Lecture 3

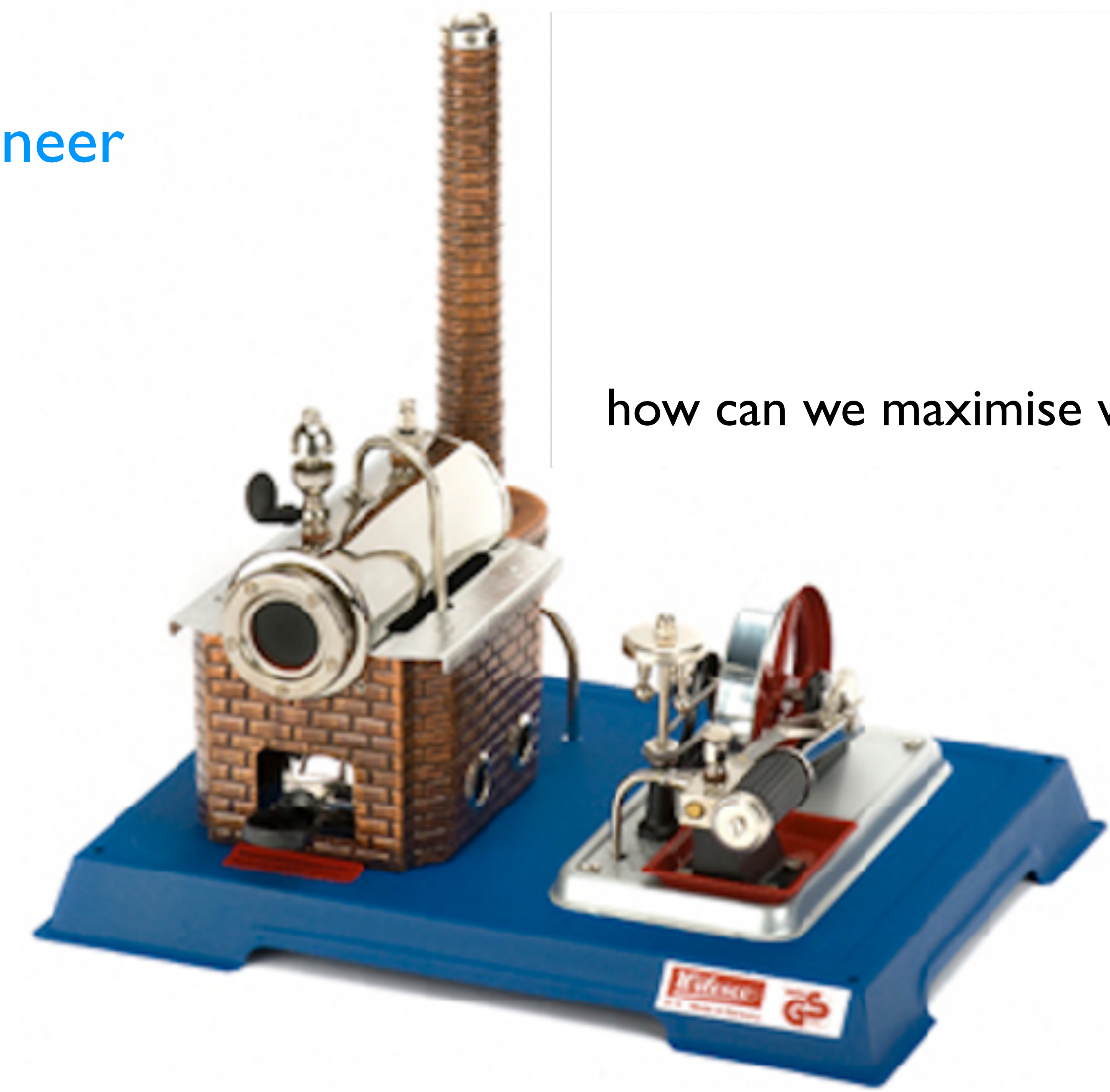
Thermodynamics

first law: conservation of energy

second law: direction of spontaneous change

important

if you're an engineer



how can we maximise work?

$$(-W_{\mathrm{u}}) \leq -\Delta A = -[\Delta U - T\Delta S]$$

Thermodynamics

Helmholtz free energy

internal energy

entropy

$$A = U - TS$$

extensive properties

Thermodynamics

Helmholtz free energy

internal energy

entropy

$$A = U - TS$$

extensive properties

chemical/physical change at constant temperature

$$\Delta A = \Delta U - T\Delta S \qquad \Delta A = -T\Delta S^{\mathrm{tot}}$$

spontaneous

$$\Delta A < 0$$

equilibrium

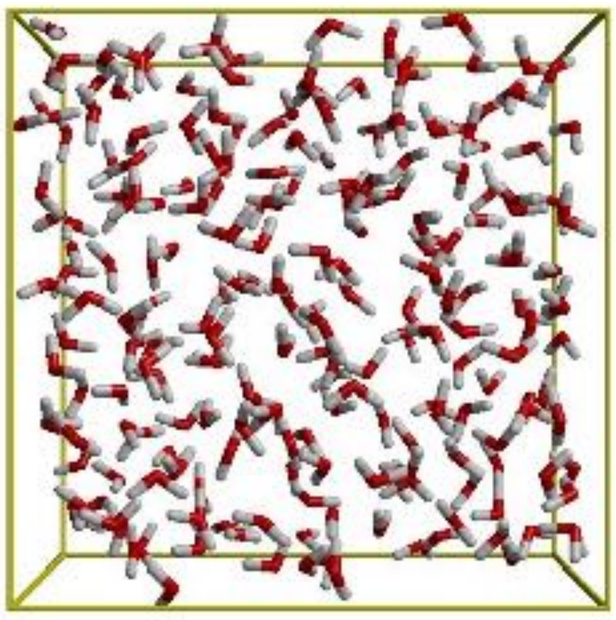
$$\Delta A = 0$$

Thermodynamics

entropy of isolated system

micro-states (realisations)

box with 216 waters:



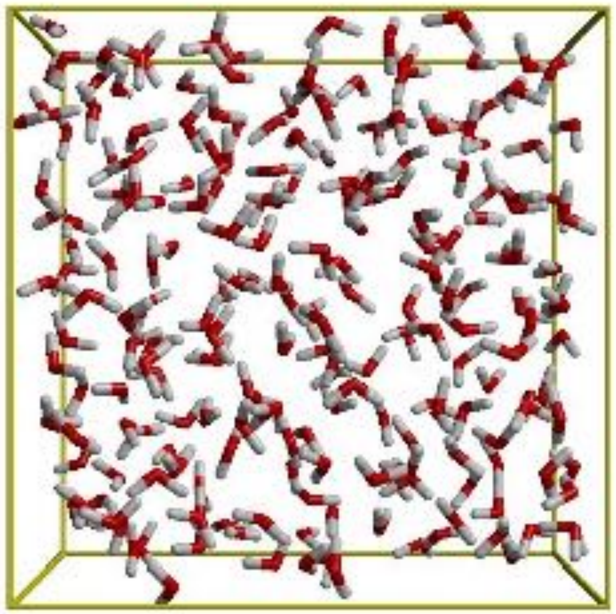
microstate 1

Thermodynamics

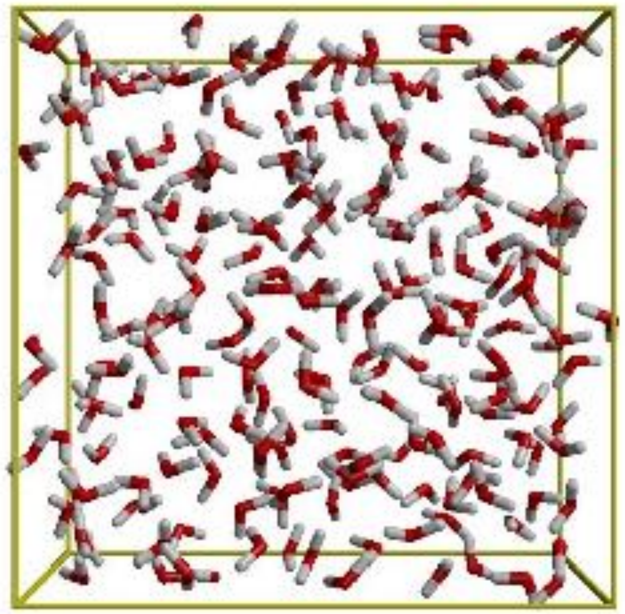
entropy of isolated system

micro-states (realisations)

box with 216 waters:



microstate 1



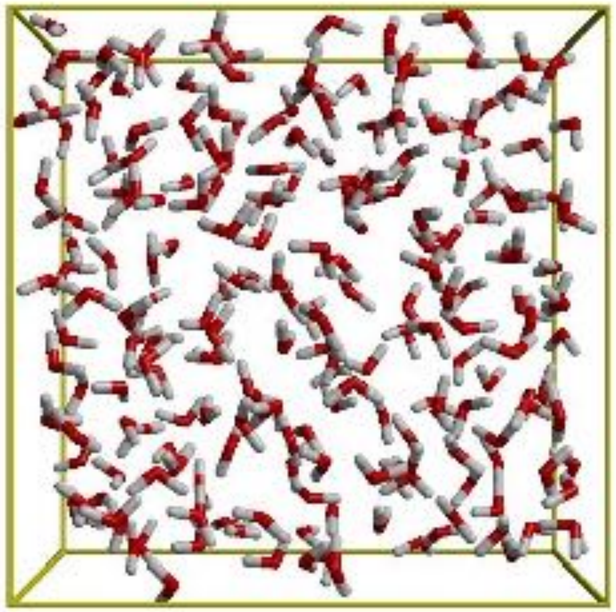
microstate 2

Thermodynamics

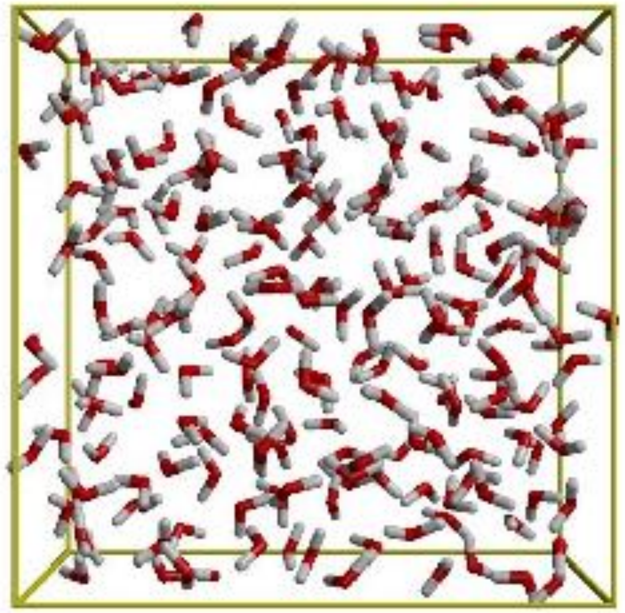
entropy of isolated system

micro-states (realisations)

