# Termodinamica statistica

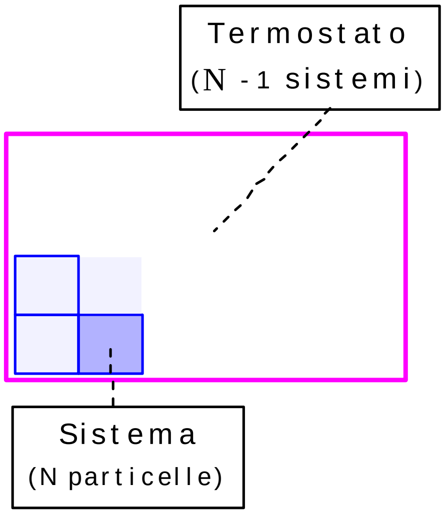
## Energia interna

- **Sistema in equilibrio termico**

Energia ≠ costante

Distribuzione canonica:

$$P_i = \frac{N_i}{N} = \frac{\exp(-E_i / k_B T)}{Z}$$

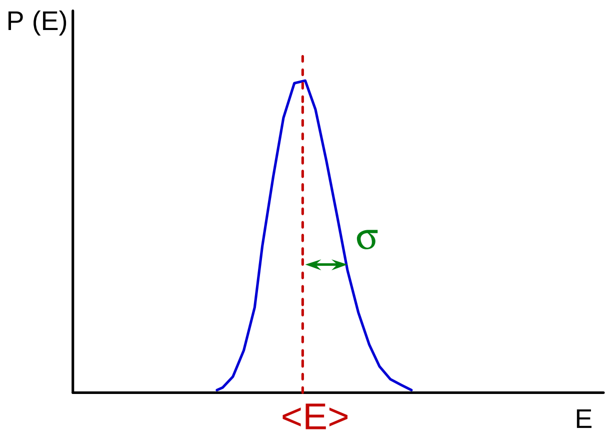



- **Energia media e fluttuazioni**

$$\langle E \rangle = \frac{E_{tot}}{N} = \sum E_i P_i \propto N$$

$$s^2 = \langle E^2 \rangle - \langle E \rangle^2 \propto N$$

$$\frac{s}{\langle E \rangle} \propto \frac{1}{\sqrt{N}}$$



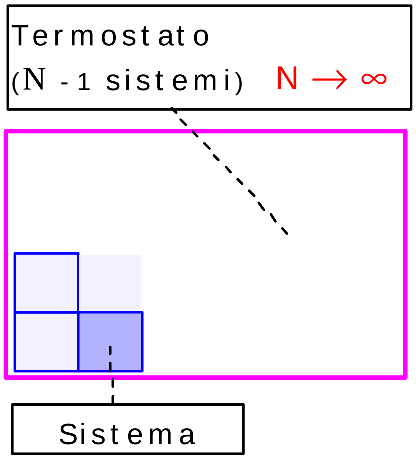

**N ≈ $10^{23}$ ⇒ E ≈ <E> = U**

**Energia interna**

⟹ **Stato di equilibrio termodinamico macroscopico !**

# Entropia

- **Insieme statistico**




Insieme isolato in equilibrio:
$\Omega_{ins}$ microstati equiprobabili

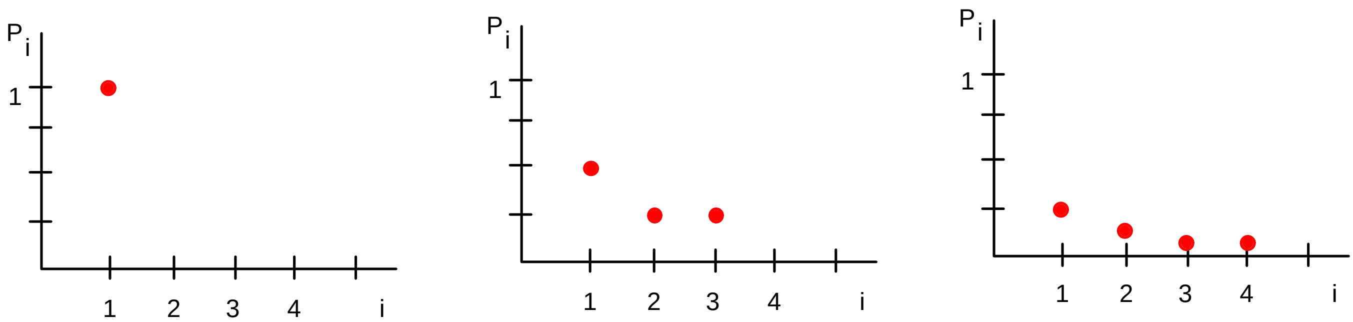
$$S_{ins} = k_B \ln \Omega_{ins}$$

$$\Omega_{ins} = N! \prod \frac{1}{N_i!}$$

- **Entropia del sistema**

Sistema non isolato $\rightarrow$ microstati non equiprobabili

$$\langle S \rangle = \frac{S_{ins}}{N} = \frac{k_B}{N} \ln \Omega_{ins} = -k_B \sum_i P_i \ln P_i$$




**S = 0**    **S = 1.04 $K_B$**    **S = 9 $K_B$**

**Entropia $\leftrightarrow$ dispersione rispetto agli stati**

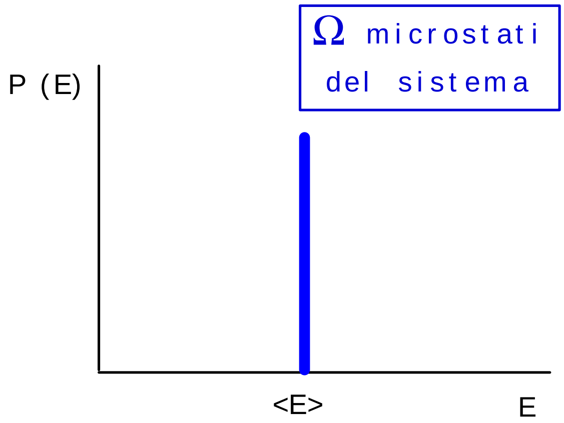
## • Sistema termodinamico

1 sistema = $10^{23}$ particelle

Concentrazione di micro-stati

Nel picco:
**microstati equiprobabili !**

Sistema quasi-isolato in equilibrio




$$P_i = \frac{1}{\Omega}$$

$$S = k_B \ln \Omega$$

## • La prospettiva molecolare

Microstati del sistema:

$\Omega$ =
- $\Omega_{MB}$ particelle distinguibili
- $\Omega_{cl}$ particelle indistinguibili (limite classico)

Entropia del sistema:

$$S = k_B \ln \Omega = \begin{cases} -Nk_B \sum p_i \ln p_i + k_B \ln N! \\ -Nk_B \sum p_i \ln p_i \end{cases}$$

