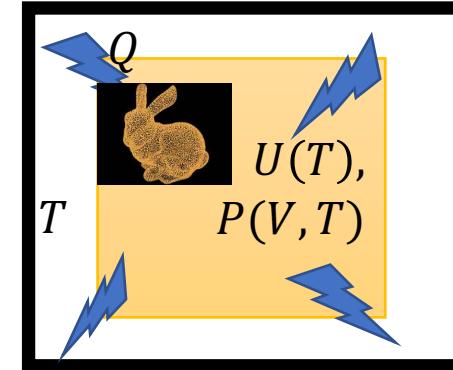
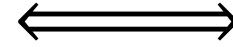
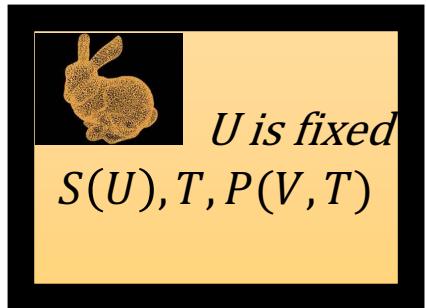


# Lecture 14

29.09.2018

Free energies and partition functions

## Equilibrium thermodynamic state



**Isolated system**

### Statistical mechanics

**System in a thermal bath**

$\Omega_N(U)$  number of **equally-likely** accessible microstates

$$S(U) = k \ln \Omega_N(U)$$

$$T = \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N}$$

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U,N}$$

$Z(T) = \sum_s e^{-\beta E_s}$  counts the microstates when they don't have the same probability at a given  $T$

$$\ln Z(T) = ?$$

- *What is the thermodynamic potential for this system that is analogue to the entropy for an isolated system?*

...

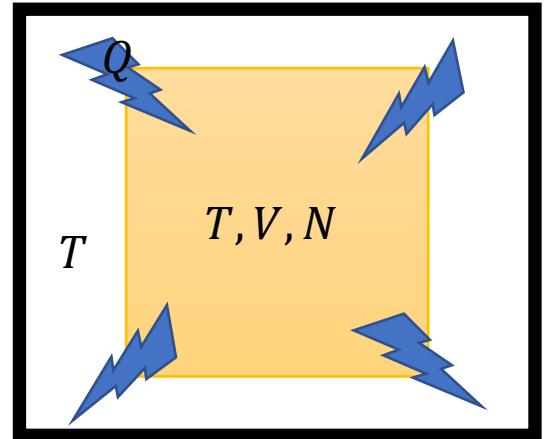
# Systems at constant $T$ and Helmholtz free energy $F(T, V, N)$

- **The Helmholtz free energy  $F$**  is the thermodynamic potential given by the internal energy of a system minus the available heat exchange with the thermal bath fixed  $T$

$$F = U - TS$$

- **Thermodynamic identity** for an infinitesimal **reversible** process

$$\begin{aligned} dF &= -SdT - PdV + \mu dN \\ dF &= \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \end{aligned}$$



- **Thermodynamic inequality** for any infinitesimal process (reversible «=», irreversible «»)

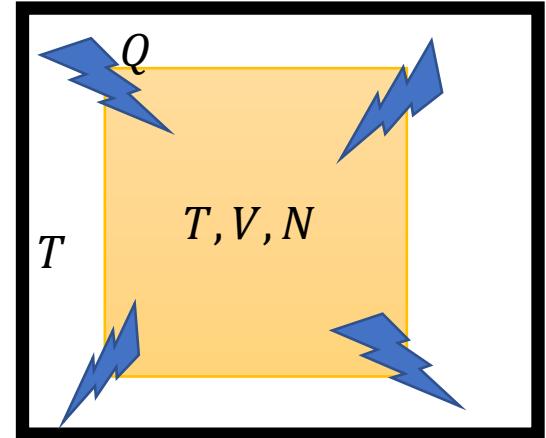
$$dF \leq -SdT - PdV + \mu dN$$

- $F$  is minimized for the equilibrium state at a given  $T$ ,  $V$  and  $N$
- Changes in  $F$  at a fixed  $T$  equals to the **available work** that a system can do  $dF = \delta W$

- $F(T, V, N)$  is the thermodynamic potential that is determined by  $Z(T, V, N)$ , just like entropy  $S(U, V, N)$  is determined by the multiplicity function  $\Omega(U, V, N)$

# System in contact with a thermal bath: Partition function $Z(T)$

- $Z(T, V, N)$  is for a system *in contact with a thermal bath*, what  $\Omega(T, V, N)$  is for an *isolated* system
- The probability that the system is in a given microstate  $s$  at equilibrium with a thermal bath depends on the energy of that microstate  $E(s)$  --- BOLTZMANN's FACTOR



System+thermal bath =  
isolated system

$$\frac{P(s_A)}{P(s_B)} = \frac{\Omega_R(s_A)}{\Omega_R(s_B)} = e^{\frac{\Delta S_R}{k}} = e^{\frac{\Delta U_R}{kT}} = e^{-\frac{\Delta E}{kT}} \rightarrow P(s) \sim e^{-\frac{E(s)}{kT}}$$

- Partition function «counts» the number of available microstates weighted by the Boltzmann's factor for a system at fixed  $T$

$$Z(T) = \sum_{\{s\}} e^{-\frac{E(s)}{kT}}, \quad \text{so that } P(s) = \frac{1}{Z} e^{-\beta E(s)}, \quad \beta = \frac{1}{kT}$$

System in contact with a thermal bath:

Partition function  $Z(T, V, N)$

- One particle in a thermal bath

$$Z_1(T) = \sum_{\{s\}} e^{-\frac{E(s)}{kT}}, \quad \text{so that } P_1(s) = \frac{1}{Z_1} e^{-\beta E(s)}, \quad \beta = \frac{1}{kT}$$