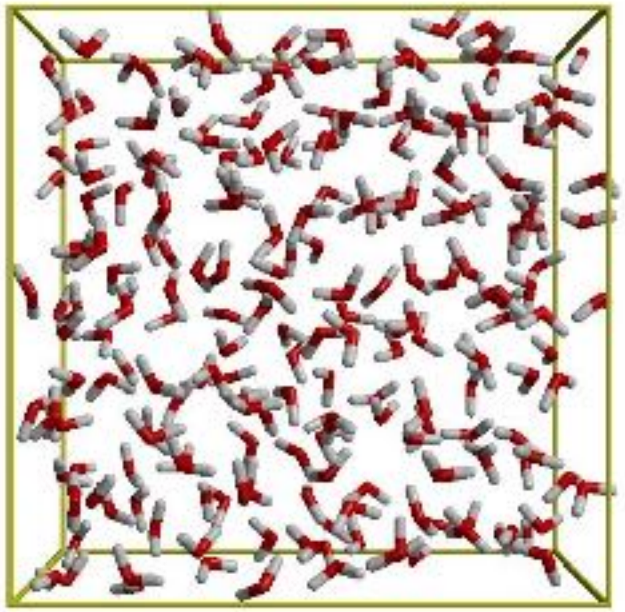
box with 216 waters:



microstate 1



microstate 2



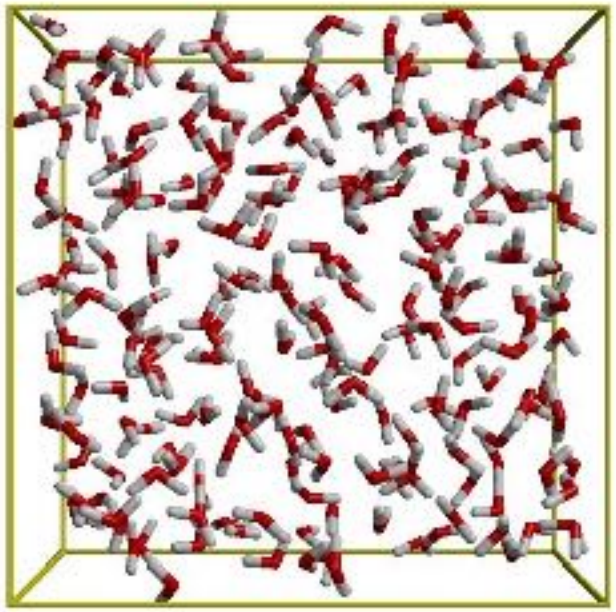
microstate 3

Thermodynamics

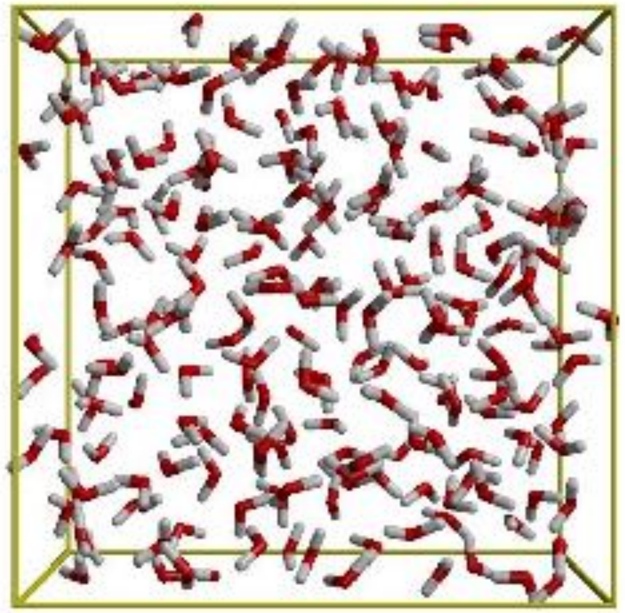
entropy of isolated system

micro-states (realisations)

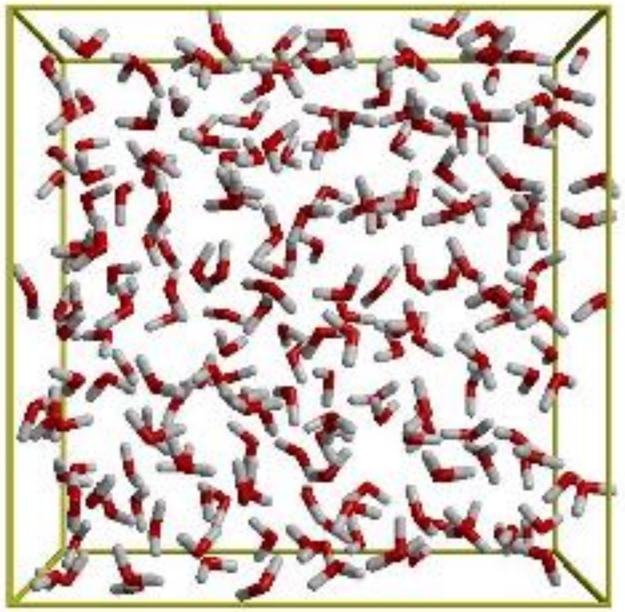
box with 216 waters:



microstate 1



microstate 2



microstate 3

total number of micro-states (realisations)

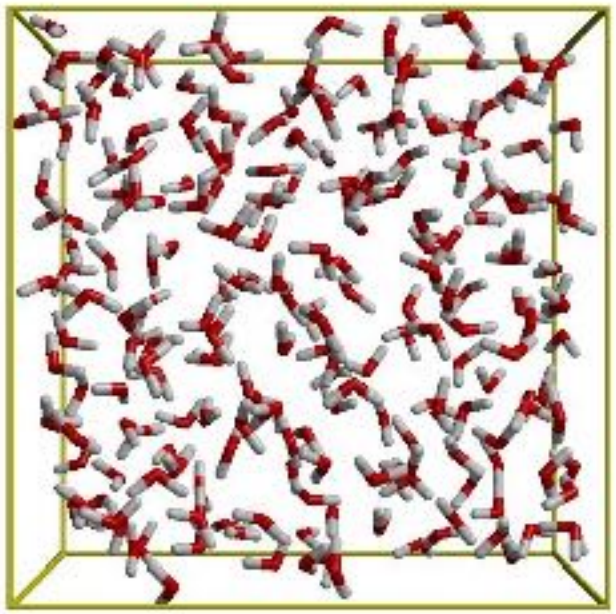
Ω

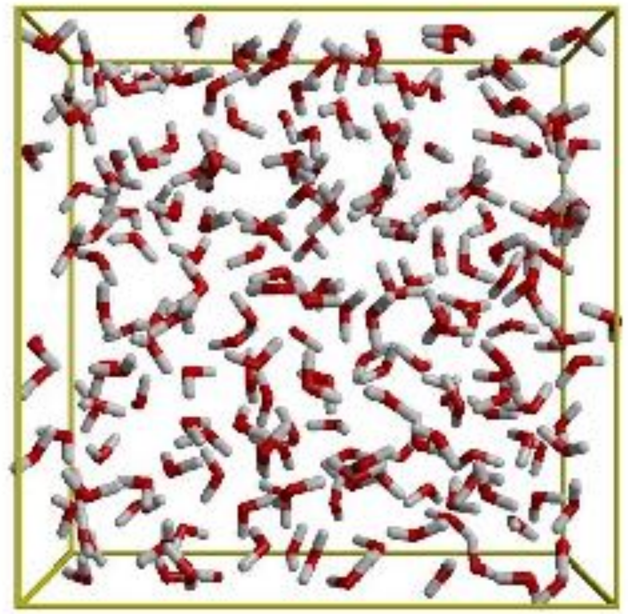
Thermodynamics

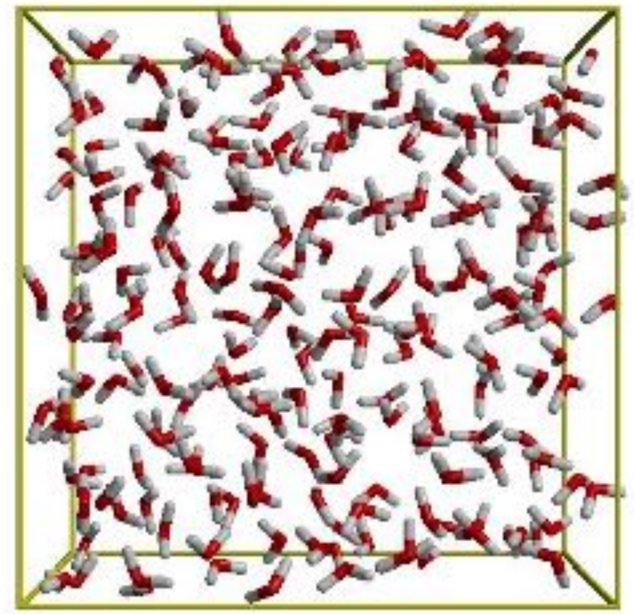
entropy of isolated system

micro-states (realisations)

box with 216 waters:


microstate 1


microstate 2


microstate 3

total number of micro-states (realisations)

Ω

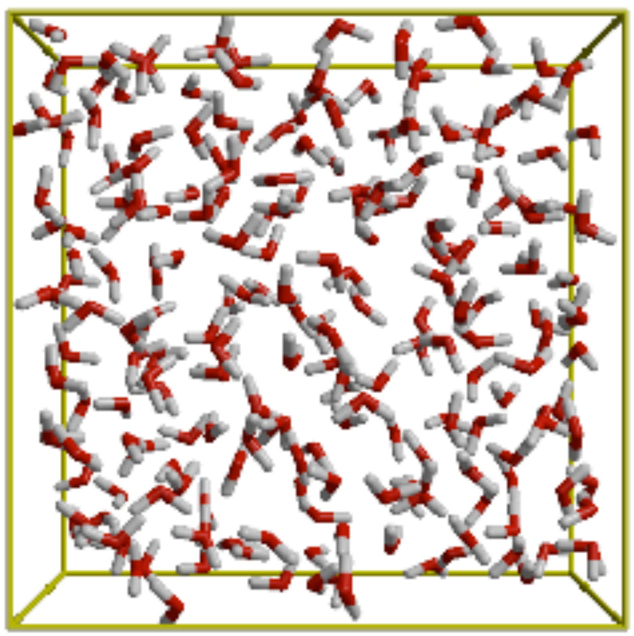
if you know how many, you pass the course today!

Thermodynamics

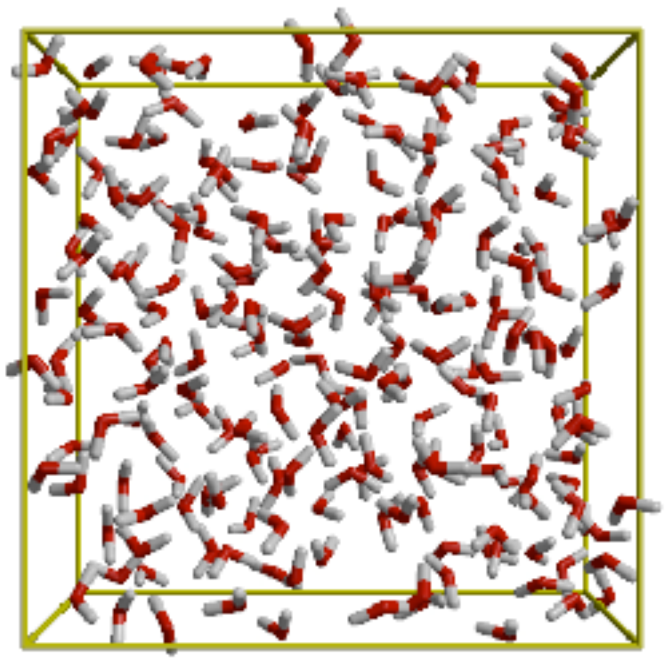
entropy of isolated system

micro-states (realisations)

two boxes of water:



box 1



box 2

total number of micro states (realisations)

