2.43 ADVANCED THERMODYNAMICS

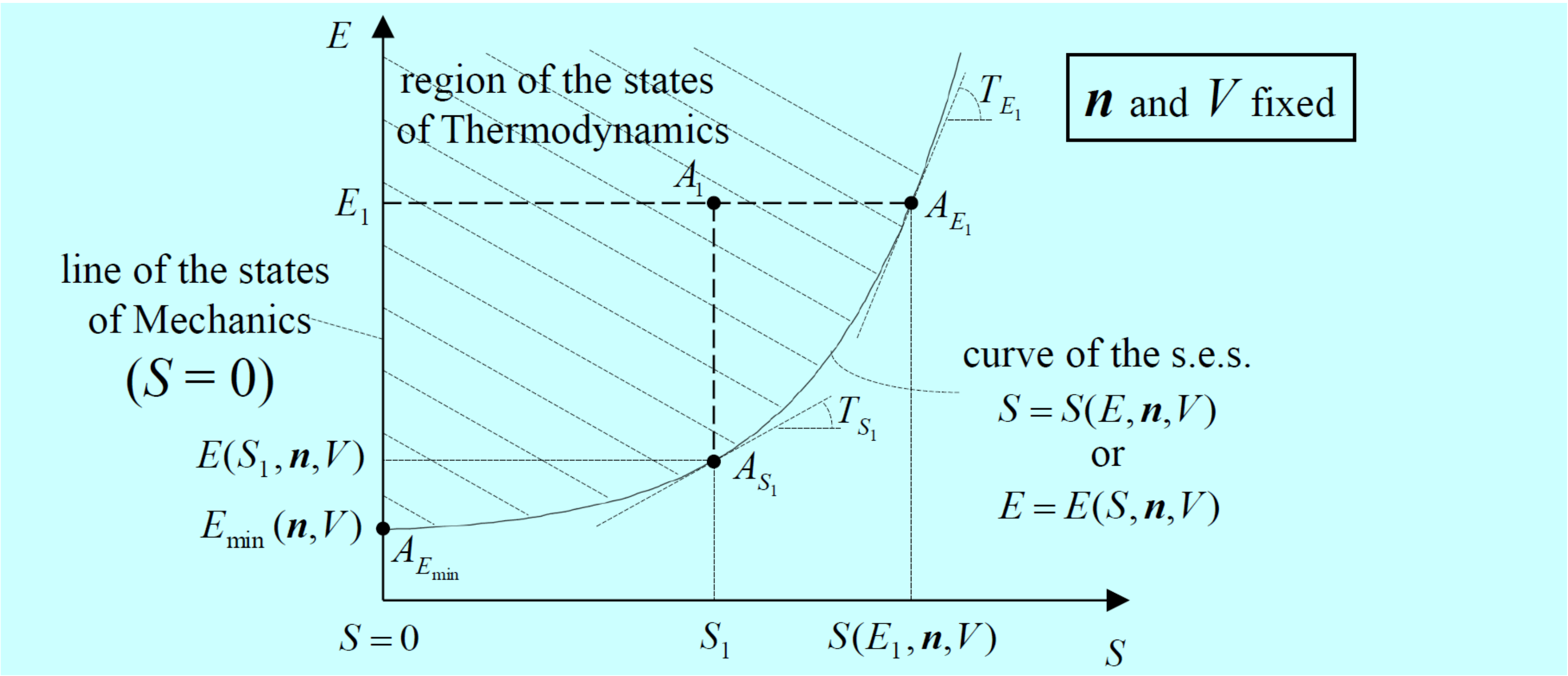
Spring Term 2024
LECTURE 04

Room 3-442
Friday, February 16, 11:00am - 1:00pm

Instructor: Gian Paolo Beretta
beretta@mit.edu
Room 3-351d

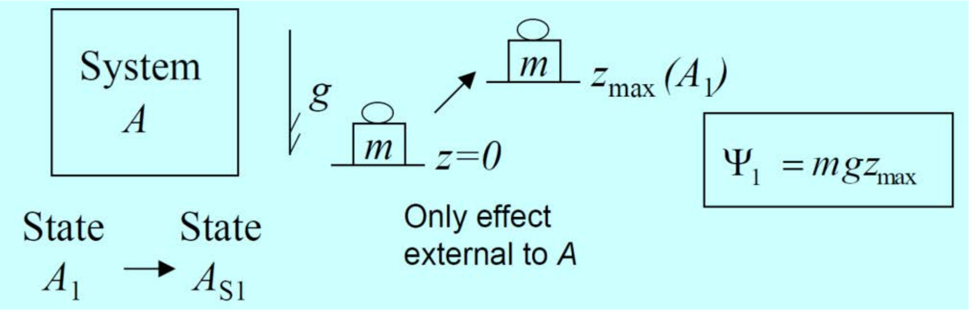
Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

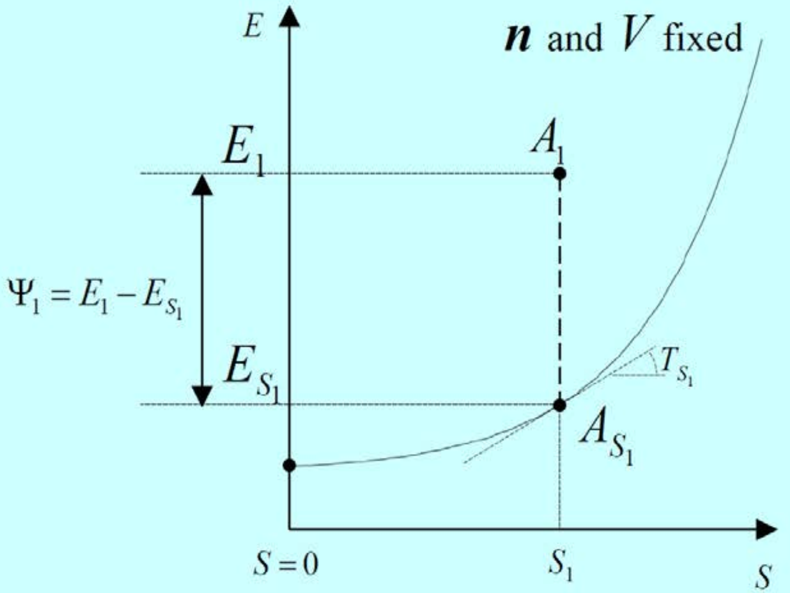
Representation of notSE states and SE states



Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

Adiabatic availability of notSE states





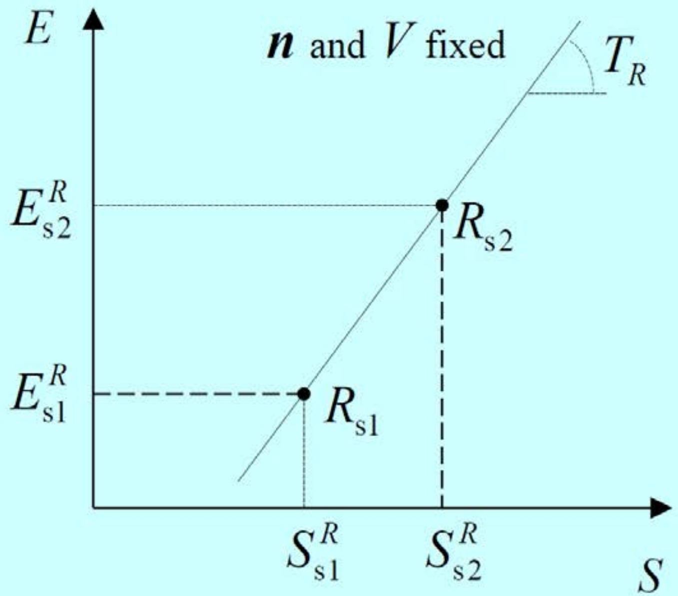
$$\Psi_1 = E_1 - E_{S_1}$$

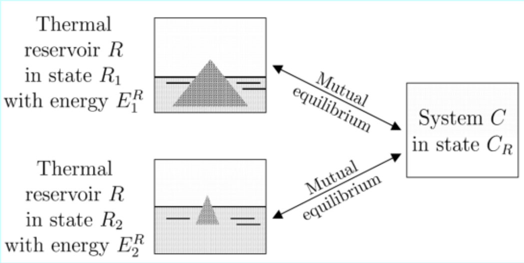
Adiabatic availability (Ψ): it is the part of the energy of *A* in a given state A_1 which can be transferred to a weight with no other external effects. It is obtained by means of rev.w.p. which ends in a stable equilibrium state, A_{s1}

