Definition of ENTROPY (valid also for nonequilibrium states!)

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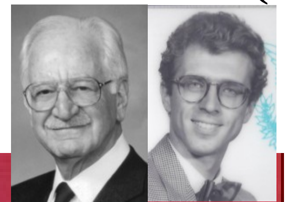

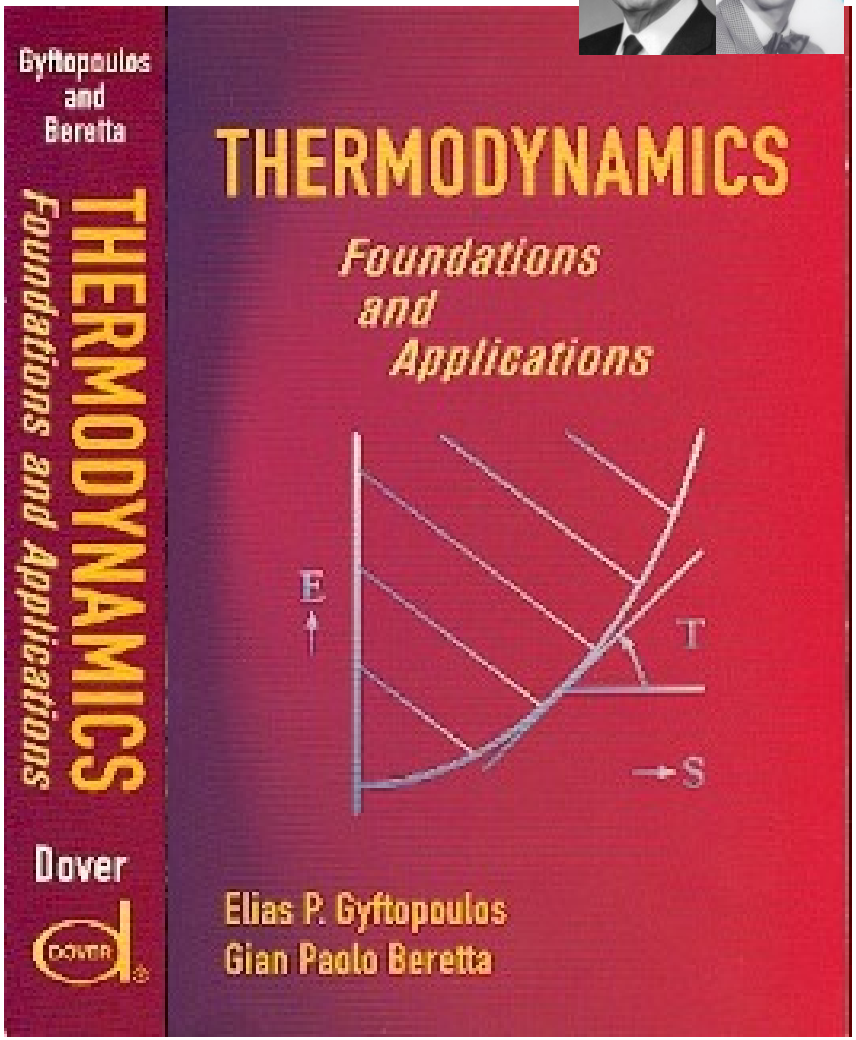

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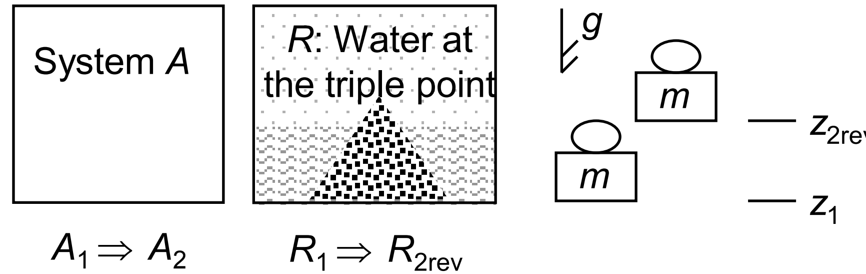

Given any pair of states A_1 and A_2 of a system A *(fixed V)*, make a reversible process for the isolated composite A*Rm,* where *m* is a weight and *R* is water at the triple point.

The SECOND LAW guarantees that such process exists!

Measure $(E_2 - E_1)^R$, divide it by $-273.16\ K$

$$(S_2 - S_1)^A = -\frac{(E_2 - E_1)^R}{273.16\ K}$$

This is the difference in entropy between state A_2 and A_1.

