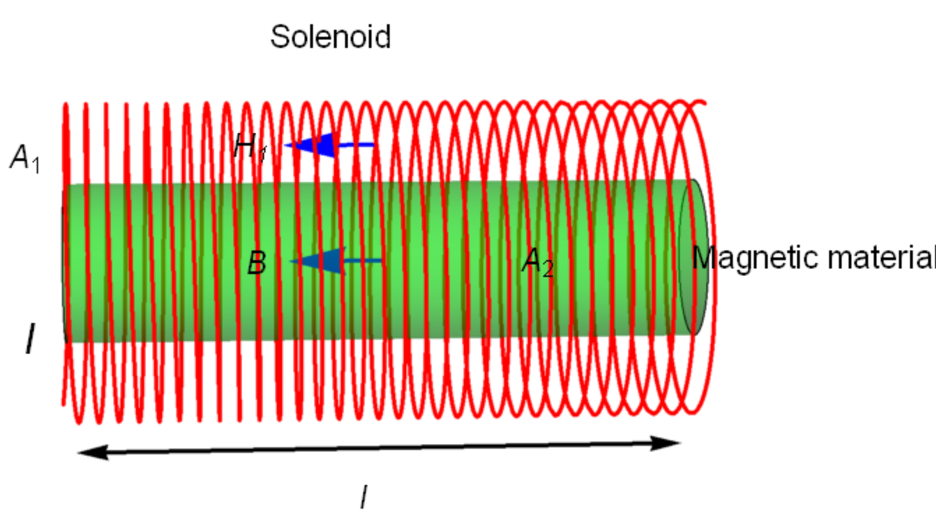


Fig. Magnetic material (cylinder) inside the solenoid with area A_1 and distance l.

The magnetic material is put inside the coil. The magnetic field is produced by current through the coil. The magnetic material can be magnetized.

For a coil having n_1 turns per unit length, we apply the Ampere's theorem.

$$\nabla \times \boldsymbol{H} = \frac{4\pi}{c}\boldsymbol{J},$$

$$\int (\nabla \times \boldsymbol{H}) \cdot d\boldsymbol{a} = \int \boldsymbol{H} \cdot d\boldsymbol{l} = \frac{4\pi}{c}\boldsymbol{J} \cdot d\boldsymbol{a} = \frac{4\pi}{c} n_1 l I_1 = H_1 l,$$

or

$$\frac{4\pi}{c} n_1 l I_1 = H_1 l$$

or

$$H_1 = \frac{4\pi}{c} n_1 I_1$$

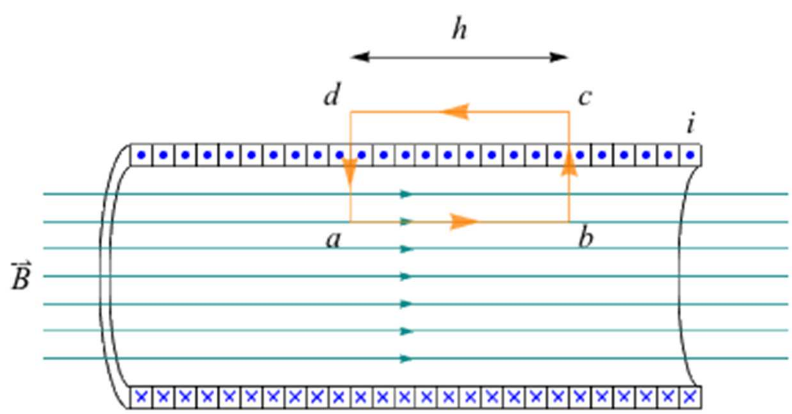


Fig. Ampere's law for the magnetic field of the solenoid

The magnetic flux density B inside the magnetic material is

$$B = H_1 + 4\pi M_0$$

where M_0 is the magnetic moment per unit volume. The magnetic flux Φ_0 is given by

$$\Phi_0 = (A_1 - A_2)H_1 + A_2 B$$

When I_1 is increased, H_1 and M_0 cahnges. Then B also changes. Thus the voltage V is generated inside the coil,

$$V = -\frac{1}{c} n_1 l \frac{d\Phi_0}{dt} = -\frac{1}{c} n_1 l [(A_1 - A_2)\frac{dH_1}{dt} + A_2 \frac{dB}{dt}]$$

The work done by the power supply during the time dt,

$$\begin{aligned} dW_K &= (-I_1 dt)V \\ &= I_1 dt(\frac{1}{c} n_1 l)[(A_1 - A_2)\frac{dH_1}{dt} + A_2 \frac{dB}{dt}] \\ &= \frac{H_1 l}{4\pi} dt[(A_1 - A_2)\frac{dH_1}{dt} + A_2 \frac{dB}{dt}] \\ &= \frac{H_1}{4\pi}(A_1 - A_2) l dH_1 + \frac{H_1}{4\pi} A_2 l dB] \\ &= (V_1 - V_2)\frac{H_1}{4\pi} dH_1 + V_2 \frac{H_1}{4\pi} dB \end{aligned}$$

where

$$H_1 = \frac{4\pi}{c} n_1 I_1, \qquad V_1 = A_1 l, \qquad V_2 = A_2 l$$

Noting that

$$B = H_1 + 4\pi M_0$$

we have

$$\begin{aligned} dW_K &= (V_1 - V_2)\frac{H_1}{4\pi}dH_1 + V_2\frac{H_1}{4\pi}dB \\ &= V_1\frac{H_1}{4\pi}dH_1 + V_2\frac{H_1}{4\pi}(dB - dH_1) \\ &= d\left(\frac{V_1 H_1{}^2}{8\pi}\right) + V_2 H_1 dM_0 \end{aligned}$$