- It is zero iff the state is a stable equilibrium state

Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

notSE and SE states of a thermal reservoir





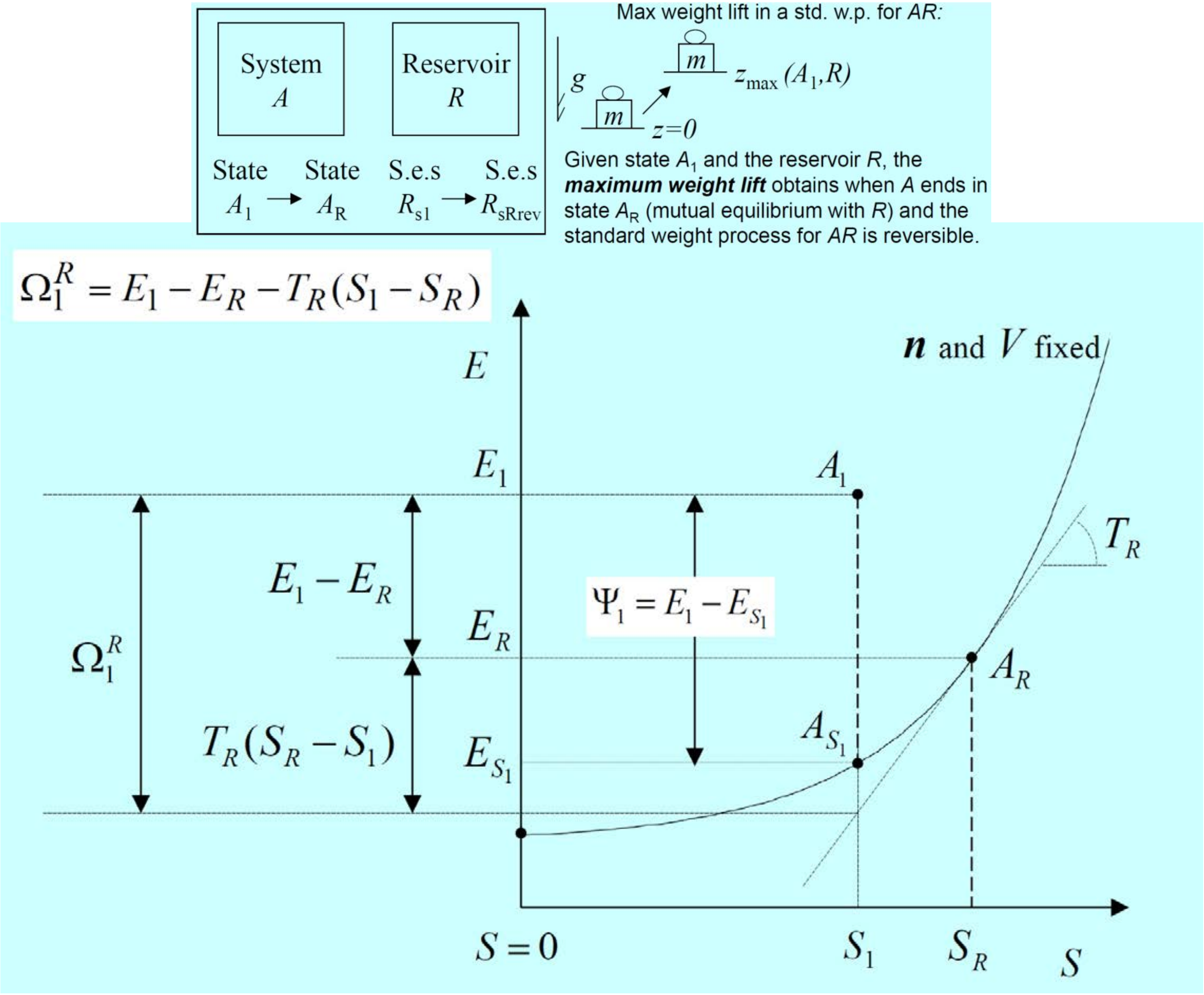
$$E^R_{s2} - E^R_{s1} = T_R\left(S^R_{s2} - S^R_{s1}\right)$$

For a reservoir *R*:

- The s.e.s. curve is a line (all states have the same temperature, T_R)

Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

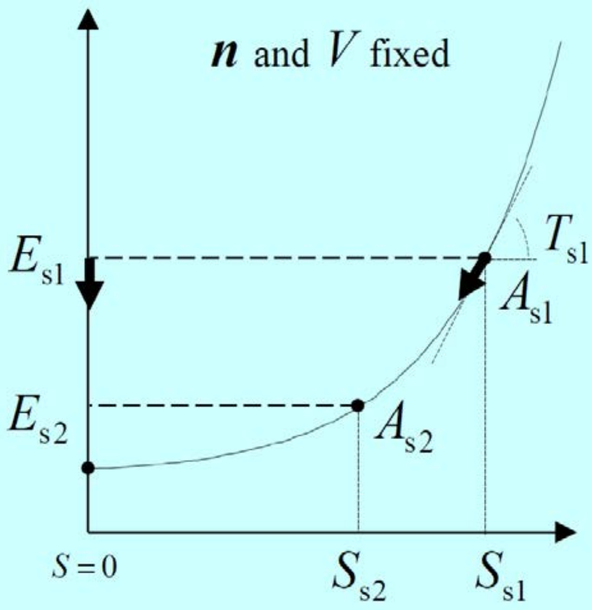
Available energy with respect to a thermal reservoir



Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

a system in a SES cannot

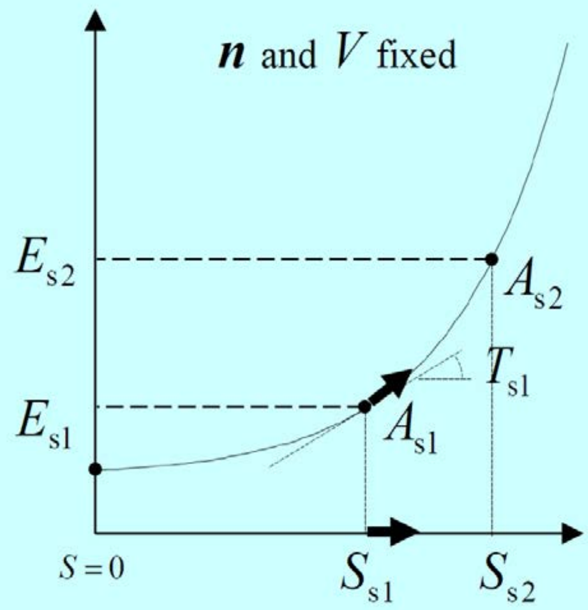
release energy unless...



To extract energy from a system in a s.e.s., we must also extract entropy

$$S_{s1} - S_{s2} > \left(E_{s1} - E_{s2}\right)/T_{s1}$$

receive entropy unless...



To give entropy to a system in a s.e.s., we must also give energy

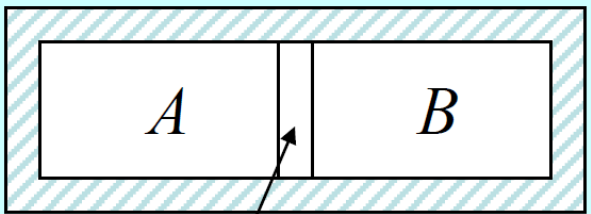
$$E_{s2} - E_{s1} > T_{s1}\left(S_{s2} - S_{s1}\right)$$

Review of basic concepts:

Necessary conditions for mutual equilibrium

Review of basic concepts: Consequences of the Maximum Entropy Principle: Necessary conditions for mutual equilibrium

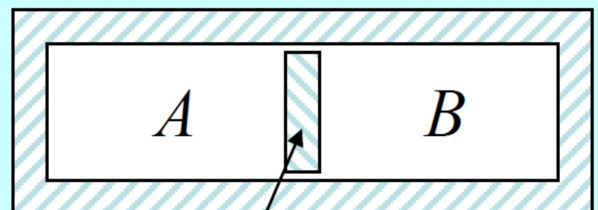
Two systems are in *mutual equilibrium* if the respective states are such that the composite system is in a stable equilbrium state.



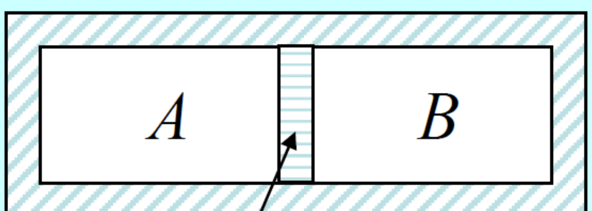
Diathermal wall

- *Equality of the* ***temperatures*** of the two systems is a n.c. for m.e. if the two systems can exchange ***energy***.

- *Equality of the* ***pressures*** of the two systems is a n.c. for m.e. if the two systems can exchange ***volume***.



Movable pistone



Wall permeable
to the i-th costituent

- *Equality of the* ***chemical potentials of the i-th constituent*** in the two systems is a n.c. for m.e. if the two systems can exchange ***the i-th constituent***.

