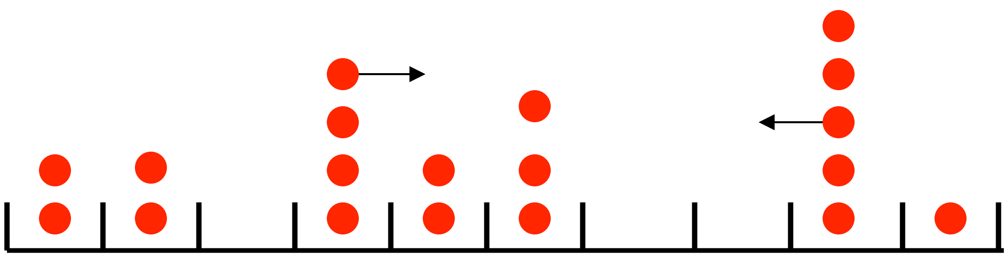
Master equation

system: *N* units ● with *z* micro-states (same energy)



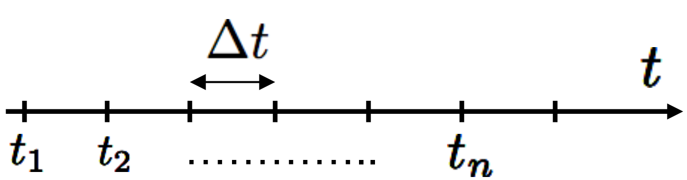
N_ν : number of units in state ν

$$\sum_{\nu=1}^{z} N_\nu = N$$

probability to find a unit in state ν

$$w_\nu = \frac{N_\nu}{N} \Rightarrow \sum_{\nu=1}^{z} w_\nu = 1$$

time evolution:



redistribution through state transitions

transitions probability in each time step

$$\nu \rightarrow \nu'$$

$$p_{\nu\nu'} = \Delta t \Gamma_{\nu\nu'}$$

transition rate

Master equation

$$\frac{dw_\nu}{dt} = -\sum_{\nu' \neq \nu} \{\Gamma_{\nu\nu'} w_\nu - \Gamma_{\nu'\nu} w_{\nu'}\}$$

leaving ν entering ν

Master equation - detailed balance

$$\frac{dw_\nu}{dt} = -\sum_{\nu' \neq \nu} \{\Gamma_{\nu\nu'} w_\nu - \Gamma_{\nu'\nu} w_{\nu'}\}$$

fixed point: $\frac{dw_\nu}{dt} = 0$ $\Longleftrightarrow$

detailed balance

$$w_\nu \Gamma_{\nu\nu'} = w_{\nu'} \Gamma_{\nu'\nu}$$

condition: ergodicity

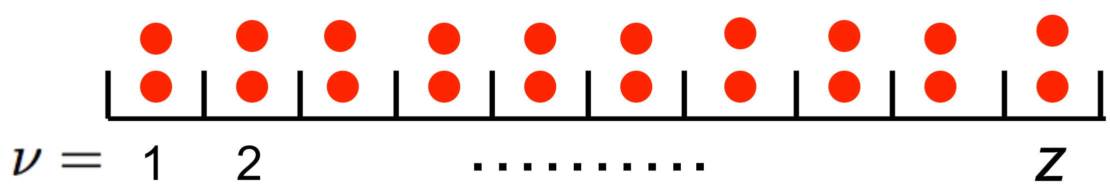
each unit reaches eventually all microstates after many transitions

time reversal symmetry

$$\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$$

rates are equal for both directions of transition

$$w_\nu = \frac{1}{z} = const.$$



Master equation - detailed balance

$$\frac{dw_\nu}{dt} = -\sum_{\nu' \neq \nu} \{\Gamma_{\nu\nu'} w_\nu - \Gamma_{\nu'\nu} w_{\nu'}\}$$

detailed balance

$$w_\nu \Gamma_{\nu\nu'} = w_{\nu'} \Gamma_{\nu'\nu}$$

state dependent quantity α_ν

mean value: $\langle\alpha\rangle(t) = \sum_\nu w_\nu(t)\alpha_\nu$

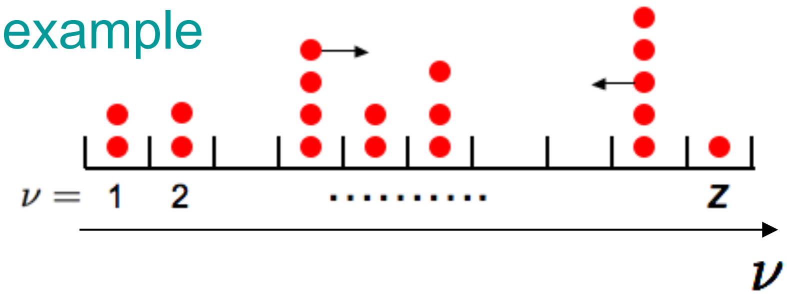
time evolution:

$$\frac{d}{dt}\langle\alpha\rangle = \frac{1}{2}\sum_{\nu,\nu'}\{\alpha_{\nu'} - \alpha_\nu\}(w_\nu - w_{\nu'})\Gamma_{\nu\nu'}$$

detailed balance

$$w_\nu = \frac{1}{z} \Rightarrow \frac{d}{dt}\langle\alpha\rangle = 0$$

example



quantity: $\alpha_\nu = \nu$ "position"

$$\frac{d}{dt}\langle\nu\rangle = \frac{1}{2}\sum_{\nu,\nu'}(\nu' - \nu)(w_\nu - w_{\nu'})\Gamma_{\nu\nu'}$$

"density inhomogeneity"

detailed balance ➡ "homogeneous density"

$$\langle\nu\rangle = \sum_\nu \nu w_\nu = \frac{z+1}{2}$$

Master equation - closed system

system: *N* units with *z* micro-states characterized by energy ϵ_ν

distribution: $w_\nu = \frac{N_\nu}{N}$

$$1 = \sum_{\nu=1}^{z} w_\nu$$

$$\langle \epsilon \rangle = \sum_{\nu=1}^{z} w_\nu \epsilon_\nu$$

closed system
energy fixed

equilibrium: maximize $H(w_\nu) = -\sum_\nu w_\nu \ln w_\nu$

with constraints

$$w_\nu = \frac{e^{-\epsilon_\nu / k_B T}}{Z}$$

$$Z = \sum_\nu e^{-\epsilon_\nu / k_B T}$$

→

equilibrium thermodynamics

internal energy

$$U = N \langle \epsilon \rangle$$

entropy

$$S = N k_B H$$

Master equation - closed system

$$\frac{dw_\nu}{dt} = \sum_{\nu_1,\nu_2,\nu_3} \{\Gamma_{\nu\nu_1;\nu_2\nu_3} w_{\nu_2} w_{\nu_3} - \Gamma_{\nu_2\nu_3;\nu\nu_1} w_\nu w_{\nu_1}\}$$

$$(\nu_2, \nu_3) \overset{\Gamma_{\nu\nu_1;\nu_2\nu_3}}{\longleftrightarrow} (\nu, \nu_1)$$

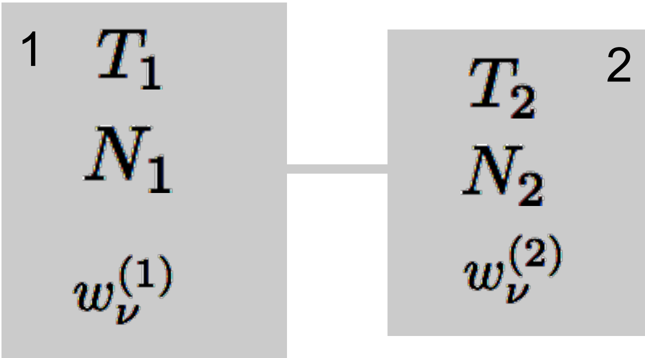
time reversal symmetry

with energy conservation $\epsilon_{\nu_2} + \epsilon_{\nu_3} = \epsilon_\nu + \epsilon_{\nu_1}$

detailed balance: $w_{\nu_2} w_{\nu_3} = w_\nu w_{\nu_1}$ $\xrightarrow[\text{maximal}]{H}$ $w_\nu = \dfrac{e^{-\epsilon_\nu/k_BT}}{Z}$

$$w_\nu w_{\nu_1} = \frac{e^{-\epsilon_\nu/k_BT} e^{-\epsilon_{\nu_1}/k_BT}}{Z^2} = \frac{e^{-\epsilon_{\nu_2}/k_BT} e^{-\epsilon_{\nu_3}/k_BT}}{Z^2} = w_{\nu_2} w_{\nu_3}$$

Master equation - irreversible process



2 subsystems each in equilibrium, weakly coupled

$$U = U_1 + U_2 = U_{01} + U_{02}$$

total equilibrium

$$U_1 = U_{01} + \tilde{U} \qquad U_2 = U_{02} - \tilde{U}$$

deviation from total equilibrium

entropy of total system: sum of subsystems

$$S(\tilde{U}) = S_1(U_{01} + \tilde{U}) + S_2(U_{02} - \tilde{U})$$

weak coupling: relaxation towards equilibrium

$$T_1 = T_2 = T_0$$

$$\frac{dS}{dt} = \tilde{U}\frac{d\tilde{U}}{dt}\left(\left.\frac{\partial^2 S_1}{\partial U_1^2}\right|_{U_{01}} + \left.\frac{\partial^2 S_2}{\partial U_2^2}\right|_{U_{02}}\right) = \frac{d\tilde{U}}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$