This is the work done on the system consisting of the sample plus field. We use M which is the total magnetic moment of the sample, the magnetic field H, and volume V as

$$V_2 M_0 = M\,, \qquad H_1 = H\,, \qquad V_1 = V$$

So we have

$$dW_K = d\left(\frac{VH^2}{8\pi}\right) + HdM \tag{1}$$

The internal energy is given by

$$dU_K = TdS + dW_K = TdS + HdM + d\left(\frac{VH^2}{8\pi}\right) \tag{2}$$

When we use ***B*** instead of H in Eq.(2), we have the final form,

$$dU_K = TdS + BdM + d\left(\frac{VB^2}{8\pi}\right) \tag{2'}$$

2. Gedanken experiment on the magnetic work by Reif

We consider the force exerted by a magnetic field H on a magnetic moment represented by a small rectangular current loop. There is a net x component of force shown in Fig. below, where I is the current and M is the magnetic moment of the loop. The force on a large sample can be regarded as due to the superposition of forces on many such infinitesimal moments.

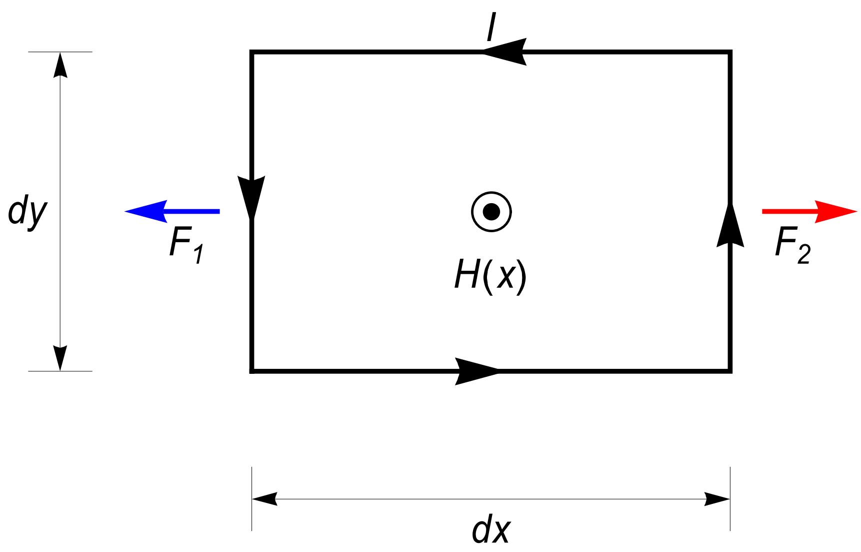


Fig. $F_2 = \frac{1}{c} Idy[H(x) + \frac{\partial H(x)}{\alpha x} dx]$, $F_1 = \frac{1}{c} IdyH(x)$

The magnetic moment is defined by

$$M = \frac{1}{c} IA = \frac{1}{c} Idxdy$$

Net x-component for the force

$$\begin{aligned} F_x &= \frac{I}{c} dy(H + \frac{\partial H}{\partial x} dx) - \frac{I}{c} dyH \\ &= \frac{I}{c} \frac{\partial H}{\partial x} dxdy \\ &= M \frac{\partial H}{\partial x} \end{aligned}$$

Then the work done by the system is

$$W_{out} = F_x dx = M \frac{\partial H}{\partial x} dx = MdH$$

The work done on the system (Reif) is

$$dW_R = -dW_{out} = -MdH \qquad (3)$$

This is the work done on the system in some given magnetic field. It is the work done on the system consisting of the sample alone. The internal energy is given by

$$dU_R = TdS - MdH \tag{4}$$

When we use ***B*** instead of H in Eq.(4), we have the final form

$$dU_R = TdS - MdB \tag{4'}$$

or

$$dU_R = TdS - d(MB) + BdM$$

3. Relation between U_K and U_R

We now consider the relation between two expressions U_K and U_R. We introduce U^* as

$$U^* = U_R + MB\,.$$

Thus we have

$$dU^* = TdS + BdM$$

The internal energy dU_K can be rewritten in the exact way, as

$$\begin{aligned} dU_K &= TdS + BdM + d\left(\frac{VB^2}{8\pi}\right) \\ &= d(U^* + \frac{VB^2}{8\pi}) \end{aligned}$$

