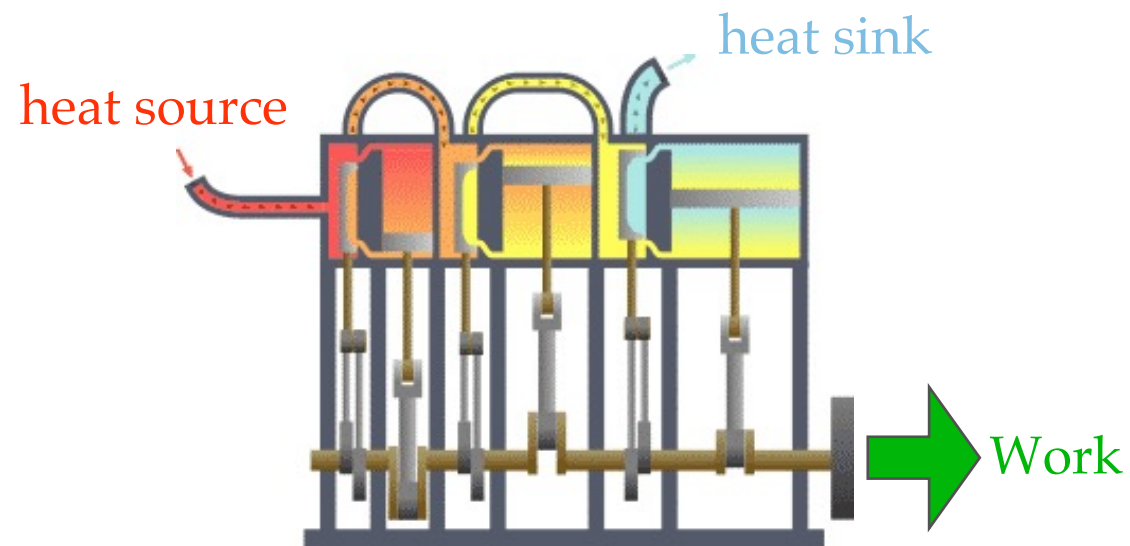


THERMODYNAMICS

MIKLÓS KELLERMAYER

WHAT IS THERMODYNAMICS?



Branch of physics studying the effects of changes in temperature, pressure and volume (energy changes).

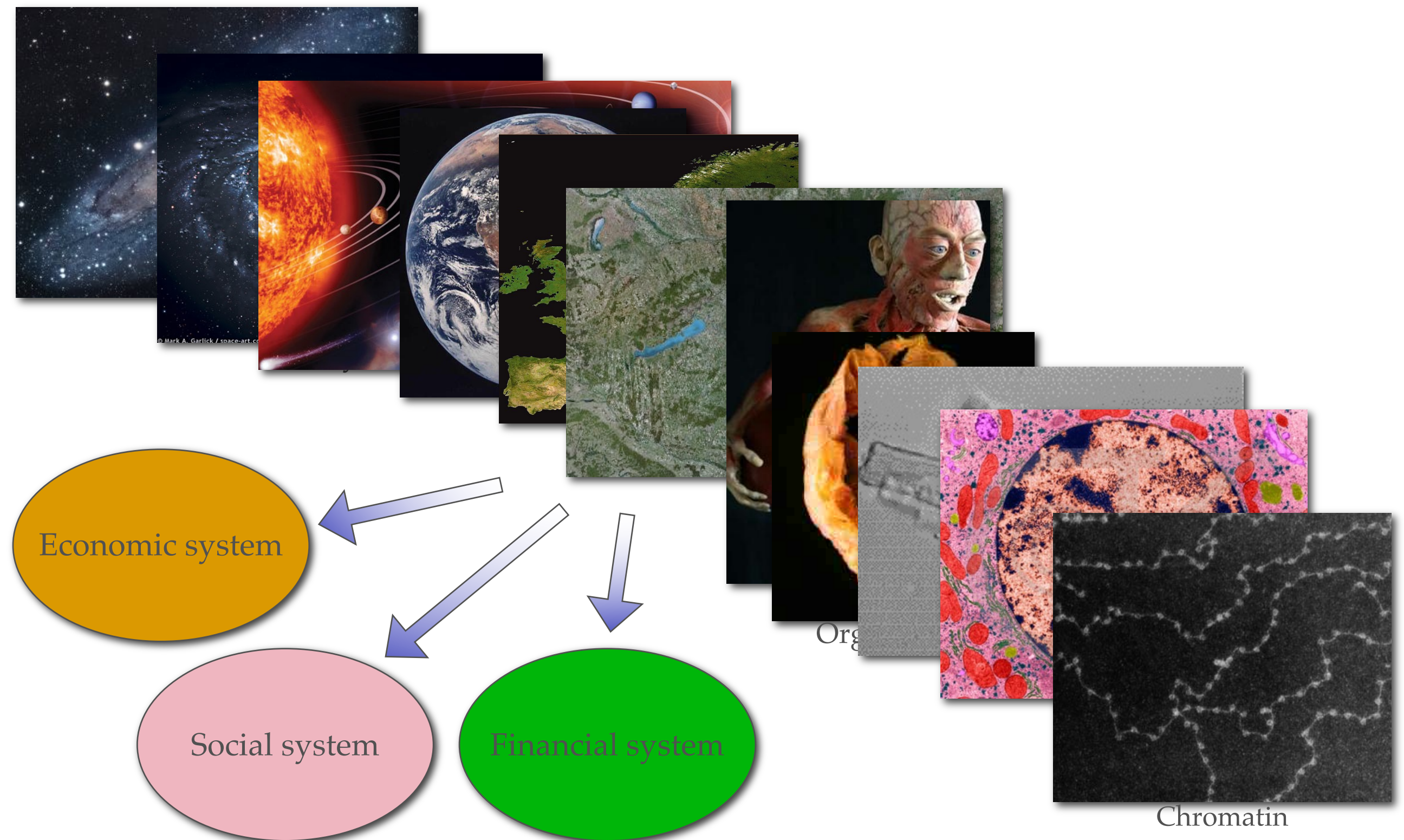
Therme (Gr) heat, *dynamis* (Gr) power.

- Its importance stems from its generality.
- It reveals the driving forces behind natural phenomena.
- Due to its generalizations, it has abstract, complex and difficult-to-understand concepts.

“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don’t understand it, but by that time your are so used to it, it doesn’t bother you any more.”

