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## Grand-canonical ensemble

characterized by fixed temperature $T$
and chemical potential $\mu$
via energy & particle exchange with particle reservoir

$$\mu = -T \frac{\partial S}{\partial N}\Big|_E$$

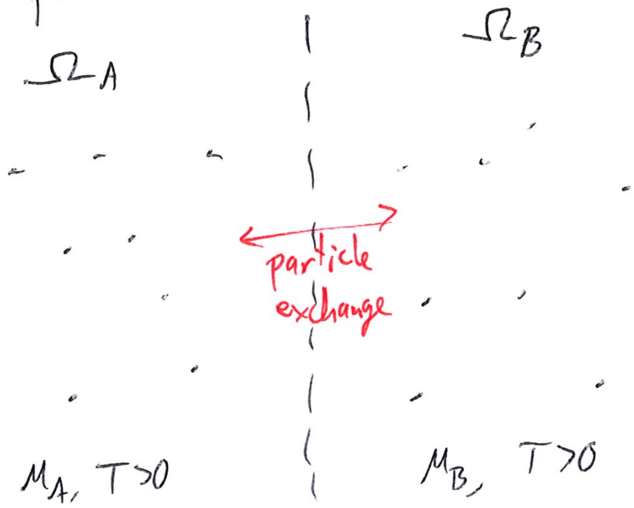
(micro-canonical therm. equil.)

$T$ — dimensions of energy, intensive quantity

For natural systems $(T>0)$
more particles → more entropy (even for fixed $E$)

$$\frac{\partial S}{\partial N} > 0 \rightarrow \mu < 0$$

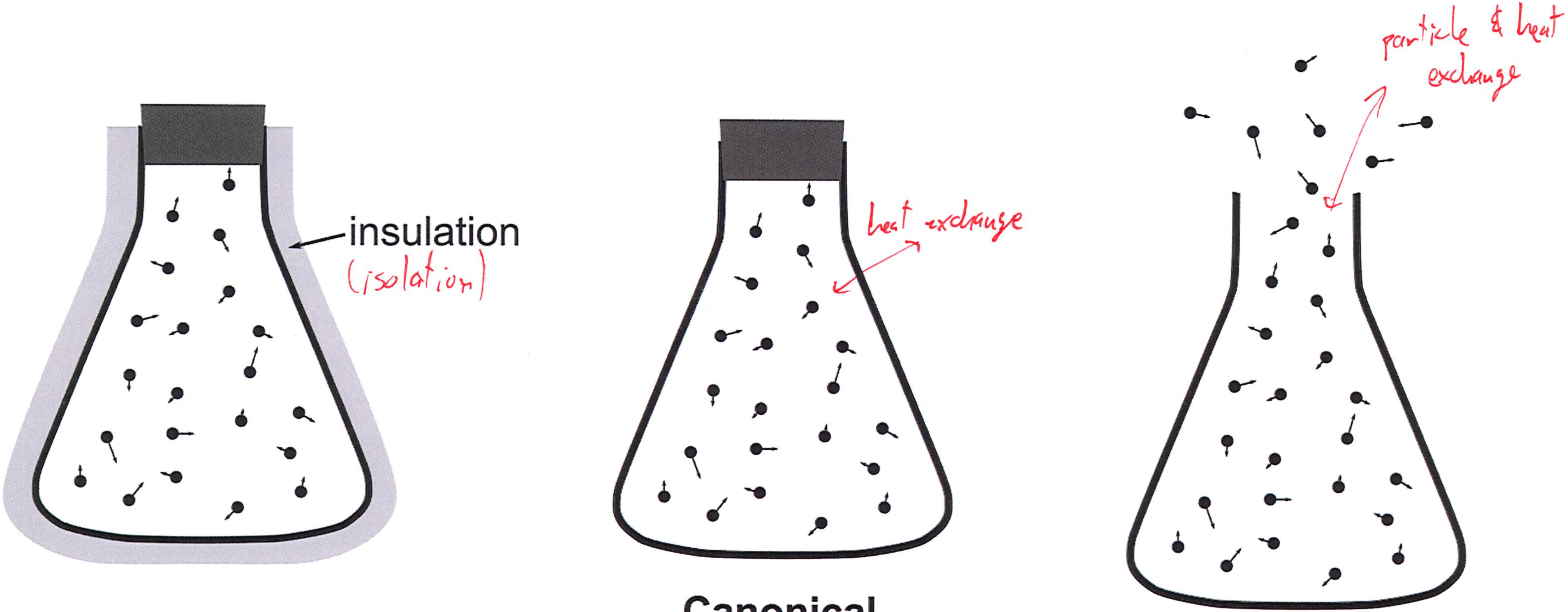
Sign is choice to aid intuition
Consider particle flow