which leads to

$$U_K = U^* + \frac{VB^2}{8\pi}, \qquad U_R = U^* - MB$$

For now we omit the term $\frac{VB^2}{8\pi}$. Then we have

$$dU_K = dU^* = TdS + BdM,$$

$$dU_R = d(U^* - MB) = TdS - MdB$$

4. Thermodynamic relations by Reif

$$dU_R = TdS - PdV = TdS - MdB$$

leading to the corresponding relation

$$P \to M, \qquad V \to B$$

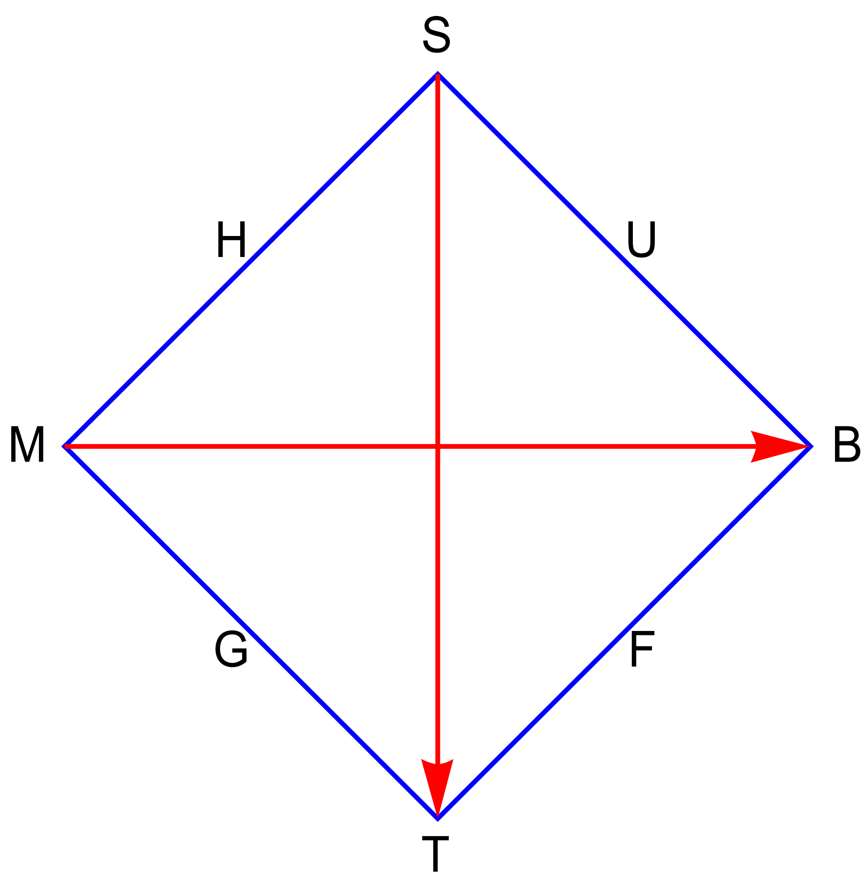


Fig. Born diagram using the definition by Reif; $P \to M$, $V \to B$

where

P, B (intensive variables)
M, V (extensive variables)

Helmholtz free energy:

$$F_R = U_R - ST\,, \qquad\qquad G_R = F_R + MB$$

$$\begin{aligned} dF_R &= dU_R - d(ST) \\ &= TdS - MdB - SdT - TdS \\ &= -SdT - MdB \end{aligned}$$

$$S = -\left(\frac{\partial F_R}{\partial T}\right)_B, \qquad M = -\left(\frac{\partial F_R}{\partial B}\right)_T$$

Gibbs free energy:

$$G_R = F_R + MB$$

$$\begin{aligned} dG_R &= dF_R + d(MB) \\ &= -SdT - MdB + MdB + BdM \\ &= -SdT + BdM \end{aligned}$$

G_R is a function of T and M.

((**Thermodynamic analysis**))

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \qquad \text{(Maxwell's relation)}$$

and

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{\partial(T,S)}{\partial(B,S)}$$
$$= \frac{\dfrac{\partial(T,S)}{\partial(T,B)}}{\dfrac{\partial(B,S)}{\partial(T,B)}}$$
$$= -\frac{\dfrac{\partial(S,T)}{\partial(B,T)}}{\dfrac{\partial(S,B)}{\partial(T,B)}}$$
$$= -\frac{\left(\dfrac{\partial S}{\partial B}\right)_T}{\left(\dfrac{\partial S}{\partial T}\right)_B}$$

or

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T\left(\dfrac{\partial S}{\partial B}\right)_T}{T\left(\dfrac{\partial S}{\partial T}\right)_B} = -\frac{T}{C_B}\left(\frac{\partial S}{\partial B}\right)_T = -\frac{T}{C_B}\left(\frac{\partial M}{\partial T}\right)_B$$

where C_B is the heat capacity at fixed *B*.

((**Example**))

For the paramagnet, M is given by

$$M = \chi(T)B$$

with

$$\chi(T) = \frac{C}{T}$$

where *C* is the Curie constant. Using the expression of *M*, we have

$$\left(\frac{\partial S}{\partial B}\right)_T = B\frac{\partial \chi(T)}{\partial T} = -B\frac{C}{T^2} < 0 \qquad \text{(Isothermal process)}$$

This means that in the isothermal process, the entropy decreases with increasing magnetic field. We also mote that

$$\left(\frac{\partial T}{\partial B}\right)_S > 0 \qquad \text{(Isentropic cooling)}$$

which means that the temperature decreases with decreasing B during the adiabatic process.