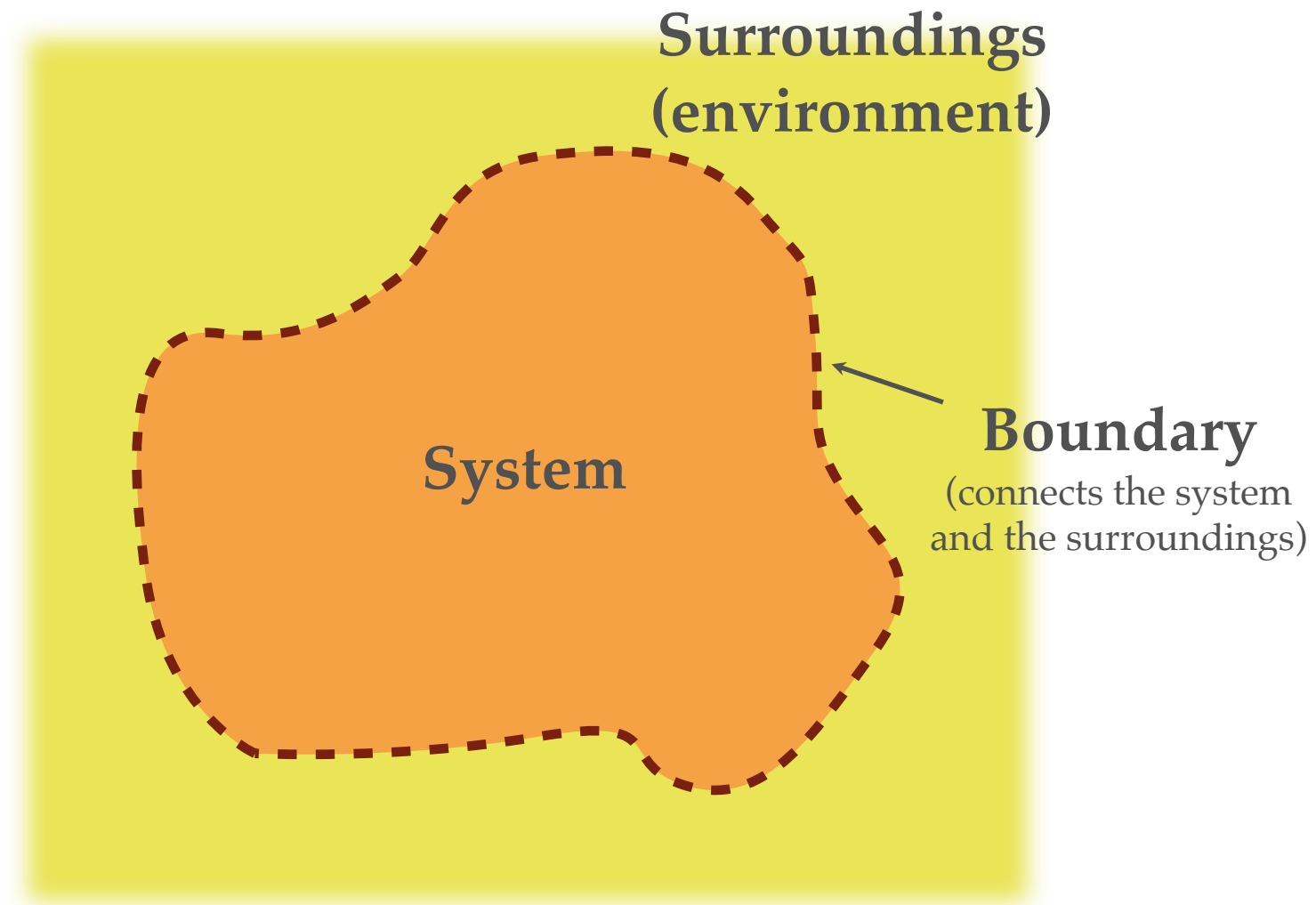
-Arnold Sommerfeld

THERMODYNAMIC SYSTEM



ABSTRACTION OF THE THERMODYNAMIC SYSTEM

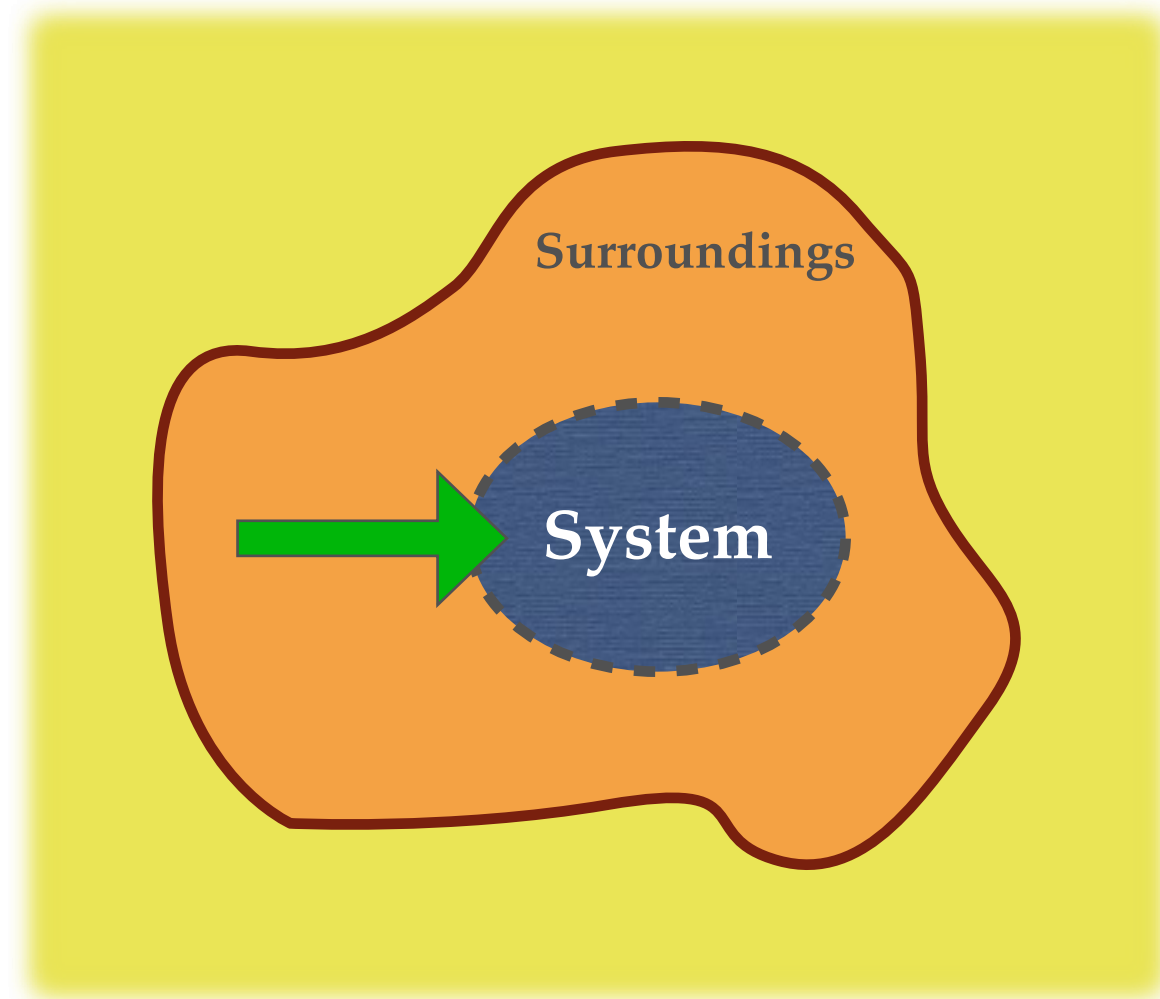
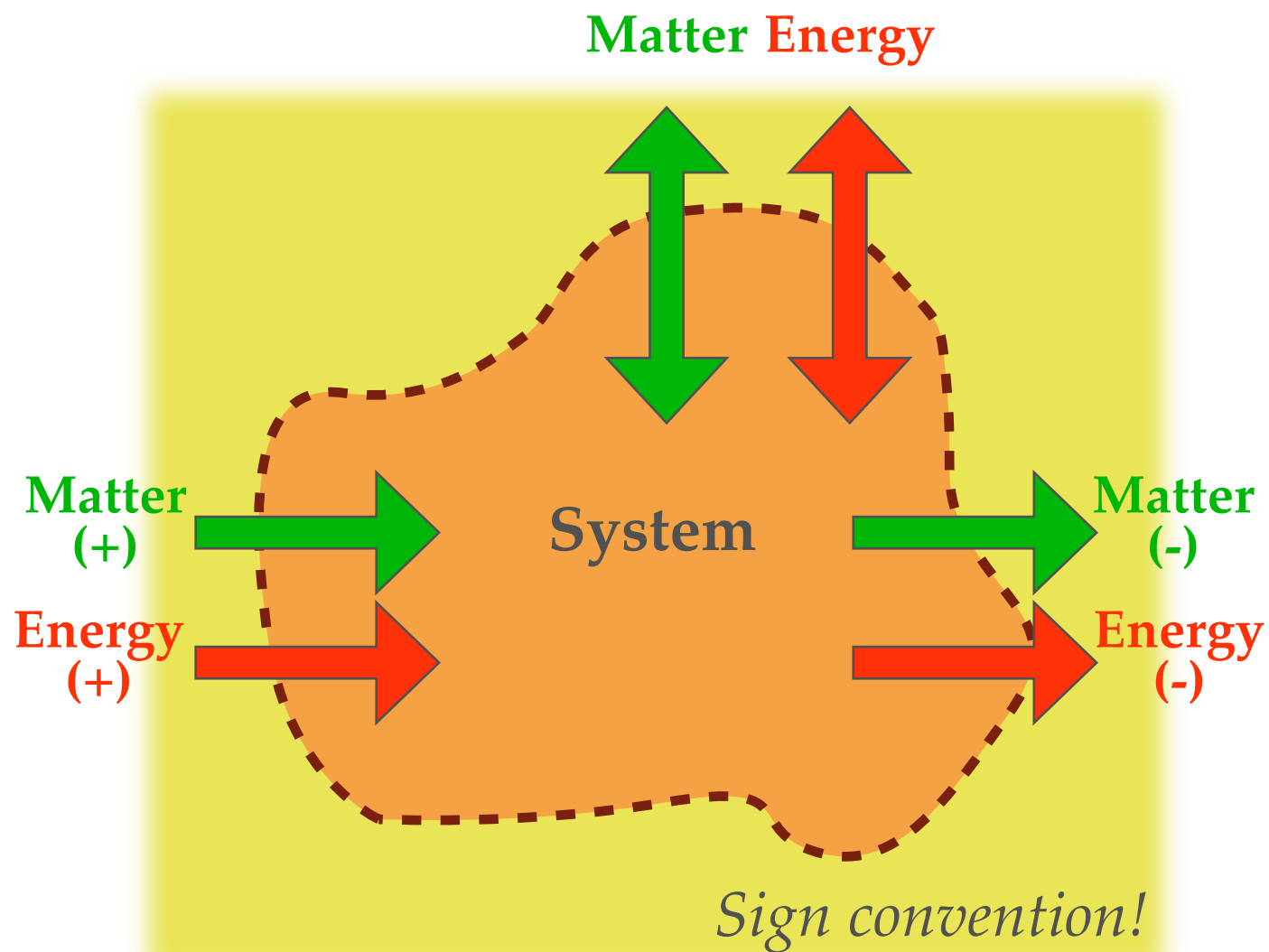
Definition: the thermodynamic system is the part of nature under investigation.



THE THERMODYNAMIC SYSTEM INTERACTS WITH THE SURROUNDINGS

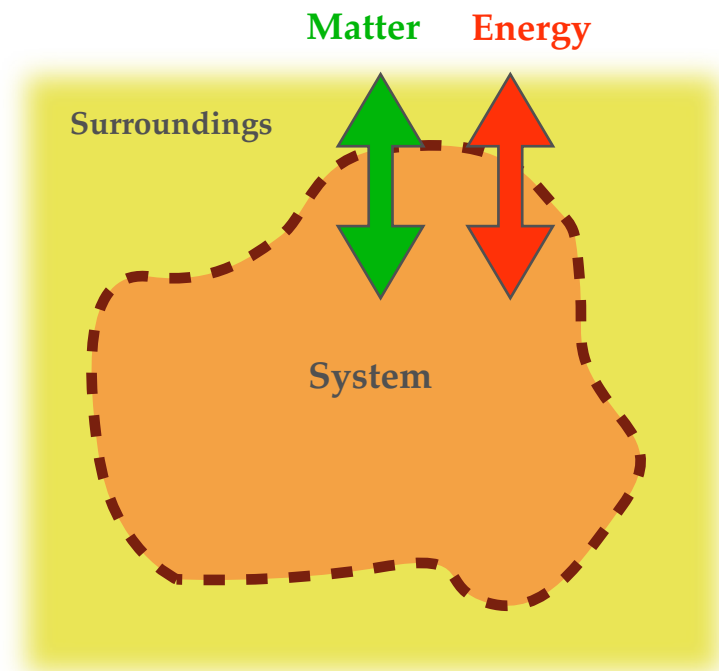
Exchange of matter and energy may occur across the boundary.

Defining the thermodynamic system has consequences for processes.