$$\mu_A < \mu_B < 0$$

$$\frac{\partial S_A}{\partial N_A} > \frac{\partial S_B}{\partial N_B} > 0$$

commons.wikimedia.org/wiki/File:Statistical_Ensembles.png




**Microcanonical (const. N E)**

**Canonical (const. N T)**

**Grand Canonical (const. μ T)**

Particle Flow $\Delta N_A = -\Delta N_B$

→ change in entropy

$$\Delta S = \Delta S_A + \Delta S_B = \left(\frac{\partial S_A}{\partial N_A}\right)\Delta N_A + \left(\frac{\partial S_B}{\partial N_B}\right)\Delta N_B \geq 0$$

by second law

$$\Delta N_A \left[\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right] \geq 0 \rightarrow \Delta N_A \geq 0$$

$\geq 0$

Particles flow from larger $\mu$ to smaller $\mu$
(same as heat flow w/ temperature)

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Grand-canonical partition function

(canonical $p_i = \frac{1}{Z} e^{-E_i/kT}$)

As for canonical ensemble
want micro-state probabilities of particle

Repeat replica trick

$$E_{tot} = E + E_{res} = \sum_{r=1}^{R} E_r$$

$$N_{tot} = N + N_{res} = \sum_r N_r$$

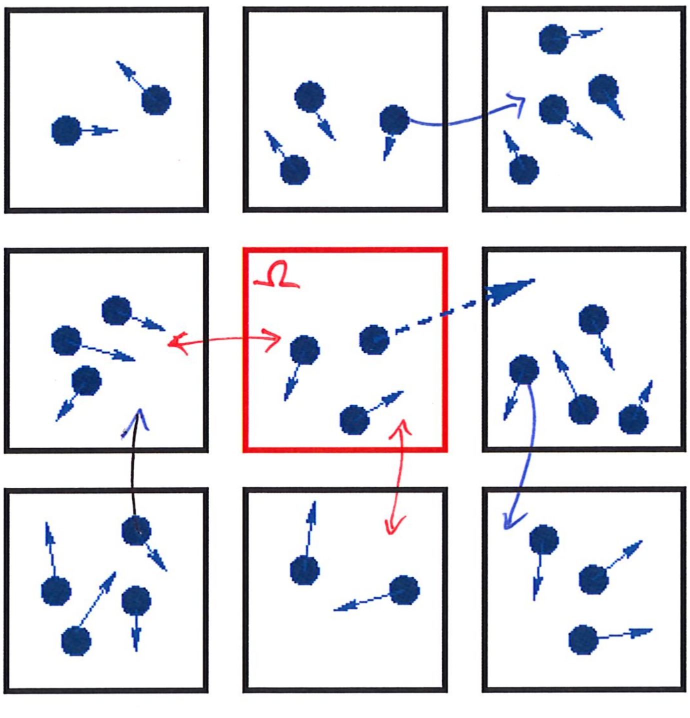
$\Omega$ has $M$ micro-states $w_i = w_1, w_2, \dots w_M$
with energy $E_i$ and $N_i$ particles
(indistinguishable)

Recall occupation numbers $n_i$ and probabilities $p_i = n_i/R$
└ replica in $w_i$

$$\sum_{i=1}^{M} n_i = R \qquad \sum_i p_i = 1$$

$$E_{tot} = \sum_i n_i E_i \qquad N_{tot} = \sum_i n_i N_i$$

$$\Omega_{tot} = \Omega \times \underbrace{\Omega_{res}}_{(R-1)\times\Omega} = R\,\Omega$$