Review of basic concepts: Consequences of the Maximum Entropy Principle:

Proof of temperature and pressure equality at mutual equilibrium

System $C = AB$

System A	System B
SES A_0	SES B_0
E_0^A	E_0^B
$\boldsymbol{n}^A$	$\boldsymbol{n}^B$
V_0^A	V_0^B

SES $C_0 = A_0 B_0$

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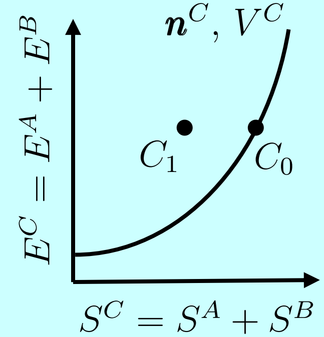
State $C_1 = A_1 B_1$ (not a SES)



If A and B are in MSE in states A_0 and B_0, then C_0 is a SES. Then, the MEP implies that C_1 cannot be a SES and therefore $S_1^C < S_0^C$ i.e. the strict inequality

$$S_1^C - S_0^C < 0$$

from entropy additivity

$$S_1^C - S_0^C = (S_1^A + S_1^B) - (S_0^A + S_0^B) = (S_1^A - S_0^A) + (S_1^B - S_0^B)$$

from the fundamental relations for A and B and assuming dE and dV infinitesimal

$$= \frac{1}{T_0^A} dE + \frac{p_0^A}{T_0^A} dV + \frac{1}{2} d_{E,V}^2 S^A + \cdots + \frac{1}{T_0^B}(-dE) + \frac{p_0^B}{T_0^B}(-dV) + \frac{1}{2} d_{E,V}^2 S^B + \ldots$$

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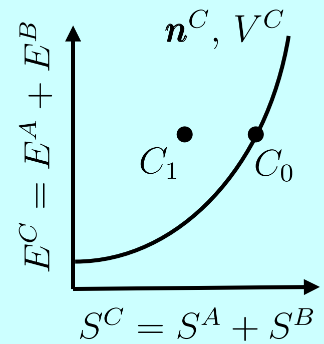

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For the inequality to hold for all choices of dE and dV, the terms in brackets must be zero. Therefore, the second-order differentials must be non-positive, i.e., the fundamental relation is concave in E and V

$$d^2_{E,V} S = \frac{\partial^2 S}{\partial E^2} (dE)^2 + 2 \frac{\partial^2 S}{\partial E \partial V} dE dV + \frac{\partial^2 S}{\partial V^2} (dV)^2 \leq 0$$

Consequences of the Maximum Entropy Principle: Proof of temperature and pressure equality at mutual equilibrium

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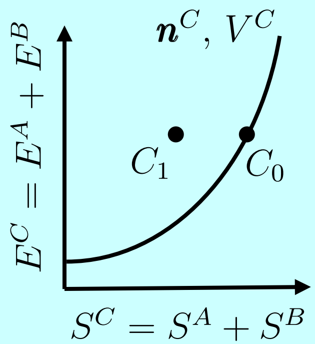

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$$\Rightarrow$$

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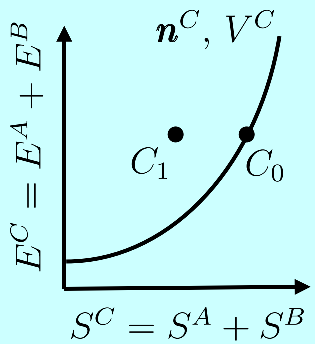

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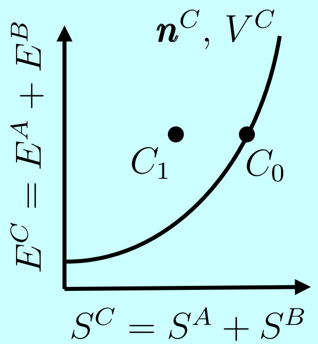

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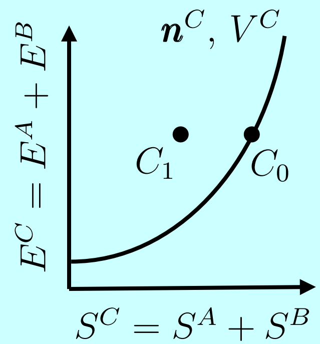

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$$\Rightarrow \begin{cases} \dfrac{\partial^2 S}{\partial E^2} \le 0 \quad \dfrac{\partial^2 S}{\partial n_i^2} \le 0 \\ \dfrac{\partial^2 S}{\partial E^2}\dfrac{\partial^2 S}{\partial n_i^2} - \left[\dfrac{\partial^2 S}{\partial E \partial n_i}\right]^2 \le 0 \end{cases}$$

 Consequences of the Maximum Entropy Principle:

Concavity of the fundamental relation

In a similar way, we can prove that the fundamental relation is concave in all its independent variables, i.e., that in any SES **the Hessian of the fundamental relation** $S = S(E, \boldsymbol{n}, V)$ **is a negative semidefinite** matrix

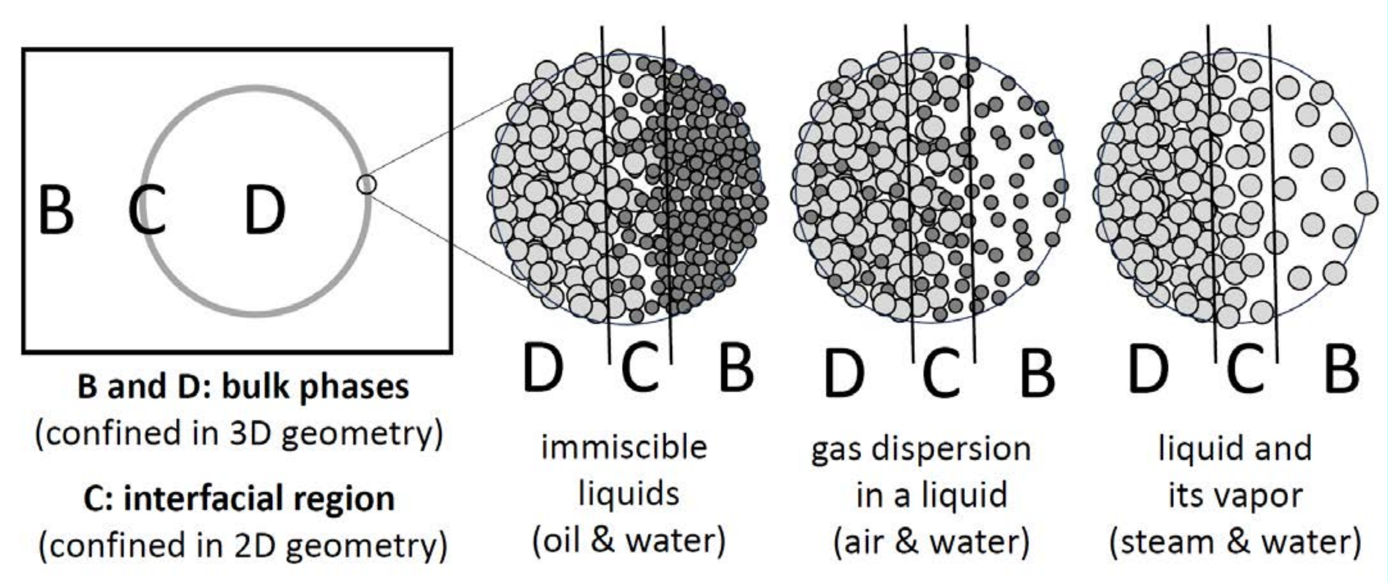
$$\text{Hessian}(S) = \begin{bmatrix} \dfrac{\partial^2 S}{\partial E^2} & \dfrac{\partial^2 S}{\partial E \partial n_1} & \cdots & \dfrac{\partial^2 S}{\partial E \partial n_r} & \dfrac{\partial^2 S}{\partial E \partial V} \\ \dfrac{\partial^2 S}{\partial n_1 \partial E} & \dfrac{\partial^2 S}{\partial n_1^2} & \cdots & \dfrac{\partial^2 S}{\partial n_1 \partial n_r} & \dfrac{\partial^2 S}{\partial n_1 \partial V} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \dfrac{\partial^2 S}{\partial n_r \partial E} & \dfrac{\partial^2 S}{\partial n_r \partial n_1} & \cdots & \dfrac{\partial^2 S}{\partial n_r^2} & \dfrac{\partial^2 S}{\partial n_r \partial V} \\ \dfrac{\partial^2 S}{\partial V \partial E} & \dfrac{\partial^2 S}{\partial V \partial n_1} & \cdots & \dfrac{\partial^2 S}{\partial V \partial n_r} & \dfrac{\partial^2 S}{\partial V^2} \end{bmatrix}$$

The full second-order differential of $S = S(E, \boldsymbol{n}, V)$ is

$$d^2 S_{E,\boldsymbol{n},V} = (dE, dn_1, \ldots, dn_r, dV) \cdot \text{Hessian}(S) \cdot (dE, dn_1, \ldots, dn_r, dV)^T \leq 0$$

From these properties it is possible to prove a number of general inequalities that must be satisfied by stable equilibrium properties.

