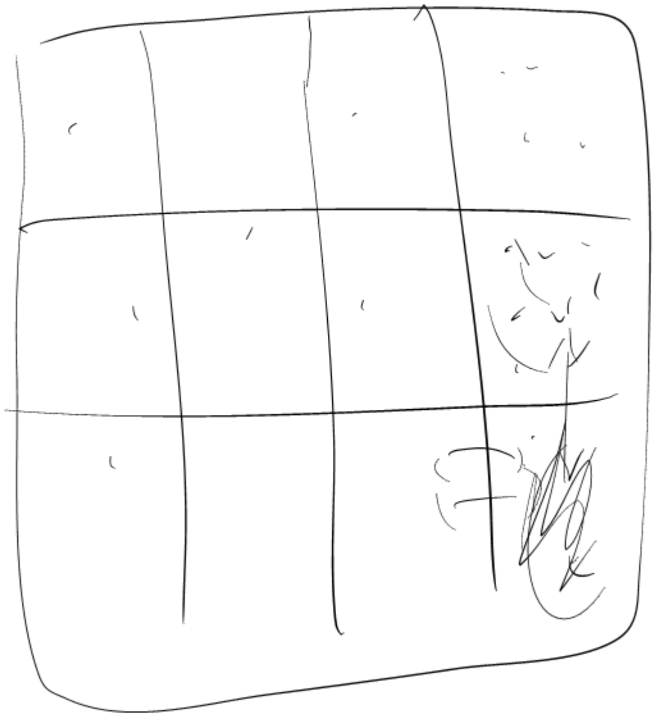
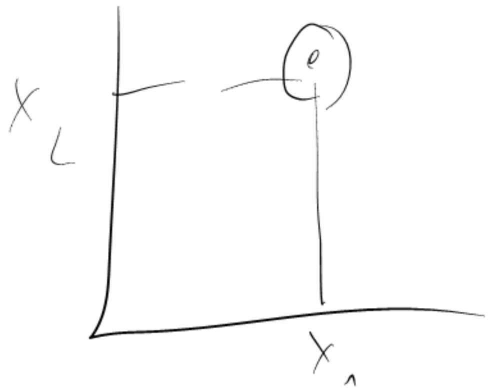




N part. in 3d space

$\swarrow$ dimension : 6N

# of quantum states in $d\Gamma = \dfrac{d\Gamma}{(2\pi\hbar)^{3N}}$

BUT particles indistinguishable $\Rightarrow$

Exchange of any two particles does not give us a new physical situation

identify all states with each other that can mapped onto each other via particle exchange!

# of permutations (of possible exchanges)

of an N-particle system is N!

$$\underbrace{\Omega(E)}_{} = \frac{1}{N!} \int \frac{d\Gamma}{(2\pi\hbar)^{3N}} \, \delta\big(H(\Gamma) - E\big) \, \Delta E$$

# of states corresponding to energy interval $[E, E + \Delta E]$

corrects for overcounting!

needed for dimension reasons, qm $\longrightarrow$ inaccuracy in measuring the energy

$\Delta p \, \Delta x \sim \hbar$, $\Delta E \Delta t \sim \hbar$

System, degrees of freedom

Hamiltonian

phase space

Structure of phase space, energy shells

$\Omega(E)$

already HERE MUCH info available!

$$\rho = \frac{1}{\Omega(E)} \Delta E \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \delta\left(H(\Gamma) - E \right) = \rho(\Gamma)$$

$$\langle A \rangle = \int d\Gamma \, \rho A$$

The Microcanonical Ensemble

Example: ((Classical) Ideal Gas

N particles in 3 dimensions, volume V, mass m

$$H = \frac{1}{2m} \sum_i \vec{p}_i^{\,2}$$

$$\Omega(E) = \frac{\Delta E}{(2\pi\hbar)^{3N} N!} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \dots \int d^3\vec{r}_N \int d^3\vec{p}_1 \int d^3\vec{p}_2 \dots \int d^3\vec{p}_N$$

$$\delta\left(\frac{1}{2m}\sum_i \vec{p}_i^{\,2} - E\right) =$$

$$= \frac{\Delta E \, V^N \, 2m}{(2\pi\hbar)^{3N} N!} \int d^3\vec{p}_1 \dots \int d^3\vec{p}_N \, \delta\left(\sum_i \vec{p}_i^{\,2} - 2mE\right)$$

