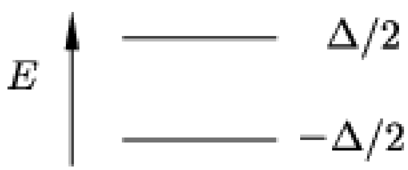
Lecture 20. *The partition function*

- Partition function

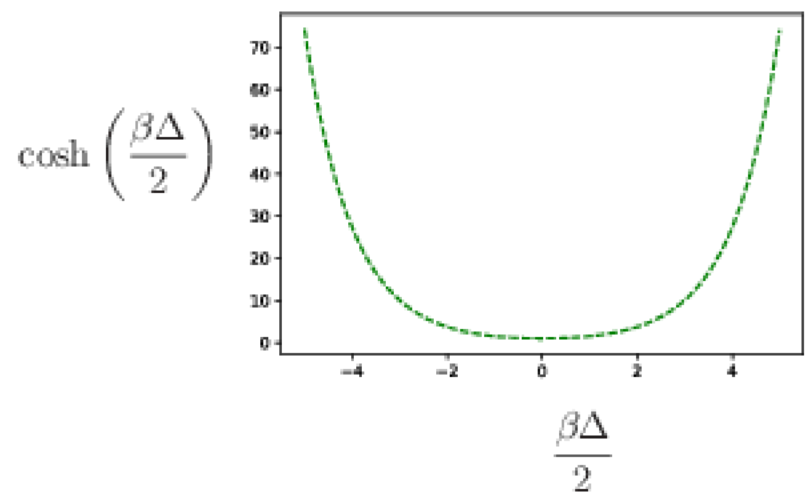
$$Z = \sum_{\alpha} \mathrm{e}^{-\beta E_\alpha}$$

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

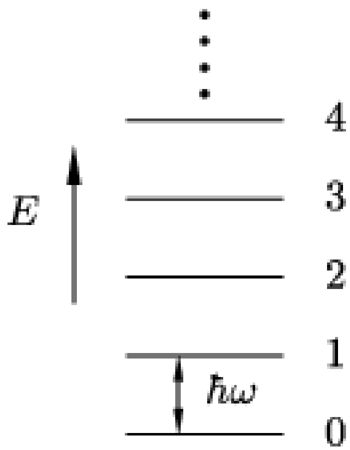
Writing the partition function: the two-level system



$$Z = \sum_\alpha e^{-\beta E_\alpha} = e^{\beta\Delta/2} + e^{-\beta\Delta/2} = 2\cosh\left(\frac{\beta\Delta}{2}\right)$$

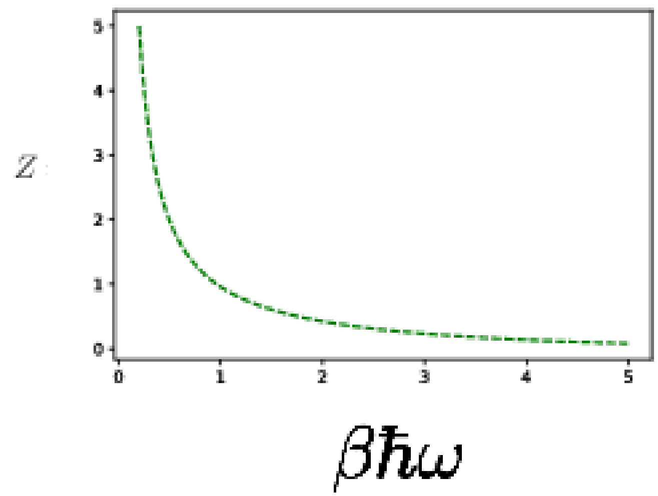


Writing the partition function: the simple harmonic oscillator

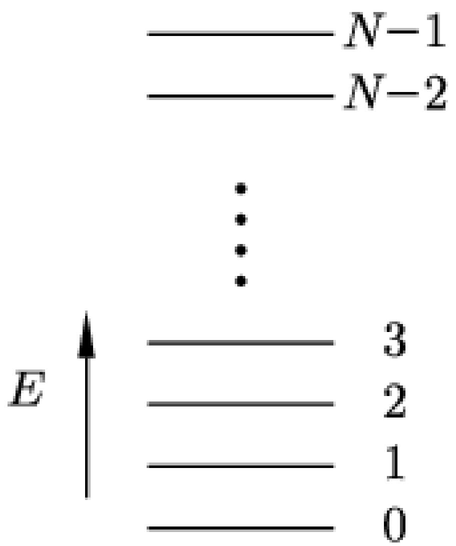


$$\left(n+\frac{1}{2}\right)\hbar\omega$$

$$Z=\sum_{\alpha} e^{-\beta E_\alpha}=\sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}=e^{-\beta\frac{1}{2}\hbar\omega}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}=\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$



