2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 07

Room 3-442
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Changing variables of the fundamental relation by means
Legendre transform

Legendre transform of a function of a single variable

Consider a curve described by the convex or concave monotonic function

$$F = F(y) \qquad \lambda(y) = \frac{\partial F}{\partial y} \qquad \boxed{L(y) = F(y) - \lambda(y)\, y}$$

Legendre's observation is that we can describe the same curve also as the envelope of the family of its tangent lines, by the function that relates the slope λ of each tangent line to its intercept L at $y = 0$.

Since the $F(y)$ is convex or concave and monotonic, $\lambda = \lambda(y)$ is monotonic and hence invertible. Using its inverse, $y = y(\lambda)$, we find the Legendre transform of $F = F(y)$

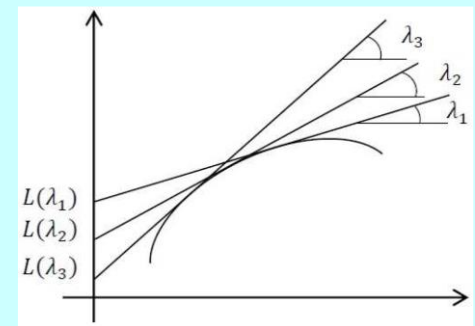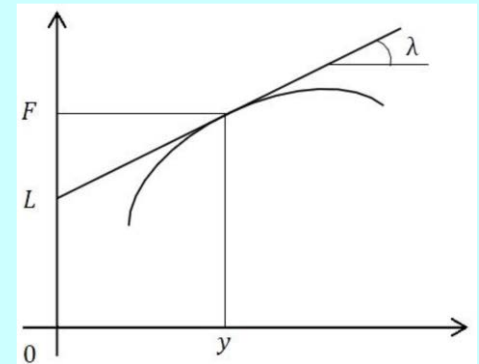$$\boxed{L = L(\lambda)} = F(y(\lambda)) - \lambda\, y(\lambda)$$

Notice that the Legendre transform of $L = L(\lambda)$ is the original $F = F(y)$. In fact, denoting the slope of its tangent line by η and its intercept by G,

$$\eta(\lambda) = \frac{\partial L}{\partial \lambda} = \frac{\partial F}{\partial y}\frac{\partial y}{\partial \lambda} - y(\lambda) - \lambda\frac{\partial y}{\partial \lambda} = -y(\lambda) \quad \Rightarrow \quad \eta = -y$$

$$G = G(\eta) = L(\lambda(\eta)) - \eta\, \lambda(\eta)$$

$$G(y) = G(-\eta) = L(\lambda(y)) + y\, \lambda(y) = F(y(\lambda(y))) - \lambda(y)\, y(\lambda(y)) + y\, \lambda(y) = F(y)$$

where we used $y(\lambda(y)) = y$ since $y = y(\lambda)$ is the inverse of $\lambda = \lambda(y)$.

Examples:
$$F(y) = e^y$$
$$L(\lambda) = \lambda - \lambda \ln \lambda$$
$$F(y) = \tfrac{1}{2} y^2$$
$$L(\lambda) = \tfrac{1}{2}\lambda^2$$
$$F(y) = \tfrac{1}{2}\underline{y} \cdot \underline{\underline{A}} \cdot \underline{y}$$
$$L(\lambda) = \tfrac{1}{2}\underline{\lambda} \cdot \underline{\underline{A}} \cdot \underline{\lambda}$$

Characteristic SES functions from
Legendre transforms of the fundamental relation in energy form