$\sum_i \vec{p}_i^{\,2} = 2mE$ $\rightarrow$ SPHERE (surface) in momentum space (dim $= 3N$)

Radius: $\sqrt{2mE}$

$$\int d^2\vec{r} \,(\text{spherically symm. Integrand}) = 2\pi \int_0^\infty dr\, r\,(\dots)$$

$$\int d^3\vec{r} \,(\quad " \quad) = 4\pi \int dr\, r^2\,(\dots)$$

$$\int d^\nu\vec{r} \,(\quad " \quad) = \Sigma_\nu \int dr\, r^{\nu-1}\,(\dots)$$

surface of a ν-dim. unit sphere

math: $\Sigma_\nu = \frac{2\pi^{\nu/2}}{\left(\frac{\nu}{2}-1\right)!}$ for even ν

(assume N even for simplic.)

$$\Omega(E) = \frac{\Delta E\, V^N 2m}{(2\pi\hbar)^{3N} N!} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \underbrace{\int_0^\infty dp\, p^{3N-1} \delta(p^2-2mE)}_{=?}$$

$x = p^2 \qquad dx = 2p\,dp \qquad p\,dp = \frac{1}{2}dx$

$$p^{3N-1}dp = p^{3N-2}\,p\,dp = \frac{1}{2}p^{3N-2}dx =$$

$$= \frac{1}{2} x^{3N/2-1} dx$$

$$\int_0^\infty dp\, p^{3N-1}\, \delta(p^2 - 2mE)$$

$$= \frac{1}{2} \int_0^\infty dx\, x^{3N/2 - 1}\, \delta(x - 2mE) =$$

$$= \frac{1}{2} (2mE)^{3N/2 - 1}$$

$$\Omega(E) = \frac{\Delta E\, V^N 2m}{(2\pi\hbar)^{3N} N!} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \frac{1}{2} (2mE)^{3N/2 - 1} =$$

$$= \frac{\Delta E}{E} \frac{V^N}{(2\pi\hbar)^{3N} N!} \frac{\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (2mE)^{3N/2}$$

ignore for $N \gg 1$

Stirling: $\ln N! \simeq \boxed{N \ln N - N} = \ln N^N - \ln e^N$

N large

$= \ln \left(\frac{N}{e}\right)^N$

$\ln N! = \ln(1 \cdot 2 \cdot 3 \cdot \ldots \cdot N) =$

$\equiv \ln 1 + \ln 2 + \ln 3 + \ldots + \ln N \equiv$

$\simeq \int_0^N dx \ln x$

$$\boxed{N! \simeq \left(\frac{N}{e}\right)^N}$$

$$\Omega(E) = \frac{\Delta E}{E} (2\pi\hbar)^{-3N} \left(\frac{Ve}{N}\right)^N \left(\frac{\pi e}{\frac{3N}{2}} \, 2mE\right)^{3N/2}$$

$$= \frac{\Delta E}{E} (2\pi\hbar)^{-3N} \left(\frac{Ve}{N}\right)^N \left(\frac{4\pi}{3} e \frac{mE}{N}\right)^{3N/2}$$

"microcanonical partition function"

ENTROPY

Define: $$S(E) = \ln \Omega(E)$$

(units: $k_B = 1$)

makes sense, why?