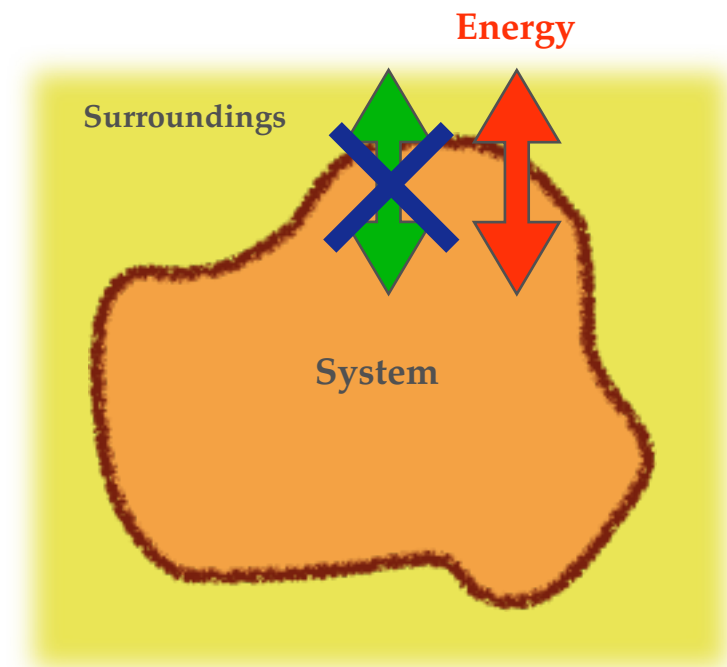
TYPES OF THERMODYNAMIC SYSTEMS

OPEN

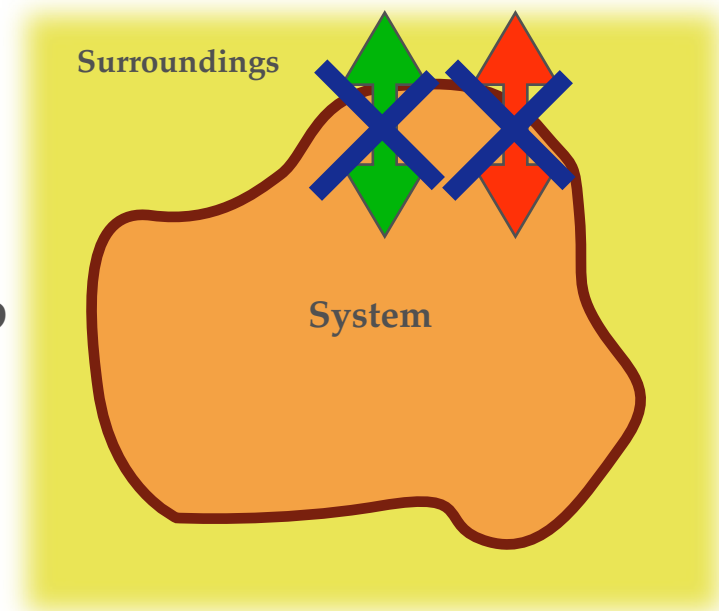


Living organisms are open systems

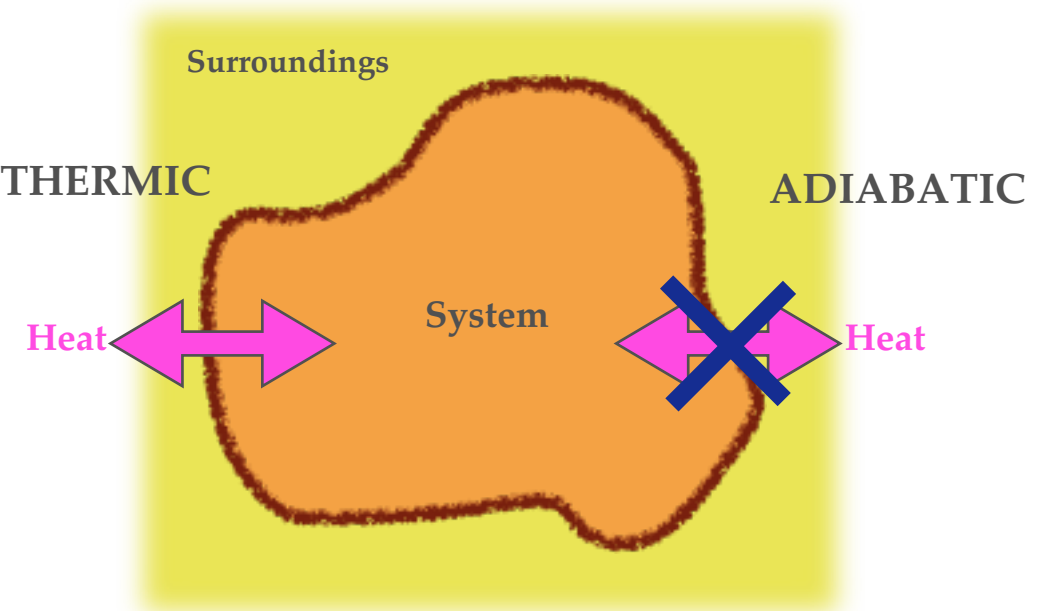
CLOSED



ISOLATED



DIATHERMIC

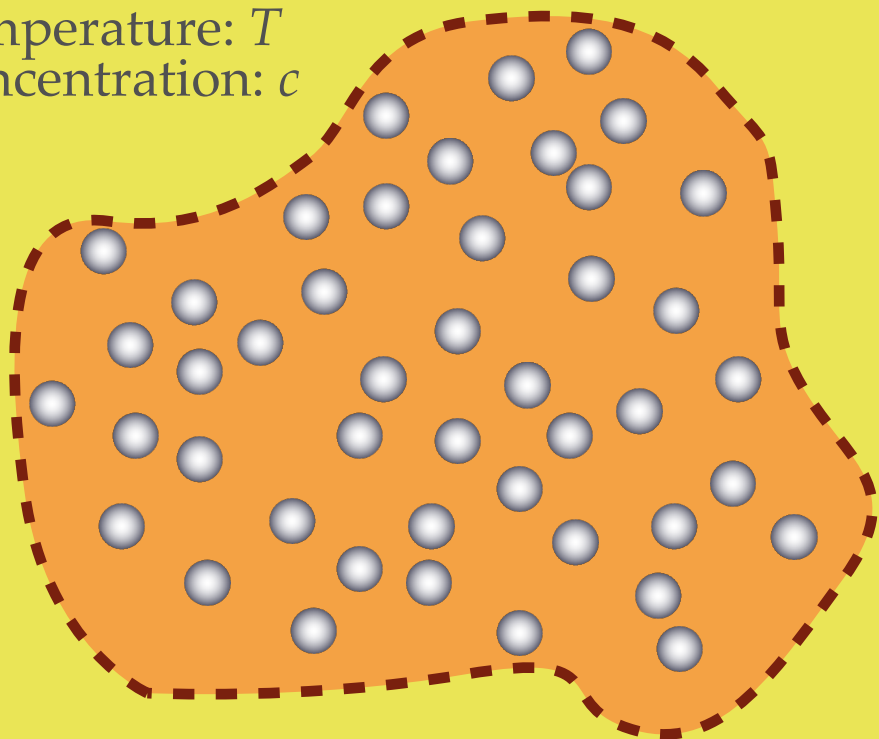


ADIABATIC

CHARACTERIZATION OF THE THERMODYNAMIC SYSTEM

Macroscopic characterization:
state variables - explicitly
determine the *state* of the system.

Pressure: p
Volume: V
Temperature: T
Concentration: c



Universal gas law: $pV=nRT$

- *Extensive* variables: their value is proportional to the size of the system
- *Intensive* variables: their value is independent of the size of the system

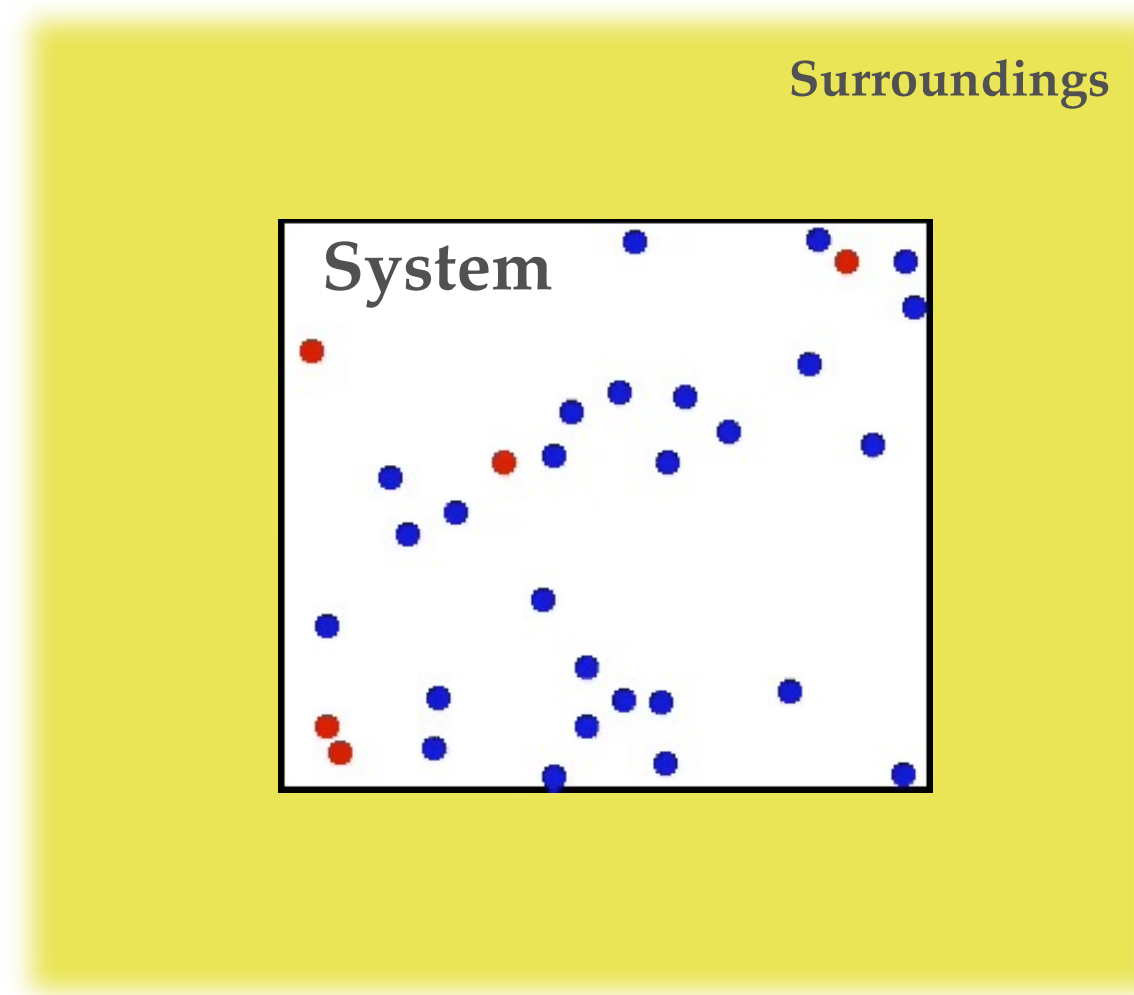
Extensive variable	Intensive variable	Product: energy change
Volume (V)	Pressure (p)	Volumetric work ($p\Delta V$)
Matter (n)	Chemical potential (μ)	Work of material transport ($\mu\Delta n$)
Charge (Q)	Electric potential (ϕ)	Electric work ($\phi\Delta Q$)
Entropy (disorder, S)	Temperature (T)	Heat exchange ($T\Delta S$)