Consequences of the Maximum Entropy Principle: Surface tension and Young-Laplace equation



Mutual equilibrium between B, C, D where:

$$S^B = S^B(E^B, V^B, \boldsymbol{n}^B) \qquad \left(\frac{\partial S^B}{\partial V^B}\right)_{E^B,\boldsymbol{n}^B} = \frac{p^B}{T^B} \quad \text{or} \quad p^B = -\left(\frac{\partial E^B}{\partial V^B}\right)_{S^B,\boldsymbol{n}^B}$$

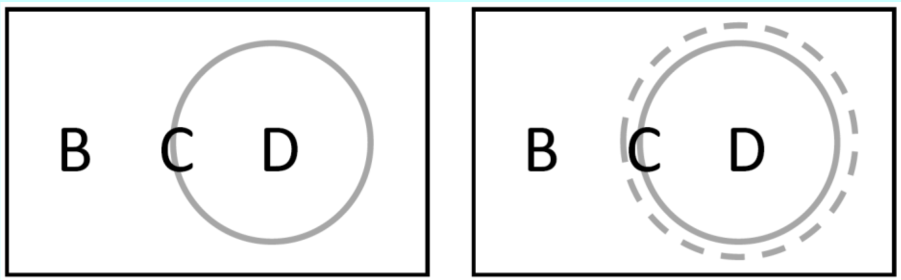
$$S^C = S^C(E^C, A^C, \boldsymbol{n}^C) \qquad \left(\frac{\partial S^C}{\partial A^C}\right)_{E^C,\boldsymbol{n}^C} = -\frac{\sigma^C}{T^C} \quad \text{or} \quad \sigma^C = \left(\frac{\partial E^C}{\partial A^C}\right)_{S^C,\boldsymbol{n}^C}$$ surface tension

$$S^D = S^D(E^D, V^D, \boldsymbol{n}^D) \qquad \left(\frac{\partial S^D}{\partial V^D}\right)_{E^D,\boldsymbol{n}^D} = \frac{p^D}{T^D} \quad \text{or} \quad p^D = -\left(\frac{\partial E^D}{\partial V^D}\right)_{S^D,\boldsymbol{n}^D}$$

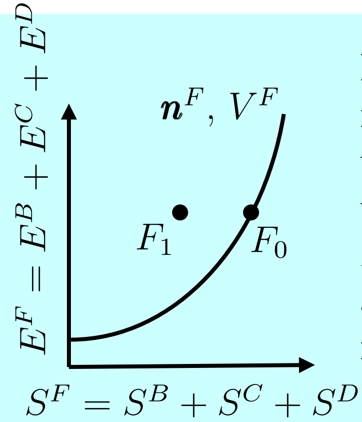
Review of basic concepts: **Consequences of the Maximum Entropy Principle:**

Surface tension and Young-Laplace equation

System $F = BCD$ — System $F = BCD$



SES $F_0 = B_0C_0D_0$ — State $F_1 = B_1C_1D_1$ (not a SES)



If B, C, D are in MSE in states B_0, C_0, D_0, then F_0 is a SES. Then, the MEP implies that F_1 cannot be a SES and therefore $S_1^F < S_0^F$ i.e. the strict inequality $S_1^F - S_0^F < 0$

from entropy additivity

$$S_1^F - S_0^F = (S_1^B + S_1^C + S_1^D) - (S_0^B + S_0^C + S_0^D) = (S_1^B - S_0^B) + (S_1^C - S_0^C) + (S_1^D - S_0^D)$$

from the fundamental relations for B, C, D, assuming infinitesimal dE's, dV's, dA

$$= \frac{1}{T_0^B} dE^B + \frac{p_0^B}{T_0^B} dV^B + \dots + \frac{1}{T_0^C} dE^C - \frac{\sigma_0^C}{T_0^C} dA^C + \dots + \frac{1}{T_0^D} dE^D + \frac{p_0^D}{T_0^D} dV^D + \dots$$

assuming $T_0^B = T_0^C = T_0^D = T_0$, $dE^B + dE^C + dE^D = 0$

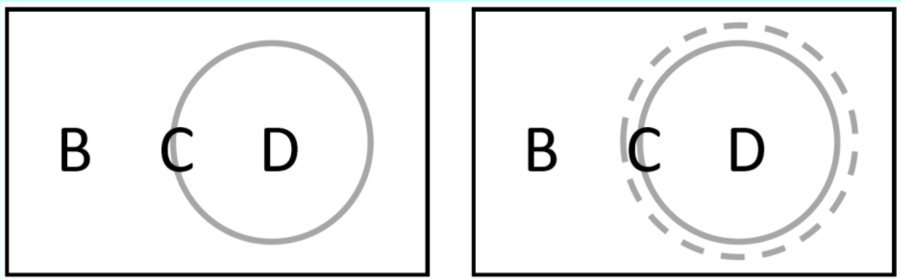
$\mu_{i0}^B = \mu_{i0}^C = \mu_{i0}^D = \mu_{i0}$, $dn_i^B + dn_i^C + dn_i^D = 0 \;\forall i$ and using $dV^B = -dV^D$

$$= \frac{1}{T_0} \underbrace{\left[\left(p_0^D - p_0^B\right) dV^D - \sigma_0^C dA^C\right]}_{=0} + \dots < 0$$

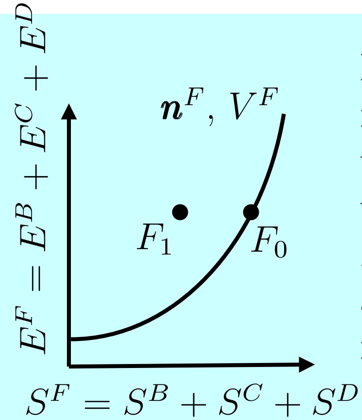
Review of basic concepts: **Consequences of the Maximum Entropy Principle:**

Surface tension and Young-Laplace equation

System $F = BCD$ System $F = BCD$



SES $F_0 = B_0C_0D_0$ State $F_1 = B_1C_1D_1$ (not a SES)



If B, C, D are in MSE in states B_0, C_0, D_0, then F_0 is a SES. Then, the MEP implies that F_1 cannot be a SES and therefore $S_1^F < S_0^F$ i.e. the strict inequality $S_1^F - S_0^F < 0$

from entropy additivity

$$S_1^F - S_0^F = (S_1^B + S_1^C + S_1^D) - (S_0^B + S_0^C + S_0^D) = (S_1^B - S_0^B) + (S_1^C - S_0^C) + (S_1^D - S_0^D)$$

from the fundamental relations for B, C, D, assuming infinitesimal dE's, dV's, dA

$$= \frac{1}{T_0^B} dE^B + \frac{p_0^B}{T_0^B} dV^B + \cdots + \frac{1}{T_0^C} dE^C - \frac{\sigma_0^C}{T_0^C} dA^C + \cdots + \frac{1}{T_0^D} dE^D + \frac{p_0^D}{T_0^D} dV^D + \ldots$$

$$= \frac{1}{T_0} \underbrace{\left[\left(p_0^D - p_0^B\right) dV^D - \sigma_0^C dA^C\right]}_{=0} + \cdots < 0$$

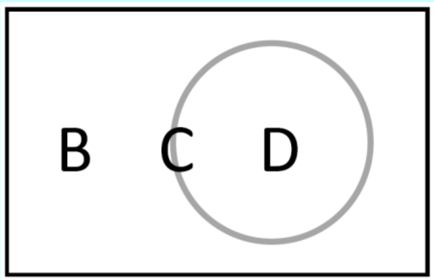
Let us first see what we get if we assume that C has **spherical shape of radius** R. For an infinitesimal displacement $d\epsilon = dR$,

$$A^C = 4\pi R^2 \qquad dV^D = 4\pi R^2\, d\epsilon \qquad dA^C = 4\pi(R + d\epsilon)^2 - 4\pi R^2 \approx 8\pi R\, d\epsilon$$

$$\underbrace{\left[\left(p_0^D - p_0^B\right) 4\pi R^2 - \sigma_0^C 8\pi R\right]}_{=0} d\epsilon = 0 \quad \forall d\epsilon \qquad \Rightarrow \qquad p_0^D - p_0^B = \frac{2\sigma_0^C}{R}$$

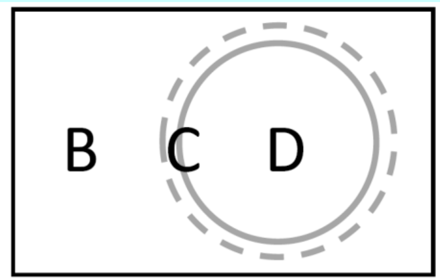
Consequences of the Maximum Entropy Principle: Surface tension and Young-Laplace equation

System $F = BCD$

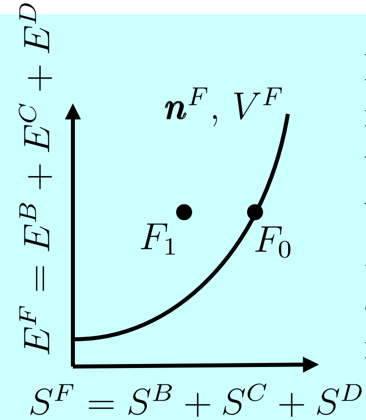


SES $F_0 = B_0C_0D_0$

System $F = BCD$



State $F_1 = B_1C_1D_1$ (not a SES)



If B, C, D are in MSE in states B_0, C_0, D_0, then F_0 is a SES. Then, the MEP implies that F_1 cannot be a SES and therefore $S_1^F < S_0^F$ i.e. the strict inequality $S_1^F - S_0^F < 0$

from entropy additivity

$$S_1^F - S_0^F = (S_1^B + S_1^C + S_1^D) - (S_0^B + S_0^C + S_0^D) = (S_1^B - S_0^B) + (S_1^C - S_0^C) + (S_1^D - S_0^D)$$

from the fundamental relations for B, C, D, assuming infinitesimal dE's, dV's, dA

$$= \frac{1}{T_0^B} dE^B + \frac{p_0^B}{T_0^B} dV^B + \cdots + \frac{1}{T_0^C} dE^C - \frac{\sigma_0^C}{T_0^C} dA^C + \cdots + \frac{1}{T_0^D} dE^D + \frac{p_0^D}{T_0^D} dV^D + \dots$$

$$= \frac{1}{T_0} [\underbrace{(p_0^D - p_0^B)\, dV^D - \sigma_0^C dA^C}_{=0}] + \cdots < 0$$