$E = E(S, V, \boldsymbol{n})$				$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$ $+\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$	fundamental relation
$F = F(y, \cdots)$	y	$\lambda = \dfrac{\partial F}{\partial y}$	$L = F - \lambda y$ $= L(\lambda, \cdots)$	$\mathrm{d}L = -y\,\mathrm{d}\lambda + \cdots$	
$E = E(S, V, \boldsymbol{n})$	S	T	$F = E - TS$ $= F(T, V, \boldsymbol{n})$	$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$ $+\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$	Helmholtz free energy
$F = F(T, V, \boldsymbol{n})$	V	$-p$	$G = F - (-p)V$ $= E - TS + pV$ $= G(T, p, \boldsymbol{n})$	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$ $+\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$	Gibbs free energy
$E = E(S, V, \boldsymbol{n})$	V	$-p$	$H = E - (-p)V$ $= H(S, p, \boldsymbol{n})$	$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$ $+\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$	Enthalpy
$H = H(S, p, \boldsymbol{n})$	S	T	$G = H - TS$ $= E - TS + pV$ $= G(T, p, \boldsymbol{n})$	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$ $+\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$	Gibbs free energy
$G = G(T, p, \boldsymbol{n})$	n_i	μ_i	$Eu_i = G - \mu_i n_i$ $= E - TS + pV$ $-\mu_i n_i$ $= Eu_i(T, p, \mu_i, \boldsymbol{n}')$	$\mathrm{d}Eu_i = -S\,\mathrm{d}T + V\,\mathrm{d}p$ $-n_i\mathrm{d}\mu_i + \boldsymbol{\mu}'\cdot\mathrm{d}\boldsymbol{n}'$	osmotic free energy
$G = G(T, p, \boldsymbol{n})$	$\boldsymbol{n}$	$\boldsymbol{\mu}$	$Eu = G - \boldsymbol{\mu}\cdot\boldsymbol{n}$ $= E - TS + pV$ $-\boldsymbol{\mu}\cdot\boldsymbol{n}$ $= Eu(T, p, \boldsymbol{\mu})$	$\mathrm{d}Eu = -S\,\mathrm{d}T + V\,\mathrm{d}p$ $-\boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu}$	Euler free energy

Maxwell relations

From $E(S, V, \boldsymbol{n})$, $T = \left(\frac{\partial E}{\partial S}\right)_{V,\boldsymbol{n}} = T(S, V, \boldsymbol{n})$ and $p = -\left(\frac{\partial E}{\partial V}\right)_{S,\boldsymbol{n}} = p(S, V, \boldsymbol{n})$

$$\left(\frac{\partial^2 E}{\partial S \partial V}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 E}{\partial V \partial S}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad -\left(\frac{\partial p}{\partial S}\right)_{V,\boldsymbol{n}} = \left(\frac{\partial T}{\partial V}\right)_{S,\boldsymbol{n}}$$

From $F(T, V, \boldsymbol{n})$, $S = -\left(\frac{\partial F}{\partial T}\right)_{V,\boldsymbol{n}} = S(T, V, \boldsymbol{n})$ and $p = -\left(\frac{\partial F}{\partial V}\right)_{T,\boldsymbol{n}} = p(T, V, \boldsymbol{n})$

$$\left(\frac{\partial^2 F}{\partial T \partial V}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 F}{\partial V \partial T}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \left(\frac{\partial p}{\partial T}\right)_{V,\boldsymbol{n}} = \left(\frac{\partial S}{\partial V}\right)_{T,\boldsymbol{n}}$$

From $H(S, p, \boldsymbol{n})$, $T = \left(\frac{\partial H}{\partial S}\right)_{p,\boldsymbol{n}} = T(S, p, \boldsymbol{n})$ and $V = \left(\frac{\partial H}{\partial p}\right)_{S,\boldsymbol{n}} = V(S, p, \boldsymbol{n})$

$$\left(\frac{\partial^2 H}{\partial S \partial p}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 H}{\partial p \partial S}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \left(\frac{\partial V}{\partial S}\right)_{p,\boldsymbol{n}} = \left(\frac{\partial T}{\partial p}\right)_{S,\boldsymbol{n}}$$

From $G(T, p, \boldsymbol{n})$, $S = -\left(\frac{\partial G}{\partial T}\right)_{p,\boldsymbol{n}} = S(T, p, \boldsymbol{n})$ and $V = \left(\frac{\partial G}{\partial p}\right)_{T,\boldsymbol{n}} = V(T, p, \boldsymbol{n})$

$$\left(\frac{\partial^2 G}{\partial T \partial p}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 G}{\partial p \partial T}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial S}{\partial p}\right)_{T,\boldsymbol{n}}$$

Review of basic concepts:

Manipulations of SES functions

Jacobian determinants
cyclic relation

Jacobian determinants

Given two functions $f = f(x, y)$ and $g = g(x, y)$ of the independent variables x and y, the determinant of the Jacobian matrix has the properties

$$\frac{\partial(f, g)}{\partial(x, y)} = \begin{vmatrix} \left(\frac{\partial f}{\partial x}\right)_y & \left(\frac{\partial f}{\partial y}\right)_x \\ \left(\frac{\partial g}{\partial x}\right)_y & \left(\frac{\partial g}{\partial y}\right)_x \end{vmatrix} = -\frac{\partial(g, f)}{\partial(x, y)} = \frac{\partial(g, f)}{\partial(y, x)} = -\frac{\partial(f, g)}{\partial(y, x)}$$