CHARACTERIZATION OF THE THERMODYNAMIC SYSTEM

Microscopic characterization: internal energy (E)

$$E = E_{el} + E_{vib} + E_{rot} + E_{other}$$

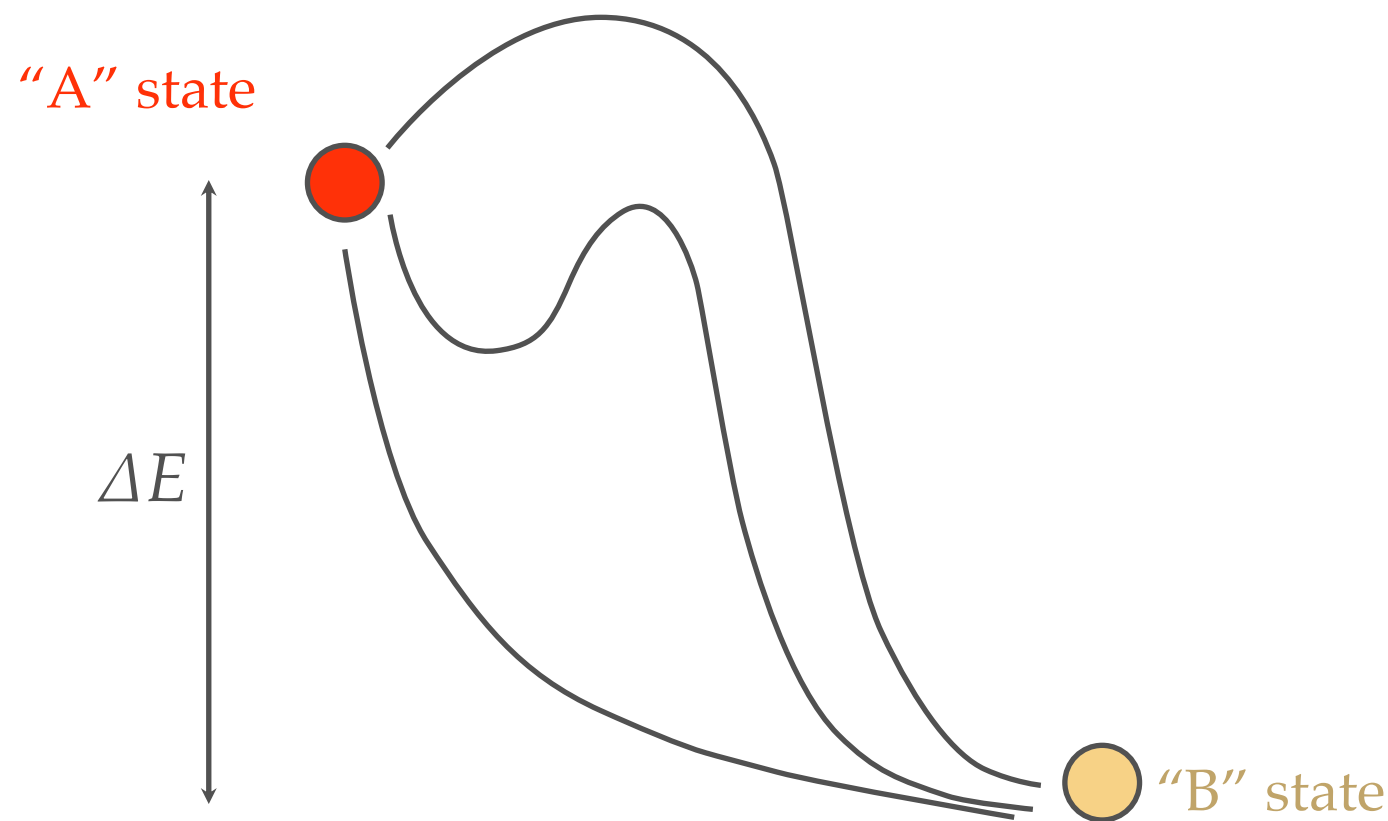
E cannot, only its change (ΔE) can be determined. (N.B.: $E = E_{Tact} - E_{0abs}$)



Internal energy does not contain the potential and kinetic energy of the macroscopic body.

INTERNAL ENERGY (E) IS A “STATE FUNCTION”

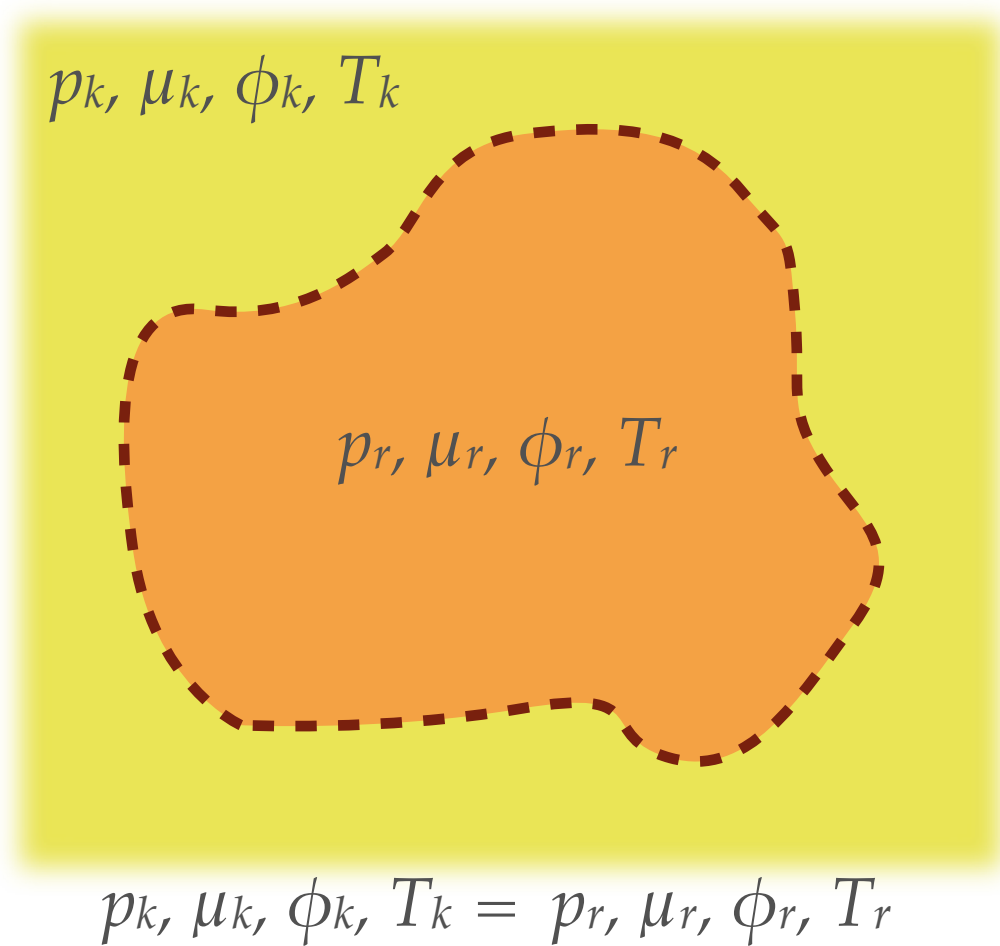
- *State functions*: single-value functions of the state variables (independent variables) of the system.
- Change in the state functions depends only on the initial and final states of the system; it is independent of the path.



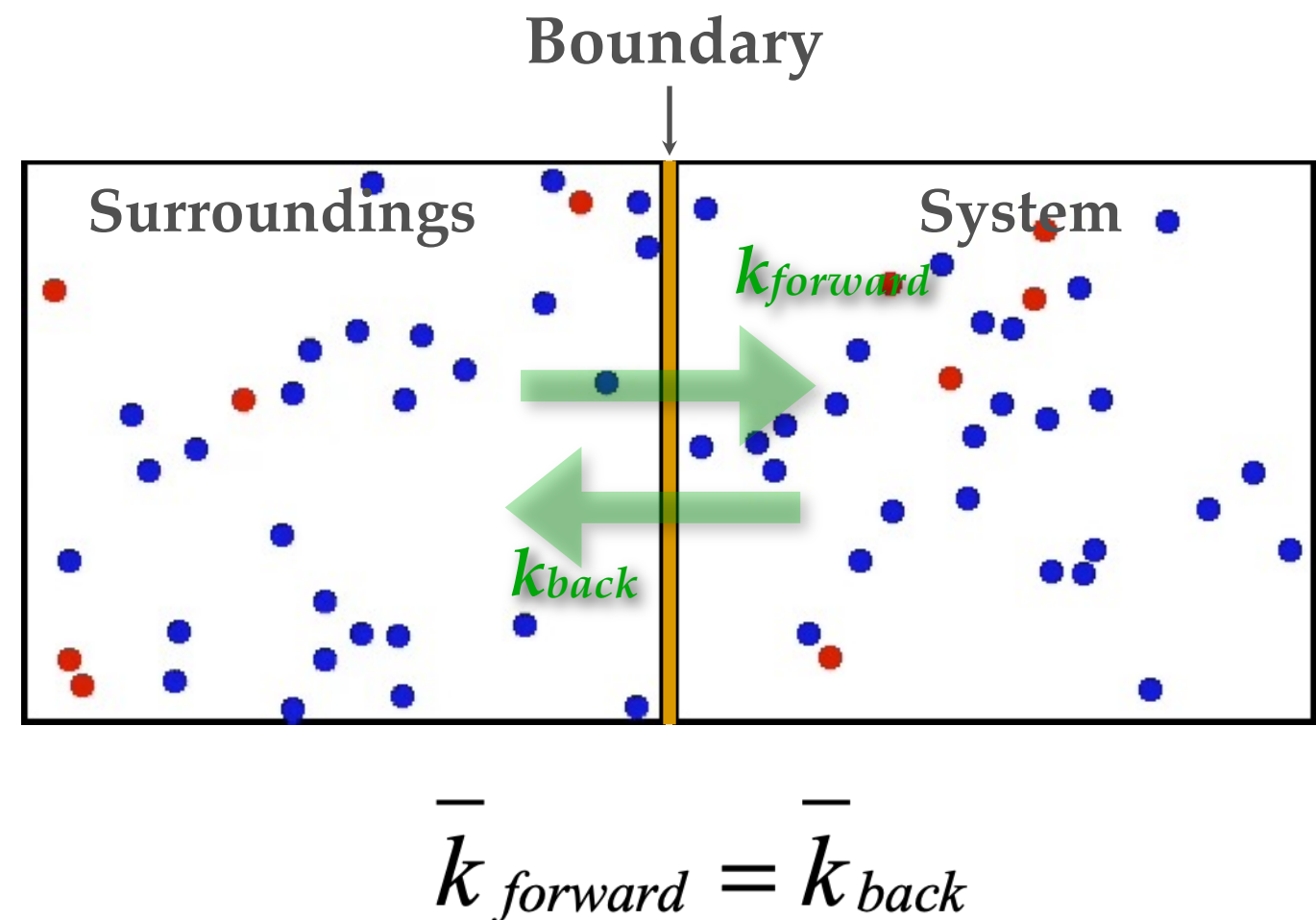
Other state functions: enthalpy (H), Helmholtz free energy (F), Gibbs free energy (G), entropy (S)

EQUILIBRIUM

Macroscopic description: intensive variables are identical (between the system and surroundings, or between different parts of the system)