Notice 1:

In this way, the entropy is:

- defined for all states (not only equilibrium)
- defined for any system (not only macroscopic)

Notice 2:

This definition does NOT require previous definition of heat and temperature.

Only later, using energy and entropy, we define temperature, find that it is 273.16 K for water at the t.p.

Later, using energy and entropy, we define work and heat interactions in a clear and unambiguous way.

Definition of ENERGY (valid also for nonequilibrium states!)

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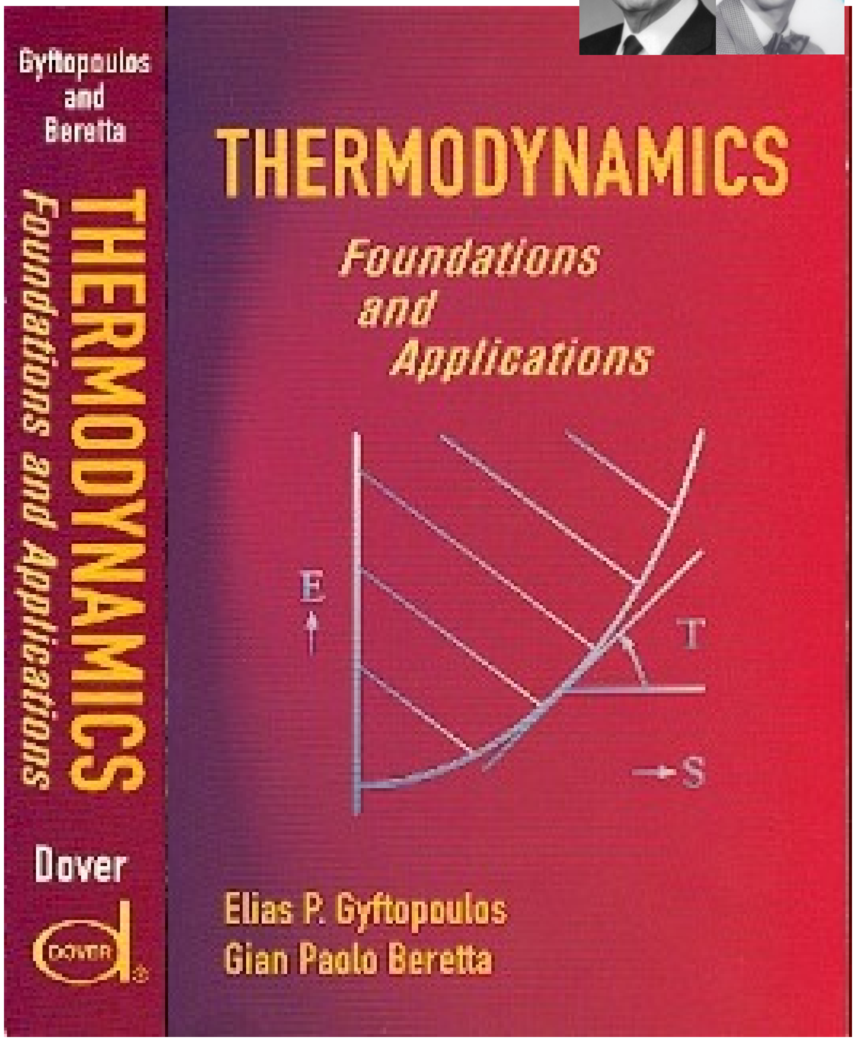

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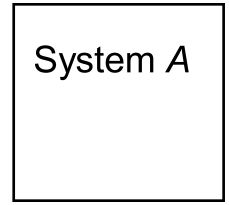

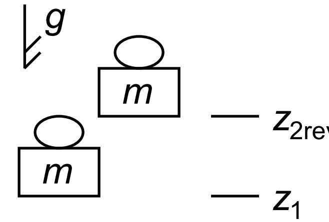

$A_1 \Rightarrow A_2$ or $A_2 \Rightarrow A_1$

Given any pair of states A_1 and A_2 of a system *A (fixed V)*, make a process for the isolated composite *Am,* where *m* is a weight.
The FIRST LAW guarantees that such process exists!
Measure $(z_{2rev} - z_1)$,

$$(E_2 - E_1)^A = -\,\mathrm{mg}\,(z_{2rev} - z_1)$$

This is the difference in energy between state A_2 and A_1

Notice 1:
In this way, the energy is:
- defined for all states (not only equilibrium)
- defined for any system (not only macroscopic)

Notice 2:
This definition does NOT require previous definition of heat, work, temperature.