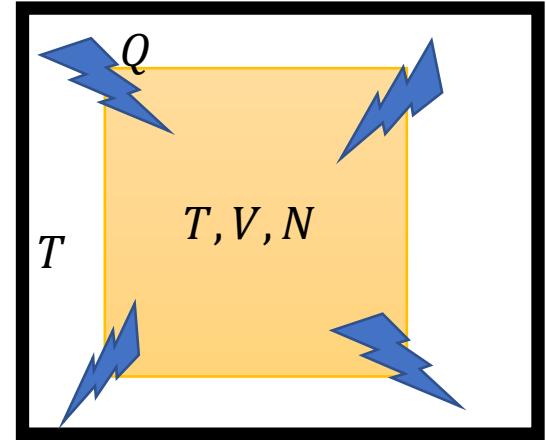
- *N-distinguishable, identical and independent* classical particles

$$Z_N(T, V) = \sum_{\{s_1, s_2 \dots s_N\}} e^{-\frac{E_N(s_1, \dots, s_N)}{kT}} = (\sum_{s_1} e^{-\beta E_1(s_1)}) (\sum_{s_2} e^{-\beta E_1(s_2)}) \dots (\sum_{s_N} e^{-\beta E_1(s_N)}) = Z_1^N(T, V)$$

- *N-indistinguishable, identical and independent* classical particles

$$Z_N(T, V) = \frac{1}{N!} Z_1^N(T, V)$$

So, if we know  $Z_1(T)$ , we know the partition function of  $N$  independent, identical particles  $Z_N(T)$

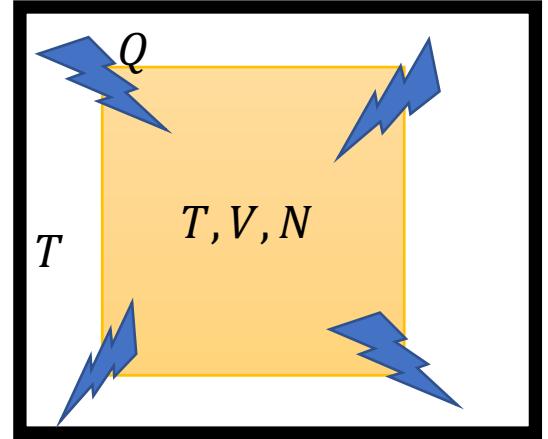


# $\ln Z$ and $F$

$F(T) \downarrow$  towards equilibrium

$\ln Z(T) \uparrow$  towards equilibrium

$$F(T) = -kT \ln Z(T)$$



Let's check that

# $\ln Z$ and $F$

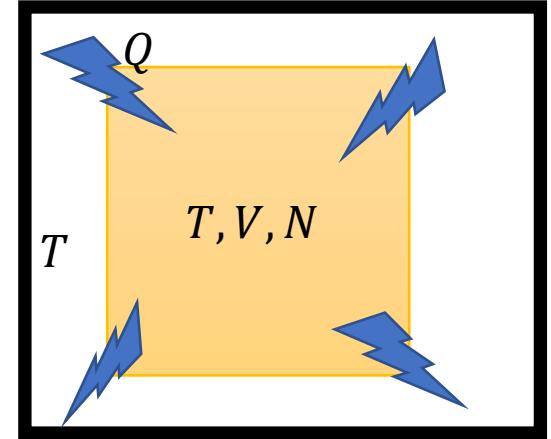
$$F(T) = -kT \ln Z(T)$$

From the Legendre transform:  $F = U - TS \rightarrow S = \frac{U-F}{T}$

From the thermodynamic identity:  $dF = -SdT - PdV + \mu dN \rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$

Thus,

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F - U}{T}$$



- Verify that this equation is also satisfied by the free energy determined by the partition function  $\tilde{F} = -kT \ln Z$

$$\frac{\partial \tilde{F}}{\partial T} = -k \ln Z - kT \frac{\partial \ln Z}{\partial T}$$

$$\frac{\partial \tilde{F}}{\partial T} = -k \ln Z + kT \frac{1}{kT^2} \frac{\partial \ln Z}{\partial \beta} \rightarrow \frac{\partial \tilde{F}}{\partial T} = -\frac{\tilde{F}}{T} - \frac{U}{T} \rightarrow F = \tilde{F} + \text{Const.}$$

- At  $T = 0K$ :  $F(0) = U_0$ ,  $Z_0 = e^{-\beta U_0} \rightarrow \tilde{F}(0) = U_0$ . Thus,  $\text{Const} = 0 \rightarrow F(T) = -kT \ln Z(T)$  ✓

# $\ln Z$ and $F$

- 1-particle

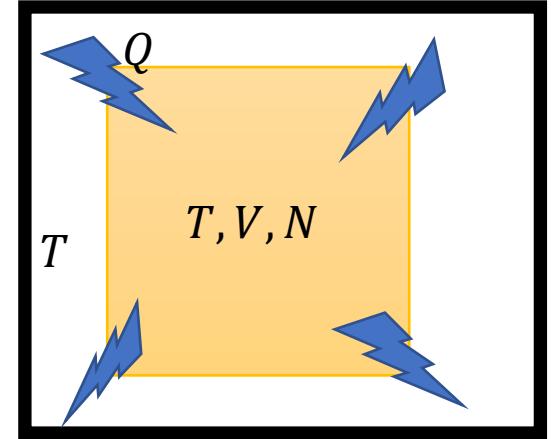
$$F_1(T) = -kT \ln Z_1(T)$$

- *N-distinguishable, identical and independent* classical particles

$$F_N(T) = -kT \ln Z_N(T) = -NkT \ln Z_1(T)$$

- *N-indistinguishable, identical and independent* classical particles

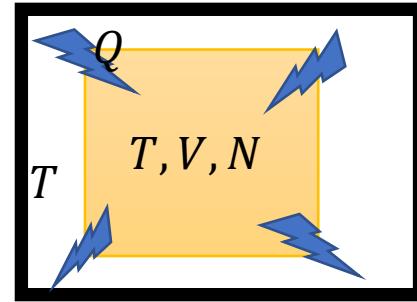
$$F_N(T) = -kT \ln \frac{Z_1^N(T)}{N!} =_{N \gg 1} -NkT \left[ \ln \left( \frac{Z_1}{N} \right) - 1 \right]$$



