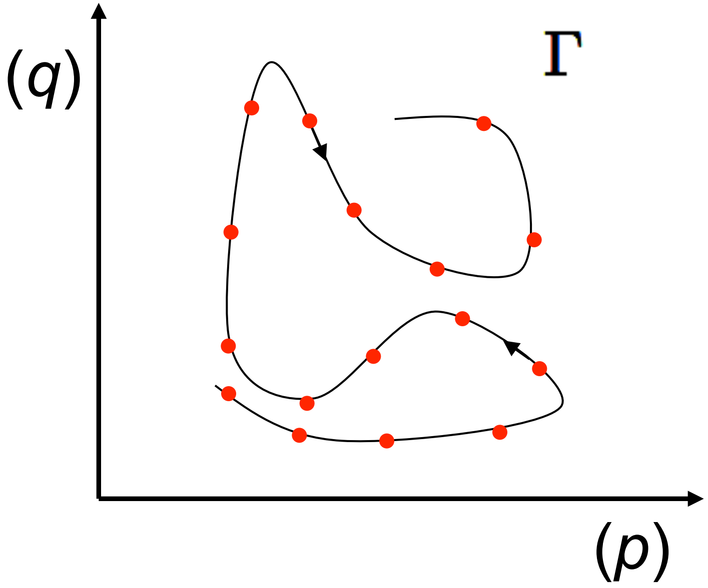
Classical statistical physics - Gibbsian concept

example: gas of *N* particles with Hamiltonian $\mathcal{H}(p,q)$

Γ *6N*-dimensional phase space $(p,q) = (p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})$

equation of motion: $\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$ and $\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$

time evolution



evolution of density in Γ

Poisson bracket

$$\rho(p,q) \longrightarrow \frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$$

equilibrium: $\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\} = 0$

$\rho(p,q)$ function of conserved quantities e.g. energy

Classical statistical physics - Gibbsian concept

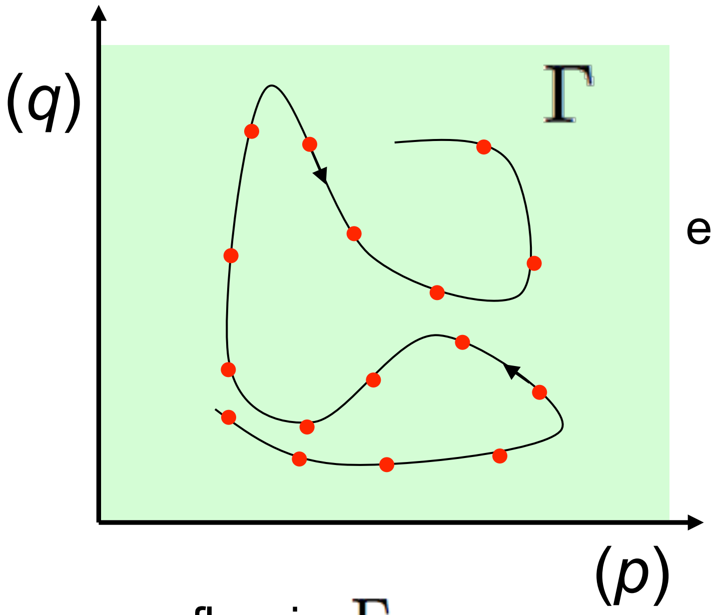
mean values in equilibrium $A(p,q) \rightarrow \langle A \rangle$

time average

$$\langle A \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T A(p(t),q(t))dt$$