Definition of PROCESS and REVERSIBLE PROCESS

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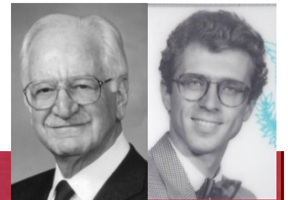

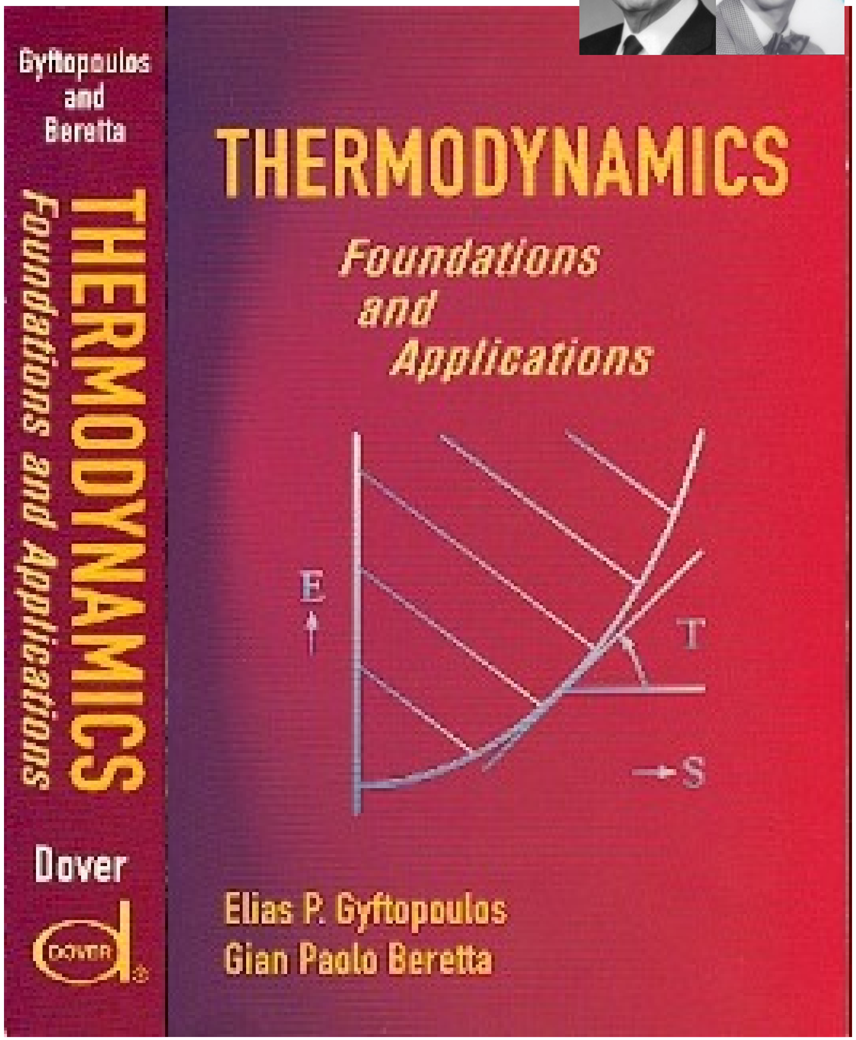

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System *A*

Environment *B*: *the relevant "rest of the universe"*

$A_1 \Rightarrow A_2$ $B_1 \Rightarrow B_2$

A **process** for a system *A (fixed V)* is defined by:
- the initial state A_1
- the final state A_2
- the effects it produces on the environment *B*, measured by its change of state from B_1 to B_2

The **process** is **reversible** if and only if there at least one process that takes the isolated composite *AB* back from state A_2B_2 to its initial state A_1B_1

ENTROPY: its physical and engineering significance

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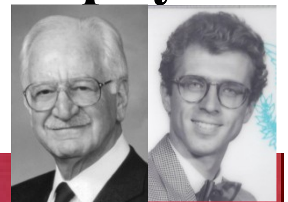

