Paramagnetism: Curie law

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In a paramagnet, the magnetic moments of electron spins are not aligned. The direction of the magnetic moment is random. So the total magnetization is zero. However, when the magnetic field is applied, the situation changes. The magnetization (the magnetic moment per volume) M appears along the direction of the magnetic field, and obeys the Curie law,

$$M \approx N\mu_B \beta \mu_B B = \frac{N\mu_B^{\ 2}}{k_B T} B = \frac{C}{T} B .$$

The thermodynamic and magnetic properties of the paramagnet are discussed using two approaches (the microcanonical ensemble and the canonical ensemble). The entropy is described by a scaling function of only a variable B/T . This property of the entropy is used for the cooling of the system (isentropic demagnetization).

1. Approach from the microcanonical ensemble

We consider the electron spin system with two energy levels in the presence of an external magnetic field B along the z axis. The spin magnetic moment $\boldsymbol{\mu}$ is given by

$$\boldsymbol{\mu} = -\frac{2\boldsymbol{S}}{\hbar}\mu_B = -\mu_B \boldsymbol{\sigma} ,$$

where $\boldsymbol{S}$ $(=\frac{\hbar}{2}\boldsymbol{\sigma})$ is the spin angular momentum, $\mu_B = \frac{e\hbar}{2mc}$ (>) is the Bohr magneton, and the charge of electron is $-e$ (e>0). In the presence of the magnetic field along the z axis, we have a Zeeman energy given by

$$\varepsilon = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -(-\mu_B\boldsymbol{\sigma})\cdot\boldsymbol{B} = \mu_B B\,\sigma_z$$

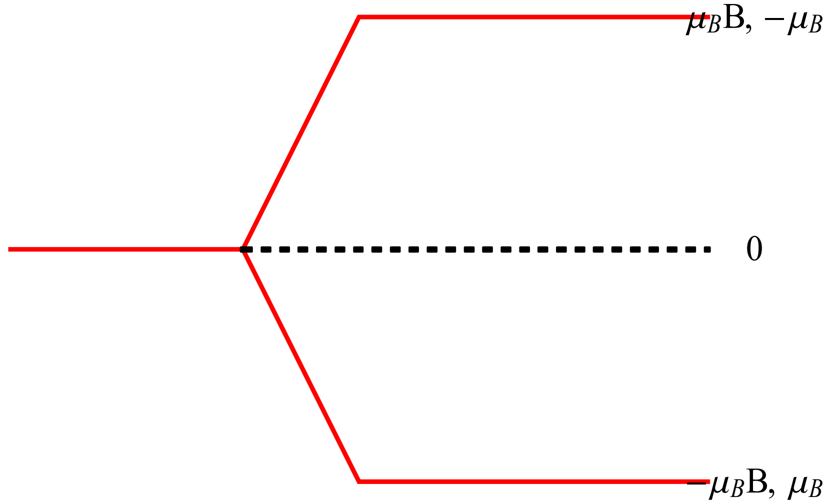
Noting that $\sigma_z\left|+z\right\rangle = \left|+z\right\rangle$ and $\sigma_z\left|-z\right\rangle = -\left|-z\right\rangle$ in quantum mechanics, the energy level splits into two levels, $\pm\mu_B B$.

(a) The energy $\mu_B B$ (higher level),

The spin state $\left|+z\right\rangle$. The spin magnetic moment is antiparallel to the z-axis $(-\mu_B)$. $\left|\downarrow\right\rangle$ state.

(b) The energy $-\mu_B B$ (lower level).

The spin state: $|-z\rangle$. The spin magnetic moment is parallel to the z-axis $(+\mu_B)$; $|\uparrow\rangle$ state.



Suppose that

$$N_\uparrow + N_\downarrow = N$$

N: the total number of spins.

$N_\uparrow$ the number of spin magnetic moment parallel to the magnetic field.

$N_\downarrow$ the number of spin magnetic moment antiparallel to the magnetic field.