# Calore e lavoro

- **Termodinamica macroscopica**

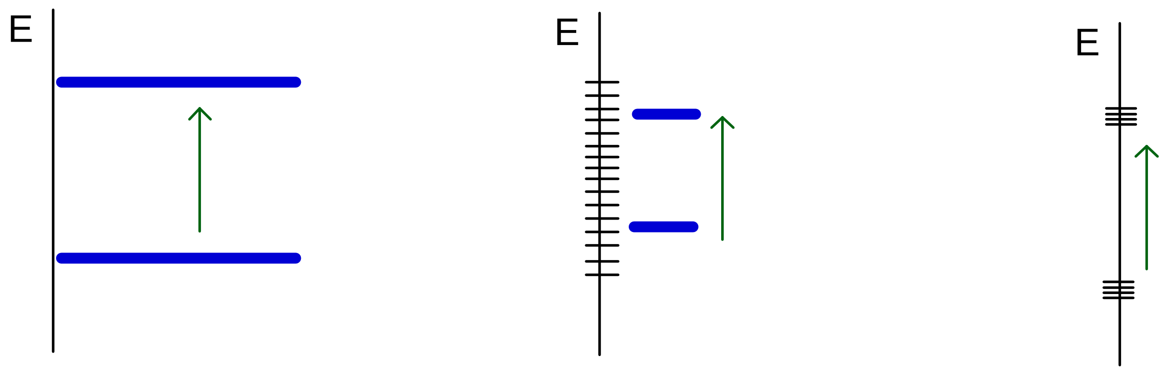
$$dU = dQ + dW$$
$$= TdS - pdV$$

- **Termodinamica statistica**

$$\langle E \rangle = \sum E_i P_i$$

$$d\langle E \rangle = \sum E_i \, dP_i + \sum P_i \, dE_i$$

Variazione di energia interna = **CALORE** (cambiano le probabilità) + **LAVORO** (si spostano i livelli)