# Entropy

$P(s)$  is the probability that the system is in a given microstate with energy  $E_s$

«Generalization» of Boltzmann's formula for entropy



$$S = -k \sum_s P(s) \ln P(s)$$

**Isolated system**

$$P(s) = \frac{1}{\Omega} \text{ is constant}$$

$\Omega(U)$  = total # of microstates at  $U$

$$S = -k \sum_s P(s) \ln P(s)$$

$$S = k \sum_s \frac{1}{\Omega} \ln \Omega = k \frac{1}{\Omega} \ln \Omega \sum_s (1)$$

$$S = k \ln \Omega$$

**System in a thermal bath**

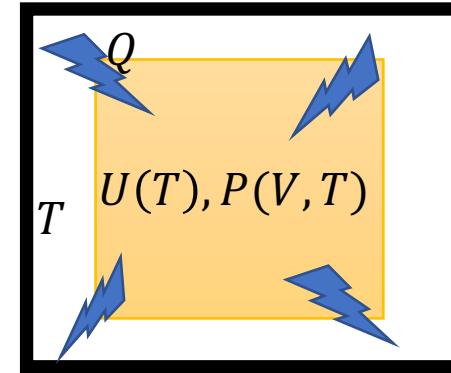
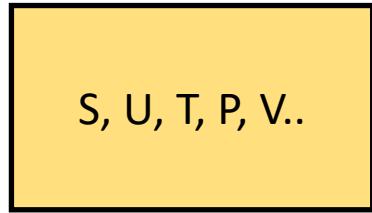
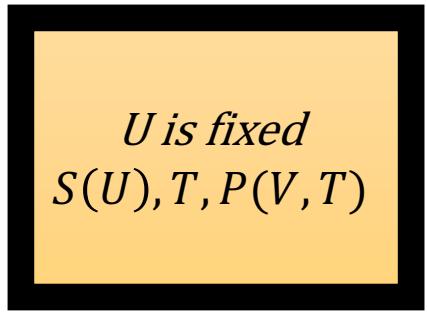
$$P(s) = \frac{1}{Z} e^{-\beta E(s)}, \quad Z = \sum_s e^{-\beta E(s)}$$

$$S = -k \sum_s P(s) \ln P(s)$$

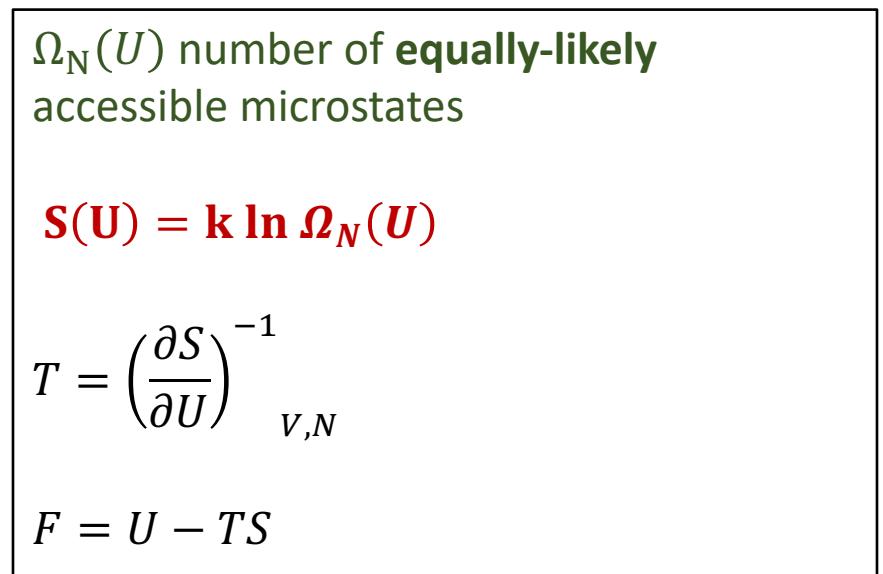
$$S = -k \sum_s P(s) \ln \left( \frac{e^{-\beta E(s)}}{Z} \right) = k\beta \sum_s P(s)E(s) + k \ln Z$$

$$S = \frac{1}{T} \langle E \rangle - \frac{1}{T} F \rightarrow F = \langle E \rangle - TS$$

## Equilibrium thermodynamic state



## Statistical mechanics



$Z(T) = \sum_s e^{-\beta E_s}$  counts the microstates when they don't have the same probability at a given  $T$

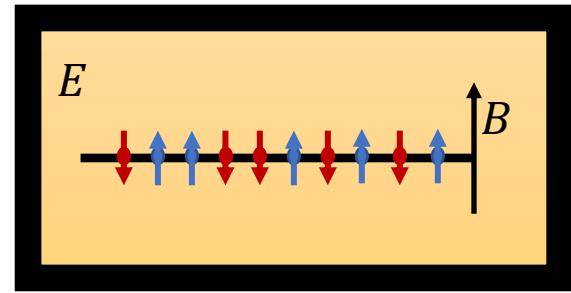
$$\mathbf{F} = -kT \ln Z(T)$$

$$U = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{V,N}$$

$$S = \frac{U - F}{T}$$

## Example: Isolated Paramagnet

(localized spins on a lattice with the dipole magnetic moment  $m_{\uparrow/\downarrow} = \pm \mu$ )



- ***N independent spins with  $N_\uparrow$  out of  $N$  spins and fixed energy set by the applied magnetic field***