The total magnetic moment M is

$$M = \mu_B N_\uparrow - \mu_B N_\downarrow = 2\mu_B s\,.$$

The total energy E is given by

$$E = -\mu_B B(N_\uparrow - N_\downarrow)$$

Here we introduce the excess spin number s.

$$N_\uparrow - N_\downarrow = 2s\,.$$

Then we have

$$N_{\uparrow} = \frac{N}{2} + s, \qquad N_{\downarrow} = \frac{N}{2} - s.$$

So the energy E is expressed by

$$E = -2s\mu_B B$$

The number of ways for choosing $N_{\uparrow}$ spins and $N_{\uparrow}$ spins out of N spins (identical) is given by

$$W(N,s) = \frac{N!}{N_{\uparrow}N_{\downarrow}} = \frac{N!}{(\frac{N}{2}+s)!(\frac{N}{2}-s)!}.$$

Using the Stirling relation, the entropy can be evaluated as

$$\begin{aligned}
S &= k_B \ln W(N,s) \\
&= k_B[\ln N! - \ln(\frac{N}{2}+s)! - \ln(\frac{N}{2}-s)!] \\
&= k_B[N\ln N - N - (\frac{N}{2}+s)\ln(\frac{N}{2}+s) + \frac{N}{2} + s - (\frac{N}{2}-s)\ln(\frac{N}{2}-s) + \frac{N}{2} - s] \\
&= k_B[N\ln N - (\frac{N}{2}+s)\ln(\frac{N}{2}+s) - (\frac{N}{2}-s)\ln(\frac{N}{2}-s)]
\end{aligned}$$

or

$$\begin{aligned}
S(N,E) = k_B[N\ln N &- (\frac{N}{2}+\frac{E}{2\mu_B B})\ln(\frac{N}{2}+\frac{E}{2\mu_B B}) \\
&- (\frac{N}{2}-\frac{E}{2\mu_B B})\ln(\frac{N}{2}-\frac{E}{2\mu_B B})]
\end{aligned}$$

Using the relation,

$$\frac{1}{T} = \frac{\partial S(N,E)}{\partial E} = \frac{k_B}{2\mu_B B}\ln\left(\frac{N\mu_B B - E}{E + N\mu_B B}\right)]$$

we have

$$E = -N\mu_B B \tanh(\beta\mu_B B)$$

Note that the total magnetization is related to the total energy as

$$E = -MB$$

Then we have

$$M = N\mu_B \tanh(\beta\mu_B B)$$

When $\beta\mu_B B << 1$, we get

$$M \approx N\mu_B \beta\mu_B B = \frac{N\mu_B{}^2}{k_B T} B = \frac{C}{T} B$$

showing the Curie law, where

$$C = \frac{N\mu_B{}^2}{k_B}.$$

((**Note**))

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

For $x << 1$, $\tanh x = x$.

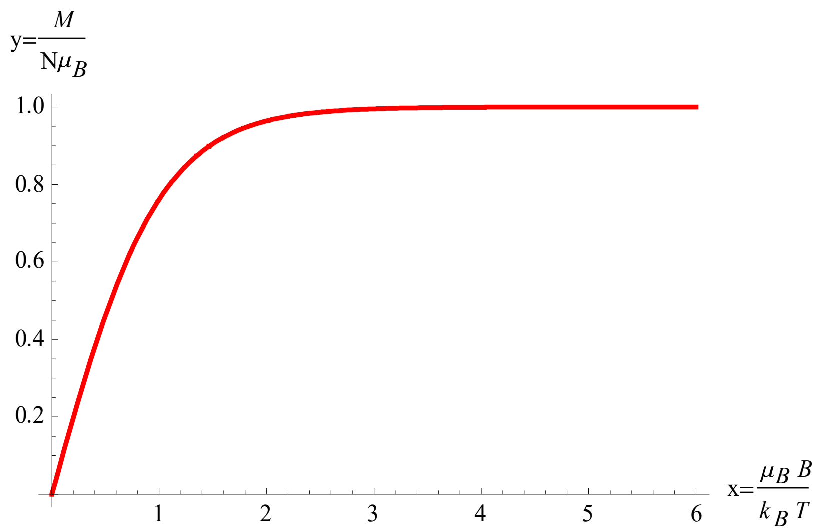


Fig. Scaling plot of the magnetization. The saturation magnetization is $N\mu_B$; $y = 1$.