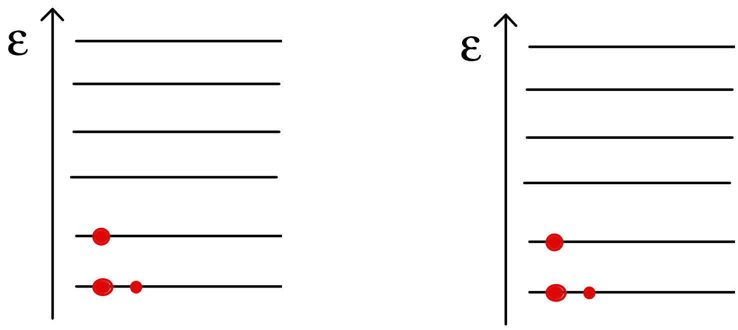
- **La prospettiva molecolare**

Livelli di energia del sistema ↔ livelli molecolari

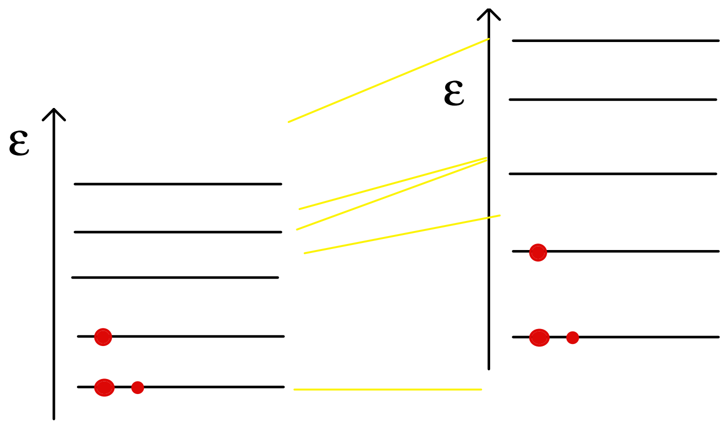
$$\langle E \rangle = \sum n_i e_i$$

$$d\langle E \rangle = \sum e_i dn_i + \sum n_i de_i$$

**CALORE**
(cambiano le popolazioni)




**LAVORO**
(si spostano i livelli)

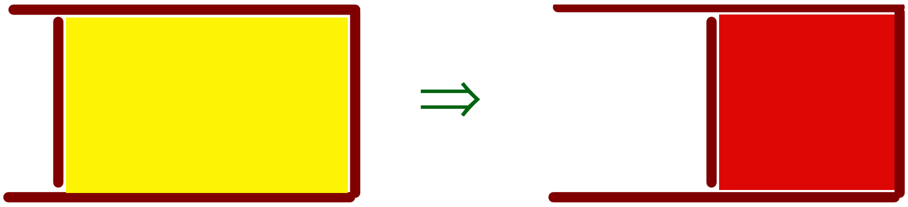


# Entropia e temperatura

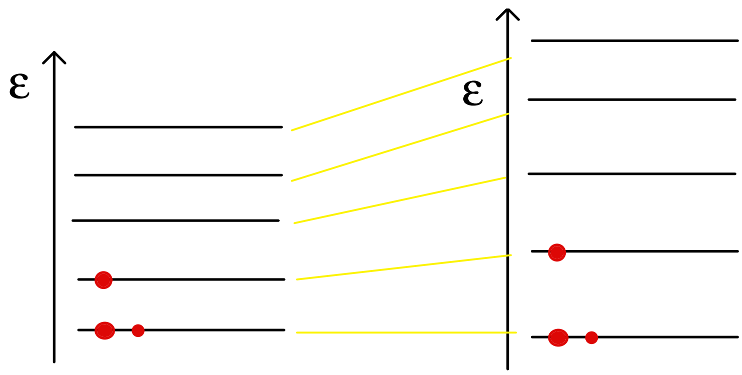
## Un esempio: gas ideale monoatomico

- **Lavoro adiabatico**

$$\Delta U = W \qquad Q = 0$$

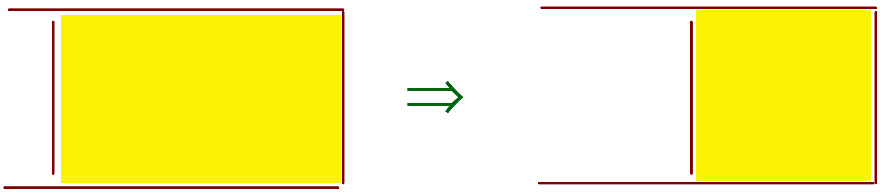