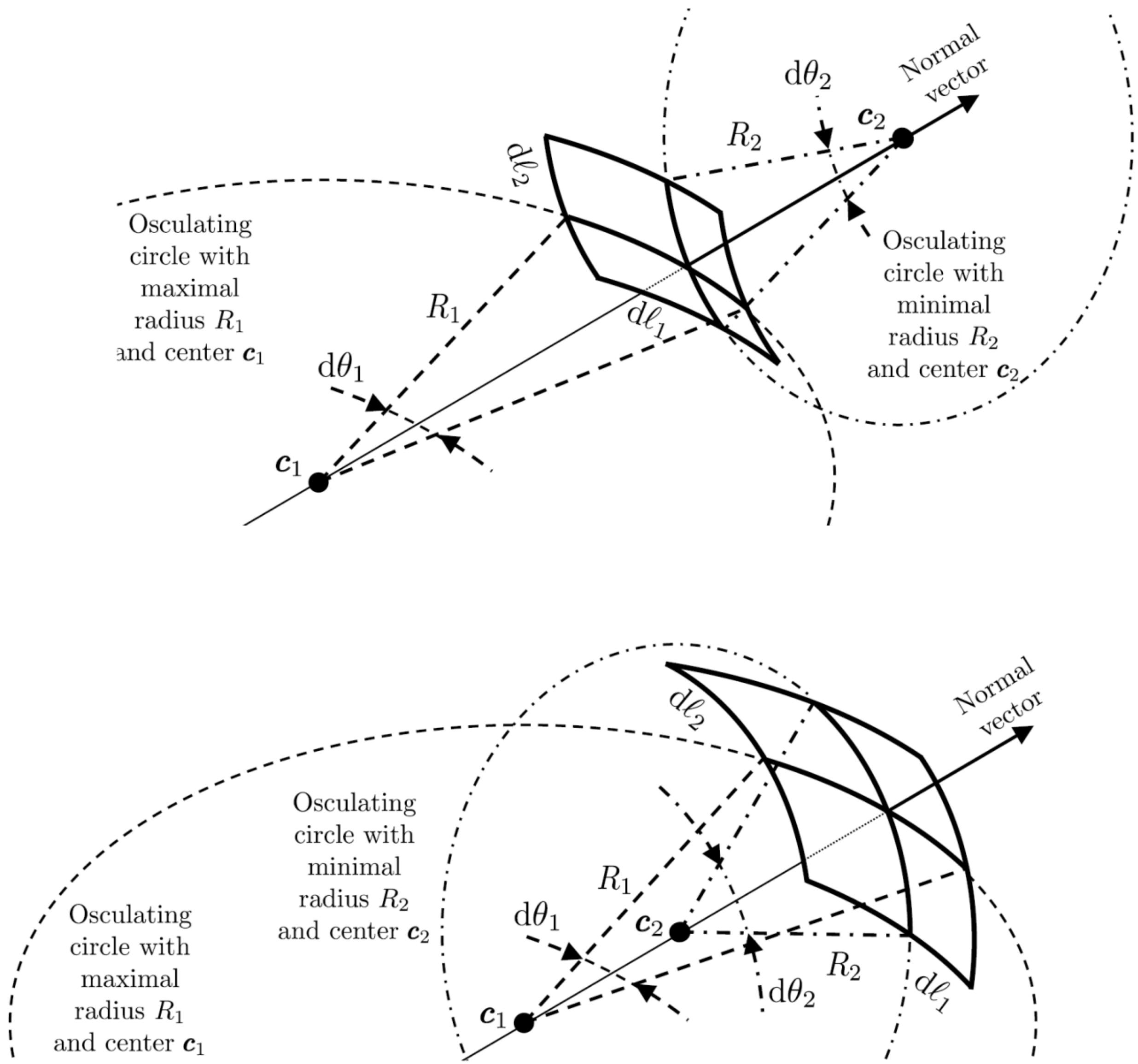
Let us assume instead that C has **cylindrical shape of radius** R and length L. For an infinitesimal displacement $d\epsilon = dR$ keeping L fixed,

$$A^C = 2\pi RL \qquad dV^D = 2\pi RL\, d\epsilon \qquad dA^C = 2\pi(R + d\epsilon)L - 2\pi RL = 2\pi L\, d\epsilon$$

$$[\underbrace{(p_0^D - p_0^B)\, 2\pi R - \sigma_0^C 2\pi}_{=0}]\, L\, d\epsilon = 0 \quad \forall d\epsilon$$

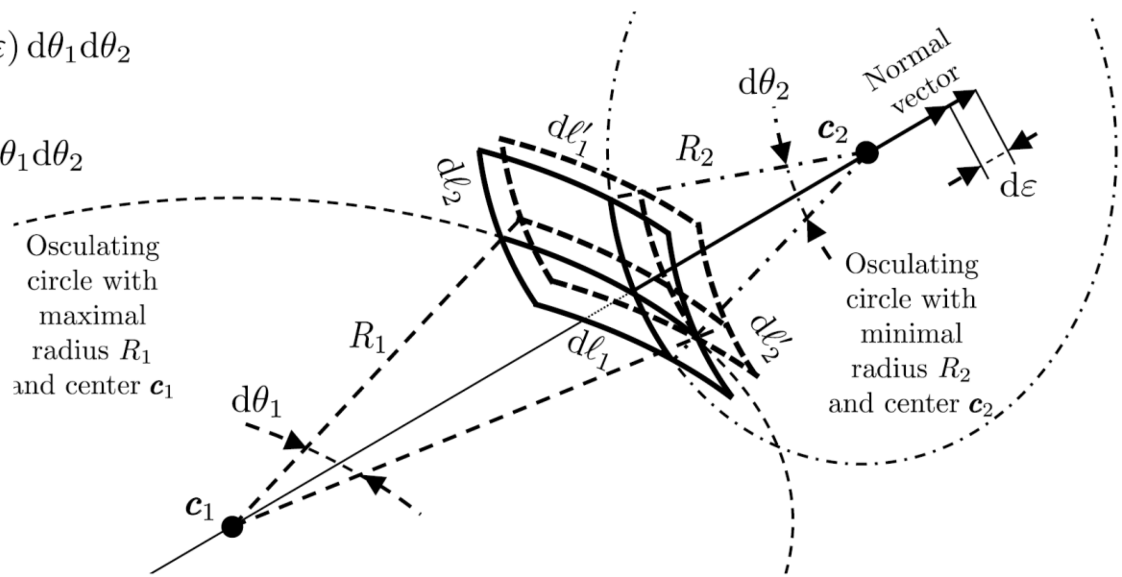
$$\Rightarrow \quad p_0^D - p_0^B = \frac{\sigma_0^C}{R}$$

Review of basic concepts: **principal radii of curvature**

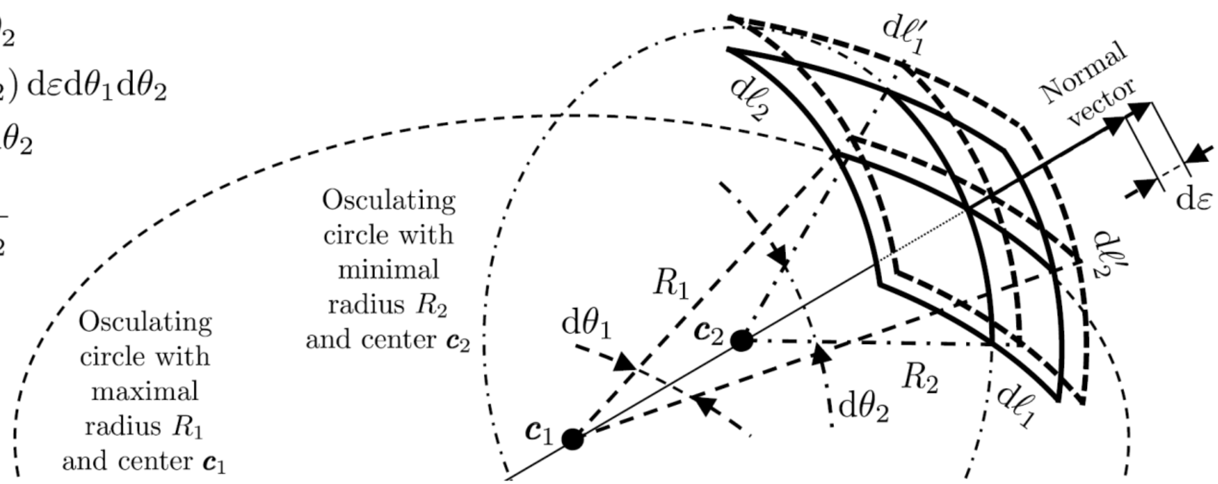


Review of basic concepts: principal radii of curvature and area-to-volume change upon surface displacement

$$\mathrm{d}A' = \mathrm{d}\ell_1'\mathrm{d}\ell_2' = (R_1 + \mathrm{d}\varepsilon)(R_2 - \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\mathrm{d}A = \mathrm{d}\ell_1\mathrm{d}\ell_2 = R_1R_2\,\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\delta A = \mathrm{d}A' - \mathrm{d}A = (-R_1 + R_2)\,\mathrm{d}\varepsilon\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\delta V = \mathrm{d}A\mathrm{d}\varepsilon = R_1R_2\,\mathrm{d}\varepsilon\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\frac{\delta A}{\delta V} = \frac{-R_1 + R_2}{R_1R_2} = \frac{1}{R_1} - \frac{1}{R_2}$$
$$\mathrm{d}\ell_1 = R_1\,\mathrm{d}\theta_1$$
$$\mathrm{d}\ell_2 = R_2\,\mathrm{d}\theta_2$$
$$\mathrm{d}\ell_1' = (R_1 + \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1$$
$$\mathrm{d}\ell_2' = (R_2 - \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1$$