5. Thermodynamic properties by Kittel (Stanley)

$$dU_K = TdS - PdV = TdS + BdM$$

leading to the corresponding relation

$$P \to B, \qquad V \to -M$$

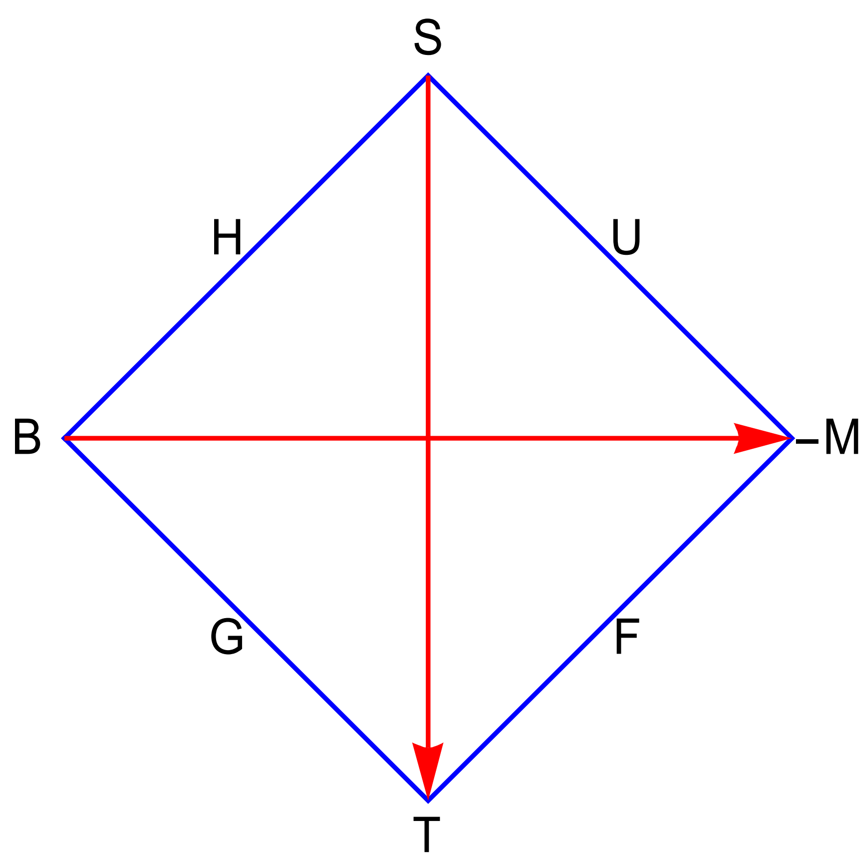


Fig. Born diagram using the definition by Kittel; $P \to B, V \to -M$

where

P, B (intensive)
M, V (extensive)

Helmholtz free energy:

$$F_K = U_K - ST\ ,$$

$$\begin{aligned} dF_K &= dU_K - d(ST) \\ &= TdS + BdM - SdT - TdS \\ &= -SdT + BdM \end{aligned}$$

$$S = -\left(\frac{\partial F_K}{\partial T}\right)_M , \qquad H = \left(\frac{\partial F_K}{\partial M}\right)_T$$

F_K is a function of T and M.

Gibbs free energy:

$$G_K = F_K - MB$$

$$\begin{aligned} dG_K &= dF_K - d(MB) \\ &= -SdT + BdM - MdB - BdM \\ &= -SdT - MdB \end{aligned}$$

G_K is a function of T and B.

$$S = -\left(\frac{\partial G_K}{\partial T}\right)_B , \qquad M = -\left(\frac{\partial G_K}{\partial B}\right)_T$$

((**Maxwell relation**))

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B , \qquad \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial B}{\partial T}\right)_M$$

$$\left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial B}{\partial S}\right)_M , \qquad \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

(a) Isothermal process

Maxwell's relation:

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \tag{2}$$

For the paramagnet, M is given by

$$M = \chi(T)B$$

with

$$\chi(T) = \frac{C}{T}$$

where C is the Curie constant. Using the expression of M, we have

$$\left(\frac{\partial S}{\partial B}\right)_T = B\frac{\partial \chi(T)}{\partial T} = -B\frac{C}{T^2} < 0$$

This means that in the isothermal process, the entropy decreases with increasing magnetic field.

(b) Isentropic process

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{\partial(T,S)}{\partial(B,S}$$

$$= -\frac{1}{\frac{\partial(S,B)}{\partial(T,B)}}\frac{\partial(T,S)}{\partial(T,B)}$$

$$= -\frac{1}{\left(\frac{\partial S}{\partial T}\right)_B}\left(\frac{\partial S}{\partial B}\right)_T$$

$$= -\frac{T}{T\left(\frac{\partial S}{\partial T}\right)_B}\left(\frac{\partial S}{\partial B}\right)_T$$

$$= -\frac{T}{C_B}\left(\frac{\partial S}{\partial B}\right)_T$$

where C_B is the heat capacity at constant B and is positive and $\left(\frac{\partial S}{\partial B}\right)_T < 0$. Thus we have

$$\left(\frac{\partial T}{\partial B}\right)_S >$$

which means that the temperature decreases with decreasing B during the adiabatic process.