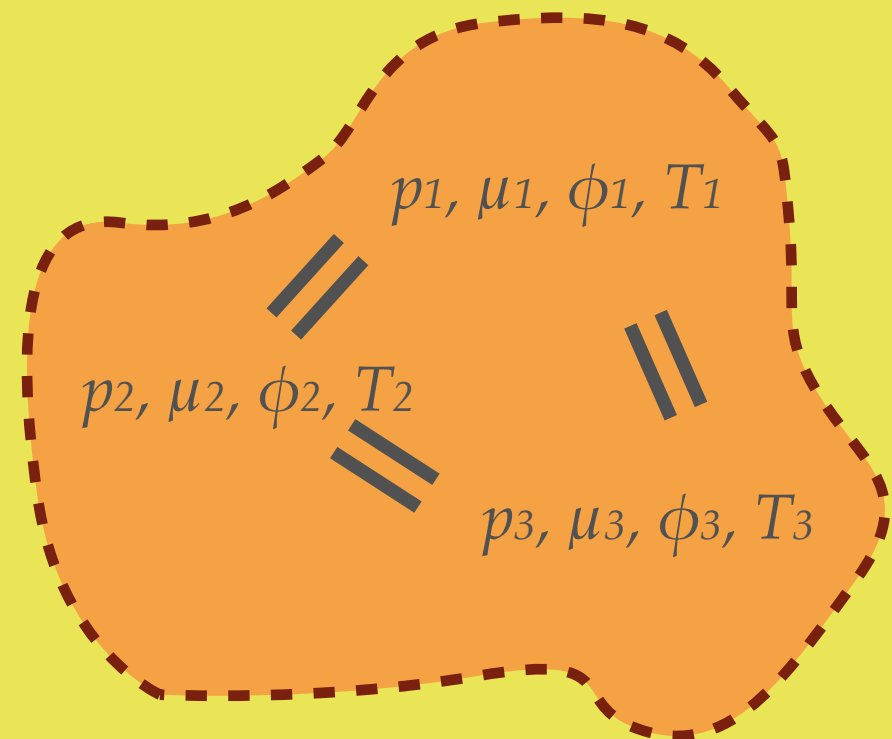
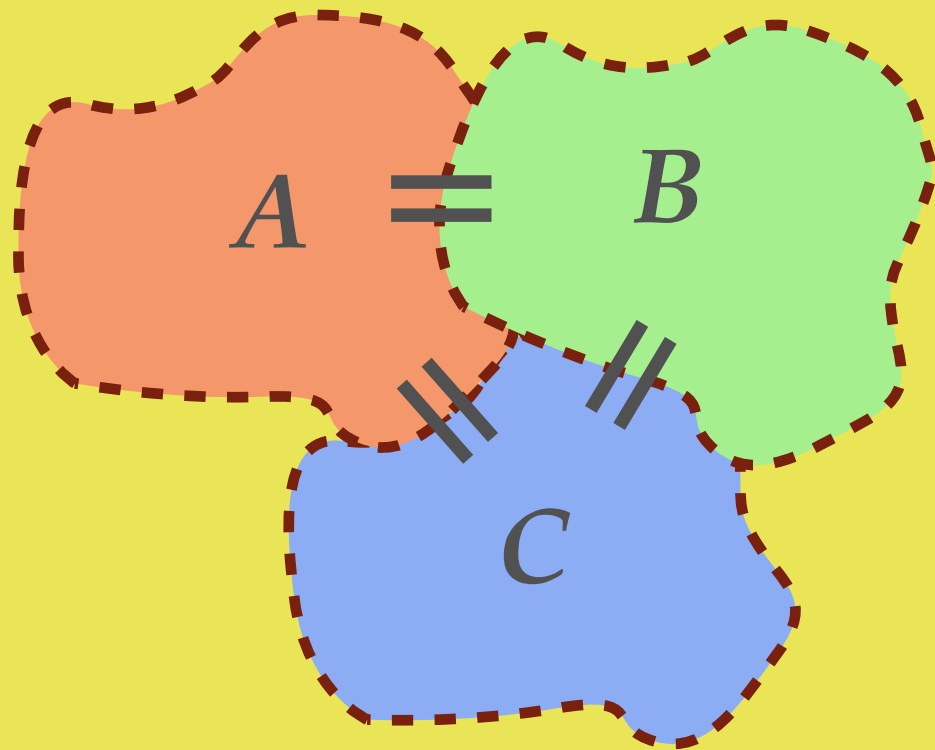


Microscopic description: average rates of forward and reverse reactions are equal.



ZEROth LAW OF THERMODYNAMICS

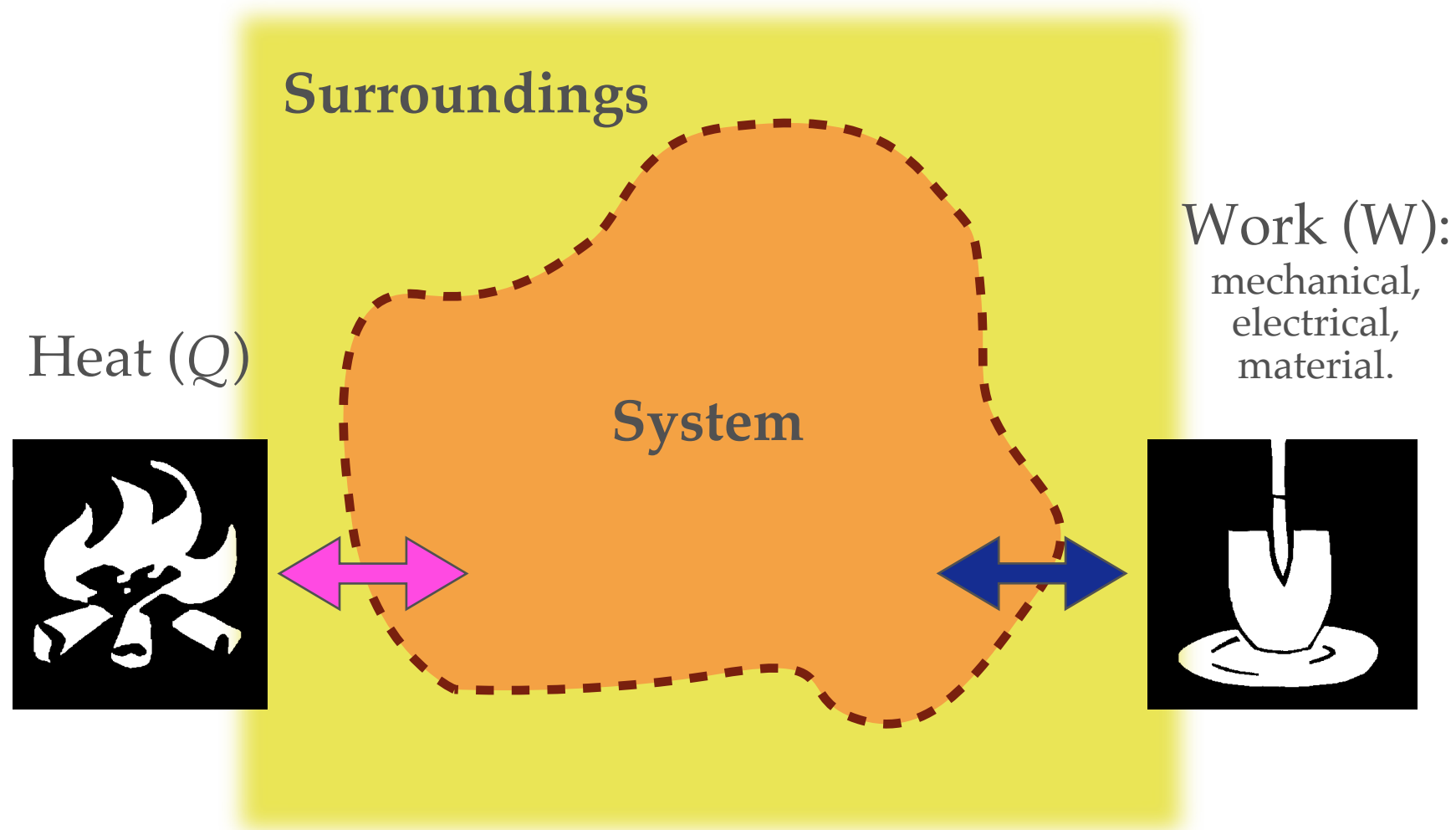
- If two systems (A and B) are independently in equilibrium with a third one (C), then they are in equilibrium with each other as well.
- Between different points of a system in equilibrium, the intensive variables are equal (i.e., there are no thermodynamic currents).



CHANGE

- Thermodynamics is interested in the changes within the system.
- Changes may be evoked by: heating, work.
- Result: internal energy of the system changes.

N.B.: any energy can be completely transformed into heat, but heat can only partly be transformed into work.



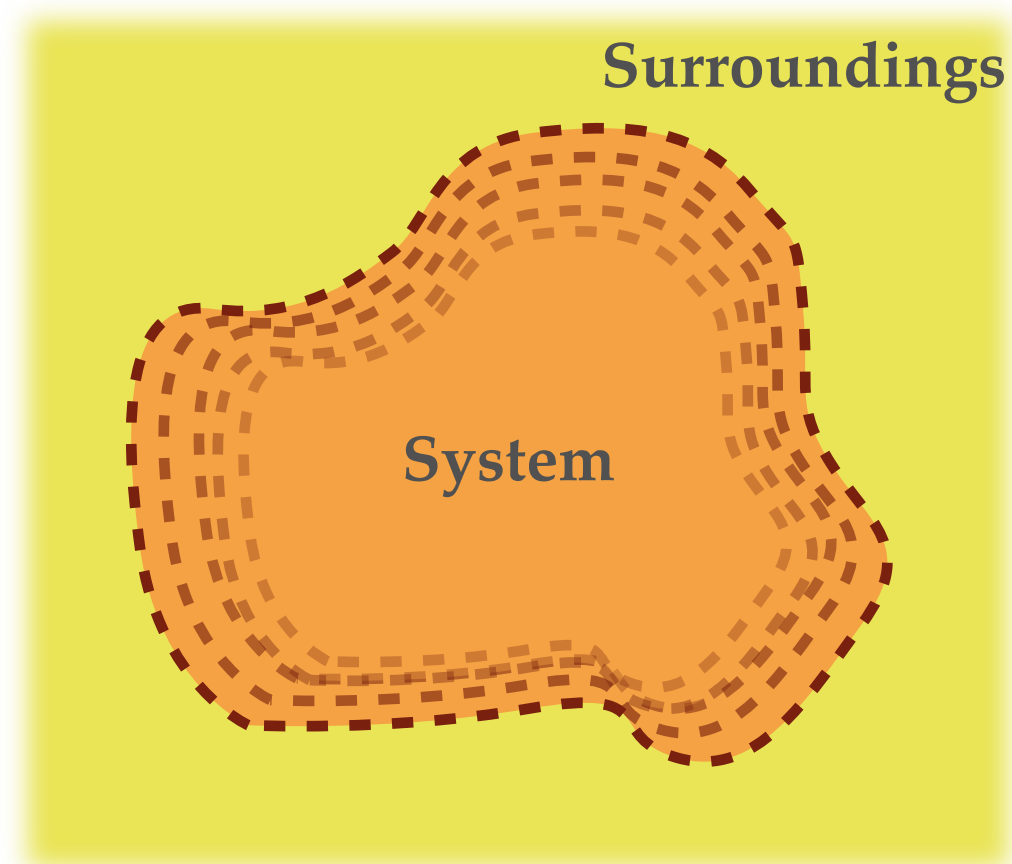
*Sign of change is +, if heat is given to the system or work is done on the system.
Sign of change is -, if the system gives off heat or does work.*

EQUILIBRIUM CHANGE

Definitions:

- Reversible change (reversibly driven process).
- Series of reversible (equilibrium, infinitesimal) steps; the system is in equilibrium during each step of the process.
- “Infinitely slow”, “quasi-static” process.
- There are no permanent (compensating) energy changes in the surroundings (work done by the system and surroundings are equal).