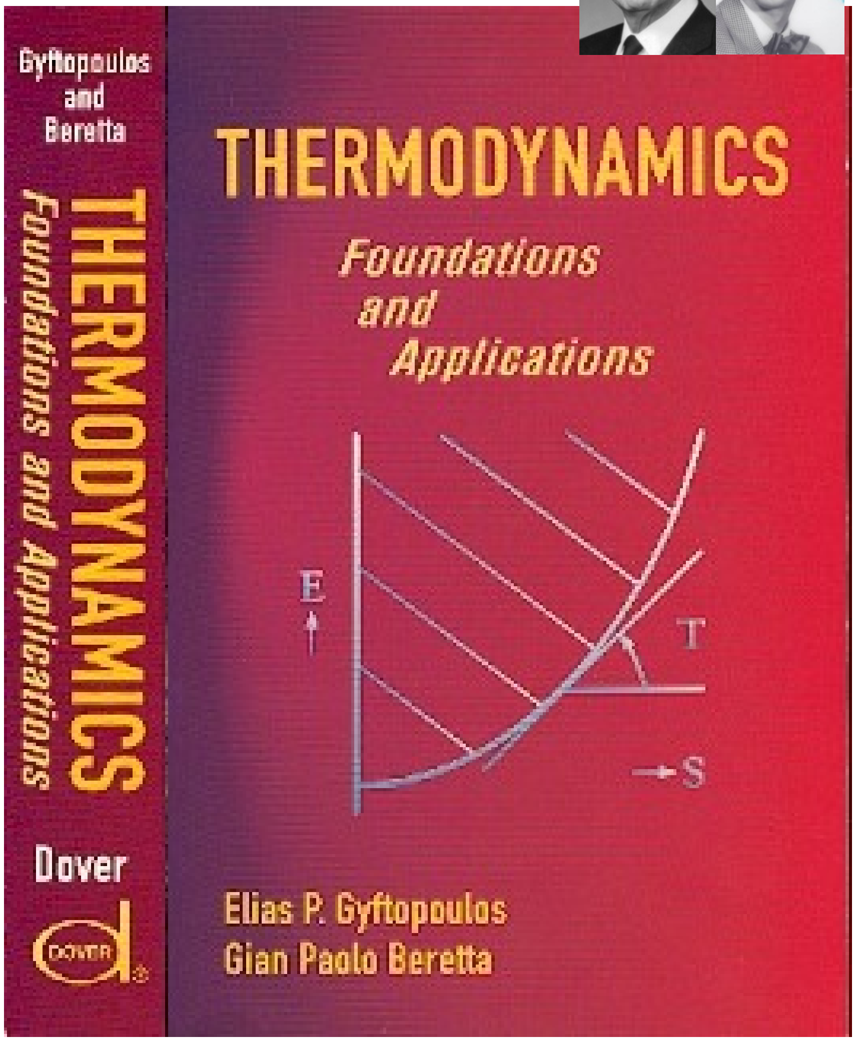

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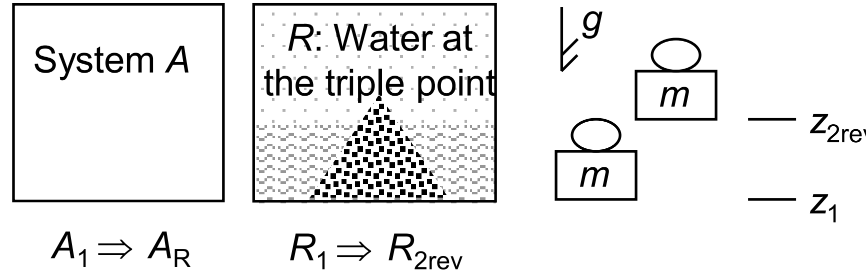

Theorem:

Given any state A_1 of a system *A (fixed V)*,

try all reversible processes for the isolated composite A*Rm,* where *m* is a weight and *R* is water at the triple point, and measure ($z_{2rev} - z_1$). The maximum weight lift obtains when *A* ends in the state A_R of mutual equilibrium with *R*.

The corresponding increase in potential energy of the weight is a property of *A* that we call **available energy with respect to water at the triple point**, that turns out to be

$$\Omega_1^{AR} = (E_1 - E_R)^A - T_R\,(S_1 - S_R)^A$$

where $T_R = 273.16\ K$. Rearranging this equation, we get

$$S_1^A = \frac{E_1^A - \Omega_1^{AR}}{273.16\ K} + \text{constant}$$

where the constant, $S_R^A - E_R^A/T_R$, is a fixed property of the given system-reservoir pair, *A* and *R*. Up to this constant, the entropy S_1^A for any state of *A* is proportional to the part of the energy of *A* that is “not available with respect to reservoir *R*”,i.e., that cannot by given to the weight.