So we note that the Maxwell's relation (1) for the Reif type is the same as that (2) for the Kittel type.

6 Magnetic work derived from quantum statistics (MacDonald)

The magnetic work is equal to zero in classical physics since the scalar product of the Lorentz force and the displacement vector is always equal to zero. On the other hand, in quantum mechanics, the magnetic work is equal to a Zeeman energy given by a form $-\boldsymbol{M}\cdot\boldsymbol{B}$. In this sense, the magnetic work should be treated in terms of the quantum mechanics. To this end we consider a simple case such as a paramagnet where the electron with the spin (S = 1/2) is under the presence of an external magnetic field $\boldsymbol{B}$.

There are two states (up state and down state) of the magnetic moment μ_B). Both states are assumed to be nondegenerate. We apply an external magnetic field B in the up direction. So that a positive magnetic moment has an negative energy $-\mu_B B$, while a nagative magnetic moment has a positive magnetic energy $+\mu_B B$. The energy difference is $2\mu_B B$.

The probability for finding the system with the positive magnetic moment is

$$P_+ = \frac{\exp(\beta\mu_B B)}{\exp(\beta\mu_B B)+\exp(-\beta\mu_B B)}$$

The probability for finding the system with the negative magnetic moment is

$$P_- = \frac{\exp(-\beta\mu_B B)}{\exp(\beta\mu_B B)+\exp(-\beta\mu_B B)}$$

The internal energy U is given by

$$\begin{aligned} U &= \mu_B B P_+ + (-\mu_B B) P_- \\ &= \frac{\mu_B B[\exp(\beta\mu_B B)-\exp(-\beta\mu_B B)]}{\exp(\beta\mu_B B)+\exp(-\beta\mu_B B)} \\ &= \mu_B B \tanh(\beta\mu_B B) \end{aligned}$$

The magnetization M:

$$\begin{aligned} M &= \mu_B P_+ + (-\mu_B) P_- \\ &= \frac{\mu_B[\exp(\beta\mu_B B)-\exp(-\beta\mu_B B)]}{\exp(\beta\mu_B B)+\exp(-\beta\mu_B B)} \\ &= \mu_B \tanh(\beta\mu_B B) \end{aligned}$$

The entropy S:

$$\begin{aligned} S &= -k_B(P_+ \ln P_+ + P_- \ln P_-) \\ &= k_B \ln[2\cosh(\beta\mu_B B)] - k_B\beta\mu_B B \tanh(\beta\mu_B B) \end{aligned}$$

Then we have

$$\begin{aligned} F &= U - ST \\ &= \mu_B B \tanh(\beta\mu_B B) - k_B T\{-\beta\mu_B B \tanh(\beta\mu_B B) + \ln[(2\cosh(\beta\mu_B B)]\} \\ &= -k_B T \ln[(2\cosh(\beta\mu_B B)]\} \end{aligned}$$

In another approach, using the partition function Z for the canonical ensemble defined by

$$\begin{aligned} Z &= \exp(\beta\mu_B B) + \exp(-\beta\mu_B B) \\ &= 2\cosh(\beta\mu_B B) \end{aligned}$$

we can also calculate the Helmholtz energy F, the entropy S, and the magnetization M as follows. The Helmholtz free energy:

$$F = -k_B T \ln Z = -k_B T \ln[2\cosh(\beta\mu_B B)]$$

The entropy S:

$$S = -\left(\frac{\partial F}{\partial T}\right)_B = k_B\{\ln[2\cosh(\beta\mu_B B)] - \beta\mu_B B \tanh(\beta\mu_B B)\}$$

The magnetization M:

$$\begin{aligned} M &= -\left(\frac{\partial F}{\partial B}\right)_T \\ &= \mu_B \tanh(\beta\mu_B B) \end{aligned}$$

The expressions of S and M thus obtained are the same as those derived above. Since F is a function of B and T, dF can be expressed by

$$dF = \left(\frac{\partial F}{\partial B}\right)_T dB + \left(\frac{\partial F}{\partial T}\right)_B dT$$

The derivatives $\left(\frac{\partial F}{\partial B}\right)_T$ and $\left(\frac{\partial F}{\partial T}\right)_B$ can be evaluated as

$$\left(\frac{\partial F}{\partial B}\right)_T = -\mu_B \tanh(\beta\mu_B B) = -M$$

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_B &= -k_B \ln(2\cosh(\beta\mu_B B)] + k_B\beta\mu_B B \tanh(\beta\mu_B B) \\ &= -S \end{aligned}$$

Thus we have

$$dF = -MdB - SdT$$

The internal energy U is related to the Helmholtz free energy F as

$$F = U - ST$$

We now consider the Gibbs free energy defined by

$$G = F + MB$$

leading to the relation

$$\begin{aligned} dG &= d(F + MB) \\ &= dF + d(MB) \\ &= -SdT - MdB + MdB + BdM \\ &= -SdT + BdM \end{aligned}$$