Characteristics: Work done by the system is maximal.



THERMODYNAMIC PROCESSES

- *Isobaric*: at constant pressure.
- *Isochoric (isometric, isovolumetric)*: at constant volume.
- *Isothermic*: at constant temperature.
- *Adiabatic*: no heat exchange.
- *Isentropic*: at constant entropy.
- *Isenthalpic*: at constant enthalpy.
- *“Steady state”*: at constant internal energy.

FIRST LAW OF THERMODYNAMICS

- Law of *conservation of energy*.
- Energy may be converted into different forms, but the total energy of the system remains constant.
- The change in the internal energy of the system is the sum of the supplied heat (Q_E) and the work (W) done on the system.

$$E_2 - E_1 = \Delta E$$

Difference between the internal energies of the initial and final states of the system.

$$\Delta E = Q_E + W$$

Work parts: *Volumetric work*
 $W_V = -p\Delta V$

Negative, because in the case of work done on the system $V_2 - V_1 < 0$.

Electric work:
 $W_Q = \phi \Delta Q$

Material transport:
 $W_n = \mu \Delta n$

Generalized:
 $W^i = y^i_{\text{int}} \Delta x^i_{\text{ext}}$

Isochoric process ($\Delta V = 0$):

$$\Delta E = Q_V$$

Change in internal energy is caused only by the heat exchange.

Isobaric process ($p = \text{constant}$):

$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

N.B.: any energy can be completely transformed into heat, but heat can only partly be transformed into work.

ENTHALPY

- “Heat content” (H)
- Total heat absorbed by the system at constant pressure.
- Thermodynamic state function, by the help of which the useful work done at constant pressure (i.e., in an isobaric process) may be calculated.
- *enthalpein* (Gr) to heat

$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

Internal energy change of the system during isobaric process.

Enthalpy: $H = E + pV$

E, p, V : equilibrium internal energy, pressure and volume.

Enthalpy change: $\Delta H = \Delta E + p\Delta V$

Isobaric process
($p = \text{constant}$):

$$\Delta H = Q_p$$

If there are no other energy changes beside volumetric work.
 Q_p = Reaction heat at constant pressure.

Isochoric process
($V = \text{constant}$):

$$\Delta E = Q_V$$

Volumetric work = 0.
 Q_V = Reaction heat at constant volume.

Standard state: 25 °C, 1 atm. Standard enthalpy of compounds (ΔH°): reaction heat of 1 mole of compound measured in standard state, at constant pressure.

SECOND LAW OF THERMODYNAMICS

- “Law of entropy.”
- Heat flows spontaneously from regions of high to low temperature.
- In an isolated system only such processes occur spontaneously which tend to equilibrate the respective intensive variables.
- During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.
- Spontaneous processes proceed towards the most probable state (irreversible).
- Statistical law.



The fallen and broken flower pot does not spontaneously return to its original place.



The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

ENTROPY

- *Entropy* (S): unavailability of the system to do useful work. State function (unit: J/K).
- Measure of “*unusable*” energy.
- Measure of thermodynamic probability.
- Measure of *disorder*.
- *entropiein* (Gr) to turn around.
- “Arrow of time”: the entropy of the universe constantly increases.

Phenomenologic description:

Energy change during
thermodynamic processes
(interactions):

$$\Delta E = \sum y^i_{\text{int}} \Delta x^i_{\text{ext}}$$

Product of intensive variables (y) and
extensive variable-changes (Δx).

Energy change during
thermal processes (thermal
interactions):

$$Q_E = T \Delta S$$

Intensive variable: temperature (T)
Extensive variable: entropy change (ΔS)

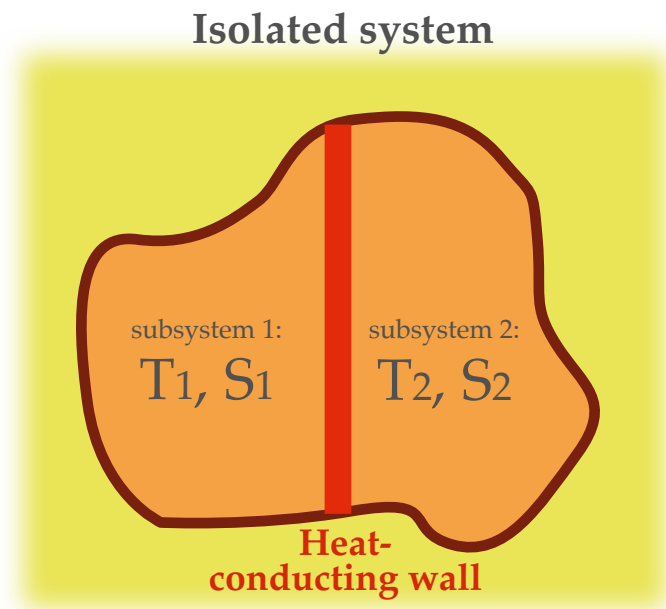
Entropy change:

$$\Delta S = \Delta Q / T$$

Measure of heat exchanged during
reversible (equilibrium) isothermal
process.

ENTROPY

- In isolated system, during temperature equilibration entropy always increases.



$$\Delta E = \Delta(E_1 + E_2) = \Delta E_1 + \Delta E_2 = 0$$

In an isolated system internal energy is constant ($\Delta E = 0$).

$$\Delta E_1 = T_1 \Delta S_1 \quad \Delta E_2 = T_2 \Delta S_2$$

Energy changes during thermal interaction.

$$\Delta S = \Delta S_1 + \Delta S_2$$

Entropy is an extensive variable.

$$\Delta S = \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} = \Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

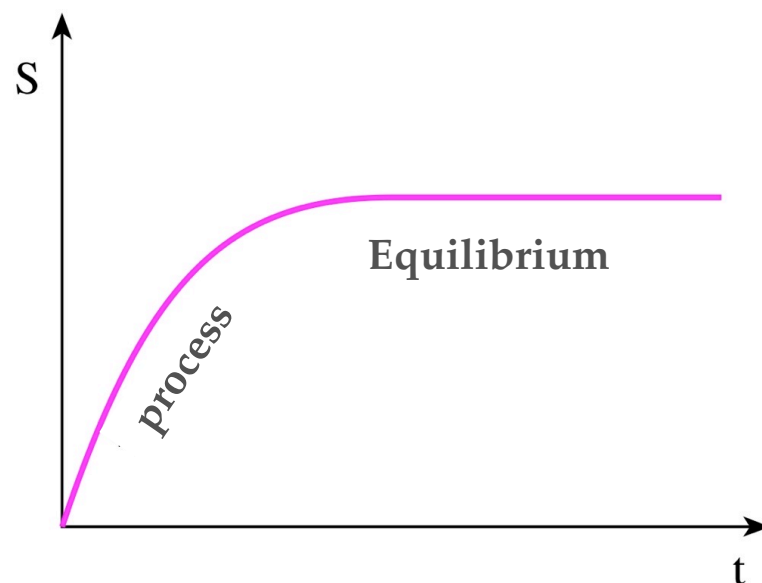
N.B.: $\Delta E_1 = -\Delta E_2$.

$$T_1 > T_2 \quad \text{or} \quad T_1 < T_2 : \Delta S > 0$$

If the initial temperatures are different, *entropy increases*.

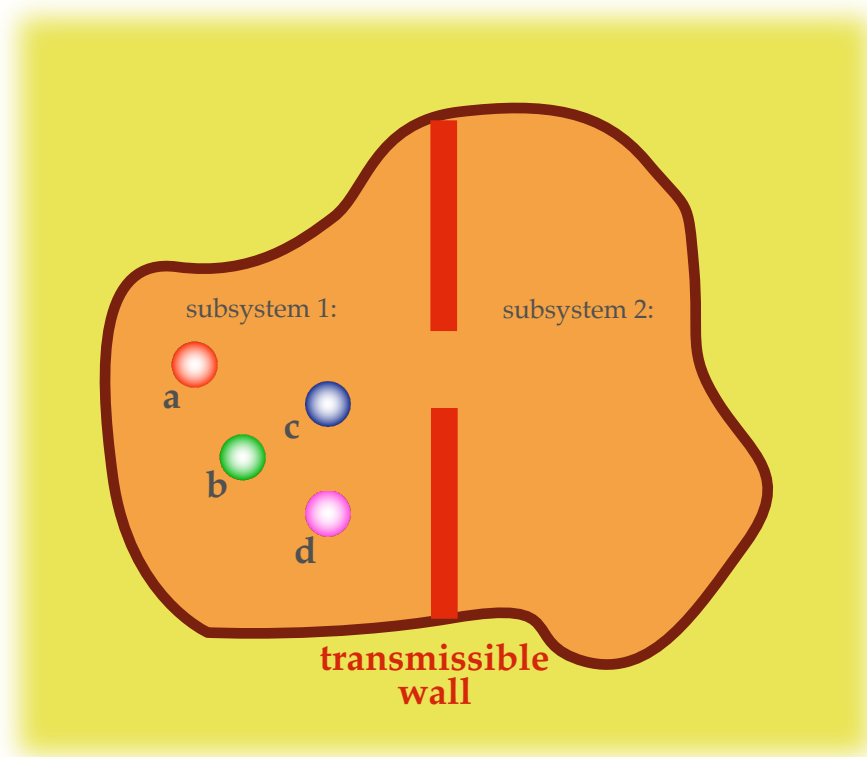
$$T_1 = T_2 : \Delta S = 0$$

If the initial temperatures are equal, entropy does not change.



STATISTICAL INTERPRETATION OF ENTROPY

- *Macrostate*: state of the system defined by state variables (e.g., p , V , T).
- *Microstate*: internal structure of the system (position, velocity of every particle)
- In the *most probable macrostate* the number of microstates is the greatest.
- Number of microstates describing a given macrostate: *thermodynamic probability* (Ω).



Macrostate	number of particles in subsystem 1	structure of subsystem 1	Number of microstates (Ω)
A	4	abcd	1
B	3	abc,abd,acd,bcd	4
C	2	ab, ac, ad, bc, bd, cd	6
D	1	a, b, c, d	4
E	0	-	1

Entropy: $S = k_B \ln \Omega$

k_B = Boltzmann's constant ($1,38 \times 10^{-23}$ J/K)

THIRD LAW OF THERMODYNAMICS

- Nernst's law.
- The entropy of mono-component, crystallizing material at 0 K temperature is 0.