ensemble average

$$\langle A \rangle = \frac{\int dpdq A(p,q)\rho(p,q)}{\int dpdq \rho(p,q)}$$



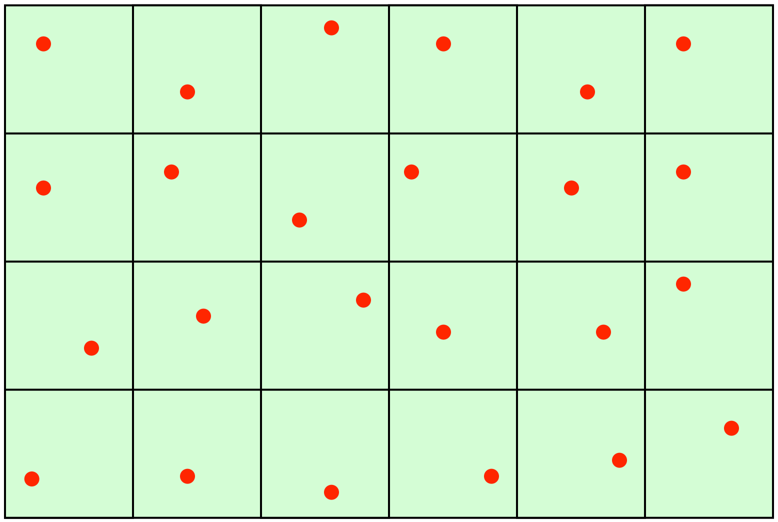
flow in Γ

egodicity

⇕

equivalence

→



ensemble of states in Γ

Classical statistical physics - microcanonical ensemble

isolated and closed system: fixed energy and particle number, ….

microcanonical phase space: system with fixed energy *E*, ….

- all states in phase space Γ within the energy interval $[E, E+\delta E]$ with same probability

- volume of microcanonical phase space $\omega(E)$: "number" of all configurations in energy interval $[E, E+\delta E]$

density function

Hamiltonian

$$\mathcal{H}(\nu)$$

$$\omega(E) = \sum_{\nu\in\Gamma}^{E\le\mathcal{H}(\nu)\le E+\delta E}$$

$$\rho(\nu) = \begin{cases} \text{const.} & E \le \mathcal{H}(\nu) \le E+\delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\nu \in \Gamma$$

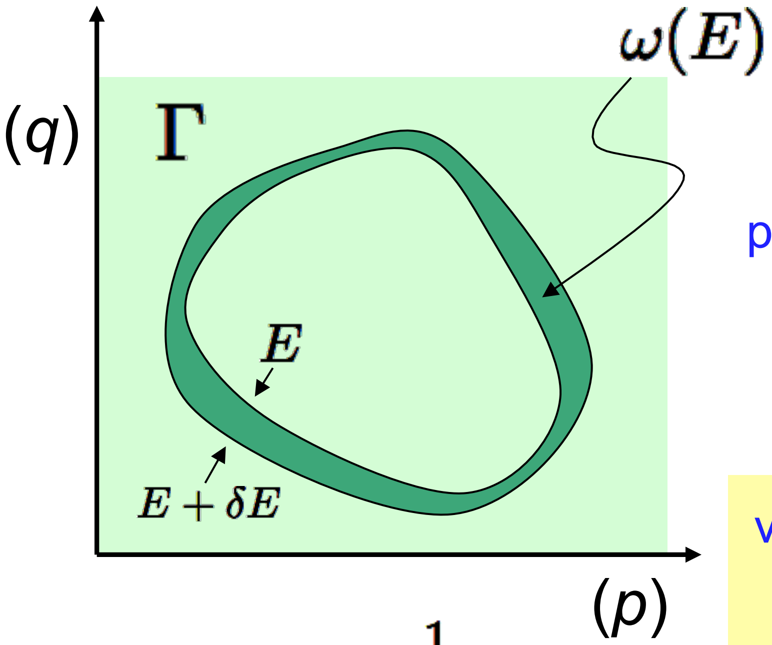
state of systems

entropy: $S(E) = k_B \ln \omega(E)$

Classical statistical physics - microcanonical ensemble

example: gas of particles with natural variables (*E*, *V*, *N*)

$$\mathcal{H}(p,q) \qquad (p,q) = (p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) \text{ in } \Gamma$$



$$\rho(🟩) = \text{const} \qquad \rho(⬜) = 0$$

phase space volume

$$\Phi(E) = \Lambda_N \int_{e \leq \mathcal{H}(p,q)} dpdq$$

$$\Lambda_N = \frac{1}{N!h^{3N}}$$

particle permutation ↗ (*N*!)