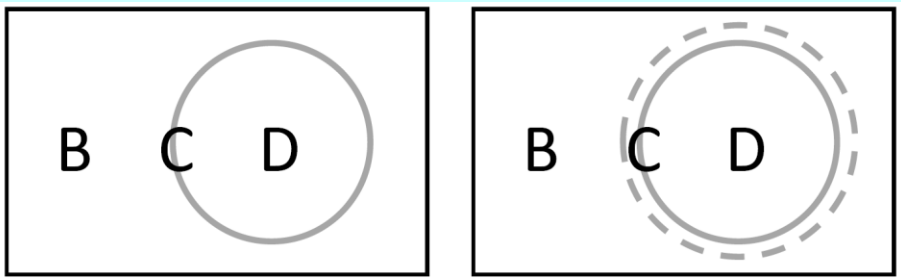
$$\mathrm{d}A' = \mathrm{d}\ell_1'\mathrm{d}\ell_2' = (R_1 + \mathrm{d}\varepsilon)(R_2 + \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\mathrm{d}A = \mathrm{d}\ell_1\mathrm{d}\ell_2 = R_1R_2\,\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\delta A = \mathrm{d}A' - \mathrm{d}A = (R_1 + R_2)\,\mathrm{d}\varepsilon\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\delta V = \mathrm{d}A\mathrm{d}\varepsilon = R_1R_2\,\mathrm{d}\varepsilon\mathrm{d}\theta_1\mathrm{d}\theta_2$$
$$\frac{\delta A}{\delta V} = \frac{R_1 + R_2}{R_1R_2} = \frac{1}{R_1} + \frac{1}{R_2}$$
$$\mathrm{d}\ell_1 = R_1\,\mathrm{d}\theta_1$$
$$\mathrm{d}\ell_2 = R_2\,\mathrm{d}\theta_2$$
$$\mathrm{d}\ell_1' = (R_1 + \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1$$
$$\mathrm{d}\ell_2' = (R_2 + \mathrm{d}\varepsilon)\,\mathrm{d}\theta_1$$



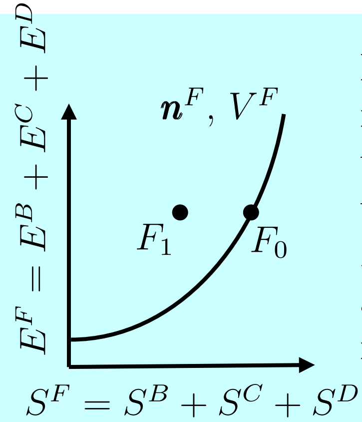
Review of basic concepts: **Consequences of the Maximum Entropy Principle:**

Surface tension and Young-Laplace equation

System $F = BCD$ System $F = BCD$



SES $F_0 = B_0C_0D_0$ State $F_1 = B_1C_1D_1$ (not a SES)



If B, C, D are in MSE in states B_0, C_0, D_0, then F_0 is a SES. Then, the MEP implies that F_1 cannot be a SES and therefore $S_1^F < S_0^F$ i.e. the strict inequality

$$S_1^F - S_0^F < 0$$

$$S_1^F - S_0^F \overset{\text{from entropy additivity}}{=} (S_1^B + S_1^C + S_1^D) - (S_0^B + S_0^C + S_0^D) = (S_1^B - S_0^B) + (S_1^C - S_0^C) + (S_1^D - S_0^D)$$

from the fundamental relations for B, C, D, assuming infinitesimal dE's, dV's, dA

$$= \frac{1}{T_0^B} dE^B + \frac{p_0^B}{T_0^B} dV^B + \cdots + \frac{1}{T_0^C} dE^C - \frac{\sigma_0^C}{T_0^C} dA^C + \cdots + \frac{1}{T_0^D} dE^D + \frac{p_0^D}{T_0^D} dV^D + \ldots$$

$$= \frac{1}{T_0} \underbrace{\left[\left(p_0^D - p_0^B\right) dV^D - \sigma_0^C\, dA^C\right]}_{=0} + \cdots < 0$$

More generally, assuming small local displacement $d\epsilon = d\epsilon|_{\theta_1,\theta_2}$ (see following slides),

$$A^C = \iint_C R_1 R_2\, d\theta_1 d\theta_2 \qquad dV^D = \iint_C R_1 R_2\, d\epsilon\, d\theta_1 d\theta_2$$

$$dA^C = \iint_C [(R_1 + d\epsilon)(R_2 \pm d\epsilon) - R_1 R_2]\, d\theta_1 d\theta_2 \approx \iint_C (\pm R_1 + R_2)\, d\epsilon\, d\theta_1 d\theta_2$$

$$\iint_C \left[\left(p_0^D - p_0^B\right) R_1 R_2 - \sigma_0^C (\pm R_1 + R_2)\right]_{\theta_1,\theta_2} d\epsilon|_{\theta_1,\theta_2}\, d\theta_1 d\theta_2 = 0 \quad \forall d\epsilon|_{\theta_1,\theta_2}$$

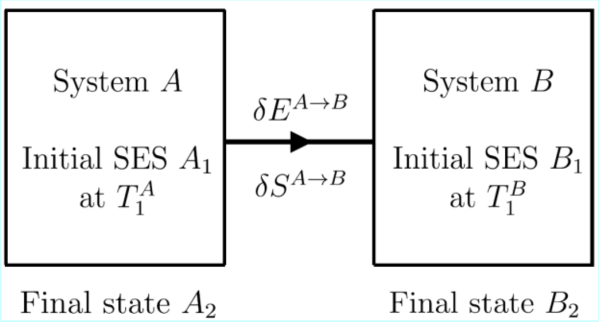
$$\Rightarrow \left[\frac{1}{R_1} \pm \frac{1}{R_2}\right]_{\theta_1,\theta_2} = \frac{p_0^D - p_0^B}{\sigma_0^C}$$

$$\Uparrow$$

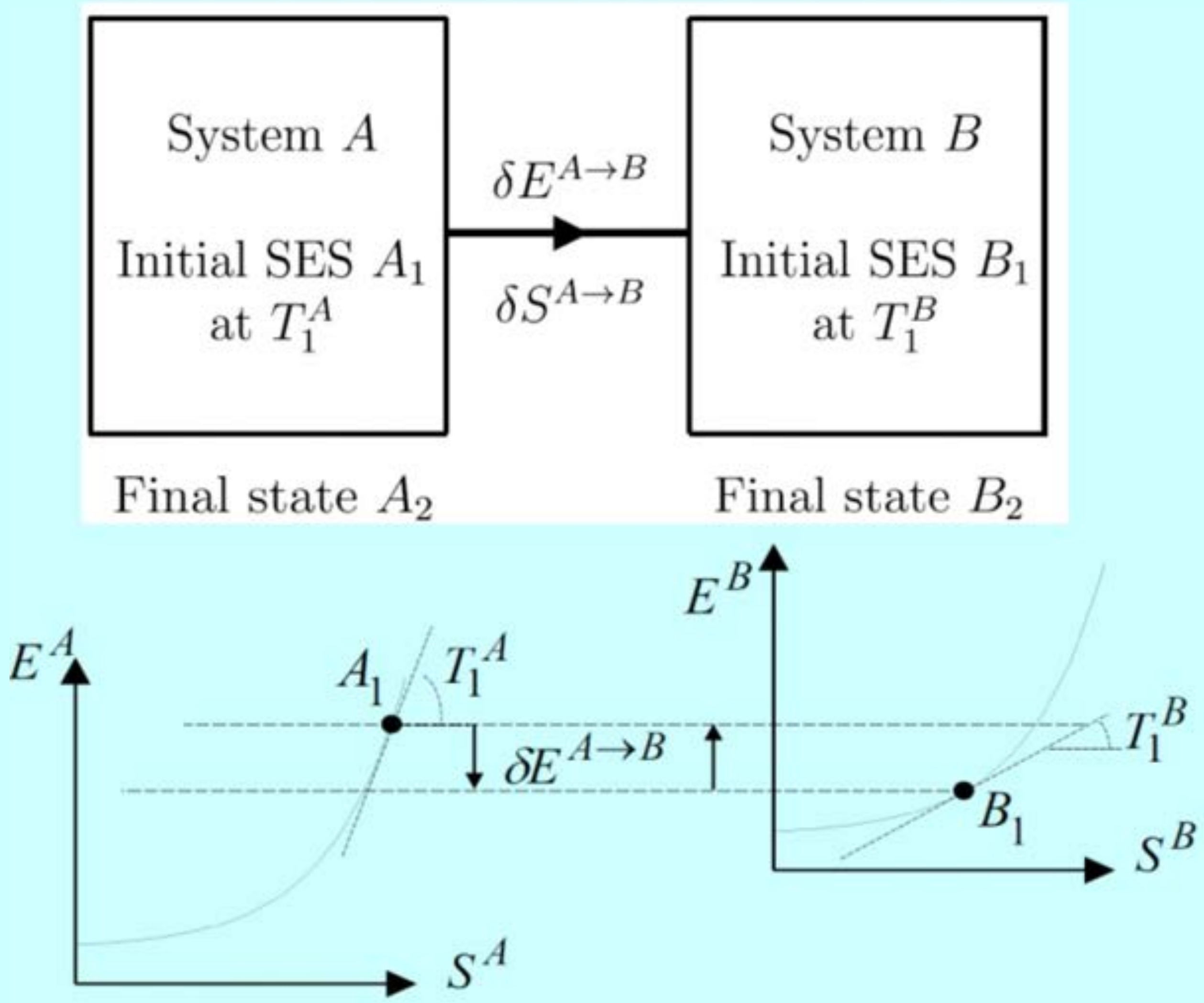
$$p_0^D - p_0^B = \sigma_0^C \left[\frac{1}{R_1} \pm \frac{1}{R_2}\right]$$