2. Approach from the canonical ensemble

(a) Thermodynamic properties: *F, G, E* and *S*

The N- partition function is given by

$$Z_{CN} = Z_{C1}{}^{N}$$

where N is the number of spins. Z_{C1} is the one-particle partition function and is given by

$$Z_{C1} = \exp(\beta\mu_B B) + \exp(-\beta\mu_B B) = 2\cosh(\beta\mu_B B).$$

The Helmholtz free energy F:

$$F = E - ST = -k_B T \ln Z_{CN} = -Nk_B T \ln Z_{C1} = -Nk_B T \ln[2\cosh(\beta\mu_B B)]$$

Since $dF = -PdV - SdT$, the pressure P is obtained as

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = 0$$

The internal energy E:

$$E = -\frac{\partial}{\partial \beta}\ln Z_{CN} = -N\frac{\partial}{\partial \beta}\ln Z_{C1} = -N\mu_B B\tanh(\beta\mu_B B)$$

(b). Magnetization M

In the present system, the Gibbs energy is equal to F (M. Kardar, Statistical Physics of Particles, Cambridge, 2007, p.117). We note that

$$dG = VdP - SdT$$

Here we use the replacement ;

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

Then we have

$$dG = -MdB - SdT$$

So the magnetization is given by

$$M = -\frac{\partial G}{\partial B} = -\frac{\partial F}{\partial B} = -k_B T \frac{\partial}{\partial B} \ln Z_{CN} = N\mu_B \tanh(\beta\mu_B B)$$

This expression can be directly derived from a view point of quantum mechanics (see the Appendix). The magnetization M can be also directly derived from the definition as

$$M = N(\mu_B P_+ - \mu_B P_-)$$

where P_+ and P_- are probabilities given by

$$P_+ = \frac{e^{\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}}, \qquad P_- = \frac{e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}}$$

Then we have

$$M = N[\frac{\mu_B e^{\beta\mu_B B} + (-\mu_B)e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = N\mu_B \tanh(\beta\mu_B B)$$

In the limit of $\frac{\mu_B B}{k_B T} \to 0$,

$$M \approx N\mu_B \frac{\mu_B B}{k_B T} = \frac{N\mu_B{}^2}{k_B}\frac{B}{T},$$

showing the Curie law. Note that

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}},$$

and for $0 < x << 1$, $\tanh x = x - \frac{x^3}{3} + \frac{2}{15}x^5 + O(x^7)$

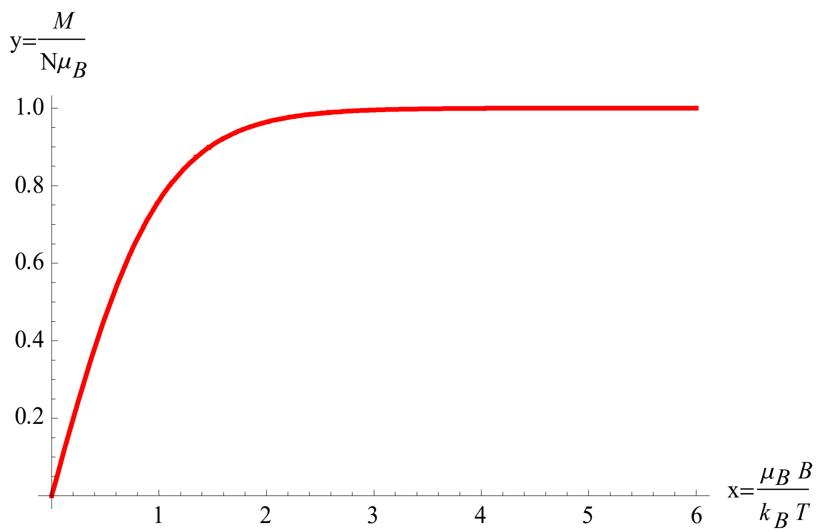


Fig. Scaling plot of the magnetization. The saturation magnetization is $N\mu_B$; $y = 1$.