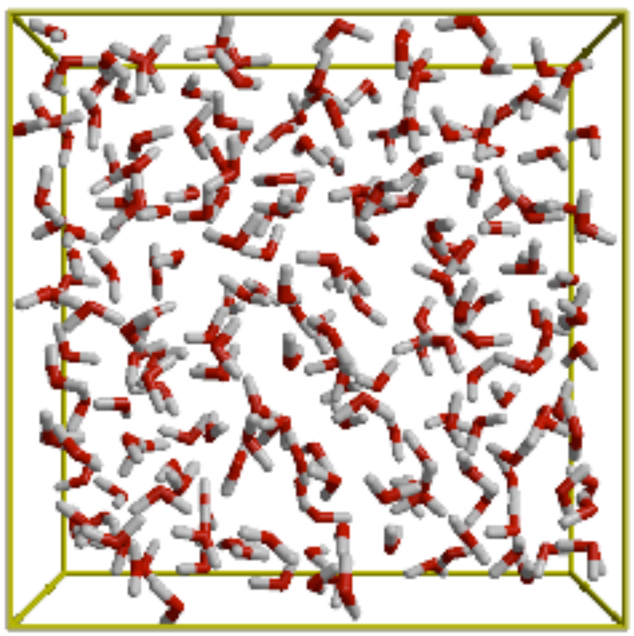
$$\Omega^{\text{tot}} =$$

Thermodynamics

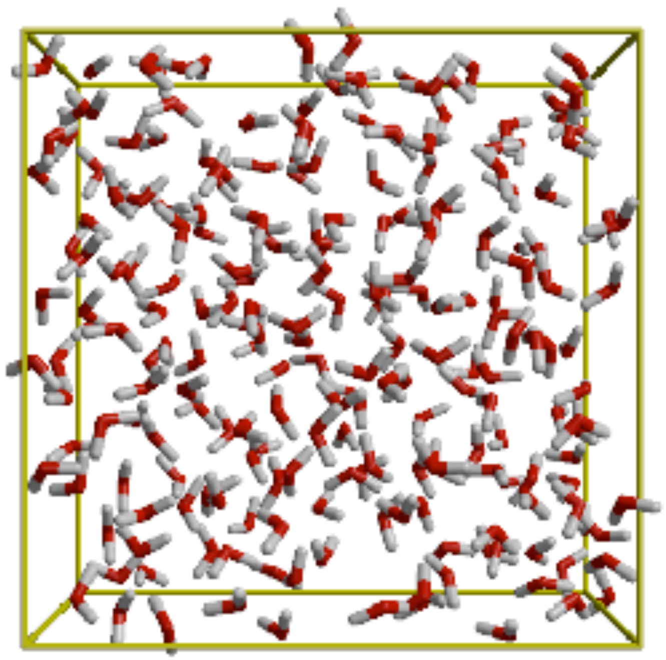
entropy of isolated system

micro-states (realisations)

two boxes of water:



box 1



box 2

total number of micro states (realisations)

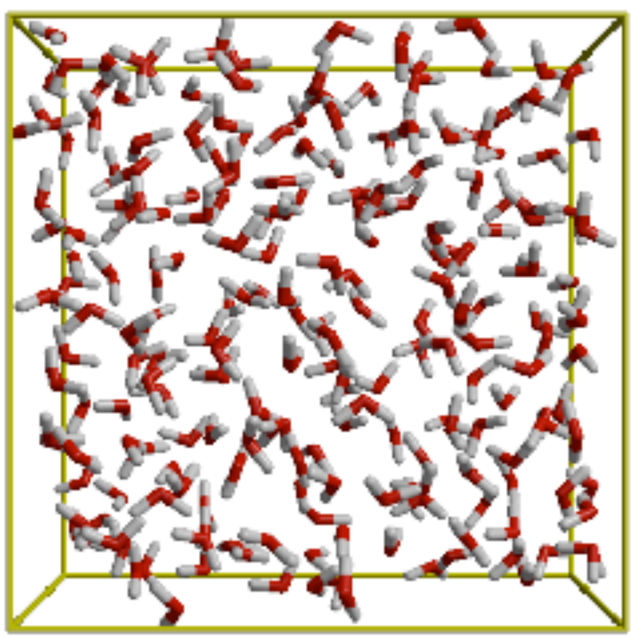
$$\Omega^{\text{tot}} = \Omega_1 \cdot \Omega_2$$

Thermodynamics

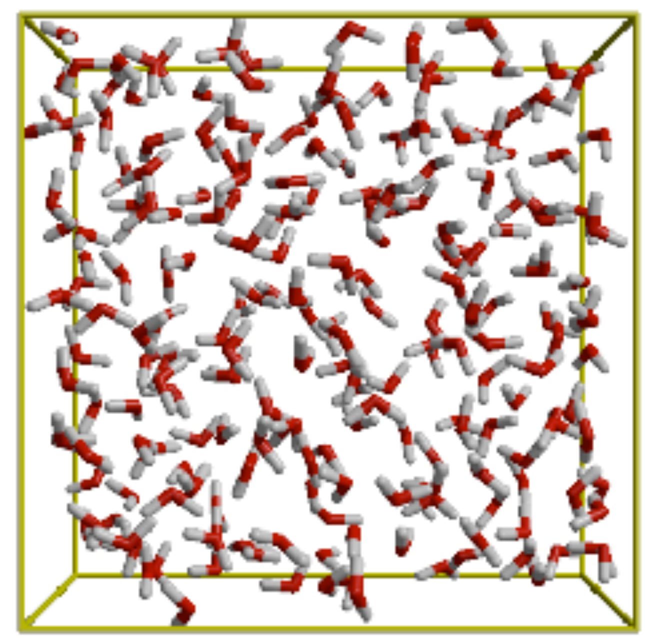
entropy of isolated system

micro-states (realisations)

two boxes of water:



box 1



box 2

total number of micro states (realisations)

$$\Omega^{\text{tot}} = \Omega_1 \cdot \Omega_2$$

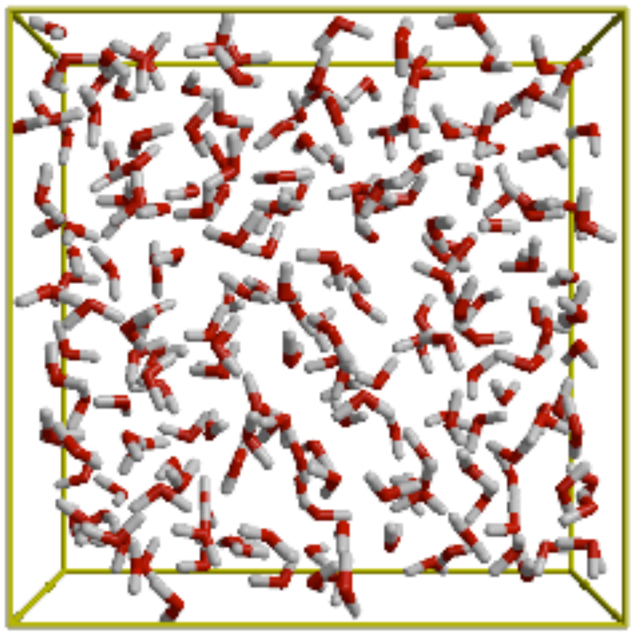
entropy is extensive, so should be sum:

Thermodynamics

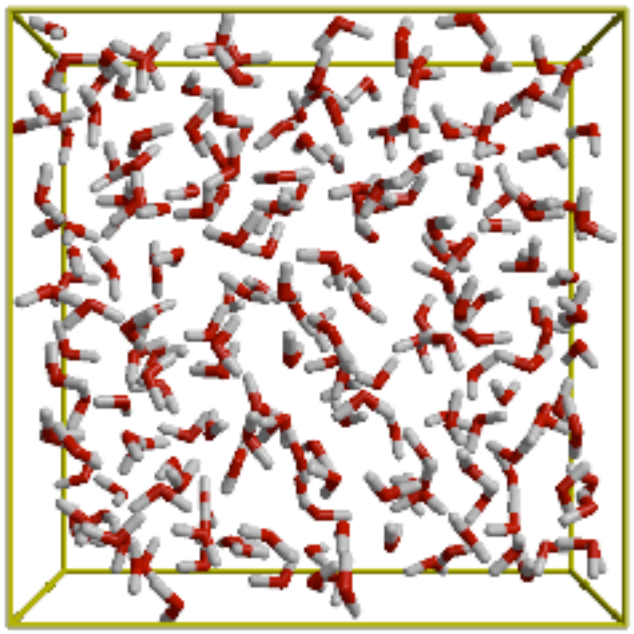
entropy of isolated system

micro-states (realisations)

two boxes of water:



box 1



box 2

total number of micro states (realisations)

$$\Omega^{\text{tot}} = \Omega_1 \cdot \Omega_2$$

entropy is extensive, so should be sum:

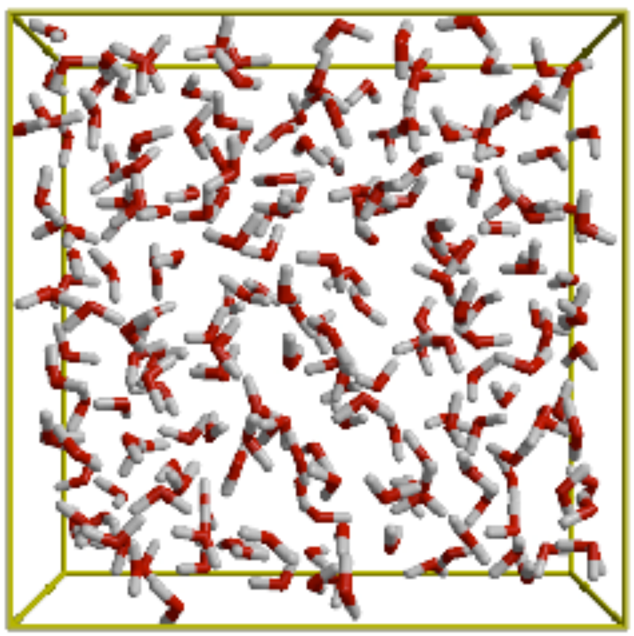
$$S = k \ln \Omega$$

Thermodynamics

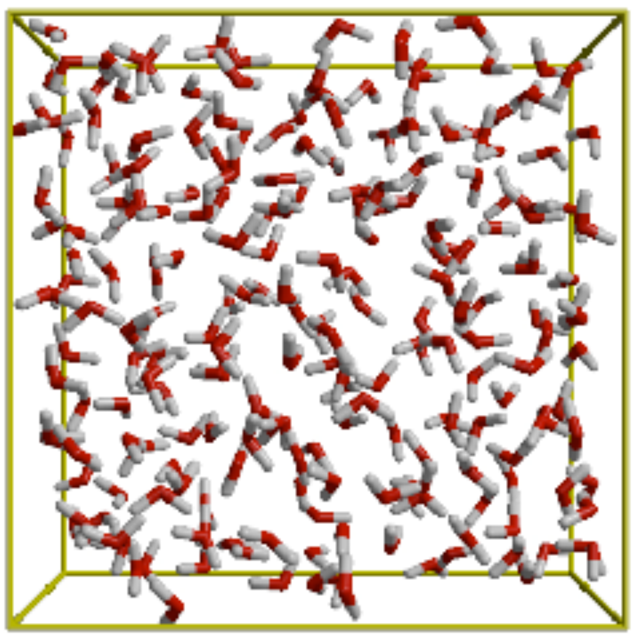
entropy of isolated system

micro-states (realisations)

two boxes of water:



box 1



box 2

total number of micro states (realisations)

$$\Omega^{\mathrm{tot}} = \Omega_1 \cdot \Omega_2$$

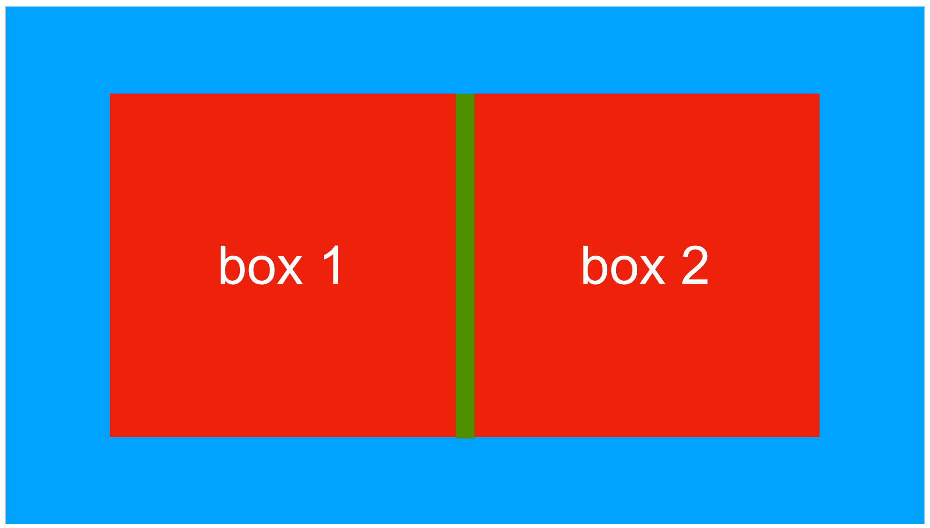
entropy is extensive, so should be sum:

$$S^{\mathrm{tot}} = k \ln[\Omega_1 \cdot \Omega_2] = k \ln \Omega_1 + k \ln \Omega_2 = S_1 + S_2$$