Review of basic concepts:

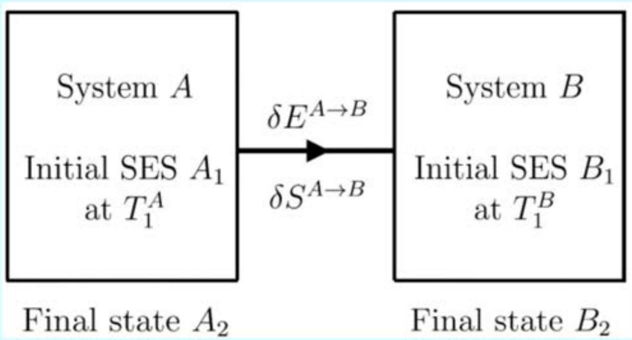
proof of Clausius statement of the Second Law

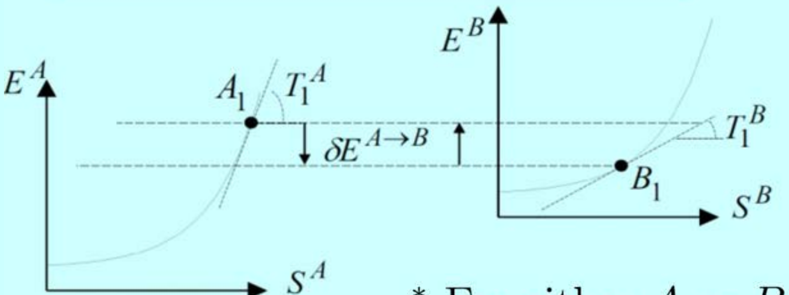


proof of Clausius statement of the Second Law (1/6)



proof of Clausius statement of the Second Law (4/6)





Principle of maximum entropy and fundamental relations of A and B:*

$$dS^A \underset{2A}{\le} \frac{dE^A}{T_1^A} + \left.\frac{\partial^2 S^A_{\rm SES}}{\partial E^2}\right|_{E_1^A} \frac{(dE^A)^2}{2} \cdots \underset{3A}{\le} \frac{dE^A}{T_1^A}$$

$$dS^B \underset{2B}{\le} \frac{dE^B}{T_1^B} + \left.\frac{\partial^2 S^B_{\rm SES}}{\partial E^2}\right|_{E_1^B} \frac{(dE^B)^2}{2} \cdots \underset{3B}{\le} \frac{dE^B}{T_1^B}$$

* For either A or B: $E_2 = E_1 + dE$, $S_2 = S_1 + dS$,

$$S_2 \le S_{2,\max} = S_{\rm SES}(E_1 + dE, V, n) = S_1 + \frac{dE}{T_1} + \left.\frac{\partial^2 S_{\rm SES}}{\partial E^2}\right|_{E_1} \frac{(dE)^2}{2} \cdots$$

Energy and entropy balances for A and B:

$$dE^A = -\delta E^{A\to B} \qquad dS^A = -\delta S^{A\to B} + \delta S^A_{\rm irr} \qquad \delta S^A_{\rm irr} \underset{1A}{\ge} 0$$

$$dE^B = \delta E^{A\to B} \qquad dS^B = \delta S^{A\to B} + \delta S^B_{\rm irr} \qquad \delta S^B_{\rm irr} \underset{1B}{\ge} 0$$

Review of basic concepts: **nonwork interactions**

proof of Clausius statement of the Second Law (5/6)

Energy and entropy balances for A and B:

$$dE^A = -\delta E^{A\to B} \qquad dS^A = -\delta S^{A\to B} + \delta S^A_{\rm irr} \qquad \delta S^A_{\rm irr} \underset{1A}{\geq} 0$$

$$dE^B = \delta E^{A\to B} \qquad dS^B = \delta S^{A\to B} + \delta S^B_{\rm irr} \qquad \delta S^B_{\rm irr} \underset{1B}{\geq} 0$$

Principle of maximum entropy and fundamental relations of A and B:*

$$dS^A \underset{2A}{\leq} \frac{dE^A}{T^A_1} + \left.\frac{\partial^2 S^A_{\rm SES}}{\partial E^2}\right|_{E^A_1} \frac{(dE^A)^2}{2} \cdots \underset{3A}{\leq} \frac{dE^A}{T^A_1}$$

$$dS^B \underset{2B}{\leq} \frac{dE^B}{T^B_1} + \left.\frac{\partial^2 S^B_{\rm SES}}{\partial E^2}\right|_{E^B_1} \frac{(dE^B)^2}{2} \cdots \underset{3B}{\leq} \frac{dE^B}{T^B_1}$$

Combine the above (eliminate dE^A, dE^B, dS^A, dS^B):

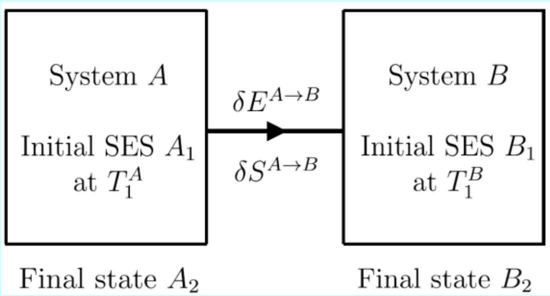
$$-\delta S^{A\to B} + \delta S^A_{\rm irr} \underset{2A,3A}{\leq} -\frac{\delta E^{A\to B}}{T^A_1} \qquad \delta S^{A\to B} + \delta S^B_{\rm irr} \underset{2B,3B}{\leq} \frac{\delta E^{A\to B}}{T^B_1}$$

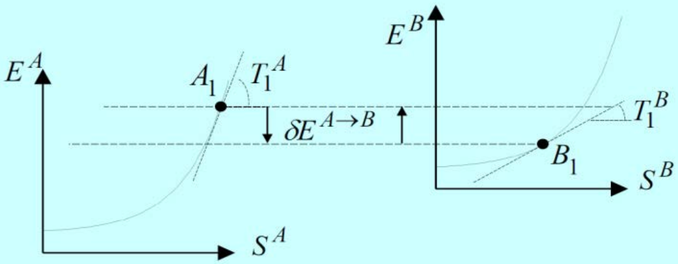
Solve for $\delta S^{A\to B}$:

$$\boxed{\frac{\delta E^{A\to B}}{T^A_1} \underset{2A,3A}{\leq} \delta S^{A\to B} - \delta S^A_{\rm irr} \underset{1A}{\leq} \delta S^{A\to B} \underset{1B}{\leq} \delta S^{A\to B} + \delta S^B_{\rm irr} \underset{2B,3B}{\leq} \frac{\delta E^{A\to B}}{T^B_1}}$$

Review of basic concepts: nonwork interactions

proof of Clausius statement of the Second Law (6/6)





Consequences of

$$\frac{\delta E^{A\to B}}{T_1^A} \le \delta S^{A\to B} \le \frac{\delta E^{A\to B}}{T_1^B}$$

Clausius statement:
$\delta E^{A\to B} \ge 0$ only if $T_1^A \ge T_1^B$

Heat interaction:
in the limit $T_1^A \to T_Q \leftarrow T_1^B$

$$\delta S^{A\to B} = \frac{\delta E^{A\to B}}{T_Q}$$

Energy and entropy balances for A and B:

$$dE^A = -\delta E^{A\to B} \qquad dS^A = -\delta S^{A\to B} + \delta S^A_{\rm irr} \qquad \delta S^A_{\rm irr} \ge_{1A} 0$$
$$dE^B = \delta E^{A\to B} \qquad dS^B = \delta S^{A\to B} + \delta S^B_{\rm irr} \qquad \delta S^B_{\rm irr} \ge_{1B} 0$$

Principle of maximum entropy and fundamental relations of A and B:*

$$dS^A \underset{2A}{\le} \frac{dE^A}{T_1^A} + \left.\frac{\partial^2 S^A_{\rm SES}}{\partial E^2}\right|_{E_1^A} \frac{(dE^A)^2}{2} \cdots \underset{3A}{\le} \frac{dE^A}{T_1^A}$$

$$dS^B \underset{2B}{\le} \frac{dE^B}{T_1^B} + \left.\frac{\partial^2 S^B_{\rm SES}}{\partial E^2}\right|_{E_1^B} \frac{(dE^B)^2}{2} \cdots \underset{3B}{\le} \frac{dE^B}{T_1^B}$$