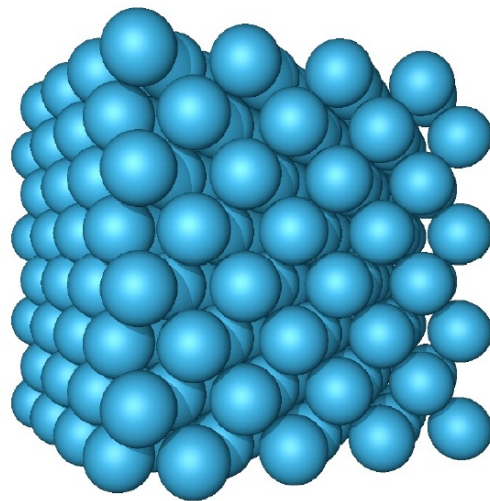
At 0 K thermal motions halt,
there are no thermal crystal faults.

$$\Omega = 1$$

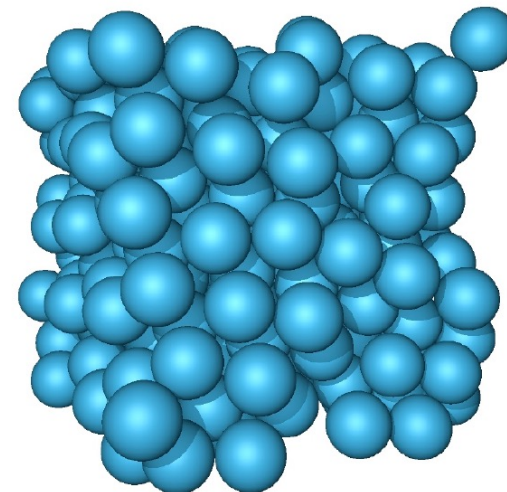
Number of microstates is 1.

Because of mono-component system,
only one type of molecular
arrangement is possible.

$$S = k_B \ln 1 = 0$$

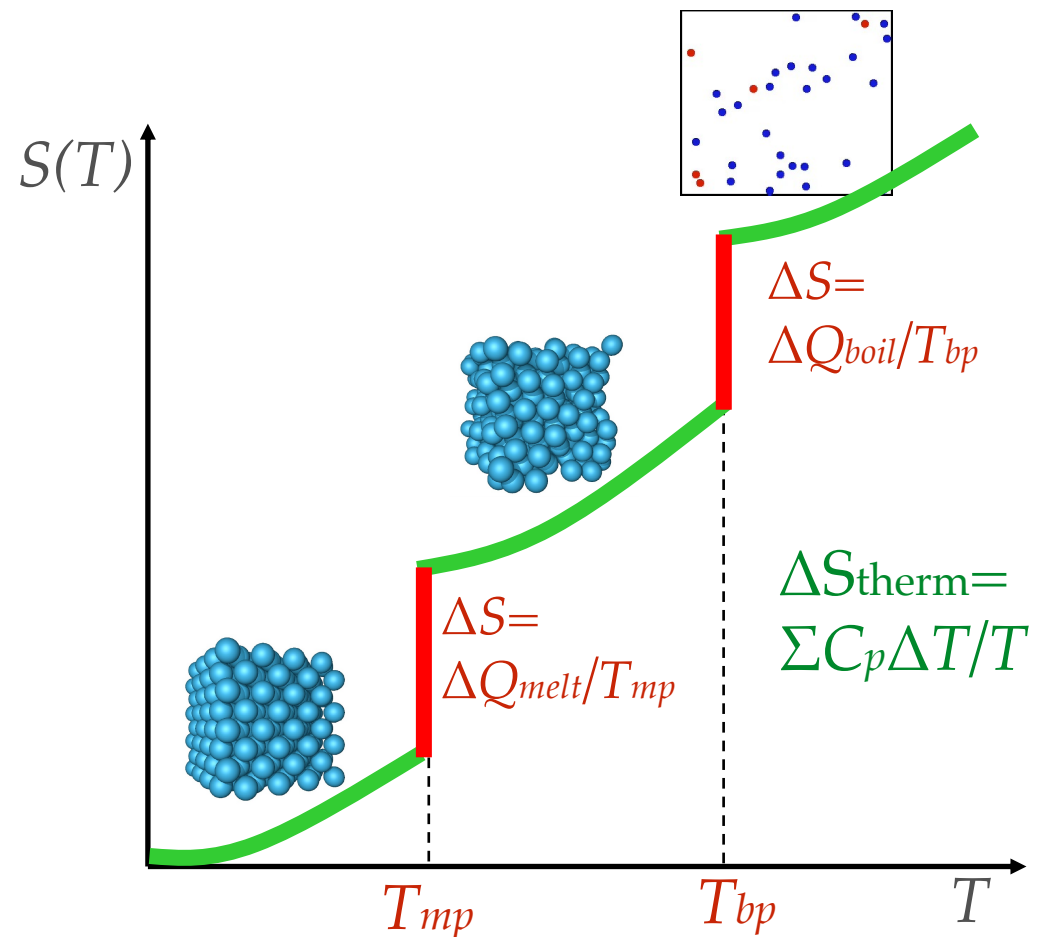
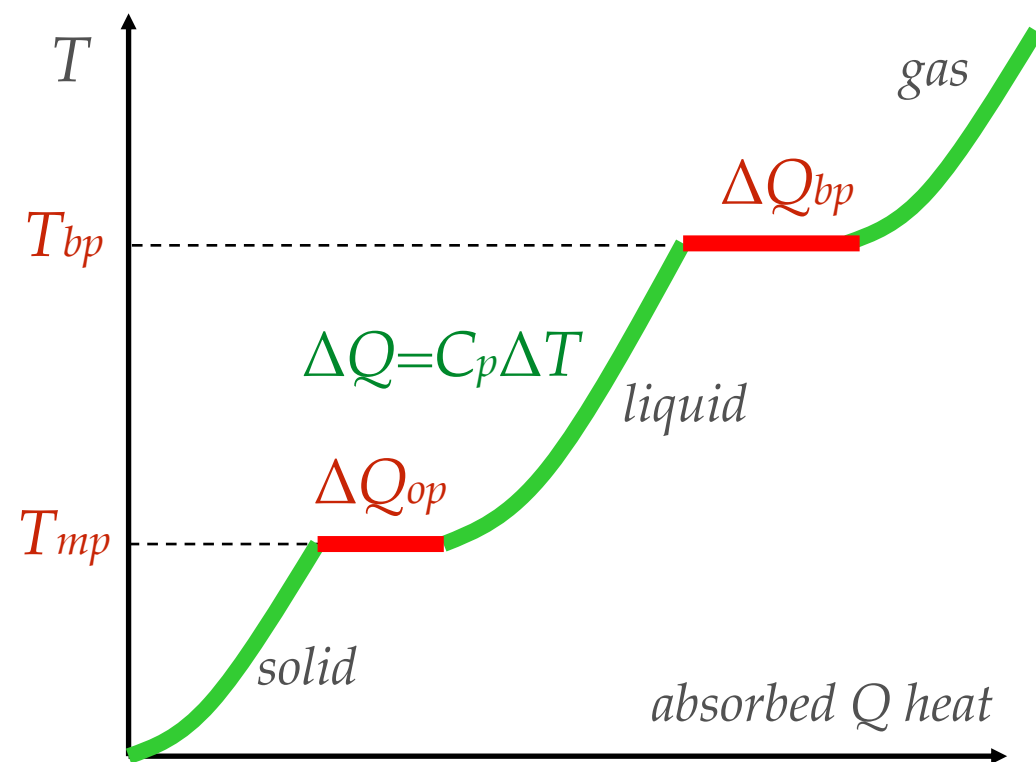
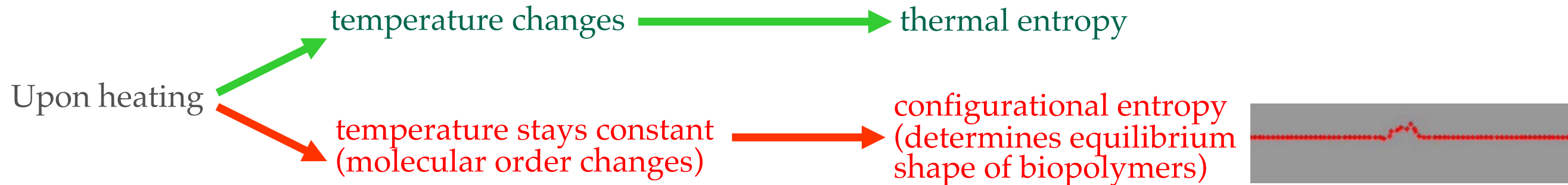


Ordered crystal:
Low entropy ($S=0$ at 0 K)



Disordered liquid:
High entropy

CHANGE IN TEMPERATURE AND ENTROPY DURING THERMAL INTERACTION



FREE ENERGY AND FREE ENTHALPY

- *Free energy*: Helmholtz free energy (F)
- Useful work extractable from isothermic, **isochoric** (constant volume) (not isolated) system.
- State function

$$F = E - TS$$

F : Helmholtz free energy
 E : internal energy
 T : absolute temperature
 S : entropy

Relationship between thermodynamic state functions:

H		
E		pV
TS	F	pV
TS	G	

- *Free enthalpy*: Gibbs free energy (G), Gibbs potential.
- Useful work extractable from isothermic, **isobaric** (not isolated) system.
- State function

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$$

$$\Delta S_{sur} = -\Delta H_{sys}/T$$

$$\Delta S_{tot} = \Delta S_{sys} - \Delta H_{sys}/T$$

$$-T\Delta S_{tot} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

S_{tot} = total entropy (entropy of the universe)
 S_{sys} = system entropy
 S_{sur} = entropy of surroundings
 H_{sys} = system enthalpy

$$H = G + TS$$

Enthalpy = $\frac{\text{useful work}}{\text{change}}$ + unusable energy

During spontaneous processes the entropy of the universe increases ($\Delta S_{tot} > 0$):

$$\Delta S_{sys} > \Delta H_{sys}/T$$

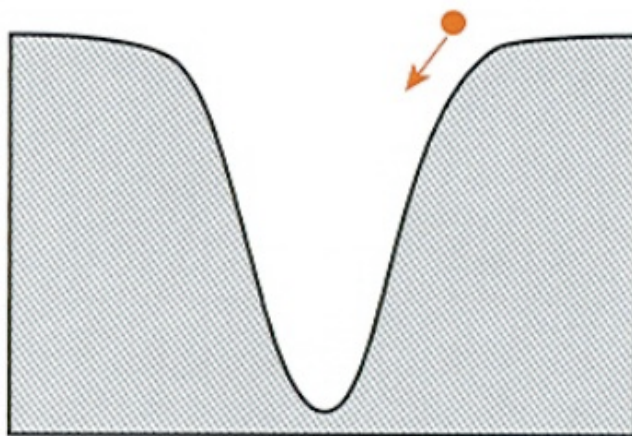
During spontaneous processes, Gibbs free energy decreases ($\Delta G < 0$):