Thermodynamics

two systems in thermal equilibrium, isolated from world

diathermic walls (only energy can transfer)



$$N_1 + N_2 = N$$

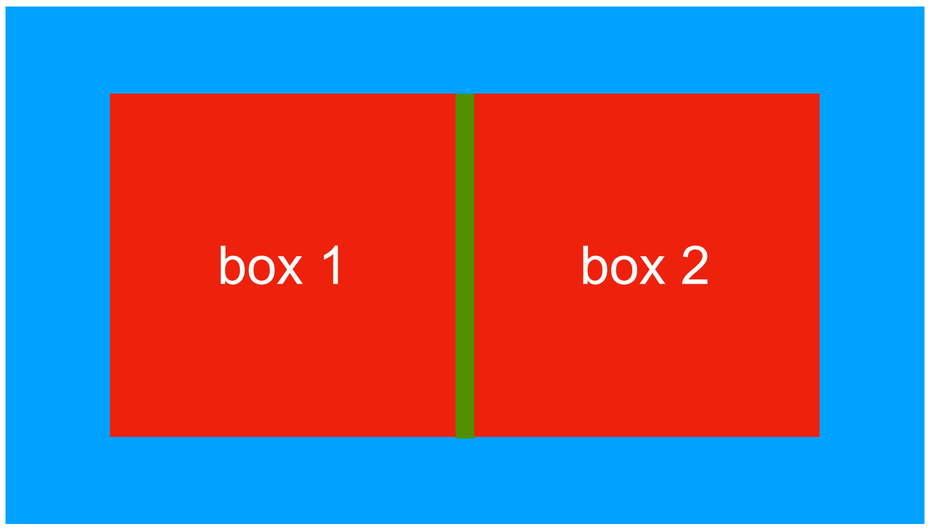
$$E_1 + E_2 = E$$

$$\frac{dE_2}{dE_1} = -1$$

Thermodynamics

two systems in thermal equilibrium, isolated from world

diathermic walls (only energy can transfer)



$$N_1 + N_2 = N$$

$$E_1 + E_2 = E$$

$$\frac{dE_2}{dE_1} = -1$$

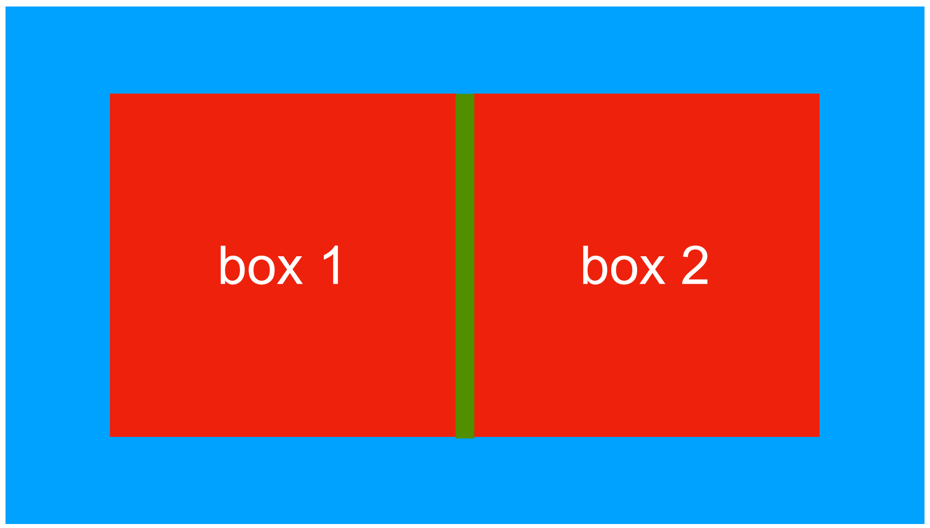
equilibrium: no net changes in total entropy

$$\frac{\partial S^{\rm tot}}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2}\frac{dE_2}{dE_1} = 0$$

Thermodynamics

two systems in thermal equilibrium, isolated from world

diathermic walls (only energy can transfer)



$$N_1 + N_2 = N$$

$$E_1 + E_2 = E$$

$$\frac{dE_2}{dE_1} = -1$$

equilibrium: no net changes in total entropy

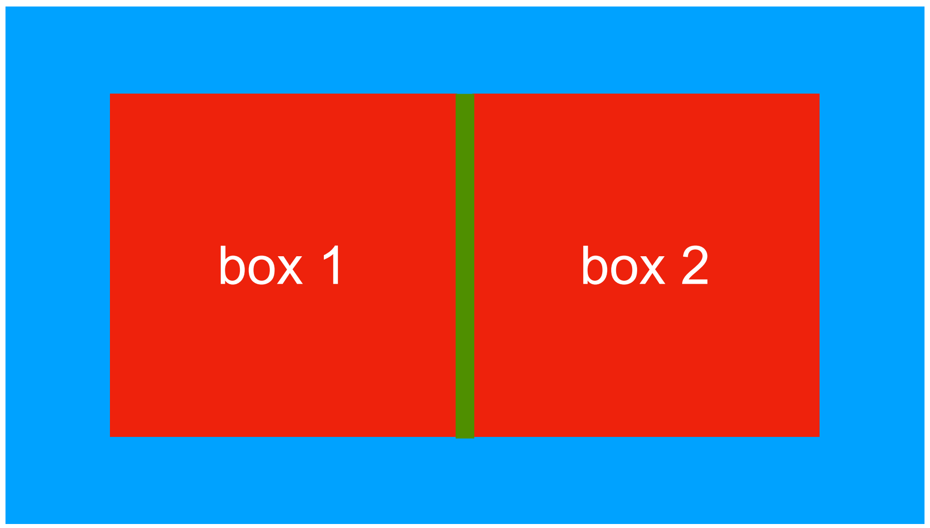
$$\frac{\partial S^{\text{tot}}}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2}\frac{dE_2}{dE_1} = 0$$

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

Thermodynamics

two systems in thermal equilibrium, isolated from world

diathermic walls (only energy can transfer)



$$N_1 + N_2 = N$$

$$E_1 + E_2 = E$$

$$\frac{dE_2}{dE_1} = -1$$

equilibrium: no net changes in total entropy

$$\frac{\partial S^{\text{tot}}}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2}\frac{dE_2}{dE_1} = 0$$

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

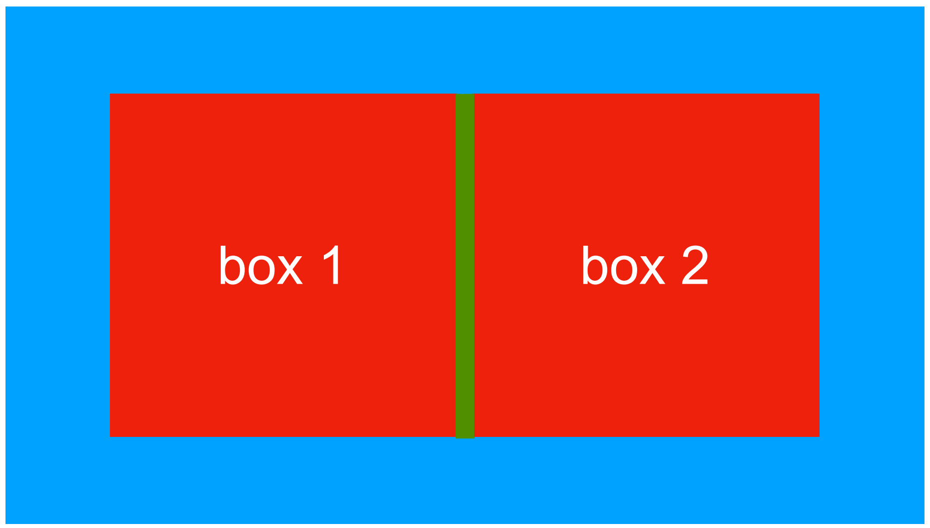
definition of temperature:

$$\frac{\partial S_1}{\partial E_1} = \frac{1}{T_1}$$

Thermodynamics

two systems in thermal equilibrium, isolated from world

diathermic walls (only energy can transfer)



$$N_1 + N_2 = N$$

$$E_1 + E_2 = E$$

no equilibrium: total entropy must increase

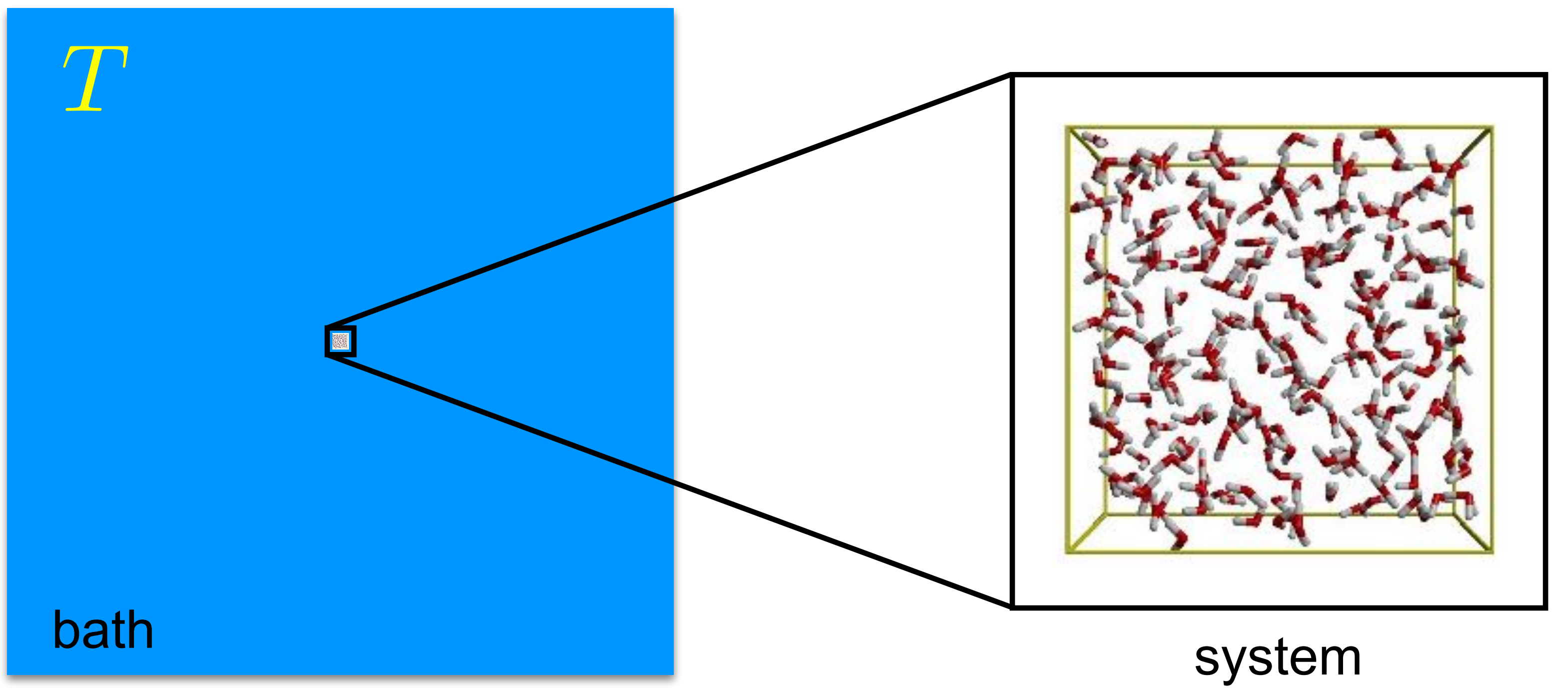
$$\frac{dS^{\text{tot}}}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} > 0$$