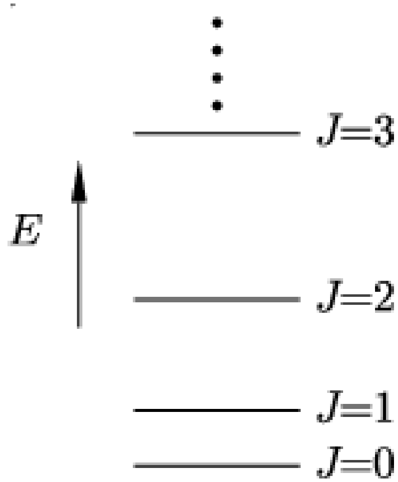
Writing the partition function: The N-level system



$$0, \quad \omega, 2 \quad \omega, \ldots, (N-1) \quad \omega.$$

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{j=0}^{N-1} e^{-j\beta \quad \omega} = \frac{1 - e^{-N\beta \quad \omega}}{1 - e^{-\beta \quad \omega}}$$

Writing the partition function: Rotational energy levels



Rotational K.E. of a molecule with moment of inertia I:

$$E = \hat{J}^2/2I$$

How to extract info from Z: (1) Internal energy

How to extract info from Z: (2) Entropy

How to extract info from Z: (3) Helmholtz function

Heat capacities

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Or $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Downarrow$$

Pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_\mathrm{B} T \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

Enthalpy

$$H = U + pV = k_{\mathrm{B}} T \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right]$$

Gibbs function

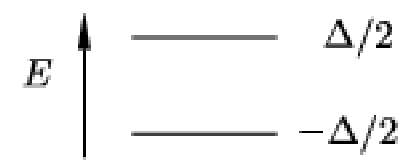
$$G = F + pV = k_{\mathrm{B}}T\left[-\ln Z + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right]$$

	Function of state	Statistical mechanical expression
U		$-\dfrac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_{\mathrm{B}}T\ln Z$
S	$=-\left(\frac{\partial F}{\partial T}\right)_V=\frac{U-F}{T}$	$k_{\mathrm{B}}\ln Z+k_{\mathrm{B}}T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
p	$=-\left(\frac{\partial F}{\partial V}\right)_T$	$k_{\mathrm{B}}T\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
H	$=U+pV$	$k_{\mathrm{B}}T\left[T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V+V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
G	$=F+pV=H-TS$	$k_{\mathrm{B}}T\left[-\ln Z+V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
C_V	$=\left(\frac{\partial U}{\partial T}\right)_V$	$k_{\mathrm{B}}T\left[2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V+T\left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$

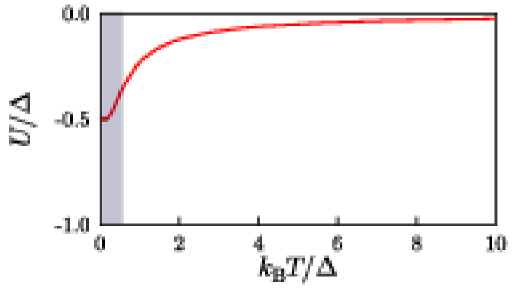
Application to the two level-system

- Internal Energy $$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = -\frac{\Delta}{2}\tanh\left(\frac{\beta\Delta}{2}\right)$$
- Heat Capacity $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_\mathrm{B}\left(\frac{\beta\Delta}{2}\right)^2 \mathrm{sech}^2\left(\frac{\beta\Delta}{2}\right)$$
- Helmholtz function $$F = -k_\mathrm{B}T\ln Z = -k_\mathrm{B}T\ln\left[2\cosh\left(\frac{\beta\Delta}{2}\right)\right]$$
- Entropy $$S = \frac{U-F}{T} = -\frac{\Delta}{2T}\tanh\left(\frac{\beta\Delta}{2}\right) + k_\mathrm{B}\ln\left[2\cosh\left(\frac{\beta\Delta}{2}\right)\right]$$