(c) Entropy *S*

The entropy *S*:

$$S = \frac{U}{T} - \frac{F}{T} = k_B(\beta U - \beta F) = k_B(-\beta \frac{\partial \ln Z_{CN}}{\partial \beta} + \ln Z_{CN})$$

or

$$S = k_B N[\ln(2\cosh(\beta\mu_B B) - \beta\mu_B B \tanh(\beta\mu_B B)]$$

or

$$\frac{S}{k_B N} = \ln[2\cosh(\frac{\mu_B B}{k_B T})] - \frac{\mu_B B}{k_B T}\tanh(\frac{\mu_B B}{k_B T}) .$$

The entropy S is expressed by a scaling function of B/T. This is an essential point to this system.
We introduce the characteristic temperature T_0 and magnetic field B_0 as

$$\mu_B B_0 = k_B T_0$$

Then we have

$$\begin{aligned}\frac{S}{k_B N} &= \ln[2\cosh(\frac{\mu_B B}{k_B T})] - \frac{\mu_B B}{k_B T}\tanh(\frac{\mu_B B}{k_B T}) \\ &= \ln[2\cosh(\frac{b}{t})] - \frac{b}{t}\tanh(\frac{b}{t})\end{aligned}$$

where

$$b = \frac{B}{B_0}, \qquad t = \frac{T}{T_0}$$

$$\frac{\mu_B B}{k_B T} = \frac{\mu_B B_0 \dfrac{B}{B_0}}{k_B T_0 \dfrac{T}{T_0}} = \frac{b}{t}$$

We make a plot of $\frac{S}{k_B N}$ as function of t, where b is changed as a parameter. In the limit of $t \to \infty$, the entropy reached

$$\frac{S}{k_B N} = \ln(2s+1) = \ln 2 = 0.693147.$$

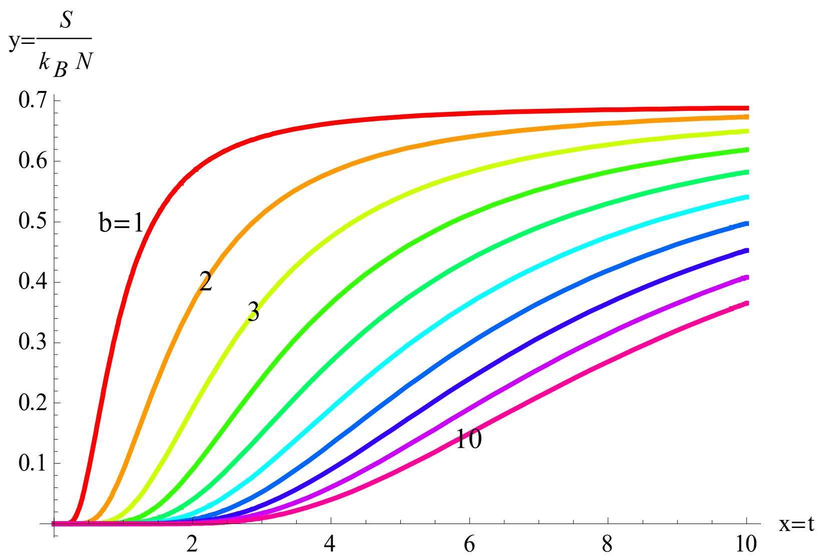


Fig. Plot of $\frac{S}{k_B N}$ as a function of a reduced temperature t (= T/T_0), where the reduced magnetic field b (= B/B_0) is changed as a parameter. Note that $\mu_B B_0 = k_B T_0$. The highest value of y is ln2 = 0.693147.