(i) numbers are much smaller

(ii) $S(E)$ is EXTENSIVE (volume-additive)

A_1

V_1

A_2

V_2

A

extensive

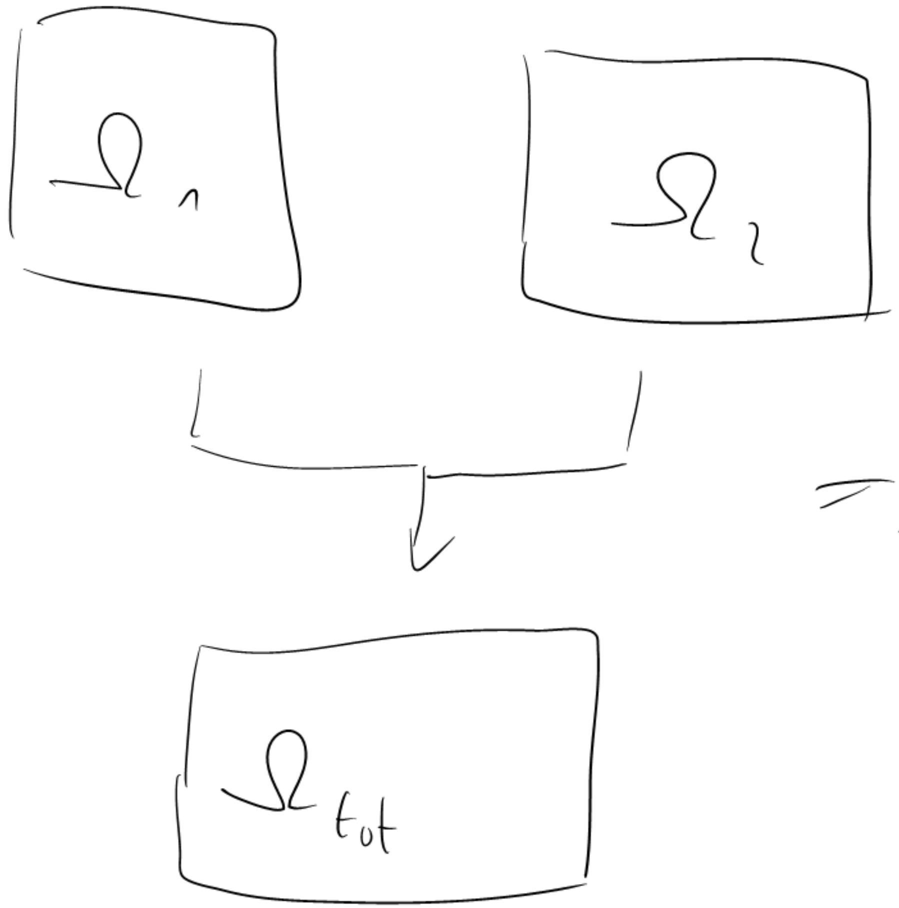
$$\boxed{A = A_1 + A_2}$$

$$V_{tot} = V_1 + V_2$$

extensive:

proportional to volume or to the particle number

$\Omega_{tot} = \Omega_1 \cdot \Omega_2$ (except for interface corrections)



$$\Rightarrow S_{tot} = \ln \Omega_1 + \ln \Omega_2$$
$$= S_1 + S_2$$

For the ideal gas:

$$S(E) = \ln \frac{\Delta E}{E} - 3N \ln(2\pi\hbar) + N \ln\left(\frac{Ve}{N}\right) + \frac{3N}{2} \ln\left(\frac{4\pi}{3} e \frac{mE}{N}\right)$$

thermodynamic limit $N \to \infty$

$$\frac{N}{V} = \text{const.} \ (\text{density}), \quad \frac{E}{N} = \text{const.}$$

(energy per particle)

$$\frac{S}{N} = \frac{1}{N} \ln \frac{\Delta E}{E} - 3\ln(2\pi\hbar) + \ln\left(\frac{Ve}{N}\right)$$
$$+ \frac{3}{2} \ln\left(\frac{4\pi}{3} e \frac{mE}{N}\right)$$

$$\frac{1}{N} \ln \frac{\Delta E}{E} = \underbrace{\frac{1}{N} \ln \Delta E}_{\substack{\to 0 \\ \text{for } N\to\infty}} - \underbrace{\frac{1}{N} \ln E}_{\substack{\to 0 \\ \text{for } N\to\infty}}$$

indeed: S is extensive

$$\boxed{\frac{S}{N} = -3\ln(2\pi\hbar) + \ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi}{3} e m \frac{E}{N}\right)}$$

intensive quantities:

remain constant for varying N or V

examples: RATIOS of extensive quantities, e.g.

$$\frac{V}{N}, \frac{E}{N}, \frac{S}{N}$$

Later: Further intensive quantities that are NOT such ratios (temperature, pressure, chemical potential) $\rightarrow$ "essential" intensive quantities (my private lingo!)