$$\Delta U > 0 \qquad \Delta T > 0 \qquad \Delta S = 0$$

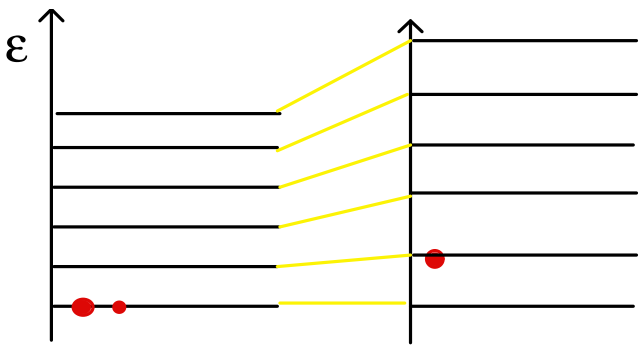



- **Lavoro isotermo**

$$\Delta U = 0 \qquad W = -Q$$

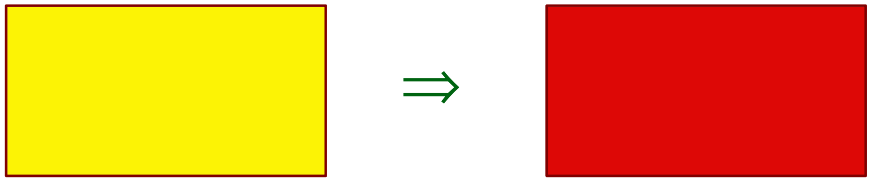


$$\Delta U = 0 \qquad \Delta T = 0 \qquad \Delta S < 0$$

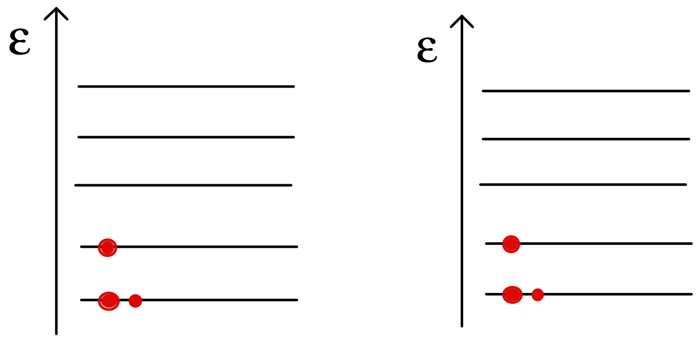


- **Riscaldamento a volume costante**

$$Q = \Delta U$$
$$W = 0$$



$$\Delta U > 0$$
$$\Delta T > 0$$
$$\Delta S > 0$$




**Temperatura:**
**dispersione rispetto ai valori dell'energia**

**Entropia:**
**dispersione rispetto ai livelli di energia**