So the Gibbs free energy G depends on T and M,

$$dG = \left(\frac{\partial G}{\partial T}\right)_M dT + \left(\frac{\partial G}{\partial M}\right)_T dM$$

We now derive the expression of magnetic field B in terms of M and T. To this end, we start with

$$\frac{M}{\mu_B} = \tanh(\beta\mu_B B) = \frac{\exp(2\beta\mu_B B) - 1}{\exp(2\beta\mu_B B) + 1}$$

The magnetic field B can be uniquely obtained as

$$\begin{aligned} B &= \frac{1}{2\beta\mu_B}\ln\left(\frac{\mu_B + M}{\mu_B - M}\right) \\ &= \frac{1}{2\beta\mu_B}\ln\left(\frac{1 + \frac{M}{\mu_B}}{1 - \frac{M}{\mu_B}}\right) \\ &= \frac{1}{2\beta\mu_B}[\ln(1 + \frac{M}{\mu_B}) - \ln(1 - \frac{M}{\mu_B})] \end{aligned}$$

Since

$$\exp(\beta\mu_B B) = \sqrt{\frac{\mu_B + M}{\mu_B - M}}$$

F can be also evaluated as

$$\begin{aligned}
F &= -\frac{1}{\beta}\ln[\exp(\beta\mu_B B) + \exp(-\beta\mu_B B)] \\
&= -\frac{1}{\beta}\ln[\sqrt{\frac{\mu_B + M}{\mu_B - M}} + \sqrt{\frac{\mu_B - M}{\mu_B + M}}] \\
&= -\frac{1}{\beta}\ln[\frac{2\mu_B}{\sqrt{(\mu_B - M)(\mu_B + M)}}] \\
&= -\frac{1}{\beta}\ln[\frac{2}{\sqrt{(1-\frac{M}{\mu_B})(1+\frac{M}{\mu_B})}}] \\
&= -\frac{1}{\beta}\ln 2 + \frac{1}{2\beta}\ln[(1-\frac{M}{\mu_B})(1+\frac{M}{\mu_B})]
\end{aligned}$$

The Gibbs free energy is obtained as

$$\begin{aligned}
G &= F + MB \\
&= -\frac{1}{\beta}\ln 2 + \frac{1}{2\beta}\ln[(1-\frac{M}{\mu_B})(1+\frac{M}{\mu_B})] + \frac{1}{2\beta}\frac{M}{\mu_B}\ln\left(\frac{1+\frac{M}{\mu_B}}{1-\frac{M}{\mu_B}}\right) \\
&= -\frac{1}{\beta}\ln 2 + \frac{1}{2\beta}[(1+\frac{M}{\mu_B})\ln(1+\frac{M}{\mu_B}) + (1-\frac{M}{\mu_B})\ln(1-\frac{M}{\mu_B})]
\end{aligned}$$

or

$$G = -\frac{1}{\beta}\ln 2 + \frac{1}{2\beta}[(1+\frac{M}{\mu_B})\ln(1+\frac{M}{\mu_B}) + (1-\frac{M}{\mu_B})\ln(1-\frac{M}{\mu_B})]$$

Thus we have

$$\begin{aligned}
\left(\frac{\partial G}{\partial M}\right)_T &= \frac{1}{2\beta\mu_B}[\ln(1+\frac{M}{\mu_B}) - \ln(1-\frac{M}{\mu_B})] \\
&= B
\end{aligned}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_M = -k_B\beta^2\left(\frac{\partial G}{\partial \beta}\right)_M$$
$$= -k_B \ln 2 + \frac{1}{2}k_B[(1+\frac{M}{\mu_B})\ln(1+\frac{M}{\mu_B}) + (1-\frac{M}{\mu_B})\ln(1-\frac{M}{\mu_B})]$$
$$= -S$$

Then dG can be expressed by

$$dG = \left(\frac{\partial G}{\partial T}\right)_M dT + \left(\frac{\partial G}{\partial M}\right)_T dM$$
$$= -SdT + BdM$$

Here we note that

$$\frac{S}{k_B} = \ln[2\cosh(\beta\mu_B B)] - \beta\mu_B B\tanh(\beta\mu_B B)$$
$$= \ln[\exp(\beta\mu_B B) + \exp(\beta\mu_B B)] - \beta\mu_B B\frac{M}{\mu_B}\}$$
$$= \ln[\sqrt{\frac{\mu_B + M}{\mu_B - M}} + \sqrt{\frac{\mu_B - M}{\mu_B + M}}] - \frac{M}{\mu_B}\ln\sqrt{\frac{\mu_B + M}{\mu_B - M}}$$
$$= \ln[\sqrt{\frac{1+\frac{M}{\mu_B}}{1-\frac{M}{\mu_B}}} + \sqrt{\frac{1-\frac{M}{\mu_B}}{1+\frac{M}{\mu_B}}}] - \frac{M}{\mu_B}\ln\sqrt{\frac{1+\frac{M}{\mu_B}}{1-\frac{M}{\mu_B}}}$$
$$= \ln[\frac{2}{\sqrt{1-\frac{M}{\mu_B}}\sqrt{1+\frac{M}{\mu_B}}}] - \frac{M}{\mu_B}\ln\sqrt{\frac{1+\frac{M}{\mu_B}}{1-\frac{M}{\mu_B}}}$$

or

$$S = k_B \ln 2 - \frac{1}{2}k_B[(1+\frac{M}{\mu_B})\ln(1+\frac{M}{\mu_B}) + (1-\frac{M}{\mu_B})\ln(1-\frac{M}{\mu_B})]$$