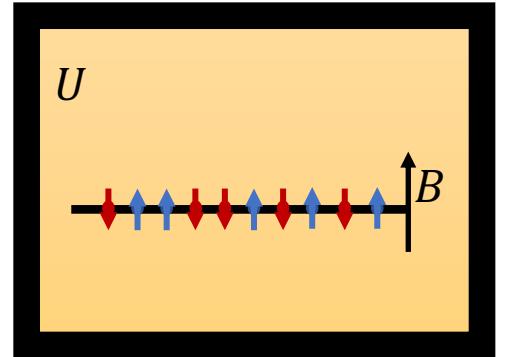
$$U = -\mu B(N_\uparrow - N_\downarrow) = -\mu B(2N_\uparrow - N)$$

➤ The multiplicity function of the macrostate at energy  $U$ :  $\Omega(U, N) = \Omega(N_\uparrow, N) = \frac{N!}{N_\uparrow!(N-N_\uparrow)!}$

➤ Entropy  $S = k_B \ln \Omega(N_\uparrow) \approx k_B [N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)]$

# Temperature $T$ and Entropy $S(U, V, N)$

**Temperature  $T$**  measures system's ability to give or received energy in order to maximize its entropy (occupy the largest macrostate)



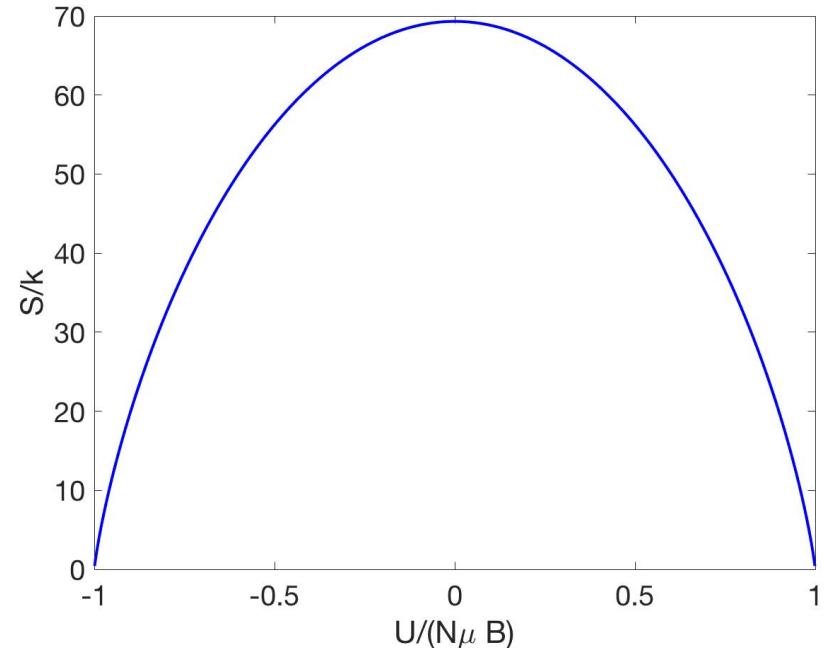
$$T = \left( \frac{\partial S}{\partial U} \right)_{N,V}^{-1}$$

*Paramagnet*

$$S = k_B [N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)]$$

$$\frac{1}{T} = \frac{\partial S}{\partial N_\uparrow} \frac{\partial N_\uparrow}{\partial U} = k(-\ln N_\uparrow - 1 + \ln(N - N_\uparrow) + 1) \frac{1}{-2\mu B}$$

$$T = \frac{2\mu B}{k} \left[ \ln \frac{N_\uparrow}{N - N_\uparrow} \right]^{-1} \rightarrow \frac{1}{T} = \frac{k}{2\mu B} \ln \frac{\frac{N}{2} - \frac{U}{2\mu B}}{\frac{N}{2} + \frac{U}{2\mu B}}$$

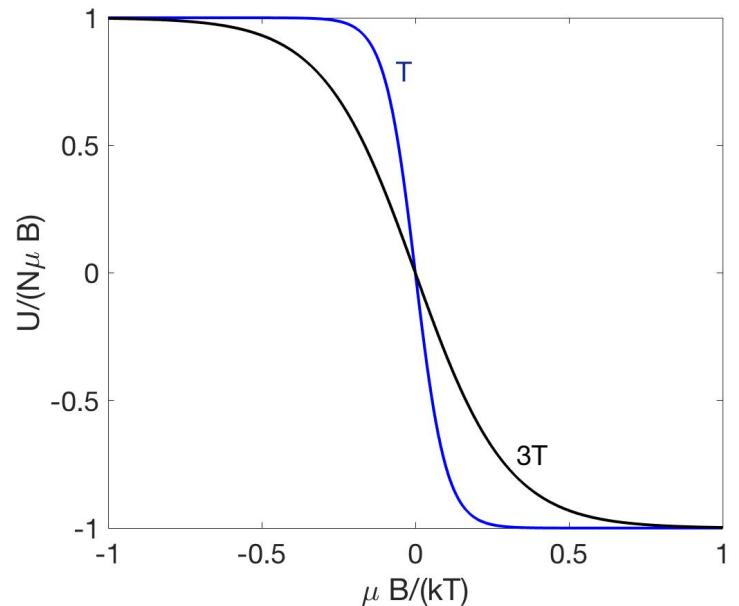
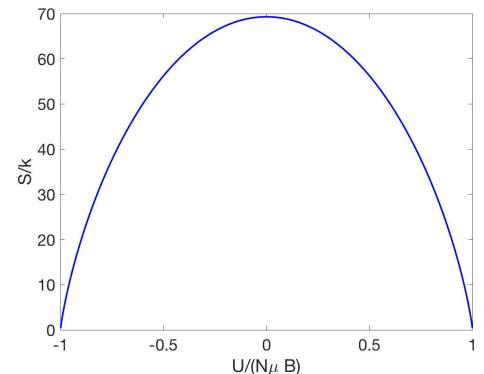
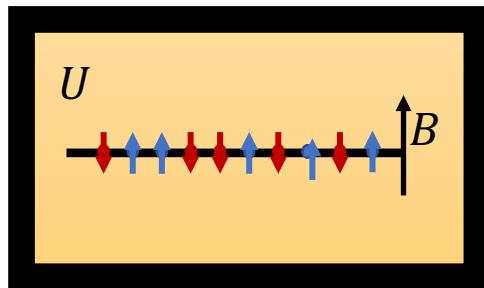