TWO systems in thermal contact

→ "essentially" intensive quantities

Aim: Study $S_{tot} = S_1 + S_2$ in more detail & scaling

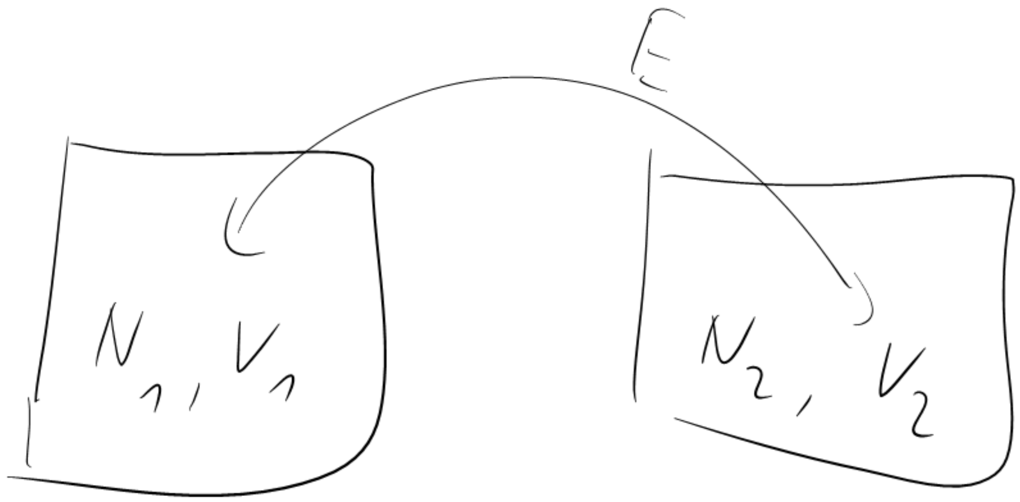
Case 1:

no exchange. Trivial

$$\Omega_{tot} = \Omega_1 \cdot \Omega_2$$

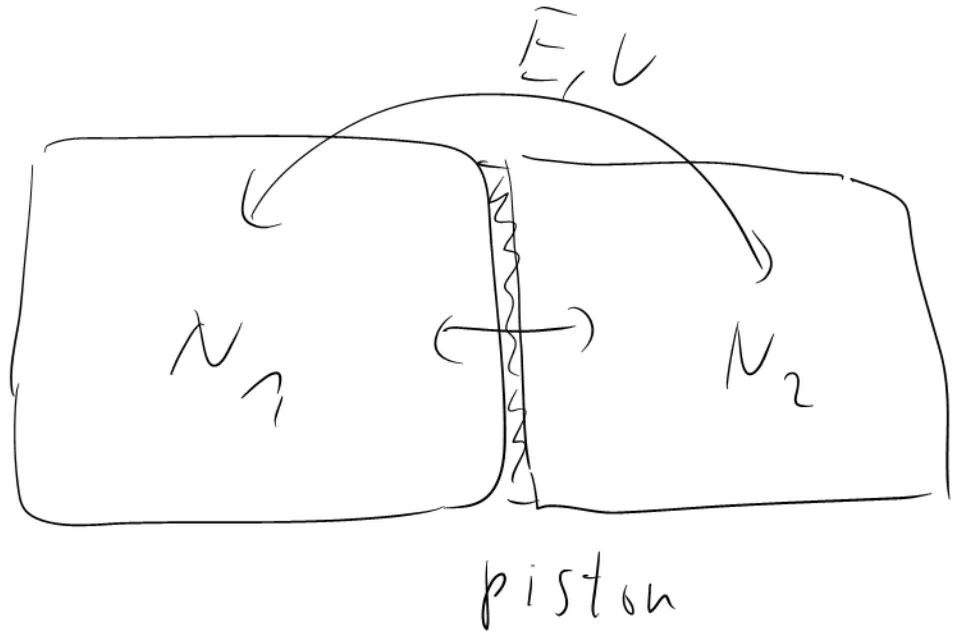
$$S_{tot} = S_1 + S_2 \quad ✓$$

Case 2



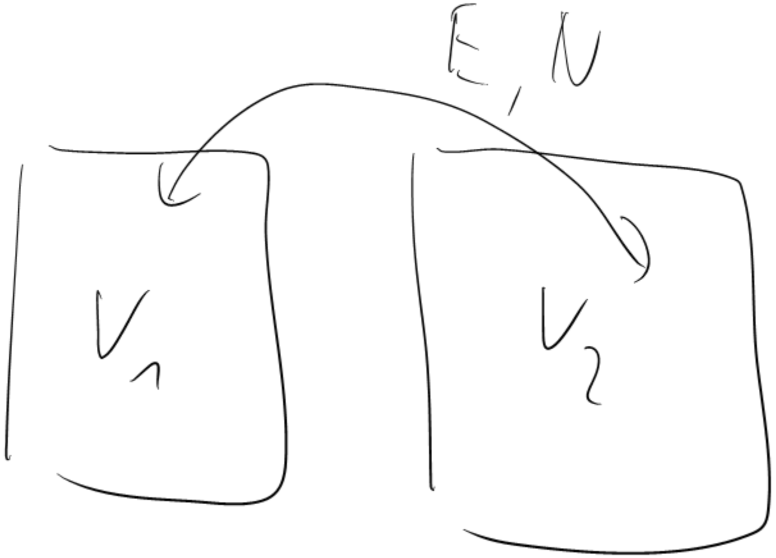
→ concept of temperature

Case 3



→ concept of pressure

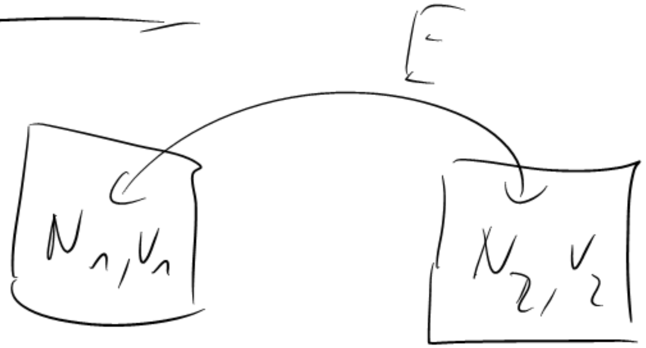
Case 4



particle exchange

→ concept of chemical potential

Temperature



assume: identical particles throughout

Let $\Omega^{\text{naive}} \equiv$ statistical weight without considering particle identity

$$\Omega_1 = \frac{1}{N_1!} \Omega_1^{\text{naive}} \quad , \quad \Omega_2 = \frac{1}{N_2!} \Omega_2^{\text{naive}}$$

$$\Omega_{tot} = \frac{1}{N_1! N_2!} \Omega_{tot}^{\text{naive}}$$

("left" vs. "right" makes particles partly distinguishable) normalization of energy:

$$E(\text{ground state}) = 0$$

$$E_1 + E_2 = E \quad \text{energy conservation}$$

$$\Omega_{tot}^{naive}(E) = \frac{1}{\Delta E} \int_0^E dE_1 \, \Omega_1^{naive}(E_1) \cdot \Omega_2^{naive}(E - E_1)$$

$$\boxed{\Omega_{tot}(E) = \frac{1}{\Delta E} \int_0^E dE_1 \, \Omega_1(E_1) \, \Omega_2(E - E_1)}$$