energy flows from higher to lower temperature

Statistical mechanics

canonical ensemble

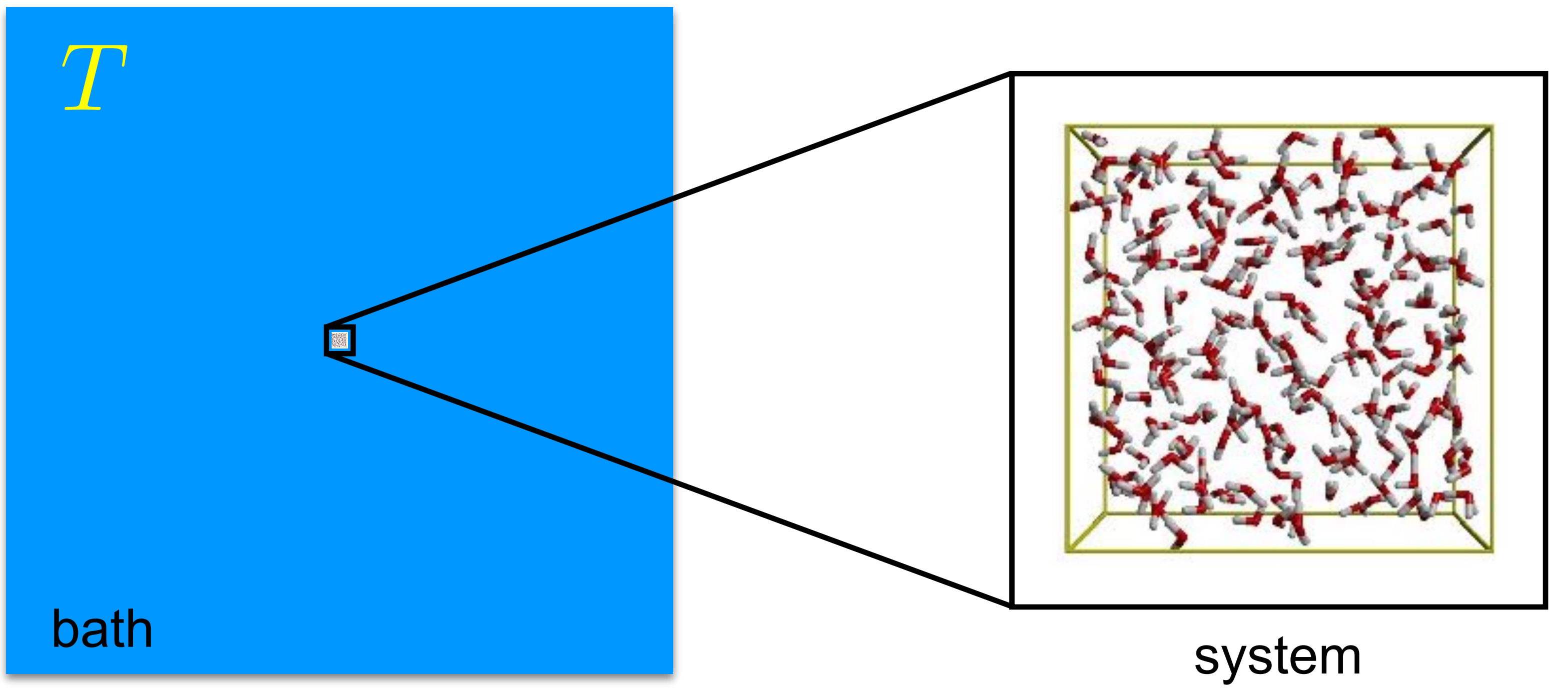
system in thermal equilibrium with bath



Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

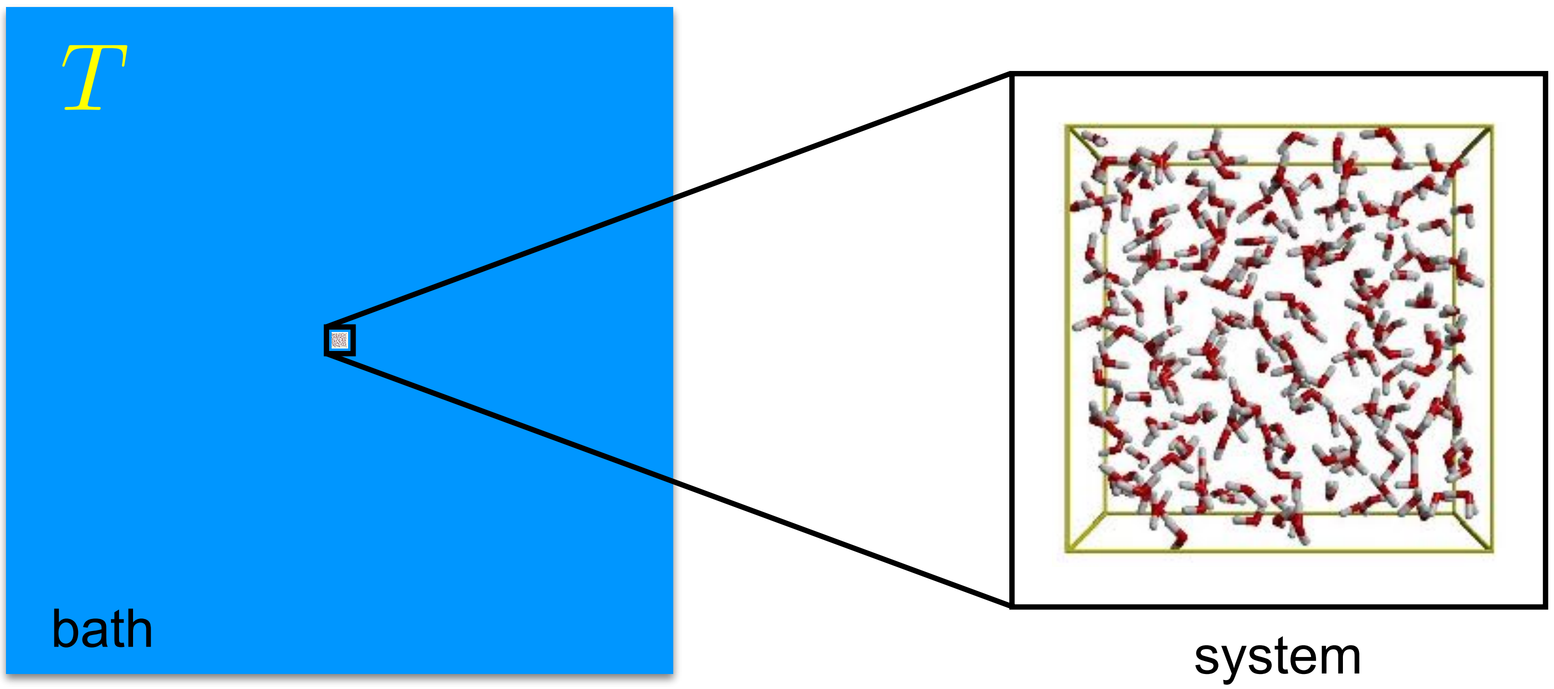
each with different energy

$$E_1 < E_2 < E_3 < \dots < E_i < \dots$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

each with different energy

$$E_1 < E_2 < E_3 < \ldots < E_i < \ldots$$

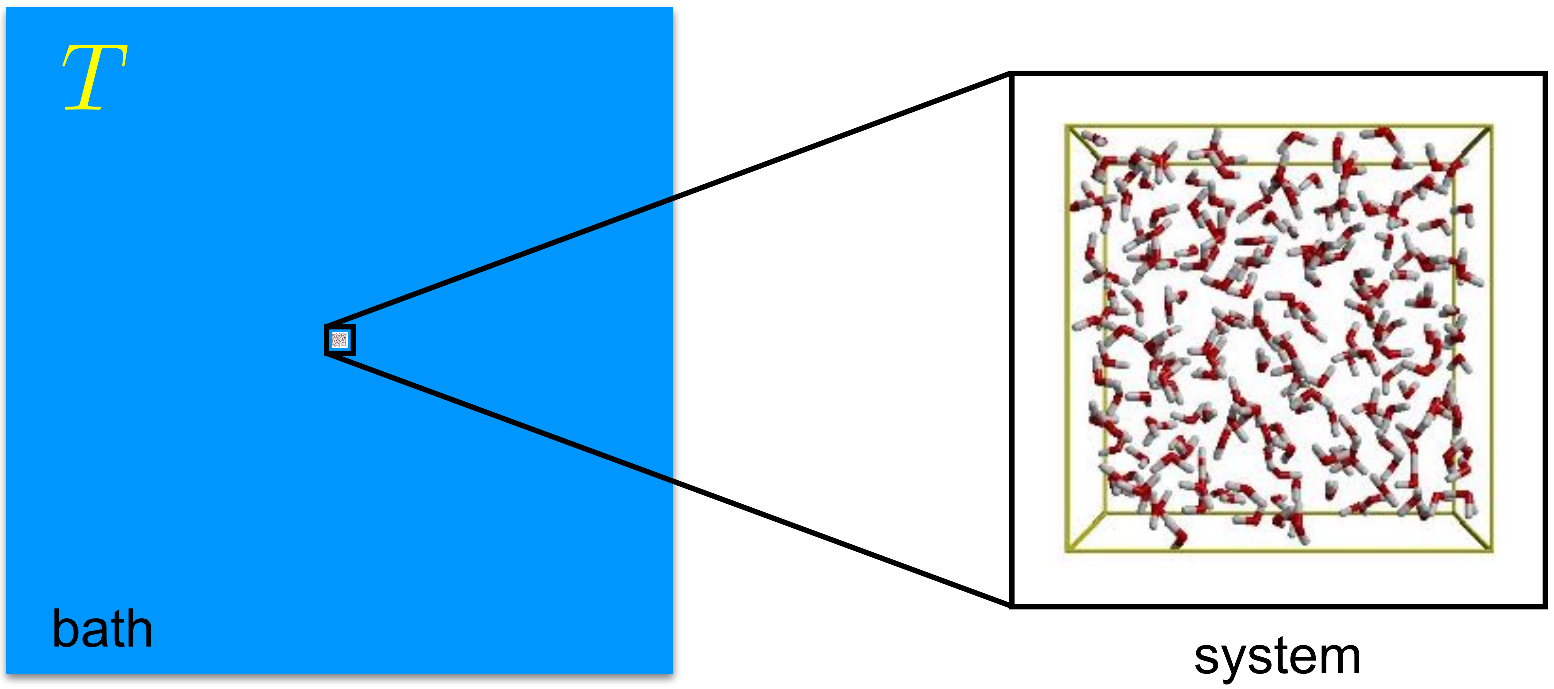
probability of micro state i proportional to number of micro states of bath

$$p_i = \mathrm{const} \cdot \Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

each with different energy

$$E_1 < E_2 < E_3 < \ldots < E_i < \ldots$$

probability of micro-state i proportional to number of micro states of bath

$$p_i = \mathrm{const} \cdot \Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)$$