# Temperature $T$ and Energy $U$

$$\frac{1}{T} = \frac{k}{2\mu B} \ln \frac{\frac{N}{2} - \frac{U}{2\mu B}}{\frac{N}{2} + \frac{U}{2\mu B}}$$

$$\frac{\frac{N}{2} - \frac{U}{2\mu B}}{\frac{N}{2} + \frac{U}{2\mu B}} = \exp\left(\frac{2\mu B}{kT}\right) \rightarrow \frac{N}{2} - \frac{U}{2\mu B} = \left(\frac{N}{2} + \frac{U}{2\mu B}\right) \exp\left(\frac{2\mu B}{kT}\right)$$

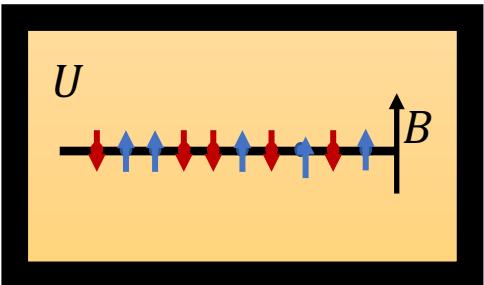
$$U = N\mu B \frac{1 - \exp\left(\frac{2\mu B}{kT}\right)}{1 + \exp\left(\frac{2\mu B}{kT}\right)} \rightarrow U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$



# Helmholtz free energy $F(T, N)$

- From  $U = -\mu B(2N_\uparrow - N) \rightarrow N_\uparrow = \frac{1}{2}(N - x)$ , with  $x = \frac{U}{\mu B}$ . Eliminate  $N_\uparrow$  from  $S(N_\uparrow, N)$  and find  $S(x, N)$

$$\begin{aligned} S(x) &= k \left[ N \ln N - \frac{N-x}{2} \ln \left( \frac{N-x}{2} \right) - \frac{N+x}{2} \ln \left( \frac{N+x}{2} \right) \right] \\ &= k \left[ N \ln N - \frac{N-x}{2} \ln \left( N \left( 1 - \frac{x}{N} \right) \right) - \frac{N+x}{2} \ln \left( N \left( 1 + \frac{x}{N} \right) \right) + \frac{N-x}{2} \ln 2 + \frac{N+x}{2} \ln 2 \right] \\ S(x) &= Nk \left[ \ln 2 - \frac{1-x/N}{2} \ln \left( 1 - \frac{x}{N} \right) - \frac{1+x/N}{2} \ln \left( 1 + \frac{x}{N} \right) \right] \end{aligned}$$



$$1 + \tanh y = \frac{e^y}{\cosh(y)}$$

$$1 - \tanh y = \frac{e^{-y}}{\cosh(y)}$$

- The equilibrium condition implies that energy and temperature are related by  $U = -N\mu B \tanh(\beta\mu B) \rightarrow \frac{x}{N} = -\tanh(\beta\mu B)$ . Find  $S(T)$ .

$$S(T) = Nk \left[ \ln 2 - \frac{1 - \tanh(y)}{2} \ln(1 - \tanh(y)) - \frac{1 + \tanh(y)}{2} \ln(1 + \tanh(y)) \right], \quad y = \beta\mu B$$

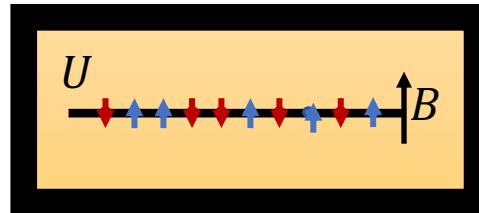
$$S(T) = Nk \left[ \ln 2 - \frac{e^y}{2 \cosh(y)} \ln \left( \frac{e^y}{\cosh(y)} \right) - \frac{e^{-y}}{2 \cosh(y)} \ln \left( \frac{e^{-y}}{\cosh(y)} \right) \right] = Nk \left[ \ln 2 - \frac{e^y}{2 \cosh(y)} y + \frac{e^{-y}}{2 \cosh(y)} y + \frac{e^y + e^{-y}}{2 \cosh(y)} \ln(\cosh(y)) \right]$$

$$S(T) = Nk[-y \tanh(y) + \ln(2 \cosh(y))] = \frac{1}{T} [-N\mu B \tanh(\beta\mu B) + NkT \ln(2 \cosh(\beta\mu B))] = \frac{U - F}{T}$$

- Helmholtz free energy:**

$$F(T, N) = -NkT \ln [2 \cosh(\beta\mu B)]$$

# Isolated Paramagnet



- Energy:

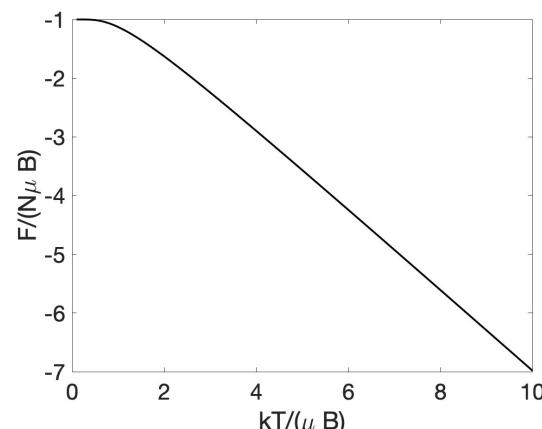
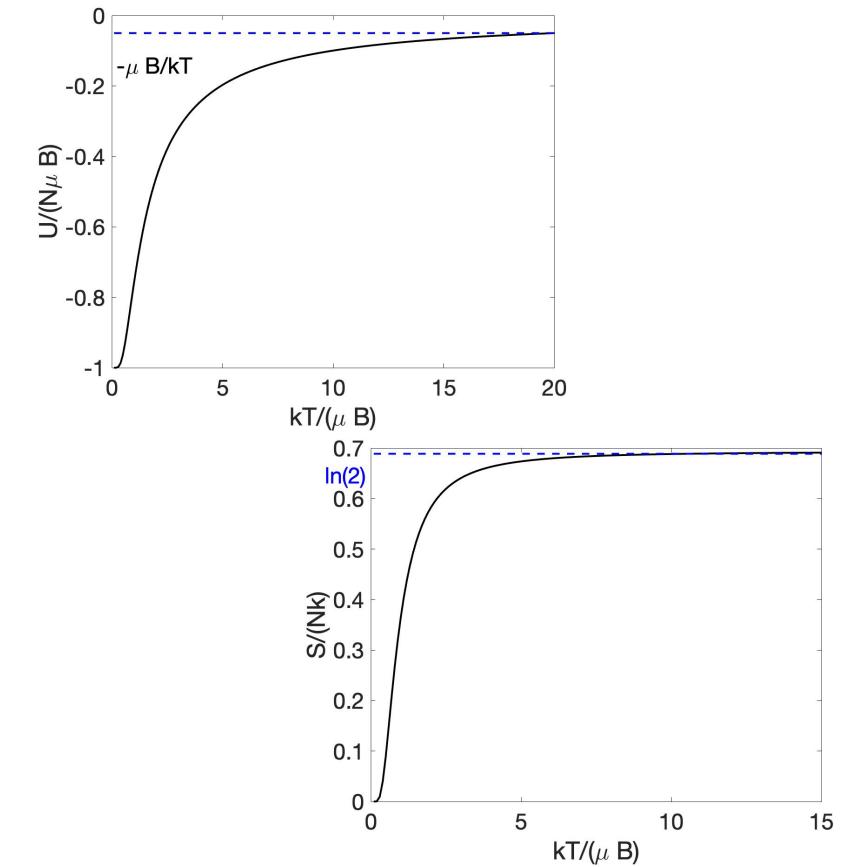
$$U = -\mu B(2N_{\uparrow} - N) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

- Entropy:

$$S = Nk[-\beta\mu B \tanh(\beta\mu B) + \ln(2 \cosh(\beta\mu B))]$$

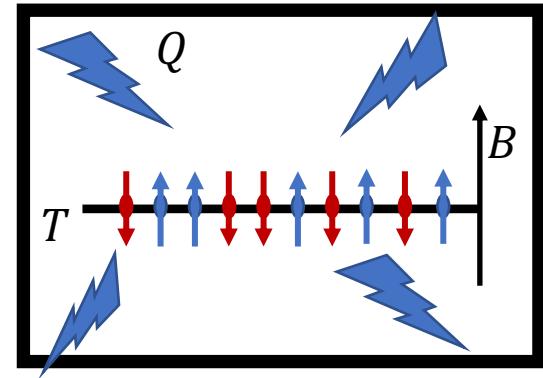
- Helmholtz free energy:

$$F = U - TS = -NkT \ln[2 \cosh(\beta\mu B)]$$



# Example: Paramagnet in a thermal bath

- 1 spin at temperature  $T$  can be in two microstates  $\epsilon_{\uparrow} = -\mu B$  or  $\epsilon_{\downarrow} = \mu B$



$$Z_1(T) = e^{-\frac{\epsilon_{\uparrow}}{kT}} + e^{-\frac{\epsilon_{\downarrow}}{kT}}$$

$$Z_1(T) = e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}} = 2 \cosh\left(\frac{\mu B}{kT}\right) = 2 \cosh(\mu B \beta), \beta = \frac{1}{kT}$$

- Average energy of 1 spin

$$\langle \epsilon \rangle = \frac{1}{Z_1} (\epsilon_{\uparrow} e^{-\beta \epsilon_{\uparrow}} + \epsilon_{\downarrow} e^{-\beta \epsilon_{\downarrow}}) = -\frac{1}{Z_1} \frac{\partial Z_1}{\partial \beta} = -\mu B \tanh(\mu B \beta)$$

# Example: Paramagnet in a thermal bath

- *N spins at temperature T*

$$Z_N(T) = Z_1^N(T) = 2^N \cosh^N \left( \frac{\mu B}{kT} \right)$$

- Average energy of N spins

$$U \equiv \langle E_N \rangle = \frac{1}{Z_N} (N_{\uparrow} \epsilon_{\uparrow} e^{-\beta N_{\uparrow} \epsilon_{\uparrow}} + N_{\downarrow} \epsilon_{\downarrow} e^{-\beta N_{\downarrow} \epsilon_{\downarrow}})$$