Considering the particularly simple function $g(x, y) = y$, for which $(\partial g/\partial x)_y = 0$ and $(\partial g/\partial y)_x = 1$, yields the identity

$$\frac{\partial(f, y)}{\partial(x, y)} = \left(\frac{\partial f}{\partial x}\right)_y \qquad \text{note also that } \frac{\partial(x, y)}{\partial(x, y)} = 1$$

If $x = x(f)$ is the inverse of a function $f = f(x)$ of a single variable only, their first derivatives are one the inverse of the other, $x'(f) = 1/f'(x)$ or $\mathrm{d}x/\mathrm{d}f = \frac{1}{\mathrm{d}f/\mathrm{d}x}$. The equivalent for

the inverse $\begin{cases} x = x(f, g) \\ y = y(f, g) \end{cases}$ of system $\begin{cases} f = f(x, y) \\ g = g(x, y) \end{cases}$ is $\dfrac{\partial(x, y)}{\partial(f, g)} = 1 \left/ \dfrac{\partial(f, g)}{\partial(x, y)}\right.$

Choosing the simple function $g(x, y) = y$, the above yields $x = x(f, y)$, which is the inversion of function $f = f(x, y)$ with respect to variable x, and proves the useful identity

$$\left(\frac{\partial x}{\partial f}\right)_y = 1 \left/ \left(\frac{\partial f}{\partial x}\right)_y \right.$$

Jacobian determinants

For a function of a single variable $f = f(x)$, if we change independent variable from x to a, with $x = x(a)$, so that $f = f(x(a))$, the chain rule reads

$$\frac{\mathrm{d}f}{\mathrm{d}a} = \frac{\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}a}$$

The equivalent for a system of two functions in two variables when we change independent variables from x, y to a, b, with $x = x(a,b)$ and $y = y(a,b)$, is

$$\frac{\partial(f,g)}{\partial(a,b)} = \frac{\partial(f,g)}{\partial(a,b)}\frac{\partial(x,y)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(x,y)}\frac{\partial(x,y)}{\partial(a,b)} = \frac{\partial(f,g)}{\partial(a,b)}$$

In the example below, for the pair (x,y) we first choose (S,p) and then (T,V), to obtain

$$\det(\mathrm{Hess}(E)) = \begin{vmatrix} \dfrac{\partial^2 E}{\partial S^2} & \dfrac{\partial^2 E}{\partial S \partial V} \\[2mm] \dfrac{\partial^2 E}{\partial V \partial S} & \dfrac{\partial^2 E}{\partial V^2} \end{vmatrix} = \begin{vmatrix} \left(\dfrac{\partial T}{\partial S}\right)_V & -\left(\dfrac{\partial p}{\partial S}\right)_V \\[2mm] \left(\dfrac{\partial T}{\partial V}\right)_S & -\left(\dfrac{\partial p}{\partial V}\right)_S \end{vmatrix} = -\frac{\partial(T,p)}{\partial(S,V)} = -\frac{\partial(T,p)}{\partial(S,V)}$$

$$= \begin{cases} -\dfrac{\partial(T,p)}{\partial(S,p)}\dfrac{\partial(S,p)}{\partial(S,V)} = \left(\dfrac{\partial T}{\partial S}\right)_p\left(\dfrac{\partial p}{\partial V}\right)_S = \dfrac{T}{C_p}\dfrac{1}{V\kappa_S} \geq 0 \\[3mm] -\dfrac{\partial(T,p)}{\partial(T,V)}\dfrac{\partial(T,V)}{\partial(S,V)} = \left(\dfrac{\partial p}{\partial V}\right)_T\left(\dfrac{\partial T}{\partial S}\right)_V = \dfrac{1}{V\kappa_T}\dfrac{T}{C_V} \geq 0 \end{cases} \Rightarrow \begin{array}{l} \text{implying} \\ \text{also the} \\ \text{identity} \end{array} \boxed{\dfrac{C_p}{C_V} = \dfrac{\kappa_T}{\kappa_S}}$$

Jacobian determinants

Recall (just used also in the previous slides) the following relations and definitions