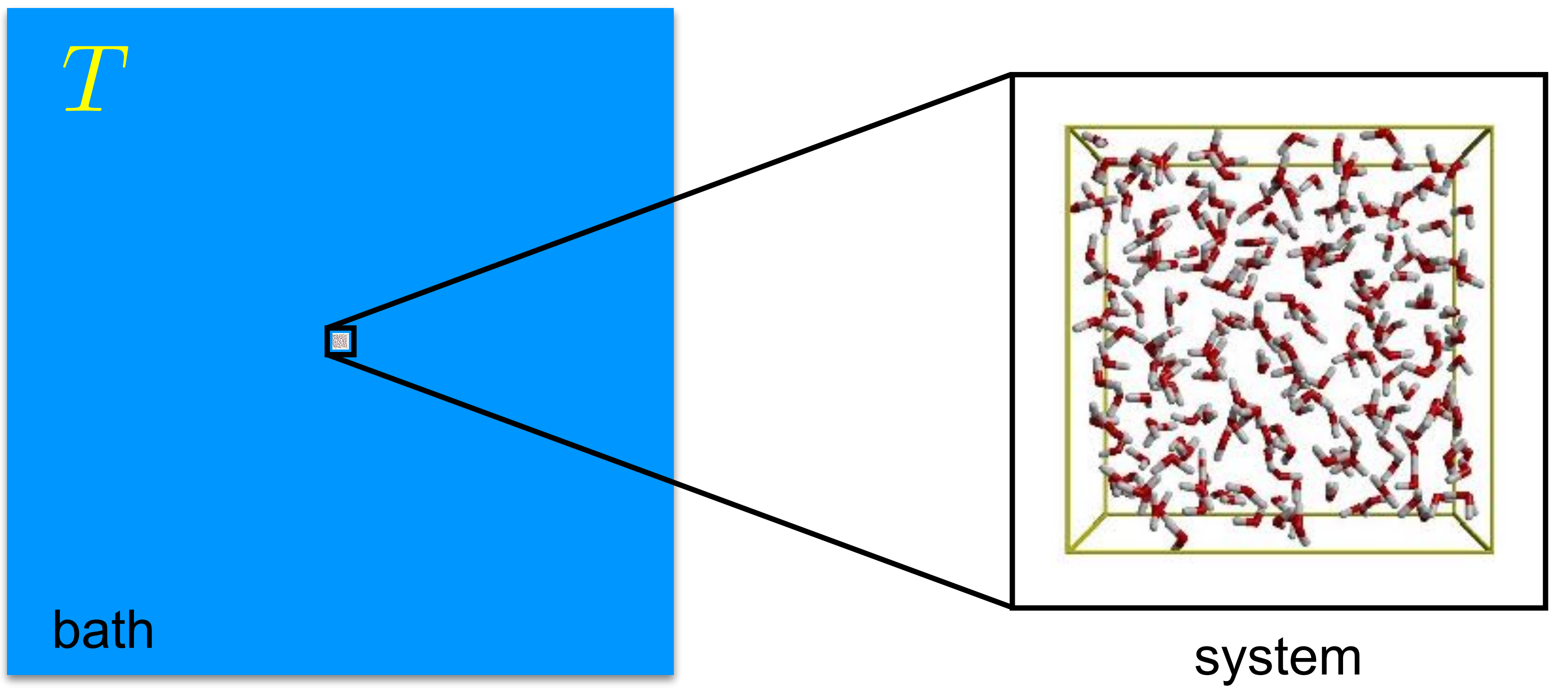
normalisation (const):

$$p_i = \frac{\Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)}{\sum_i \Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)}$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

probability of micro-state i proportional to number of micro states of bath

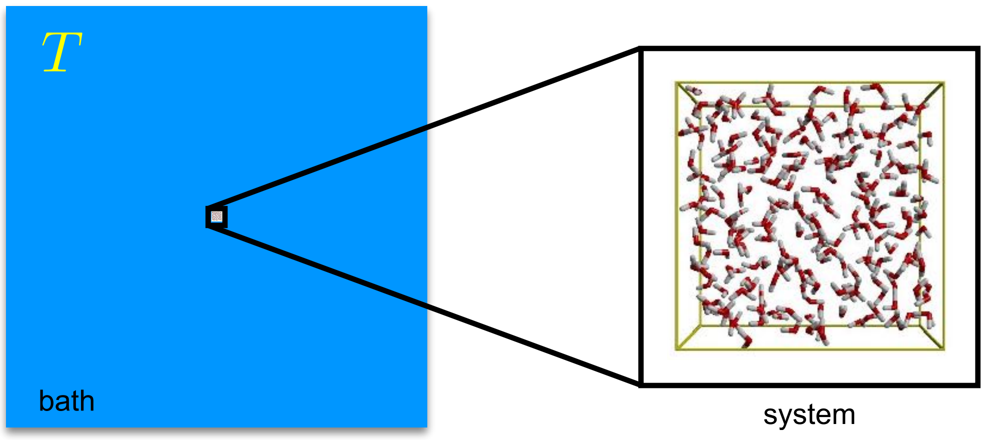
$$p_i = \text{const} \cdot \Omega_{\text{bath}}(E^{\text{tot}} - E_i)$$

normalisation (const):

$$p_i = \frac{\Omega_{\text{bath}}(E^{\text{tot}} - E_i)}{\sum_i \Omega_{\text{bath}}(E^{\text{tot}} - E_i)}$$

Statistical mechanics

canonical ensemble



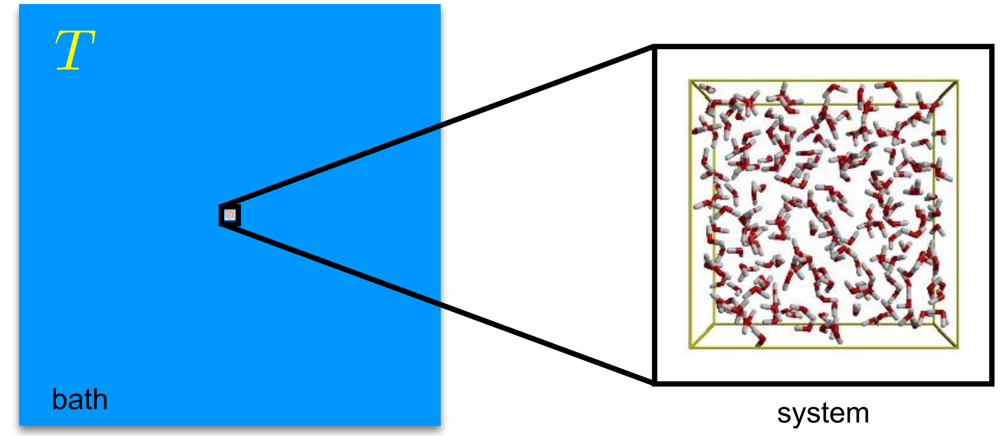
system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \text{const} \cdot \Omega_{\text{bath}}(E^{\text{tot}} - E_i)$$

Statistical mechanics



canonical ensemble

system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)$$

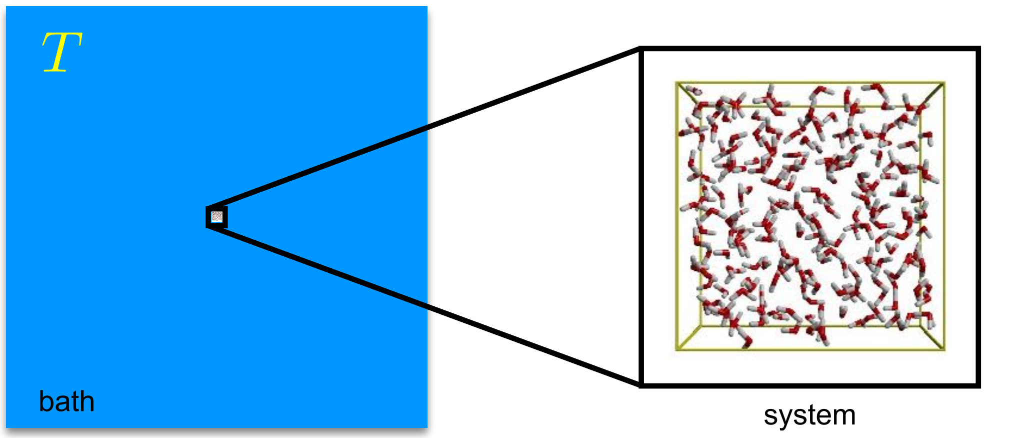
with definition of entropy: $S = k \ln \Omega$

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \Omega_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)$$

with definition of entropy: $S = k \ln \Omega$

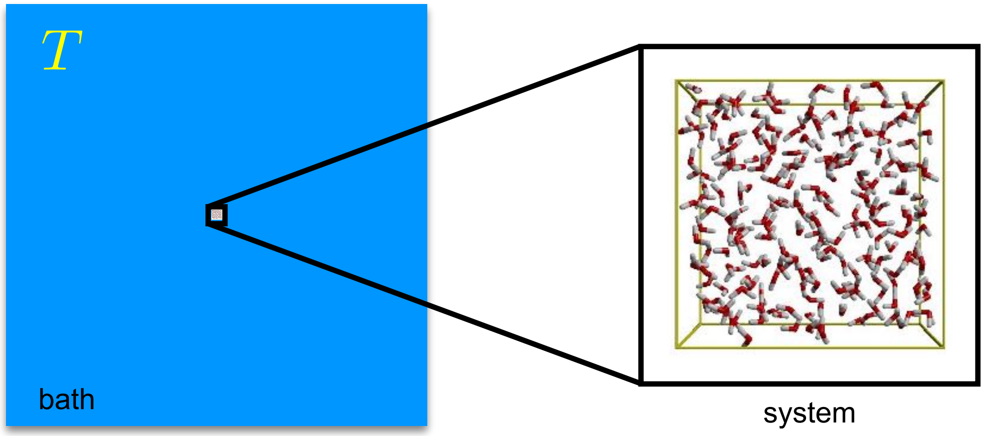
$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

bath much larger than system:

$$E^{\mathrm{tot}} \gg E_i$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro states of bath

$$p_i = \text{const} \cdot \Omega_{\text{bath}}(E^{\text{tot}} - E_i)$$

with definition of entropy: $S = k \ln \Omega$

$$p_i = \text{const} \cdot \exp[S_{\text{bath}}(E^{\text{tot}} - E_i)/k]$$

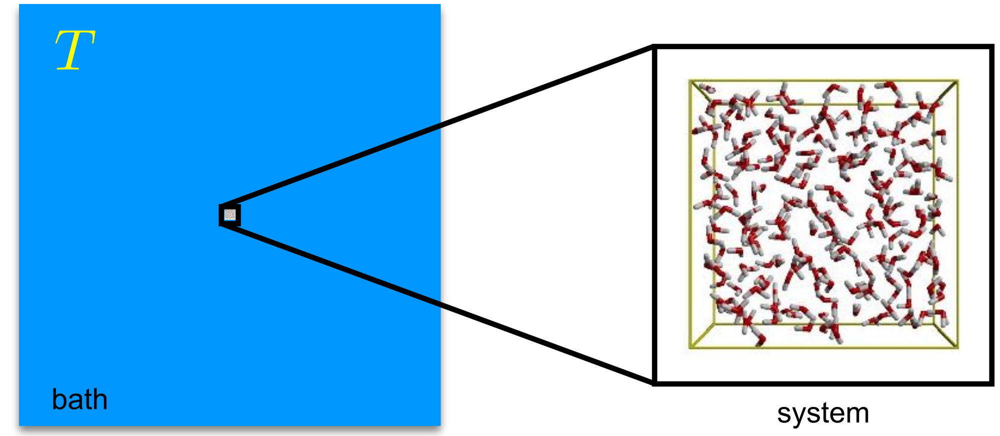
bath much larger than system:

$$E^{\text{tot}} \gg E_i$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\text{bath}}(E^{\text{tot}} - E_i) = \frac{1}{k} S_{\text{bath}}(E^{\text{tot}}) - \frac{E_i}{k} \left. \frac{\partial S_{\text{bath}}(E)}{\partial E} \right|_{E=E^{\text{tot}}} + \ldots$$