No need to assume "macroscopicity" for the first 16 chapters!

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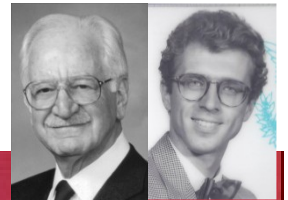

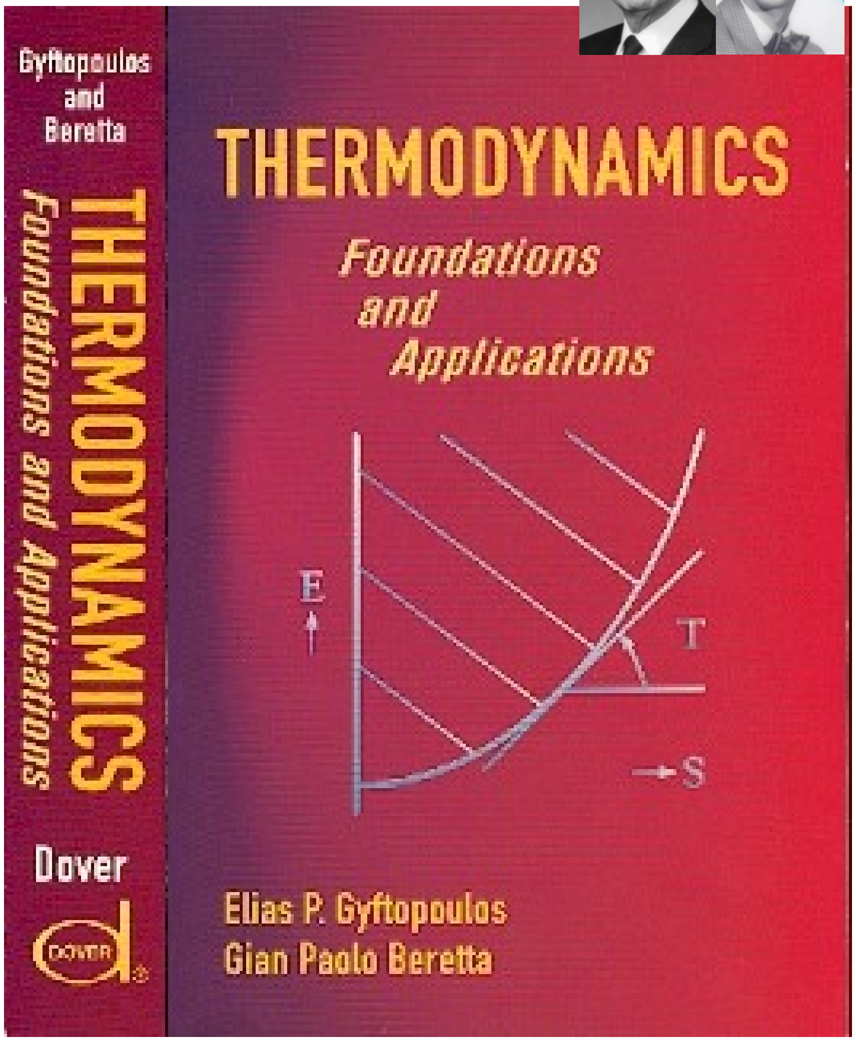

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Chapter 17:
The SIMPLE SYSTEM model.

The study of the equilibrium states of "macroscopic" systems can be significantly simplified by an important approximation.

Under this approximation, which has a very clear physical explanation, in addition to the fundamental equilibrium relation (which holds for all systems)