3. Proof of $\frac{S}{k_B N} \to 0$ in the limit of $t \to 0$

Noting that $e^{b/t} >> 1$ and $e^{-b/t} << 1$, we can approximate the expression of entropy as

$$\begin{aligned}
\frac{S}{k_B N} &= \ln[2\cosh(\frac{b}{t})] - \frac{b}{t}\tanh(\frac{b}{t}) \\
&= \ln(e^{b/t} + e^{-b/t}) - \frac{b}{t}\left(\frac{e^{b/t} - e^{-b/t}}{e^{b/t} + e^{-b/t}}\right) \\
&= \ln[e^{b/t}(1 + e^{-2b/t})] - \frac{b}{t}\left(\frac{1 - e^{-2b/t}}{1 + e^{-2b/t}}\right) \\
&\approx \frac{b}{t} + e^{-2b/t} - \frac{b}{t}\left(1 - 2e^{-2b/t}\right) \\
&\approx \frac{2b}{t} e^{-2b/t}
\end{aligned}$$

where we use the approximation

$$\ln(1+x) \approx x, \qquad \frac{1-x}{1+x} \approx 1-2x \qquad \text{for } 0 < x << 1$$

In the limit of $t \to 0$, we have

$$\lim_{t \to 0} S = 0$$

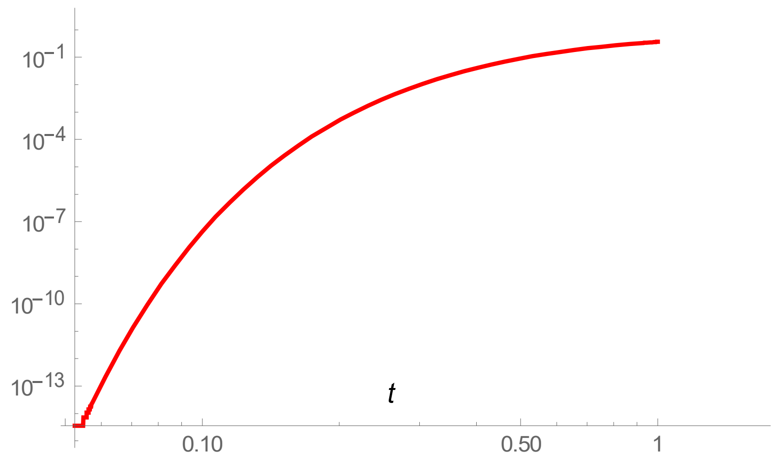


Fig. The entropy of $S/(Nk_B)$ as a function of t. b = 1. The system settles into ground state; the multiplicity becomes 1: and the entropy goes to zero.

4. Isentropic demagnetizion

The principle of magnetically cooling a sample is as follows. The paramagnet is first cooled to a low starting temperature. The magnetic cooling then proceeds via two steps.

Suppose that the spin system is kept at temperature T_1 in the presence of magnetic field B_1. The system is insulated ($\Delta S = 0$) and the field removed, the system follows the constant entropy path AB, ending up at the temperature T_2 (isentropic process). If B_Δ is the effective field that corresponds to the local interactions, the final temperature T_2 reached in an isentropic demagnetization process is

$$\frac{T_2}{B_\Delta} = \frac{T_1}{B_1}.$$

since the entropy is a function of only B/T.