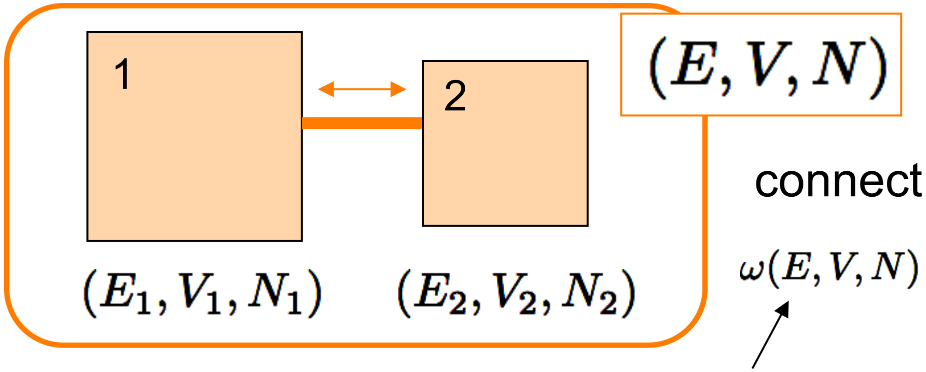
units ↖ (h^{3N}) [*h*]=[*pq*]=*Js*

volume of microcanonical ensemble

$$\omega(E) = \Lambda_N \int_{e \leq \mathcal{H}(p,q) \leq E + \delta E} dpdq$$
$$= \frac{d\Phi}{dE} \delta E$$

Classical statistical physics - microcanonical ensemble

composite systems of 2 subsystems:



$$E = E_1 + E_2 \quad V = V_1 + V_2 \quad N = N_1 + N_2$$

connect the two systems → equilibriation

$$\omega(E,V,N) = \sum_{\substack{0 \le E' \le E \\ 0 \le V' \le V \\ 0 \le N' \le N}} \omega_1(E',V',N')\omega_2(E-E',V-V',N-N')$$

volume of total microcan. ensemble

largest term dominates sum

$$\omega_1(E_0',V_0',N_0')\omega_2(E-E_0',V-V_0',N-N_0')$$

search the maximum

$$\left.\frac{\partial \omega_1(E',V',N')\omega_2(E-E',V-V',N-N')}{\partial E'}\right|_{E'=E_0',V'=V_0',N'=N_0'} = 0$$

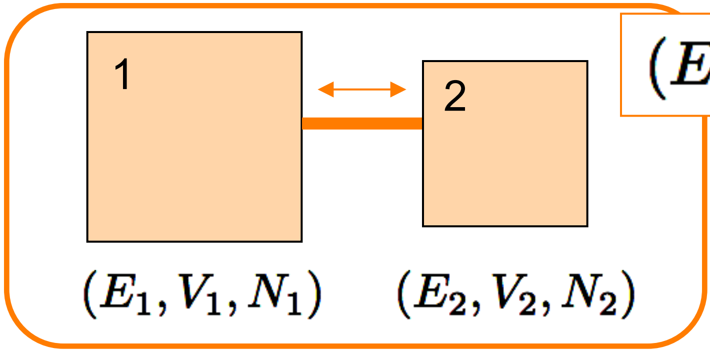
$$\left.\frac{\partial \omega_1(E',V',N')\omega_2(E-E',V-V',N-N')}{\partial V'}\right|_{E'=E_0',V'=V_0',N'=N_0'} = 0$$

$$\left.\frac{\partial \omega_1(E',V',N')\omega_2(E-E',V-V',N-N')}{\partial N'}\right|_{E'=E_0',V'=V_0',N'=N_0'} = 0$$

→ equilibrium conditions

Classical statistical physics - microcanonical ensemble

composite systems of 2 subsystems:



$$\boxed{(E, V, N)}$$

$$E = E_1 + E_2 \quad V = V_1 + V_2 \quad N = N_1 + N_2$$

connect the two systems → equilibriation

$$\tilde{E}_1 = E_0' \qquad \tilde{V}_1 = V_0' \qquad \tilde{N}_1 = N_0'$$

$$\tilde{E}_2 = E - E_0' \qquad \tilde{V}_2 = V - V_0' \qquad \tilde{N}_2 = N - N_0'$$

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{\tilde{E}_1,\tilde{V}_1,\tilde{N}_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{\tilde{E}_2,\tilde{V}_2,\tilde{N}_2} \longrightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

$$\left.\frac{\partial S_1}{\partial V_1}\right|_{\tilde{E}_1,\tilde{V}_1,\tilde{N}_1} = \left.\frac{\partial S_2}{\partial V_2}\right|_{\tilde{E}_2,\tilde{V}_2,\tilde{N}_2} \longrightarrow \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\left.\frac{\partial S_1}{\partial N_1}\right|_{\tilde{E}_1,\tilde{V}_1,\tilde{N}_1} = \left.\frac{\partial S_2}{\partial N_2}\right|_{\tilde{E}_2,\tilde{V}_2,\tilde{N}_2} \longrightarrow \frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$

equilibrium parameters

$T_1 = T_2$ temperature

$p_1 = p_2$ pressure

$\mu_1 = \mu_2$ chem. pot.