$$S = S(E,V,n_1,n_2,\dots,n_r)$$

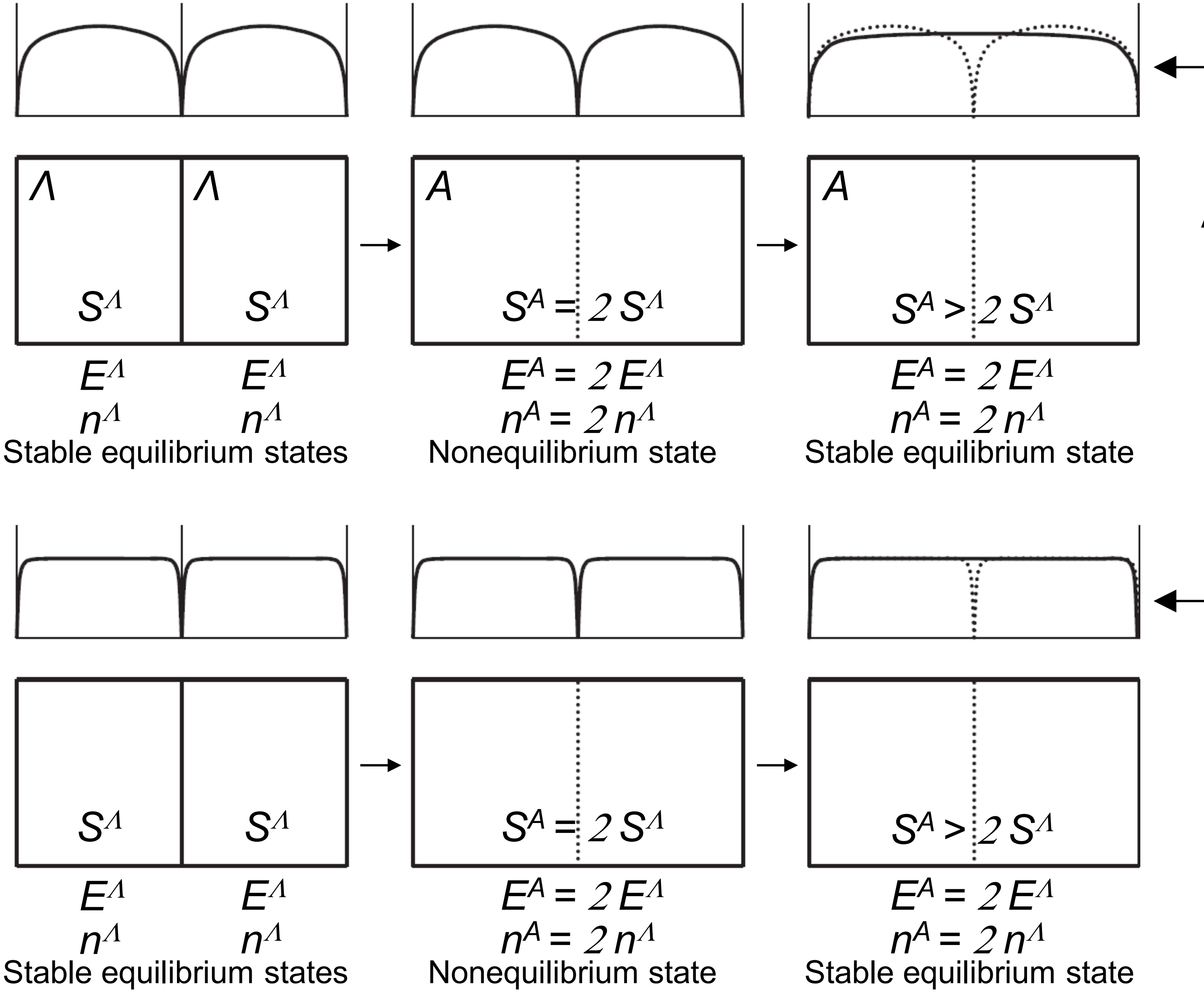
we gain also the Euler relation

$$E = TS - pV + \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_r n_r$$

from which it follows that from the study of the equilibrium properties of 1 kg of a substance, we can infer immediately the properties of any other amount.

This is not true for few particle systems: the equilibrium properties of a two-particle system cannot be inferred from the equilibrium properties of a one-particle system, even if the particles are identical.

The effect of removing a partition



Few particles per partition
(microscopic systems)

At stable equilibrium

$$S^{\Lambda} = S\left(E^{\Lambda}, V^{\Lambda}, n^{\Lambda}\right)$$

$$S^{A} = S\left(2E^{\Lambda}, 2V^{\Lambda}, 2n^{\Lambda}\right)$$

Many particles per partition
(macroscopic systems)

$$S^{A} \approx 2\, S^{\Lambda}$$

$$\frac{S^{A} - 2S^{\Lambda}}{S^{A}} << 1$$

"Simple system" model: $S\left(2E, 2V, 2\mathbf{n}\right) \approx 2\, S\left(E, V, \mathbf{n}\right)$