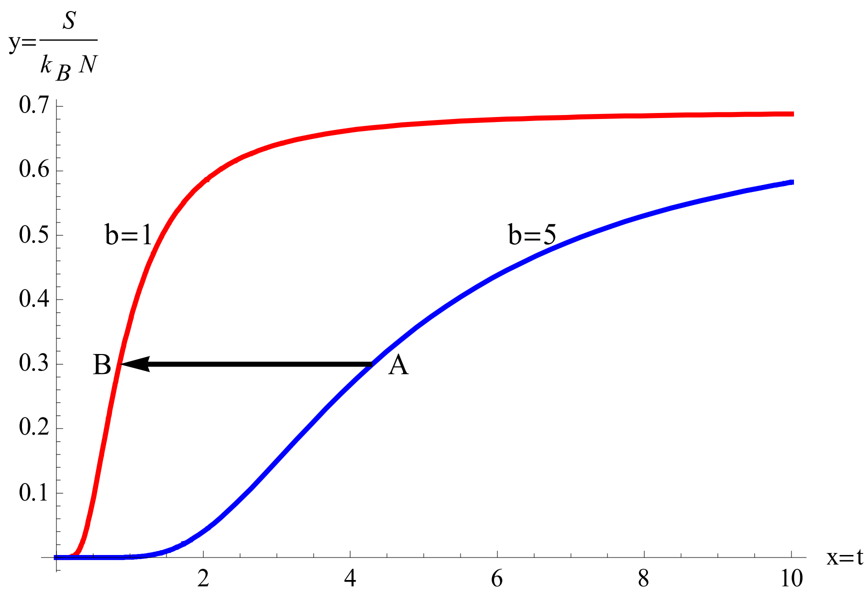
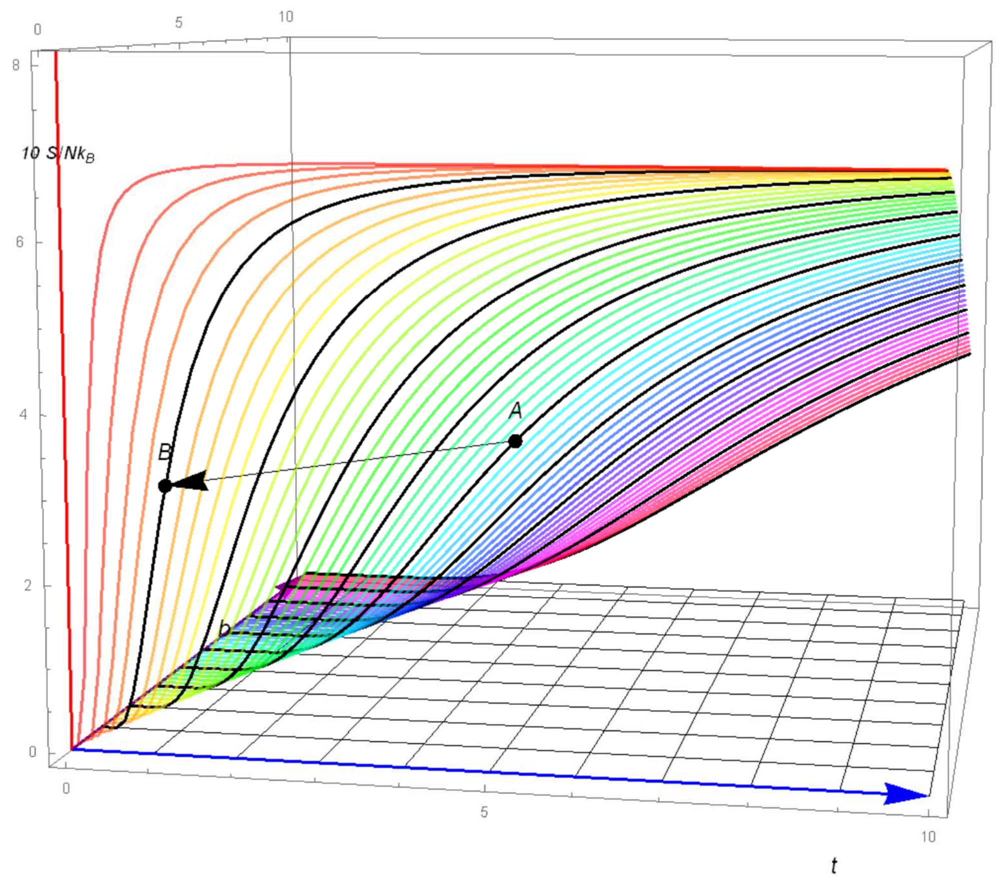