Two-level system

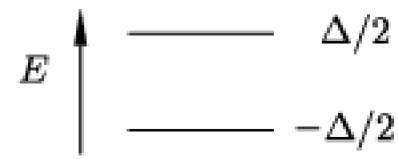


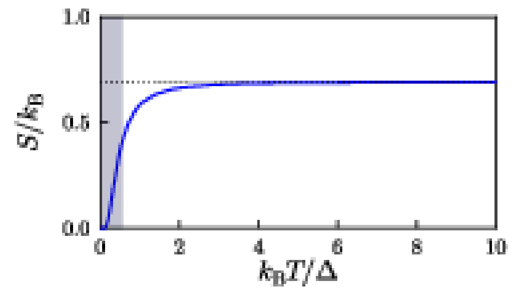
$$Z = 2\cosh\left(\frac{\beta\Delta}{2}\right)$$



Low-T: $U = -\Delta/2$ (lowest state occupied)

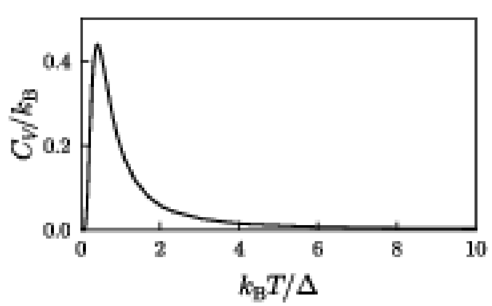
High-T: $U = 0$ (both states occupied)





Low-T: $S = 0$ (one microstate; higher order)

High-T: $S = k_B \ln 2$ (two microstates)

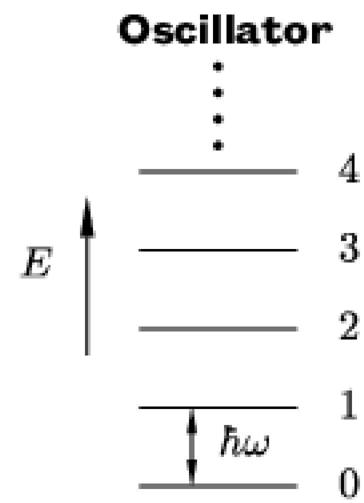


$k_B T << \Delta$ and $k_B T >> \Delta$:: system cannot absorb heat

$k_B T \approx \Delta$: the capacity is at a maximum (**Schottky anomaly**)

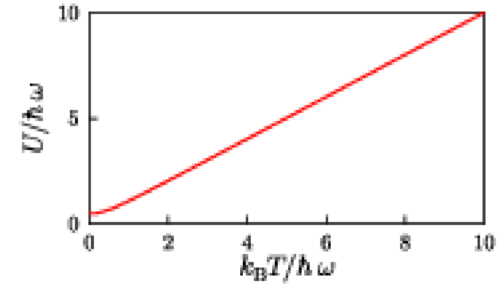
Application to the harmonic oscillator

- Internal Energy $$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = \ \omega\left(\frac{1}{2} + \frac{1}{\mathrm{e}^{\beta\ \omega} - 1}\right)$$
- Heat Capacity $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_\mathrm{B}(\beta\ \omega)^2 \frac{\mathrm{e}^{\beta\ \omega}}{(\mathrm{e}^{\beta\ \omega} - 1)^2}$$
- Helmholtz function $$F = -k_\mathrm{B} T \ln Z = \frac{\omega}{2} + k_\mathrm{B} T \ln(1 - \mathrm{e}^{-\beta\ \omega})$$
- Entropy $$S = \frac{U - F}{T} = k_\mathrm{B}\left(\frac{\beta\ \omega}{\mathrm{e}^{\beta\ \omega} - 1} - \ln(1 - \mathrm{e}^{-\beta\ \omega})\right)$$