Combine the above (eliminate dE^A, dE^B, dS^A, dS^B):

$$-\delta S^{A\to B} + \delta S^A_{\rm irr} \underset{2A,3A}{\le} -\frac{\delta E^{A\to B}}{T_1^A} \qquad \delta S^{A\to B} + \delta S^B_{\rm irr} \underset{2B,3B}{\le} \frac{\delta E^{A\to B}}{T_1^B}$$

Solve for $\delta S^{A\to B}$:

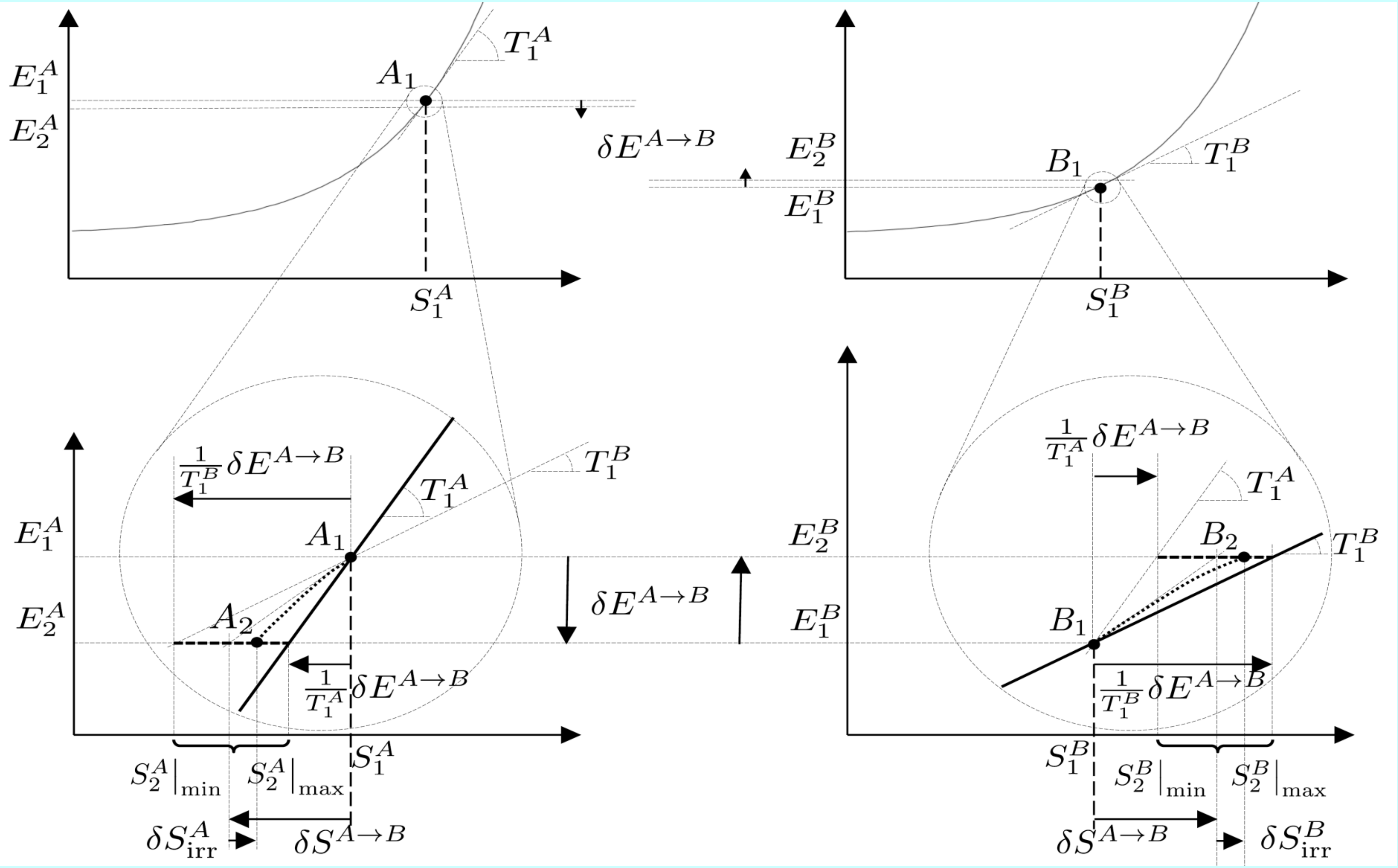
$$\frac{\delta E^{A\to B}}{T_1^A} \underset{2A,3A}{\le} \delta S^{A\to B} - \delta S^A_{\rm irr} \underset{1A}{\le} \delta S^{A\to B} \underset{1B}{\le} \delta S^{A\to B} + \delta S^B_{\rm irr} \underset{2B,3B}{\le} \frac{\delta E^{A\to B}}{T_1^B}$$

* For either A or B: $E_2 = E_1 + dE$, $S_2 = S_1 + dS$,

$$S_2 \le S_{2,\max} = S_{\rm SES}(E_1 + dE, V, n) = S_1 + \frac{dE}{T_1} + \left.\frac{\partial^2 S_{\rm SES}}{\partial E^2}\right|_{E_1} \frac{(dE)^2}{2} \cdots$$

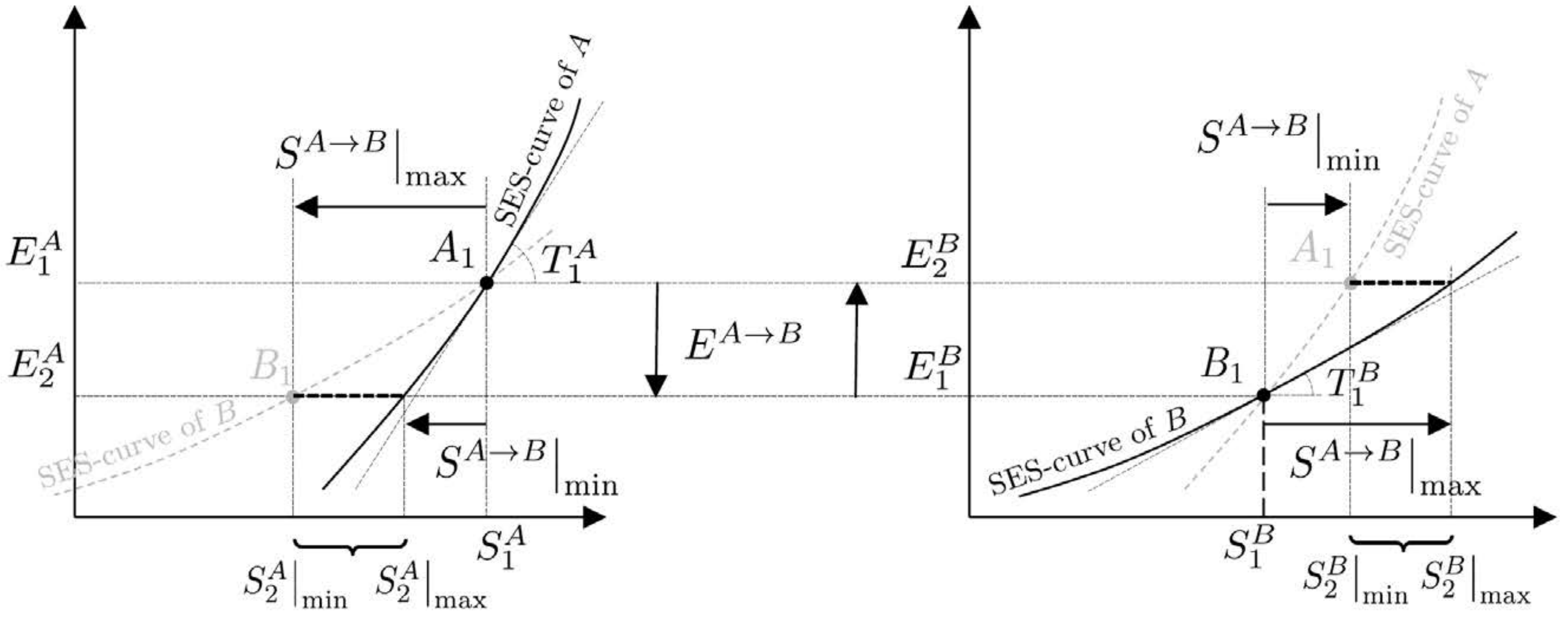
graphical proof of Clausius inequality (infinitesimal transfers)

$$\frac{\delta E^{A\to B}}{T_1^A} \underset{2A,3A}{\leq} \delta S^{A\to B} - \delta S_{\rm irr}^A \underset{1A}{\leq} \delta S^{A\to B} \underset{1B}{\leq} \delta S^{A\to B} + \delta S_{\rm irr}^B \underset{2B,3B}{\leq} \frac{\delta E^{A\to B}}{T_1^B}$$



graphical proof of a more precise Clausius inequality
valid for finite transfers of energy and entropy

$$S^B_{\mathrm{SES}}(E^B_1 + E^{A\to B}, V^B, n^B) - S^B_1 \le S^{A\to B} \le S^A_1 - S^A_{\mathrm{SES}}(E^A_1 - E^{A\to B}, V^A, n^A)$$



Systems A and B are initially in SES and interact directly without other effects by exchanging a finite amount $E^{A\to B}$ of energy. Such exchange can occur only if there is also an entropy $S^{A\to B}$ transfer, at least $S^{A\to B}|_{\min}$ but no more than $S^{A\to B}|_{\max}$.

Next:

Work interactions
Adiabatic process

Non-Work interactions
Heat interactions