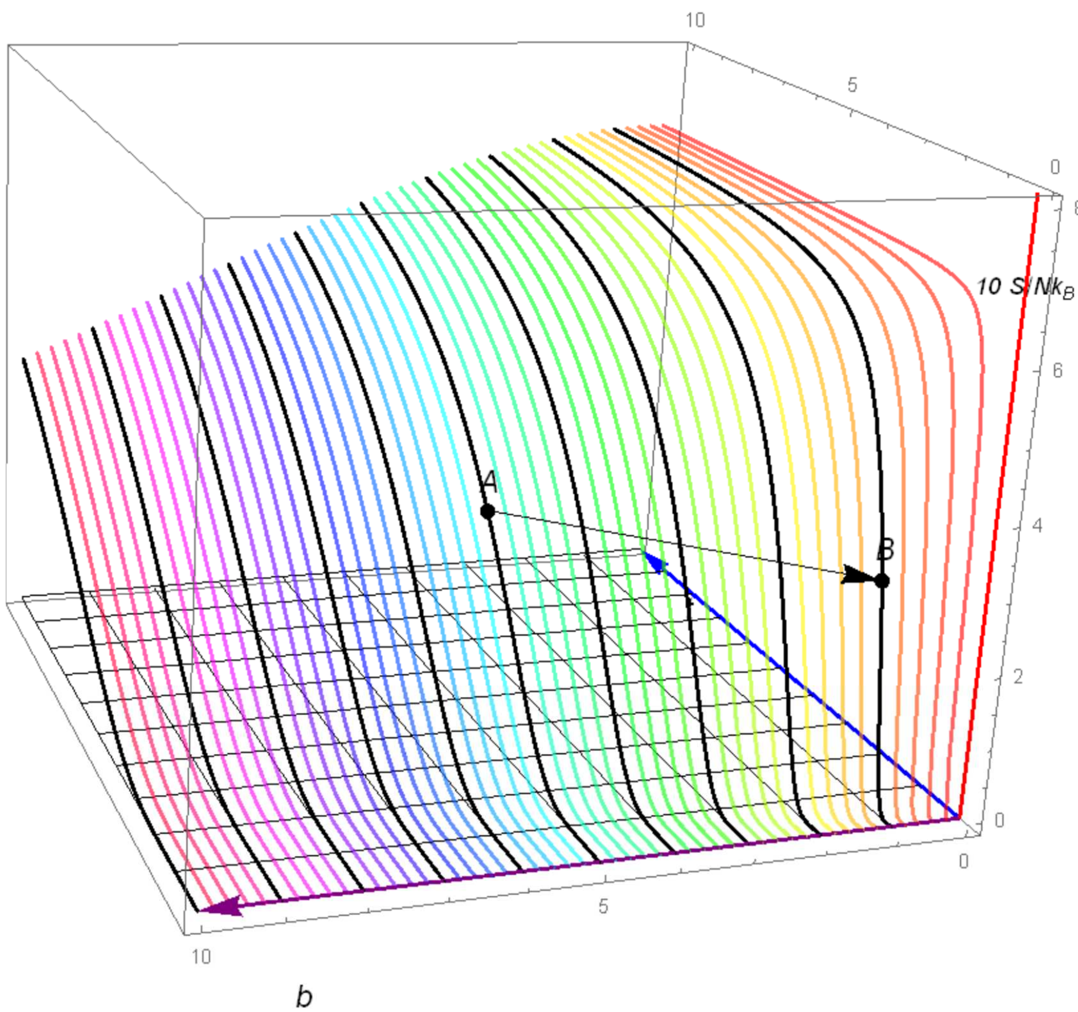
Fig. Point A (t_A = 4.29726, y_A = 0.3) on the line with $\frac{B_A}{B_0} = 1$. Point B (t_B= 0.859452, , y_A = 0.3) on the line with $\frac{B_B}{B_0} = 5$. The path AB is the isentropic process (y = 0.3).

Note that

$$\frac{t_A}{B_A} = \frac{t_B}{B_B}.$$



10 S/Nk_B
A
B
b
t



5. Specific heat

The heat capacity is given by

$$\frac{C}{Nk_B} = (\frac{\mu_B B}{k_B T})^2 \sec h^2 (\frac{\mu_B B}{k_B T})$$

Using the energy gap parameter

$$k_B \Delta = 2\mu_B B$$

$$\frac{C}{Nk_B} = (\frac{\Delta}{2T})^2 \sec h^2 (\frac{\Delta}{2T}) = \frac{1}{4}(\frac{\Delta}{T})^2 \sec h^2 (\frac{\Delta}{2T}) = \frac{1}{4}(\frac{\Delta}{T})^2 \frac{e^{T/\Delta}}{(1+e^{T/\Delta})^2}$$