Statistical mechanics



canonical ensemble

system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

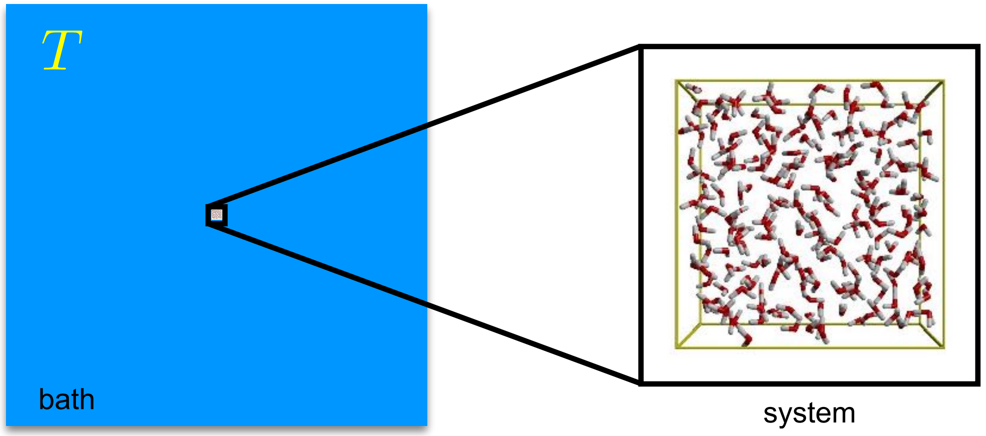
$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{E_i}{k} \frac{\partial S_{\mathrm{bath}}(E)}{\partial E}\bigg|_{E=E^{\mathrm{tot}}} + \ldots$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{E_i}{k} \frac{\partial S_{\mathrm{bath}}(E)}{\partial E}\bigg|_{E=E^{\mathrm{tot}}} + \ldots$$

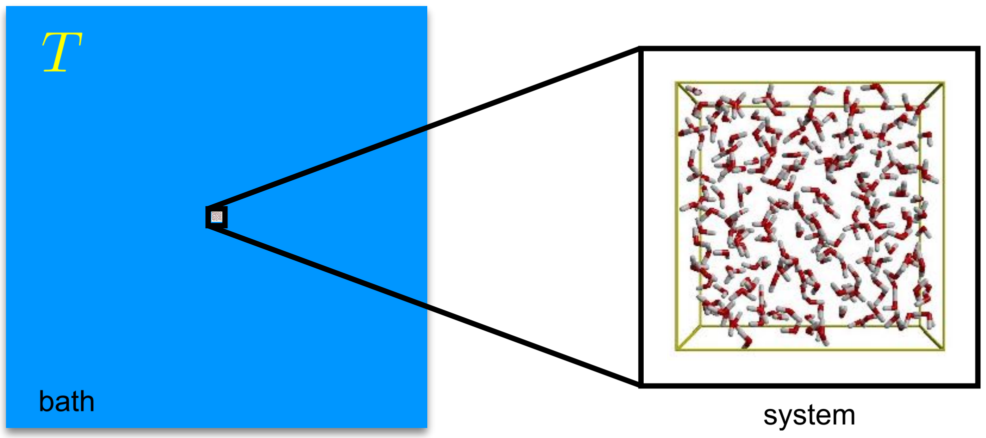
with definition of temperature

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{1}{kT} E_i$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro-state i proportional to number of micro-states of bath

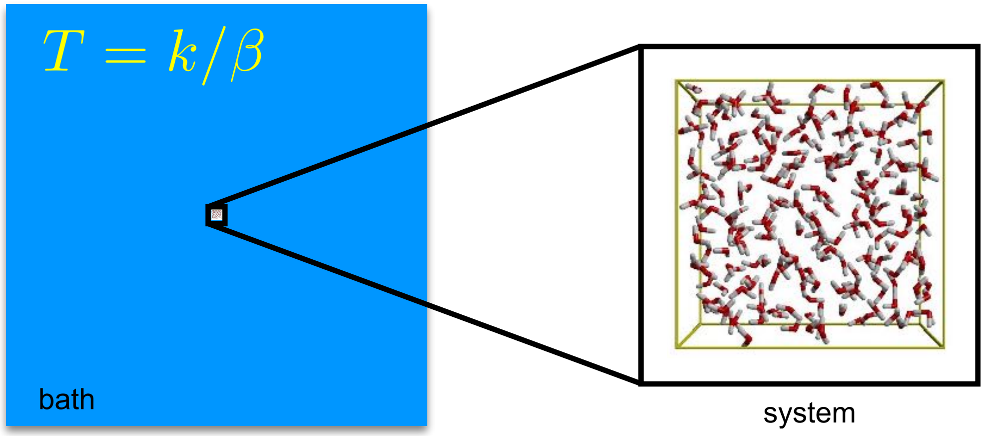
$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{1}{kT} E_i$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro-state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

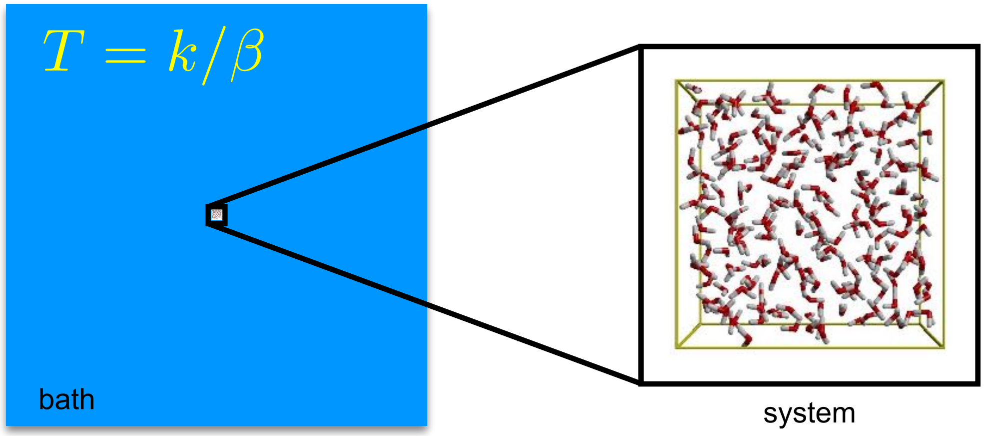
$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{1}{kT} E_i$$

define

$$\beta \equiv \frac{1}{kT}$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro-state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \frac{1}{kT} E_i$$

define

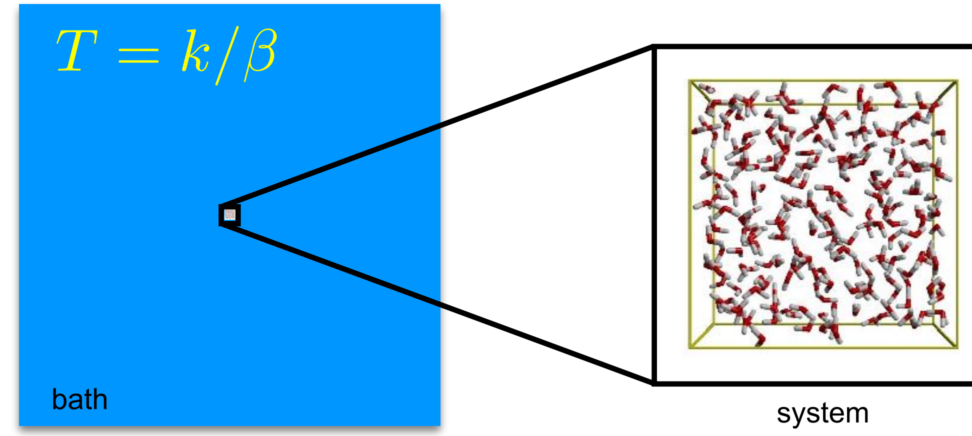
$$\beta \equiv \frac{1}{kT}$$

so that

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \beta E_i$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

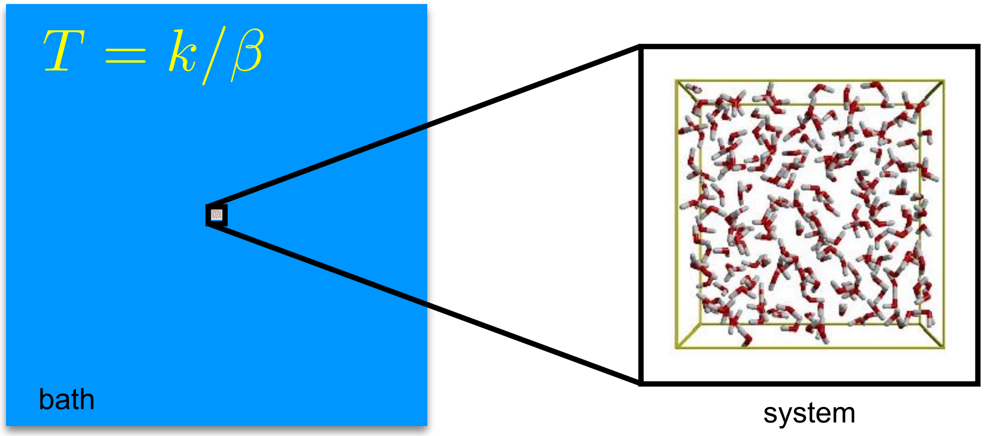
Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \beta E_i$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \beta E_i$$

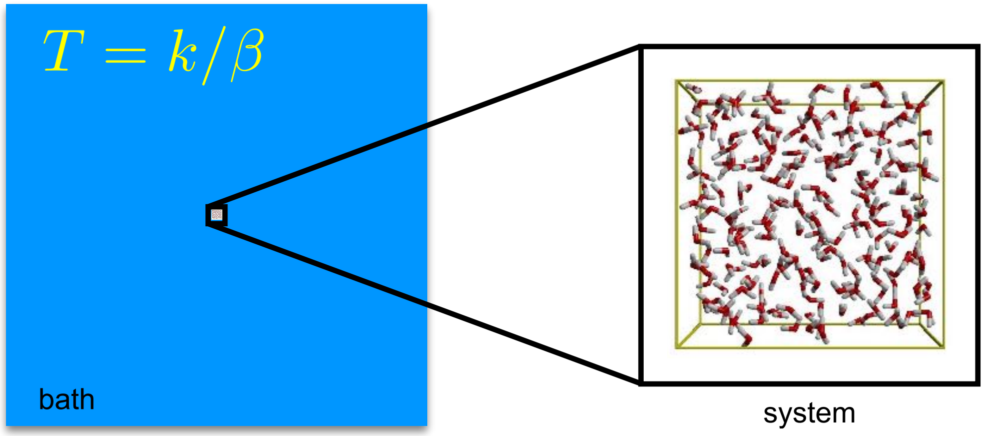
probability of micro-state i

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \text{const} \cdot \exp[S_\text{bath}(E^\text{tot} - E_i)/k]$$