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,\boldsymbol{n}} = T\left(\frac{\partial S}{\partial T}\right)_{V,\boldsymbol{n}}$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,\boldsymbol{n}} = T\left(\frac{\partial S}{\partial T}\right)_{p,\boldsymbol{n}}$$

$$\mathrm{d}V|_{\boldsymbol{n}} = V\alpha_p\,\mathrm{d}T - V\kappa_T\,\mathrm{d}p$$

$$V\alpha_p = \left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}}$$

$$V\kappa_T = -\left(\frac{\partial V}{\partial p}\right)_{T,\boldsymbol{n}}$$

$$V\kappa_S = -\left(\frac{\partial V}{\partial p}\right)_{S,\boldsymbol{n}}$$

Cyclic relation

Using Jacobians it is easy to prove the cyclic relation

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

that holds between the three functions

$$\begin{cases} x = x(y,z) \\ y = y(z,x) \\ z = z(x,y) \end{cases}$$

that represent the same surface $f(x,y,z) = 0$. In fact, expressing partial derivatives in term of Jacobians and using their properties

$$\frac{\partial(x,z)}{\partial(y,z)}\frac{\partial(y,x)}{\partial(z,x)}\frac{\partial(z,y)}{\partial(x,y)} = \overbrace{\frac{\partial(x,z)}{\partial(z,x)}}^{-1}\overbrace{\frac{\partial(y,x)}{\partial(x,y)}}^{-1}\overbrace{\frac{\partial(z,y)}{\partial(y,z)}}^{-1} = -1$$

For example, the cyclic relation for the three equivalent equations of state $V = V(T, p, \boldsymbol{n})$, $T = T(V, p, \boldsymbol{n})$, $p = p(V, T, \boldsymbol{n})$ which represent the p–V–T surface for the SES of equal given composition $\boldsymbol{n}$, is

$$\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} \left(\frac{\partial T}{\partial p}\right)_{V,\boldsymbol{n}} \left(\frac{\partial p}{\partial V}\right)_{T,\boldsymbol{n}} = -1$$

As another example, using this cyclic relation and a Maxwell relation, to obtain

$$\left(\frac{\partial S}{\partial V}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial p}{\partial T}\right)_{V,\boldsymbol{n}} = -\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} \left(\frac{\partial p}{\partial V}\right)_{T,\boldsymbol{n}} = \frac{\alpha_p}{\kappa_T}$$

Mayer relation between C_p, C_V, α_p, κ_T

To prove the relation

$$C_p = C_V + \frac{VT\alpha_p^2}{\kappa_T}$$

Start from the definition of C_p (drop $\boldsymbol{n}$ for simplicity)

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,\boldsymbol{n}} = T\left(\frac{\partial S}{\partial T}\right)_{p,\boldsymbol{n}} = T\frac{\partial(S,p)}{\partial(T,p)} = T\frac{\partial(S,p)}{\partial(T,p)} =$$

$$= T\frac{\partial(S,p)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(T,p)} = \frac{\partial(S,p)}{\partial(T,V)}T\left(\frac{\partial V}{\partial p}\right)_T = -\frac{\partial(S,p)}{\partial(T,V)}TV\kappa_T$$

Next compute the Jacobian and substitute

$$\frac{\partial(S,p)}{\partial(T,V)} = \begin{vmatrix} \left(\dfrac{\partial S}{\partial T}\right)_V & \left(\dfrac{\partial S}{\partial V}\right)_T \\ \left(\dfrac{\partial p}{\partial T}\right)_V & -\left(\dfrac{\partial p}{\partial V}\right)_T \end{vmatrix} = \begin{vmatrix} \dfrac{C_V}{T} & \dfrac{\alpha_p}{\kappa_T} \\ \dfrac{\alpha_p}{\kappa_T} & -\dfrac{1}{V\kappa_T} \end{vmatrix} = -\frac{C_V}{TV\kappa_T} - \frac{\alpha_p^2}{\kappa_T^2}$$
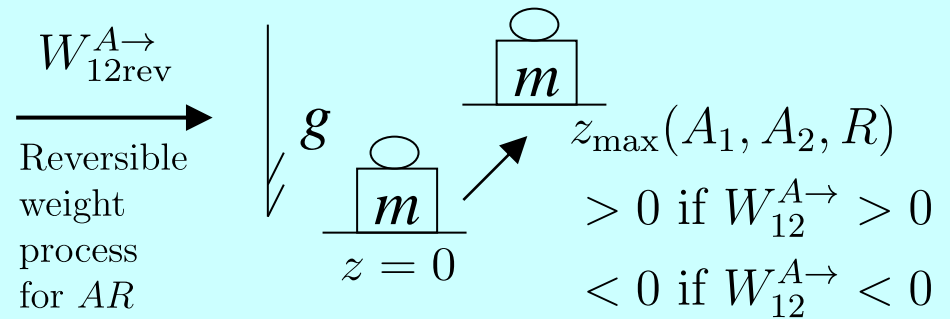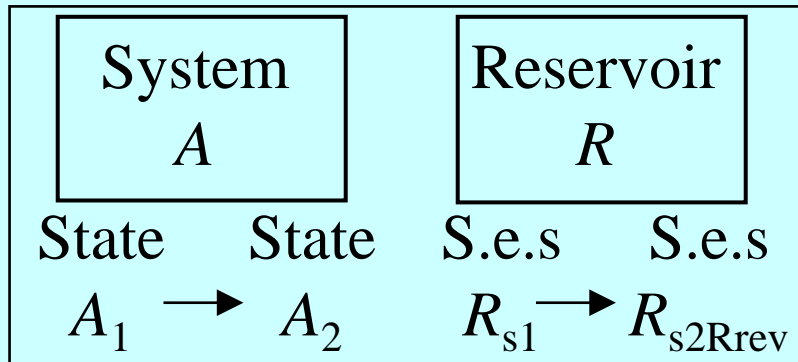
Review of basic concepts:

**availabile energy with respect to
various types of thermal reservoirs**

availability functions

stability conditions

LeChatelier-Braun principle

Available energy with respect to a
thermal reservoir with fixed volume and amounts

System A	Reservoir R
State State	S.e.s S.e.s
$A_1 \longrightarrow A_2$	$R_{s1} \longrightarrow R_{s2Rrev}$

$W_{12rev}^{A\to}$

Reversible weight process for AR

g m $z=0$ m $z_{\max}(A_1, A_2, R)$

> 0 if $W_{12}^{A\to} > 0$

< 0 if $W_{12}^{A\to} < 0$

Energy balance: $(E_2^A - E_1^A) + (E_2^R - E_1^R) = -W_{12}^{A\to}$

Entropy balance: $(S_2^A - S_1^A) + (S_2^R - S_1^R) = S_{\text{gen}}$

Fund.rel. for R: $E_2^R - E_1^R = T_R \left(S_2^R - S_1^R \right)$

Eliminate $(E_2^R - E_1^R)$ and $(S_2^R - S_1^R)$ from the above to yield:

$W_{12}^{A\to} = E_1^A - E_2^A - T_R \left(S_1^A - S_2^A \right) - T_R S_{\text{gen}} = W_{12rev}^{A\to} - T_R S_{\text{gen}}$

$W_{12rev}^{A\to} = \left(\Omega^R \right)_1^A - \left(\Omega^R \right)_2^A = \Gamma_1^A - \Gamma_2^A$

where $\left(\Omega^R \right)^A = E^A - E_R^A - T_R \left(S^A - S_R^A \right) = \Gamma^A - \Gamma_R^A$