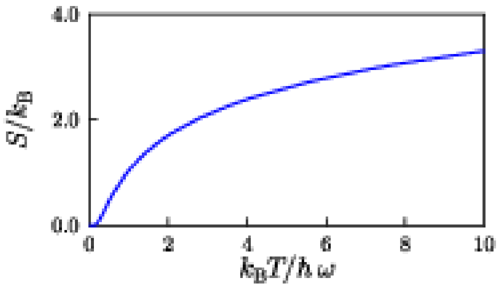
$$\left(n + \tfrac{1}{2}\right)\ \omega$$

$$Z = \frac{\mathrm{e}^{-\frac{1}{2}\beta\ \omega}}{1 - \mathrm{e}^{-\beta\ \omega}}$$



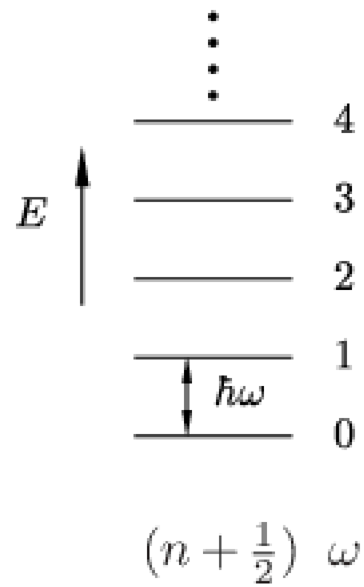
Low-T: $U = \hbar\omega/2$ (lowest state occupied)

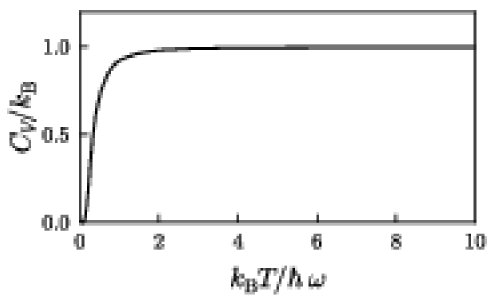
High-T: U increases without limit (~k_BT)



Low-T: $S = 0$ (one microstate; higher order)