Compute (intensive) $T$ and $\mu$ of micro-canonical $\Omega_{tot}$

Need therm. equilibrium $\rightarrow$ maximize $S_{tot}$ with constraints

Same $$M_{tot} = \frac{R!}{n_1!\, n_2! \cdots n_M!} \rightarrow S_{tot} = -R \sum_{i=1}^{M} p_i \log p_i \qquad n_i \gg 1$$

Third Lagrange multiplier:

$$\bar{S} = -R \sum_i p_i \log p_i + \alpha \left( \sum_i p_i - 1 \right) - \beta \left( R \sum_i p_i E_i - E_{tot} \right) + \gamma \left( R \sum_i p_i N_i - N_{tot} \right)$$

$$\frac{\partial \bar{S}}{\partial p_k} = 0 = -R(\log p_k + 1) + \alpha - \beta R E_k + \gamma R N_k$$

$$\log p_k = -1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k$$

$$p_k = \exp\left[ -\left(1 - \frac{\alpha}{R}\right) - \beta E_k + \gamma N_k \right]$$

$$= \frac{\exp[-\beta E_k + \gamma N_k]}{\exp\left[1 - \frac{\alpha}{R}\right]} = \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k}$$

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Impose constraint

$$1 = \sum_i p_i = \frac{1}{Z_g} \sum_i e^{-\beta E_i + \gamma N_i} \rightarrow Z_g(\beta, \gamma) = \sum_i e^{-\beta E_i + \gamma N_i}$$

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Grand-canonical partition func

$T$ and $\mu$ come from entropy

$$S_{tot} = -R \sum_i p_i \log p_i = -R \sum_i p_i \left( -\log Z_g - \beta E_i + \gamma N_i \right)$$

$$= R \log Z_g + \beta E - \gamma N$$

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$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = R\left(\frac{\partial \beta}{\partial E}\underline{\frac{\partial}{\partial \beta}\log Z_g} + \frac{\partial \gamma}{\partial E}\underline{\frac{\partial}{\partial \gamma}\log Z_g}\right) + E\frac{\partial \beta}{\partial E} + \beta - N\frac{\partial \gamma}{\partial E}$$

$$\frac{1}{Z_g}\frac{\partial}{\partial \beta}\sum_i e^{-\beta E_i + \gamma N_i} = \frac{1}{Z_g}\sum_i (-E_i)\, e^{-\beta E_i + \gamma N_i}$$

$$= -\sum_i p_i E_i = \frac{-E}{R}$$

$$\frac{1}{Z_g}\frac{\partial}{\partial \gamma}\sum_i e^{-\beta E_i + \gamma N_i} = \frac{N}{R}$$

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$$\frac{1}{T} = -E\frac{\partial \beta}{\partial E} + N\frac{\partial \gamma}{\partial E} + E\frac{\partial \beta}{\partial E} + \beta - N\frac{\partial \gamma}{\partial E}$$

$$\beta = 1/T$$

$$-\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_E = R\left(\frac{\partial \beta}{\partial N}\frac{\partial}{\partial \beta}\log Z_g + \frac{\partial \gamma}{\partial N}\frac{\partial}{\partial \gamma}\log Z_g\right) + E\frac{\partial \beta}{\partial N} - N\frac{\partial \gamma}{\partial N} - \gamma$$

($\frac{\partial}{\partial \beta}\log Z_g \to -E/R$, $\frac{\partial}{\partial \gamma}\log Z_g \to N/R$)

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$$\gamma = \mu/T$$

Putting everything together,

we have derived the micro-state probabilities

$$p_i = \frac{1}{Z_g} e^{-E_i/T + \mu N_i/T} = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)} \qquad \beta = 1/T$$

$$Z_g = \sum_i e^{-\beta(E_i - \mu N_i)}$$

Both $E_i$ and $N_i$ fluctuate

Reservoir unknowable except for fixing $T$ and $\mu$