Using the relations

$$dG = -SdT + BdM$$

$$dF = -MdB - SdT$$

$$G = F + MB = U - ST + MB$$

we get

$$U = G + ST - MB$$

and

$$\begin{aligned} dU &= dG + d(ST) - d(MB) \\ &= -SdT + BdM + SdT + TdS - MdB - BdM \\ &= TdS - MdB \end{aligned}$$

In summary, it is reasonable to conclude that from a view point of quantum statistical physics,

$$dU = TdS - MdB \qquad \text{and} \qquad dG = -SdT + BdM$$

The expression for dU is the same as that derived by Reif and the expression for dG is the same as that derived by Kittel. We agree with the comment by Robertson that the magnetic work done on the system by the mutual energy must be $-MdB$

7. Problem and solution (1)
K. Huang
Introduction to Statistical mechanics, second edition (CRC Press, 2010)

((Problem 3-8))
Thermodynamic variables for magnetic system are B, M, T, where B is the magnetic field, M is the magnetization, and T the absolute temperature. The magnetic work is

$$dW = BdM ,$$

and the first law states $dU = TdS + BdM$. The equation of state is given by Curie's law

$$M = C\frac{B}{T} ,$$

where C (>0) is the Curie constant. This is valid only at small B and high T. The heat capacity at constant B is denoted by C_B, and that at constant M is C_M. Many thermodynamics relations can be obtained from those of a *PVT* system by the correspondence $B \to P$, $V \to -M$

(a) Show

$$C_M = \left(\frac{\partial U}{\partial T}\right)_M, \qquad C_B = \left(\frac{\partial U}{\partial T}\right)_B - B\left(\frac{\partial M}{\partial T}\right)_B$$

(b) From the analog of the energy equation and Curie's law, show that

$$\left(\frac{\partial U}{\partial M}\right)_T = 0$$

This is the analog of the statement that the internal energy of the ideal gas is independent of the volume.

(c) Show

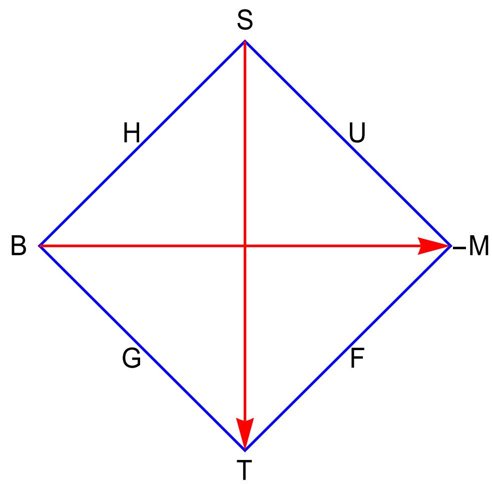
$$C_B - C_M = \frac{CB^2}{T^2} = \frac{M^2}{C}$$

Here we use the correspondence relations such that

$P \to B$ (intensive quantity)

$V \to -M$ (extensive quantity)

$dU = TdS - PdV \qquad dU = TdS + HdM$



((**Solution**))
(a)

$$dU = TdS + HdM$$

The heat capacity:

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M,$$

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial U}{\partial T}\right)_H - H\left(\frac{\partial M}{\partial T}\right)_H$$

(b)

$$\left(\frac{\partial U}{\partial M}\right)_T = H + T\left(\frac{\partial S}{\partial M}\right)_T = H - T\left(\frac{\partial H}{\partial T}\right)_M$$

where we use the Maxwell's relation:

$$\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M$$

M is given by the Curie law as

$$M = \frac{C}{T}B$$

Noting that

$$\left(\frac{\partial B}{\partial T}\right)_M = \frac{M}{C} = \frac{B}{T}$$

we have

$$\left(\frac{\partial U}{\partial M}\right)_T = B - T\left(\frac{\partial B}{\partial T}\right)_M = 0$$

(c)

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M = T\frac{\partial(S,M)}{\partial(T,M)} = T\frac{\frac{\partial(S,M)}{\partial(T,B)}}{\frac{\partial(T,M)}{\partial(T,B)}} = T\frac{\frac{\partial(S,M)}{\partial(T,B)}}{\left(\frac{\partial M}{\partial B}\right)_T}$$

or

$$\begin{aligned} C_M &= \frac{T}{\left(\frac{\partial M}{\partial B}\right)_T}\begin{vmatrix} \left(\frac{\partial S}{\partial T}\right)_B & \left(\frac{\partial S}{\partial B}\right)_T \\ \left(\frac{\partial M}{\partial T}\right)_B & \left(\frac{\partial M}{\partial B}\right)_T \end{vmatrix} \\ &= \frac{T}{\left(\frac{\partial M}{\partial B}\right)_T}[\left(\frac{\partial S}{\partial T}\right)_B\left(\frac{\partial M}{\partial B}\right)_T - \left(\frac{\partial S}{\partial B}\right)_T\left(\frac{\partial M}{\partial T}\right)_B] \\ &= T\left(\frac{\partial S}{\partial T}\right)_B - \frac{T\left(\frac{\partial S}{\partial B}\right)_T\left(\frac{\partial M}{\partial T}\right)_B}{\left(\frac{\partial M}{\partial B}\right)_T} \end{aligned}$$