High-T: S keeps increasing

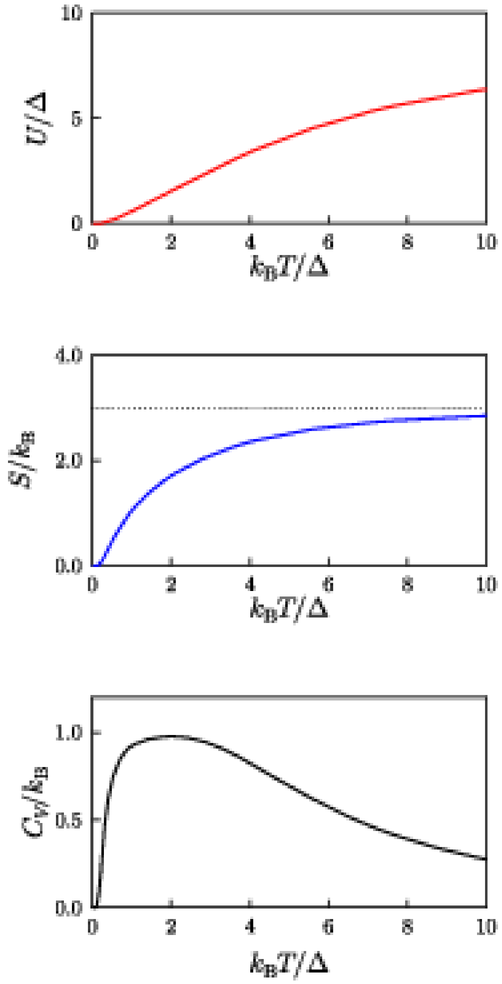




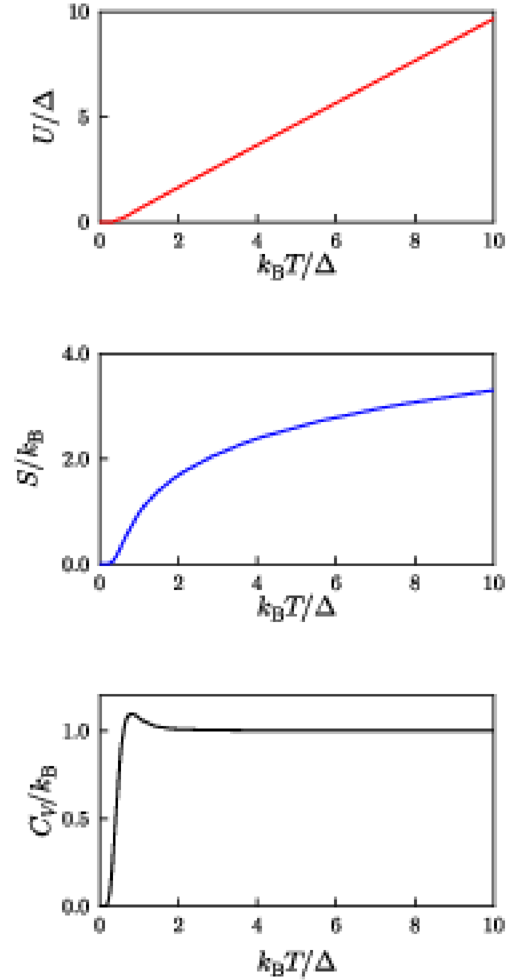
Low-T: $C_V = 0$

High-T: $C_V = k_B$ (equipartition limit)

N-level system (N=20)



Rotating of diatomic molecule



Big Idea of statistical mechanics

(0) Obtain the energy levels of a system

(1) Write down Z

(2) Evaluated thermodynamic functions

	Function of state	Statistical mechanical expression
U		$-\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_\mathrm{B}T\ln Z$
S	$=-\left(\frac{\partial F}{\partial T}\right)_V=\frac{U-F}{T}$	$k_\mathrm{B}\ln Z+k_\mathrm{B}T\left(\frac{\partial\ln Z}{\partial T}\right)_V$
p	$=-\left(\frac{\partial F}{\partial V}\right)_T$	$k_\mathrm{B}T\left(\frac{\partial\ln Z}{\partial V}\right)_T$
H	$=U+pV$	$k_\mathrm{B}T\left[T\left(\frac{\partial\ln Z}{\partial T}\right)_V+V\left(\frac{\partial\ln Z}{\partial V}\right)_T\right]$
G	$=F+pV=H-TS$	$k_\mathrm{B}T\left[-\ln Z+V\left(\frac{\partial\ln Z}{\partial V}\right)_T\right]$
C_V	$=\left(\frac{\partial U}{\partial T}\right)_V$	$k_\mathrm{B}T\left[2\left(\frac{\partial\ln Z}{\partial T}\right)_V+T\left(\frac{\partial^2\ln Z}{\partial T^2}\right)_V\right]$

Interpretation hinges on using $k_B T$ as the relevant scale

Combining partition functions

Imagine the energy of a system is decomposed in different contributions from (a) and (b) and the energy levels are

$$E_{i,j} = E_i^{(a)} + E_j^{(b)}$$

$$Z = \sum_i \sum_j \mathrm{e}^{-\beta(E_i^{(a)} + E_j^{(b)})} = \sum_i \mathrm{e}^{-\beta E_i^{(a)}} \sum_j \mathrm{e}^{-\beta E_j^{(b)}} = Z_a Z_b$$

$$\ln Z = \ln Z_a + \ln Z_b$$

Contributions to functions of state that depend on ln will be additive!

Application: N independent harmonic oscillators

Partition function of a simple harmonic oscillator: $Z_{\mathrm{SHO}} = \mathrm{e}^{-\frac{1}{2}\beta \omega}/(1-\mathrm{e}^{-\beta \omega})$

Partition function of N simple harmonic oscillators: $Z = Z_{\mathrm{SHO}}^{N}$

Application: diatomic molecule

Vibrational degree of freedom: $Z_{\text{vib}} = \mathrm{e}^{-\frac{1}{2}\beta\hbar\omega}/(1 - \mathrm{e}^{-\beta\hbar\omega})$

Curie's law: the spin 1/2 paramagnetic

Spin $s = 1/2$, two possible projections on the (*e.g.*) z-axis: $|\uparrow\rangle$

Spin 1/2 paramagnet: N non-interacting spin 1/2

Most stable state: $\cdots\uparrow\cdots$ *Unlikely (only one micro state)*

Many more states are 50% up and 50% down! $\cdots\uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\downarrow\downarrow\uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\downarrow\uparrow\uparrow\downarrow\downarrow\downarrow\uparrow\cdots$