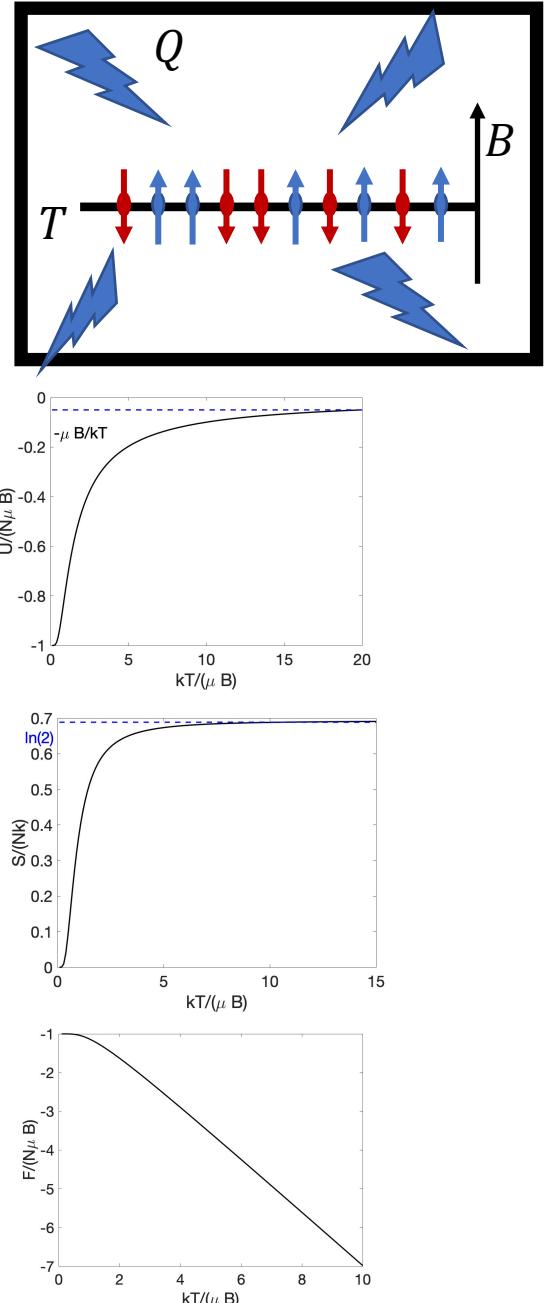
$$U = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\mu B N \tanh(\mu B \beta) = N \langle \epsilon \rangle$$

- Helmholtz free energy

$$F = -NkT \ln[2^N \cosh^N(\beta \mu B)]$$

- Entropy

$$S = \frac{U - F}{T} = -N\beta\mu B \tanh(\mu B \beta) + Nk \ln[2^N \cosh^N(\beta \mu B)]$$



## Example: harmonic oscillator in a thermal bath

- N identical, non-interacting harmonic oscillators. Each harmonic oscillator has the available energies:  $0, \epsilon, 2\epsilon, 3\epsilon, \dots$ , where  $\epsilon = \hbar\omega$
- One-particle partition function

$$Z_1 = \sum_s e^{-\beta\epsilon_s} = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} \dots = \frac{1}{1 - e^{-\beta\epsilon}}$$

- Average energy of one harmonic oscillator at energy  $T$

$$\langle \epsilon \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\partial \ln(1 - e^{-\beta\epsilon})}{\partial \beta} = \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}}$$

- Average energy of N harmonic oscillators at energy  $T$

$$U = \langle E_N \rangle = \frac{N\epsilon}{e^{\beta\epsilon} - 1}$$

- Helmholtz free energy

$$F = -kT \ln Z_1^N = NkT \ln(1 - e^{-\beta\epsilon})$$

- Entropy

$$S = \frac{U - F}{T} = Nk \left[ \frac{\beta\epsilon}{e^{\beta\epsilon} - 1} - \ln(1 - e^{-\beta\epsilon}) \right]$$

## Example: harmonic oscillator in a thermal bath

- Average energy of  $N$  harmonic oscillators at energy  $T$

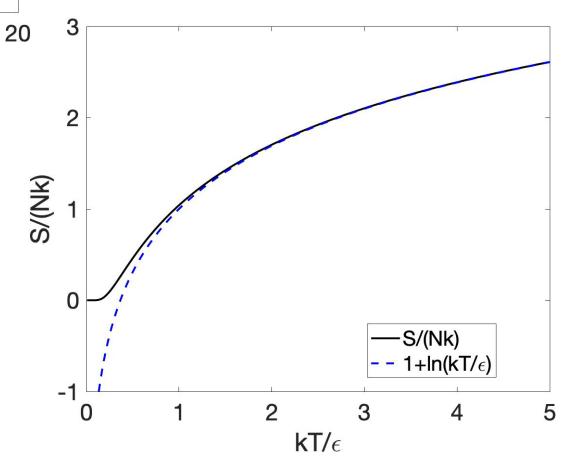
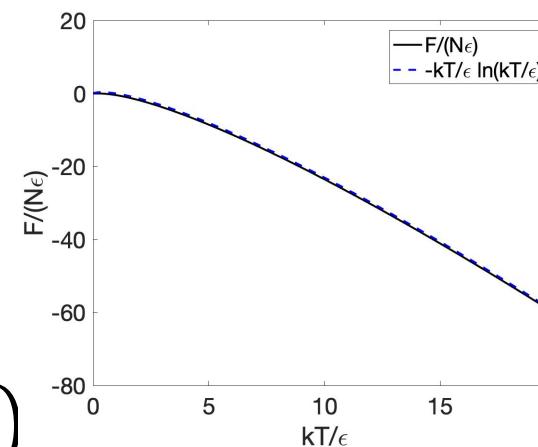
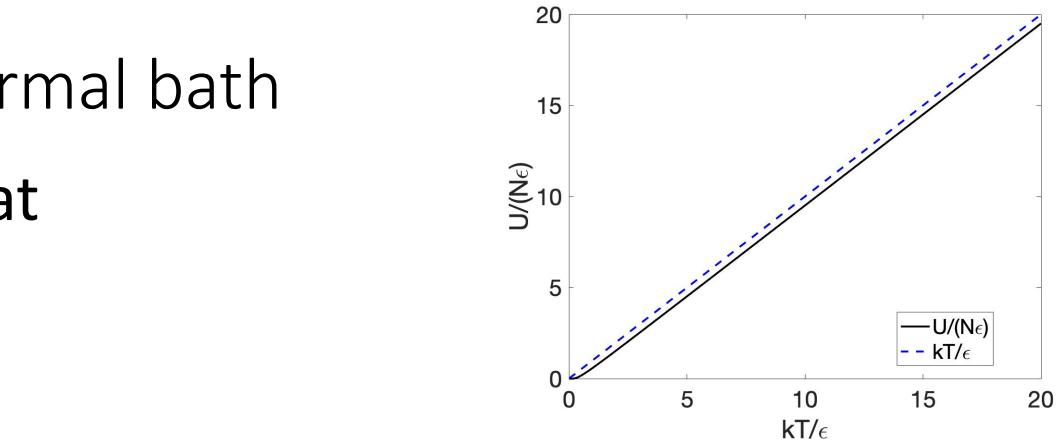
$$U = \langle E_N \rangle = \frac{N\epsilon}{e^{\beta\epsilon} - 1} \xrightarrow{T \rightarrow \infty} NkT$$