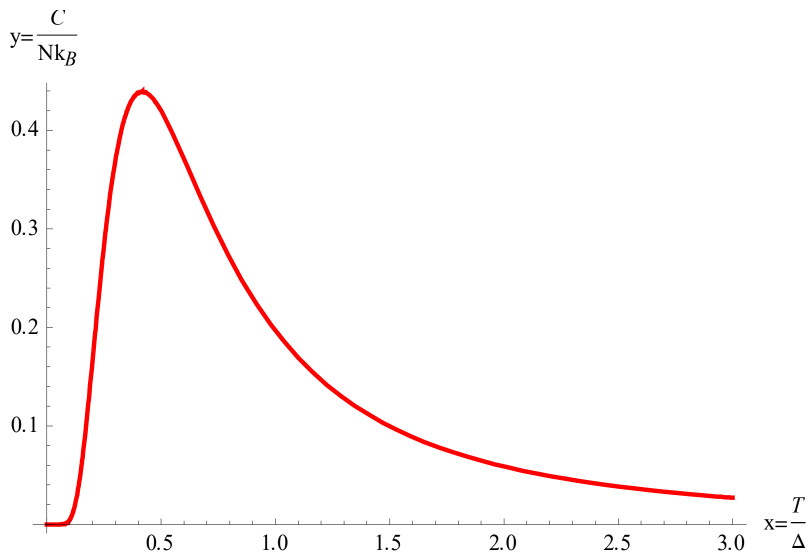


Fig. Plot of the heat capacity C/k_B as a function of T/Δ. It show a peak at T/Δ = 0.416778.

The heat capacity as a function of temperature, has a peak at

$$\frac{T}{\Delta} = 0.416778\,.$$

((Schottky anomaly))

The Schottky anomaly is an observed effect in solid state physics where the specific heat capacity of a solid at low temperature has a peak. It is called anomalous because the heat capacity usually increases with temperature, or stays constant. It occurs in systems with a limited number of energy levels so that $E(T)$ increases with sharp steps, one for each energy level that becomes available. Since Cv =(dE/dT), it will experience a large peak as the temperature crosses over from one step to the next.

REFERENCES

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APPENDIX Quantum mechanical treatment for the expression of Magnetization

The spin Hamiltonian for the spin 1/2 system in the presence of a magnetic field along the z axis, is given by the Zeeman energy as

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B} = -(-\frac{2\mu_B}{\hbar}\hat{\boldsymbol{S}}) \cdot \boldsymbol{B} = \mu_B B \hat{\sigma}_z$$

where $\hat{\boldsymbol{\mu}} = -\frac{2\mu_B}{\hbar}\hat{\boldsymbol{S}} = \mu_B \hat{\sigma}_z$ is the spin magnetic moment operator. The on-particle partition function is given by

$$Z_{C1} = Tr[e^{-\beta \hat{H}}] = Tr[e^{-\beta \mu_B B \hat{\sigma}_z}]$$

We can evaluate the average magnetic moment as

$$-\frac{1}{\beta}\frac{\partial}{\partial B} Z_{C1} = Tr[\mu_B \hat{\sigma}_z e^{-\beta \mu_B B \hat{\sigma}_z}] = Z_{C1}\langle \mu_z \rangle$$

or

$$\langle \mu_z \rangle = -\frac{1}{\beta}\frac{\partial}{\partial B}\ln Z_{C1}$$

The magnetization for the N particle system, we have

$$M = N\langle \mu_z \rangle = -Nk_B T\frac{\partial}{\partial B}\ln Z_{C1}.$$

Bohr magneton

$\mu_B = 9.27400915$ x 10^{-21} emu

$\frac{\mu_B}{k_B} = 6.71713$ x 10^{-5} (K/Oe)

Nuclear magneton

$\mu_N = 5.050783699$ x 10^{-24} emu

$$\frac{\mu_N}{k_B} = 3.65826 \text{ x } 10^{-8} \text{ (K/Oe)}$$

scaling

universality