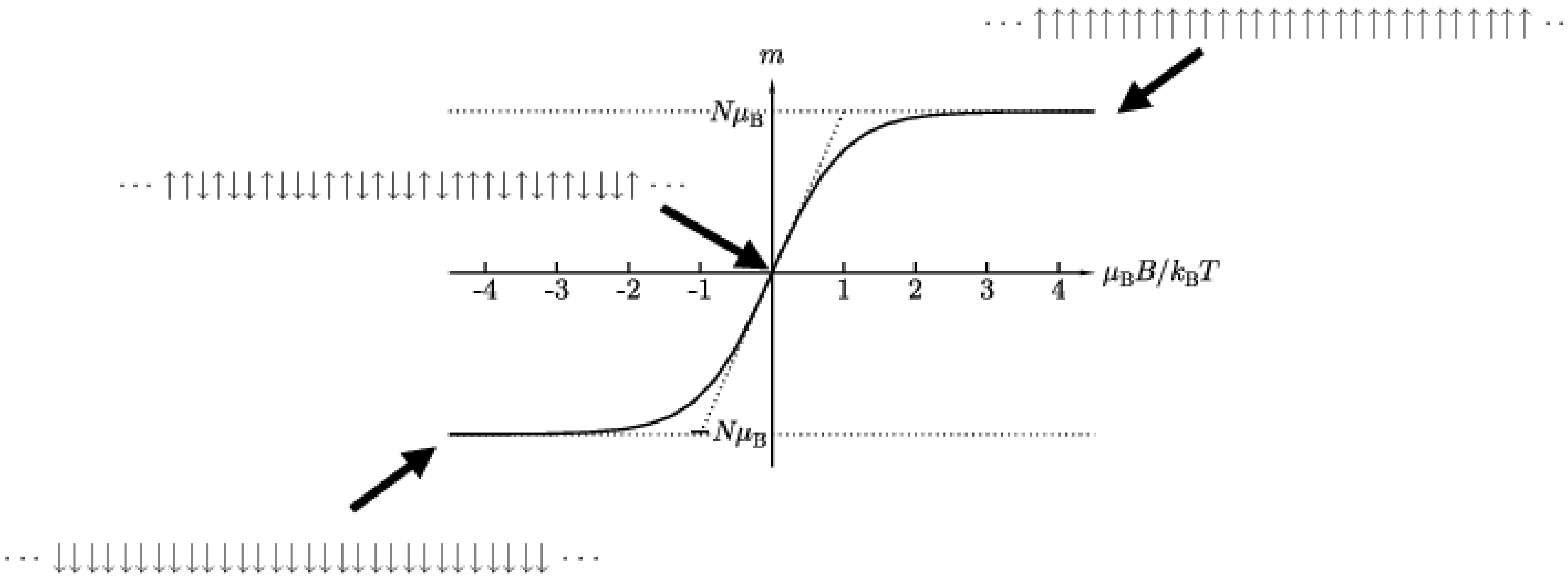
How does that factor in the thermodynamics? $F = U - TS$ Helmholtz

Partition function: $Z_N = Z_1^N$

<u>Helmholtz function:</u> $F = -k_\mathrm{B}T\ln Z_N = -Nk_\mathrm{B}T\ln\left[2\cosh(\beta\mu_\mathrm{B}B)\right]$

<u>Magnetic moment:</u> $m = -\left(\frac{\partial F}{\partial B}\right)_T = N\mu_\mathrm{B}\tanh(\beta\mu_\mathrm{B}B)$

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



Magnetization

$$M = \frac{m}{V} = \frac{N\mu_B}{V}\tanh(\beta\mu_B B)$$

- Magnetic susceptibility is computed at low field $\tanh(x) \sim x$

$$M \approx \frac{N\mu_B^2 B}{V k_B T} \quad \Longrightarrow \quad M \approx \chi H$$

$$\chi \ll 1$$

At low field

Summary

	Function of state	Statistical mechanical expression
U		$-\dfrac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_\mathrm{B}T\ln Z$
S	$= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_\mathrm{B}\ln Z + k_\mathrm{B}T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
p	$= -\left(\frac{\partial F}{\partial V}\right)_T$	$k_\mathrm{B}T\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
H	$= U + pV$	$k_\mathrm{B}T\left[T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
G	$= F + pV = H - TS$	$k_\mathrm{B}T\left[-\ln Z + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
C_V	$= \left(\frac{\partial U}{\partial T}\right)_V$	$k_\mathrm{B}T\left[2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + T\left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$