Taylor expansion of S_bath around E^tot

$$\frac{1}{k} S_\text{bath}(E^\text{tot} - E_i) = \frac{1}{k} S_\text{bath}(E^\text{tot}) - \beta E_i$$

probability of micro-state i

Boltzmann distribution

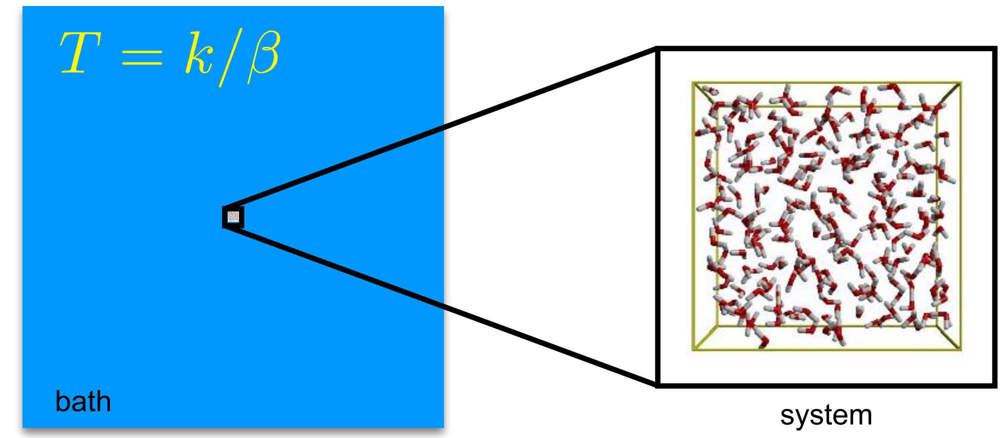
$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

partition function

$$Z = \sum_i e^{-\beta E_i}$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

micro-states of system

probability of micro state i proportional to number of micro-states of bath

$$p_i = \mathrm{const} \cdot \exp[S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i)/k]$$

Taylor expansion of S_{bath} around E^{tot}

$$\frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}} - E_i) = \frac{1}{k} S_{\mathrm{bath}}(E^{\mathrm{tot}}) - \beta E_i$$

probability of micro state i

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

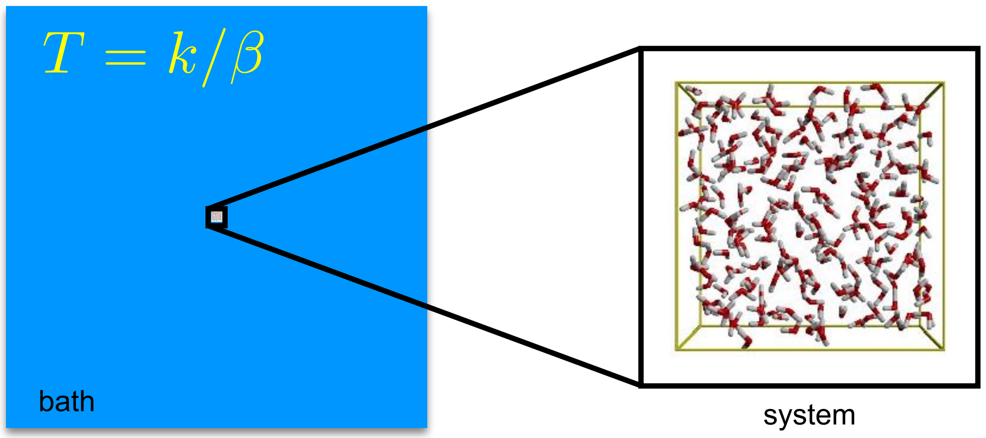
partition function

$$Z = \sum_i e^{-\beta E_i}$$

from microscopic to macroscopic with partition function

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

entropy of system

probability of micro-state i

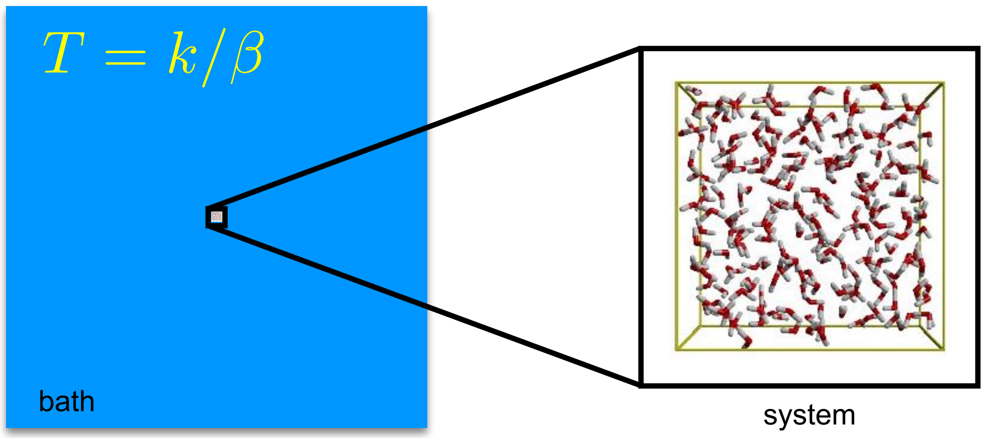
$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath

entropy of system



probability of micro-state i

$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

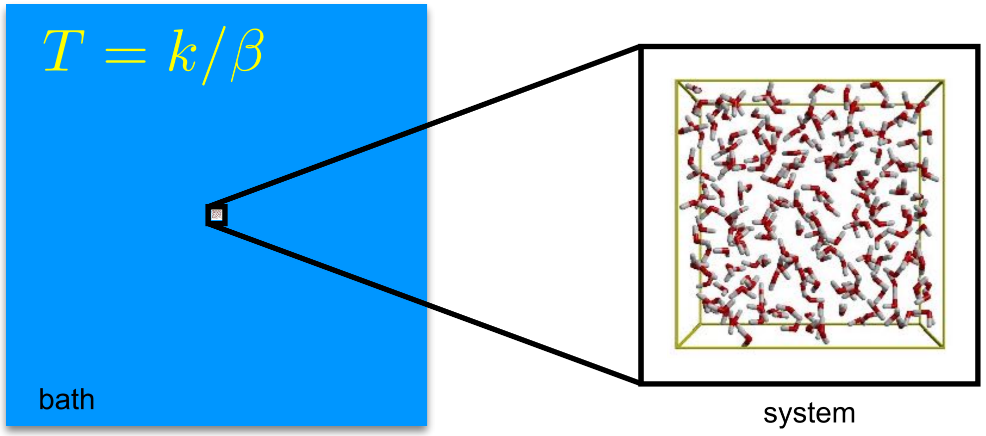
average energy of system

$$\langle E \rangle =$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



entropy of system

probability of micro-state i

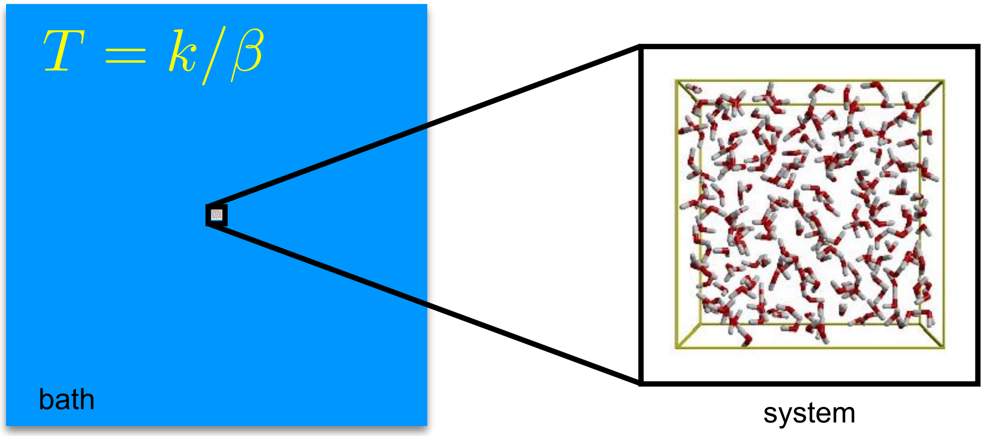
$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

average energy of system

$$\langle E \rangle = \sum_i p_i E_i$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

entropy of system

probability of micro-state i

$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

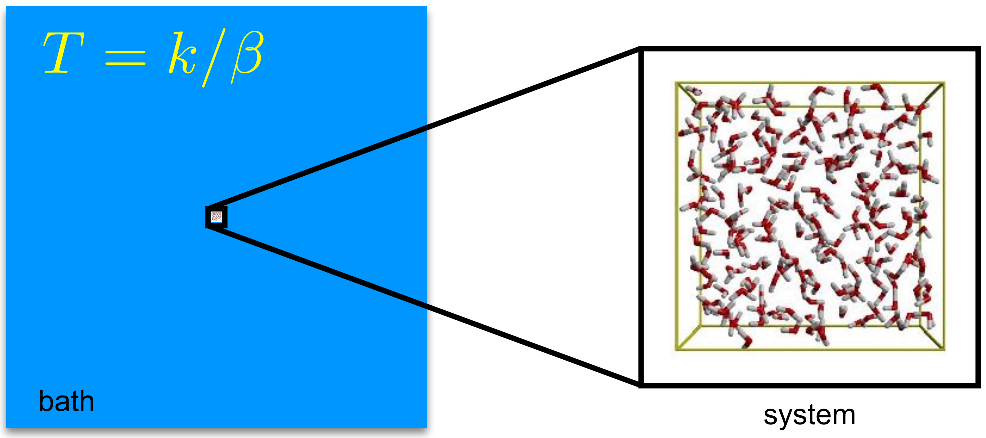
average energy of system

$$\langle E \rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



entropy of system

probability of micro-state i

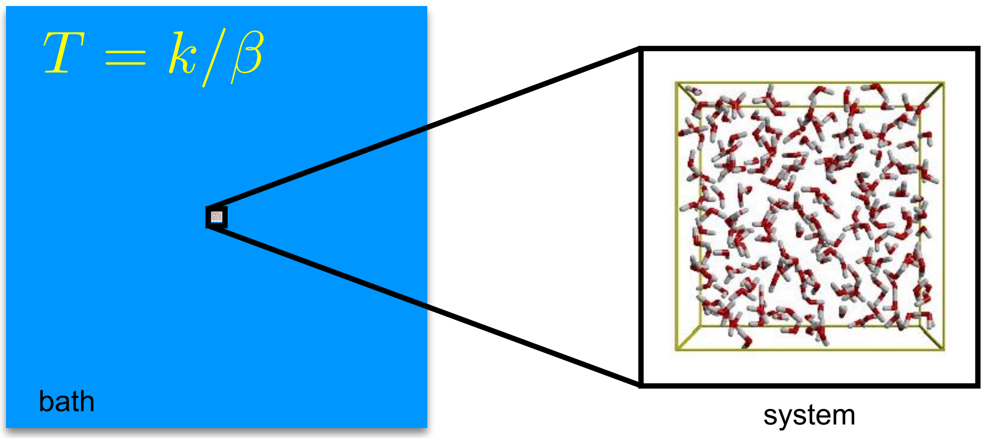
$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

average energy of system

$$\langle E \rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial \ln Z}{\partial \beta}$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

entropy of system

probability of micro state i

$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

average energy of system

$$\langle E \rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial \ln Z}{\partial \beta}$$

what about entropy?