- Helmholtz free energy

$$F = -kT \ln Z_1^N = NkT \ln(1 - e^{-\beta\epsilon})$$

- Entropy

$$S = Nk \left[ \frac{\beta\epsilon}{e^{\beta\epsilon} - 1} - \ln(1 - e^{-\beta\epsilon}) \right]$$



# Example: isolated harmonic oscillator

- N identical, non-interacting harmonic oscillators and  $q = \frac{U}{\epsilon}$  energy units

- Multiplicity function of that equilibrium macrostate

$$\Omega(q, N) = \frac{(q + N - 1)!}{q! (N - 1)!} \approx \frac{(q + N)!}{q! N!}$$

- Entropy

$$S = k \ln \Omega = k [(q + N) \ln(q + N) - q \ln q + q - N \ln N + N]$$

$$S(q, N) = k \left[ q \ln \left( 1 + \frac{N}{q} \right) + N \ln \left( 1 + \frac{q}{N} \right) \right]$$

- Temperature of the equilibrium state

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{dq}{dU} \frac{\partial S}{\partial q} = \frac{k}{\epsilon} \left[ \ln \left( 1 + \frac{N}{q} \right) - \frac{q^2}{q+N} \frac{N}{q^2} + \frac{N}{q+N} \right] = \frac{k}{\epsilon} \ln \left( 1 + \frac{N\epsilon}{U} \right)$$

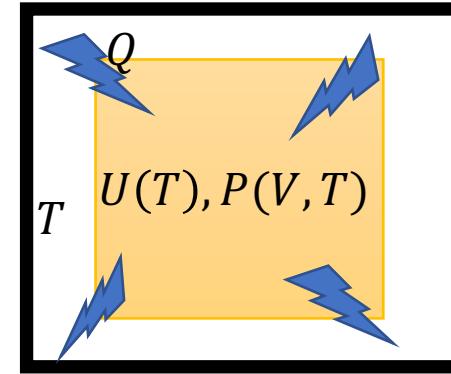
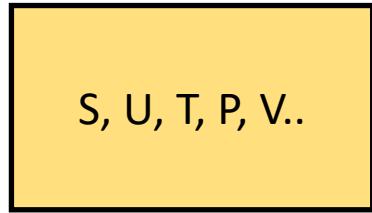
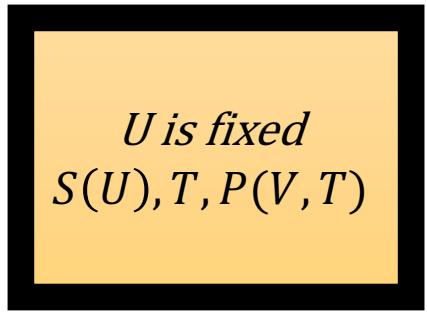
- Energy as a function of temperature

$$U = \frac{N\epsilon}{e^{\beta\epsilon} - 1}$$

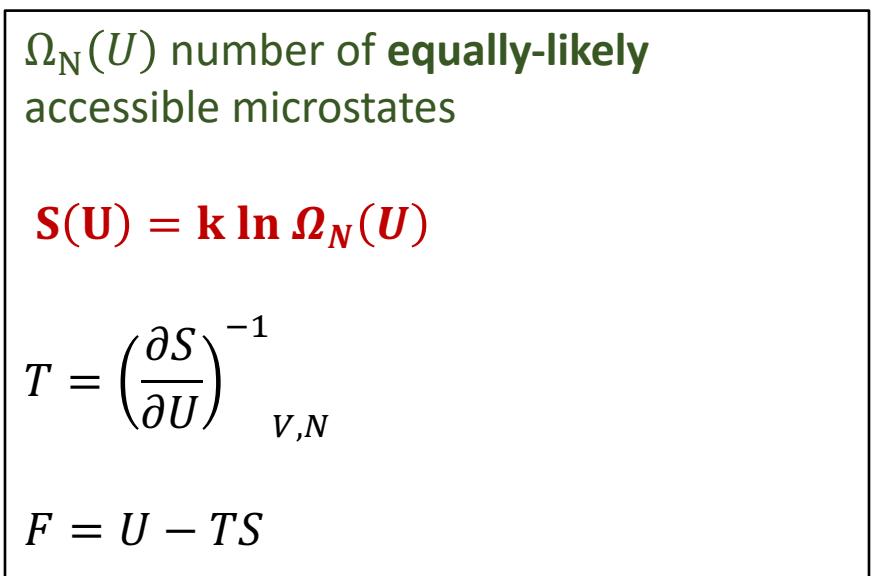
- Helmholtz free energy

$$F = U - TS \dots \text{After more algebra of expressing } S(T) \dots \text{we arrive at the same expression } F = NkT \ln(1 - e^{-\beta\epsilon})$$

## Equilibrium thermodynamic state



## Statistical mechanics



$Z(T) = \sum_s e^{-\beta E_s}$  counts the microstates when they don't have the same probability at a given  $T$

$$F = -kT \ln Z(T)$$

$$U = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{V,N}$$

$$S = \frac{U - F}{T}$$