Using the Maxwell's relation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

Then we get

$$C_M - C_B = -\frac{T\left(\frac{\partial M}{\partial T}\right)_B^2}{\left(\frac{\partial M}{\partial B}\right)_T}$$

For the paramagnetic system,

$$M = \frac{C}{T}B$$

$$C_M - C_B = -\frac{CB^2}{T^2}$$

or

$$C_B - C_M = \frac{CB^2}{T^2} = \frac{M^2}{C}$$

8. Problem and solution (2)

K. Huang
Introduction to Statistical mechanics, second edition (CRC Press, 2010)

((Problem 3-9))
Define the free energy $F(M,T)$ and Gibbs energy $G(B,T)$ of a magnetic system by analogy with the PVT system.
(a) Show

$$dF = -SdT + BdM\,, \qquad dG = -SdT - MdB$$

(b) Show

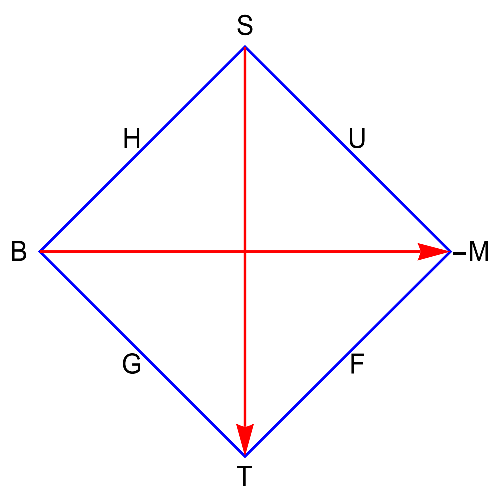
$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

hence

$$\left(\frac{\partial S}{\partial B}\right)_T = -\frac{CB}{T^2}.$$

(c) With the help of the chain rule, show

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{CB}{C_B T}$$



((**Solution**))
Helmholtz free energy F
Gibbs free energy G

$$dU = TdS - PdV \to TdS + HdM$$

$$F = U - ST, \qquad G = F + PV \to F - HM$$

where $P \to B$, $V \to -M$ (Kittel)

(a)

$$\begin{aligned} dF &= d(U - ST) \\ &= dU - SdT - TdS \\ &= TdS + BdM - SdT - TdS \\ &= -SdT + BdM \end{aligned}$$

$$
\begin{aligned}
dG &= d(F - BM) \\
&= -SdT + BdM - BdM - MdB \\
&= -SdT - MdB
\end{aligned}
$$

(b)

$$
S = -\left(\frac{\partial G}{\partial T}\right)_B, \quad M = -\left(\frac{\partial G}{\partial B}\right)_T
$$

$$
\begin{aligned}
\left(\frac{\partial S}{\partial B}\right)_T &= -\left(\frac{\partial}{\partial B}\right)_T \left(\frac{\partial G}{\partial T}\right)_B \\
&= -\frac{\partial^2 G}{\partial B \partial T} \\
&= -\frac{\partial^2 G}{\partial T \partial B} \\
&= -\left(\frac{\partial}{\partial T}\right)_B \left(\frac{\partial G}{\partial B}\right)_T \\
&= \left(\frac{\partial M}{\partial T}\right)_B
\end{aligned}
$$

Since

$$
M = \frac{C}{T} B, \qquad \left(\frac{\partial M}{\partial T}\right)_B = -\frac{CB}{T^2}
$$

$$
\left(\frac{\partial S}{\partial B}\right)_T = -\frac{CB}{T^2}
$$

(b)

Noting that

$$
\frac{\partial(T,S)}{\partial(B,S)} \frac{\partial(S,B)}{\partial(T,B)} \frac{\partial(B,T)}{\partial(S,T)} = -1
$$

we get the relation

$$\left(\frac{\partial T}{\partial B}\right)_S \left(\frac{\partial S}{\partial T}\right)_B \left(\frac{\partial B}{\partial S}\right)_T = -1$$

Since

$$\left(\frac{\partial B}{\partial S}\right)_T = \frac{1}{\left(\frac{\partial S}{\partial B}\right)_T} = -\frac{T^2}{CB}$$

$$T\left(\frac{\partial S}{\partial T}\right)_B = \left(\frac{\partial Q}{\partial T}\right)_B = C_B$$

we have

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T = -\frac{\left(\frac{\partial S}{\partial B}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_B} = \frac{\frac{CB}{T^2}}{\frac{C_B}{T}} = \frac{CB}{C_B T}$$

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