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys} < 0$$

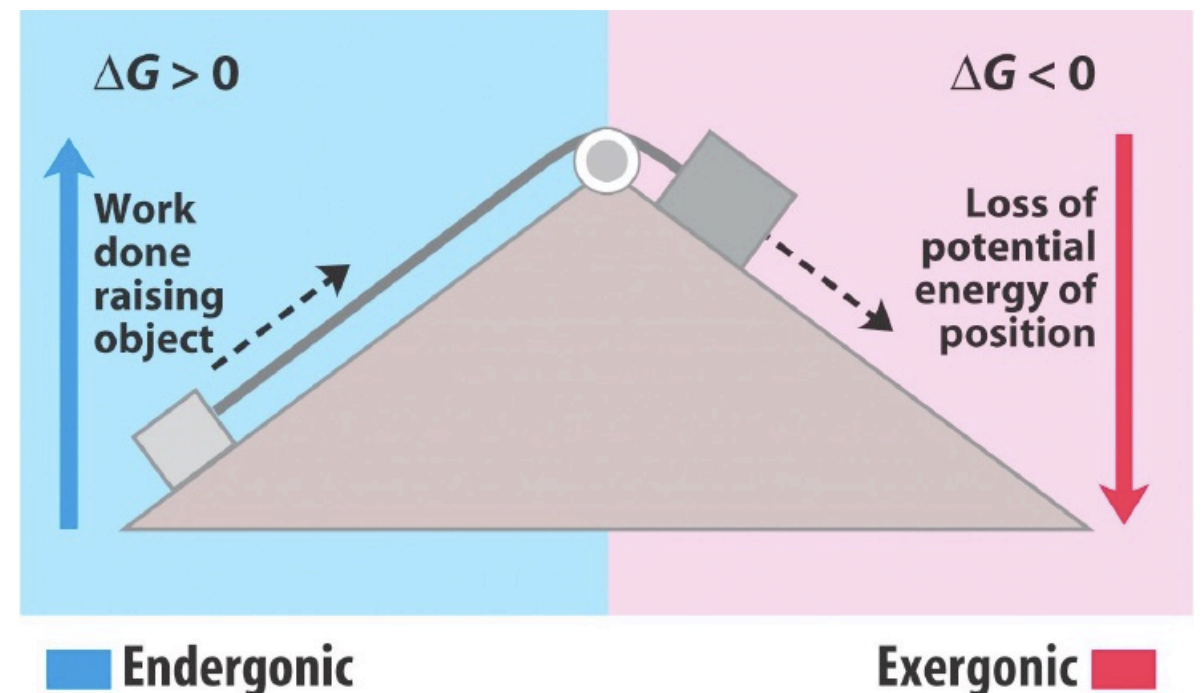
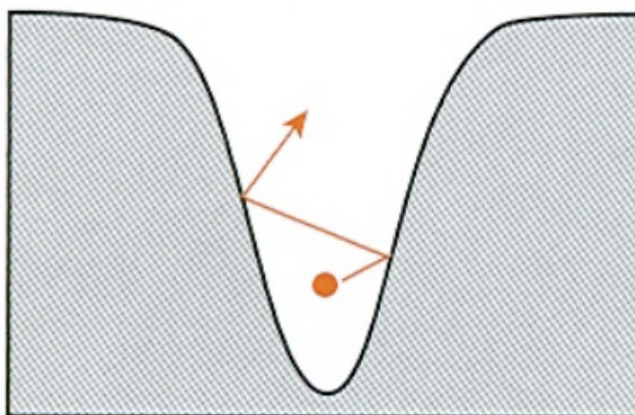
SIGNIFICANCE OF ENTROPY AND GIBBS FREE ENERGY

- Spontaneous processes are those, during which Gibbs free energy decreases ($\Delta G < 0$) and the entropy of the universe increases ($S_{tot} > 0$).

Decrease in free energy:
stabilizes



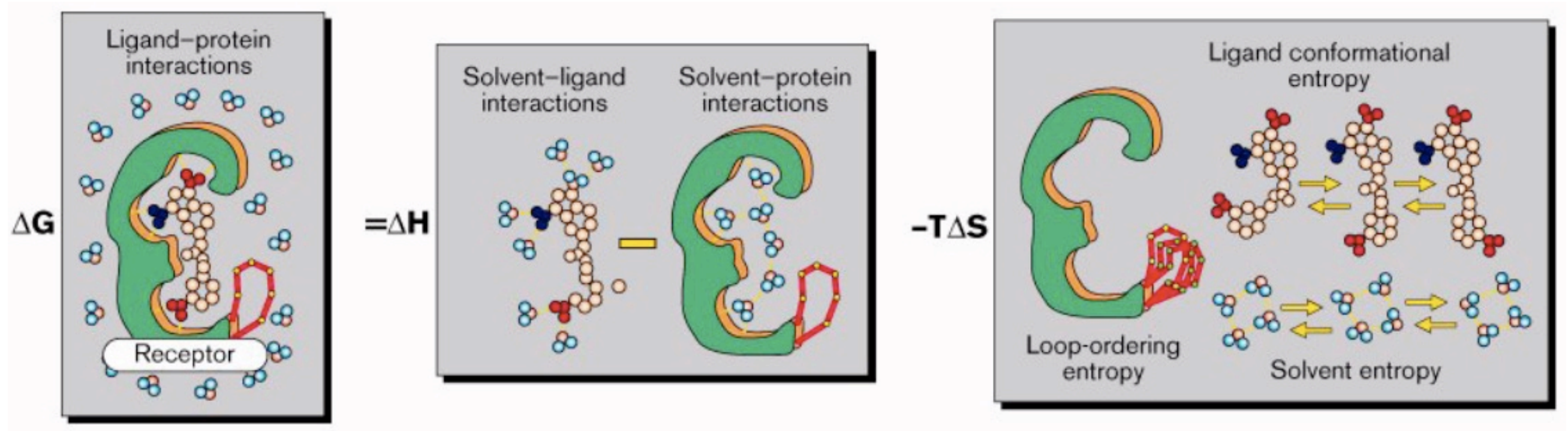
Increase in entropy:
randomizes



- Useful work is done by exergonic processes.
- Endergonic processes can be driven by coupling to exergonic processes.
- Entropy can be decreased locally.
- Life consumes entropy (its entropy is decreased at the expense of increasing total entropy).

SIGNIFICANCE OF ENTROPY AND GIBBS FREE ENERGY

- *Enthalpic* component: molecular interactions (covalent, van der Waals, electrostatic, hydrogen bond)
- *Entropic* component: internal structural disorder (arrangement of solvent molecules and counter-ions, degrees of freedom, rotational and translational arrangements)



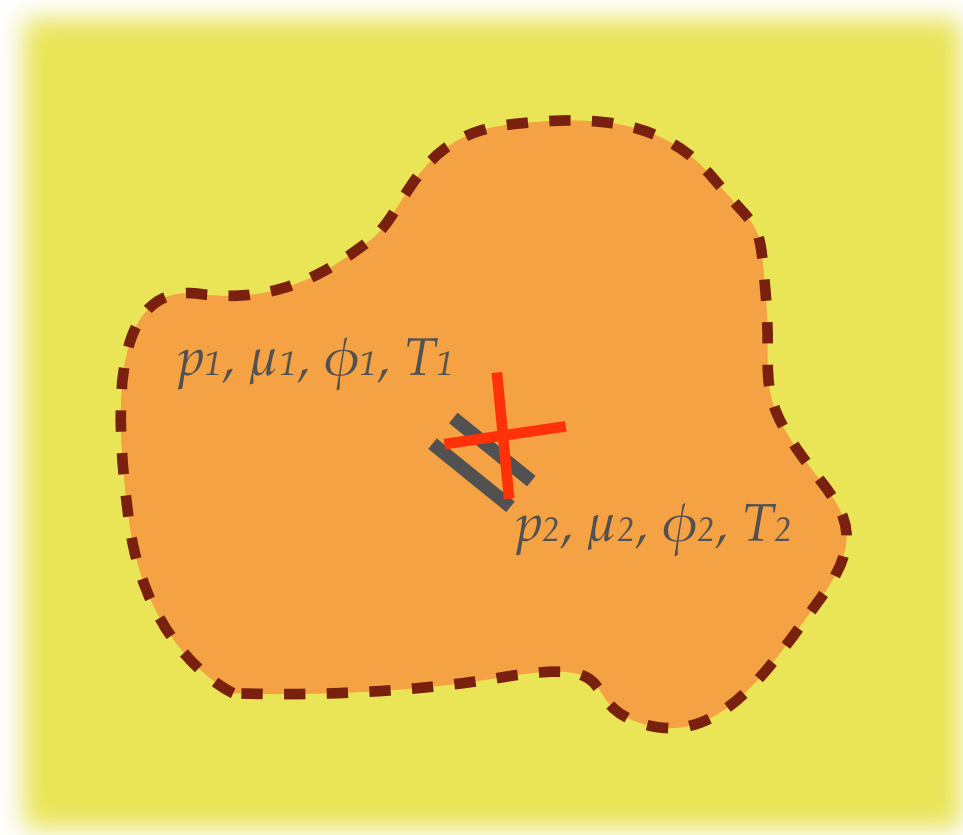
Gibbs free-energy change associated with receptor-ligand interaction binding

Enthalpic component: changes in molecular interactions

Entropic component: conformational changes

THERMODYNAMIC CURRENTS

- Natural processes are rarely reversible.
- If there are inequalities in the intensive variables at different locations within the system, thermodynamic **currents** arise.
- Thermodynamic currents (**irreversible** processes) aim at the restoration of equilibrium.
- Irreversible processes are described by irreversible thermodynamics.



Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Heat flow	Temperature (T)	$J_E = -\lambda \frac{\Delta T}{\Delta x}$	Fourier
Volumetric flow	Pressure (p)	$J_V = -\frac{R^2}{8\eta} \frac{\Delta p}{\Delta x}$	Hagen-Poiseuille
Electric current	Electric potential (ϕ)	$J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$	Ohm
Material transport (diffusion)	Chemical potential (μ)	$J_n = -D \frac{\Delta c}{\Delta x}$	Fick

ONSAGER'S LINEAR FUNCTION

- Lars Onsager (1903-1976), Nobel prize (1968)
- General relationship between transport processes.

$$J=LX$$

Flow intensity of transported
extensive variable
(thermodynamic current, J)

$$J = \frac{\Delta x_{ext}}{A\Delta t}$$

=

Coefficient of
conductance
(thermodynamic
coefficient, L)

x

Change in intensive variable
across a distance of Δx
("gradient", thermodynamic force,

$$X = -\frac{\Delta y_{int}}{\Delta x}$$

A thermodynamic current may be evoked by several different intensive variables. E.g., thermodiffusion (material transport evoked by temperature gradient).

Feedback



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