we define the **canonical availability function** $\Gamma = E - T_R S$

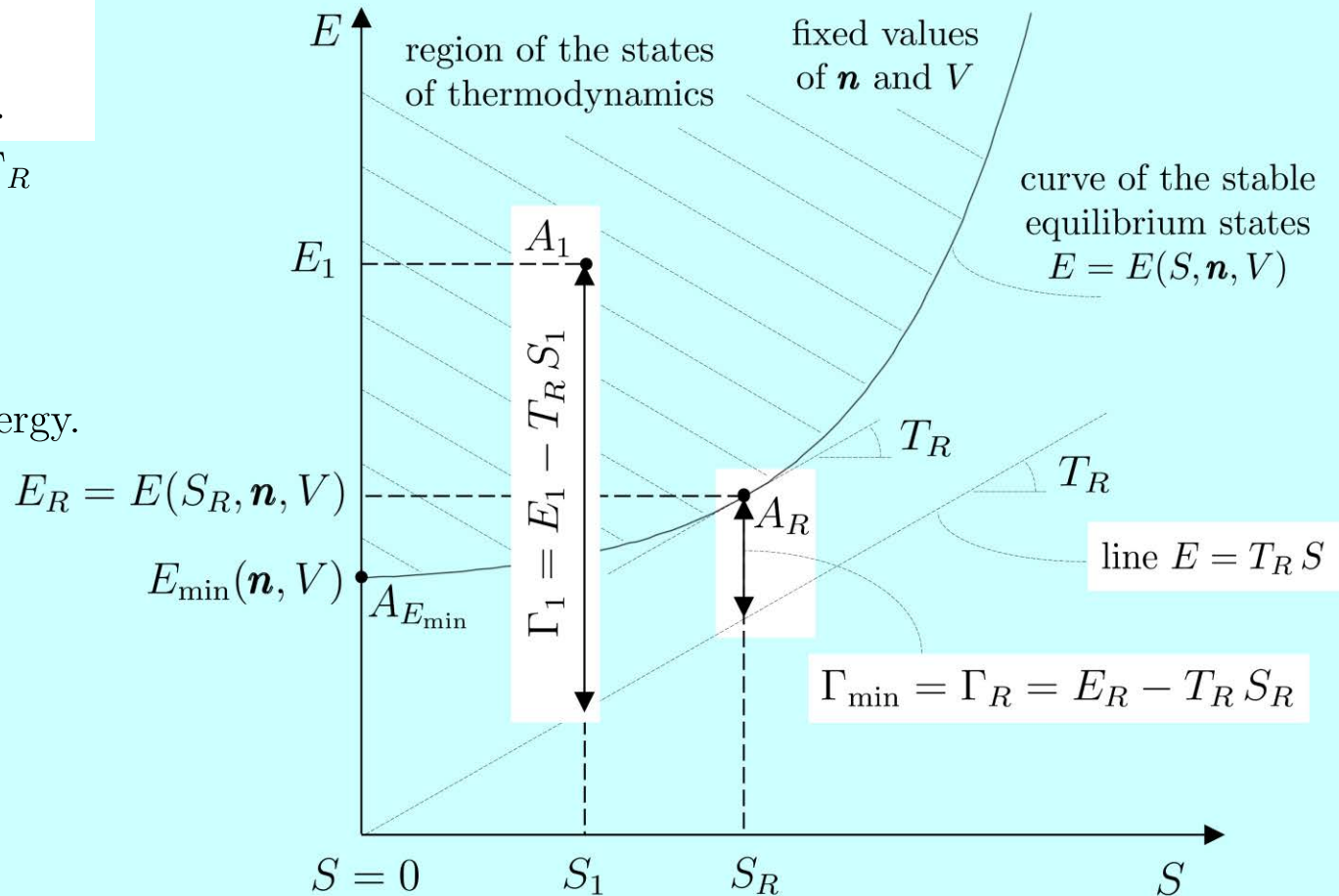Note that Γ is **minimum at state** A_R with $T_R^A = T_R$, where $\Gamma_R = F_R$

Availability function $\Gamma = E - T_R\,S$:

From $\left(\Omega^R\right)_1^A = \Gamma_1^A - \Gamma_R^A \begin{cases} = 0 \text{ if } A_1 = A_R \\ > 0 \text{ if } A_1 \neq A_R \end{cases}$

follows that $\Gamma > \Gamma_R$ for
any state of A that
is not of MSE with R.
The minimum value Γ_R
is achieved only at
the MSE state A_R,
where $\Gamma_R = F_R$,
the Helmholtz free energy.

region of the states
of thermodynamics

fixed values
of $\boldsymbol{n}$ and V

curve of the stable
equilibrium states
$E = E(S, \boldsymbol{n}, V)$

E_1

A_1

$E_R = E(S_R, \boldsymbol{n}, V)$

T_R

T_R

A_R

$E_{\min}(\boldsymbol{n}, V)$

$A_{E_{\min}}$

$\Gamma_1 = E_1 - T_R\,S_1$

line $E = T_R\,S$

$\Gamma_{\min} = \Gamma_R = E_R - T_R\,S_R$

$S = 0$ S_1 S_R S

Stability conditions deriving from the available energy with respect to a
thermal reservoir with fixed volume and amounts

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta \Gamma^A = \Gamma_1^A - \Gamma_R^A > 0 \qquad \text{where} \quad \Gamma^A = E^A - T_R S^A$$

For example, choose A_1 to be the neighbouring SES with $\Delta S^A = dS$, and the same values of V and $\boldsymbol{n}$, so that

$$\Delta E^A = E^A(S_R + dS, V, \boldsymbol{n}) - E_R^A = T_R\, dS + \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}} + \cdots$$

This implies

$$\Delta \Gamma^A = \Delta E^A - T_R \Delta S^A = \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 E^A|_{V,\boldsymbol{n}} \geq 0}$$

Again, choose instead A_1 to be the neighbouring SES with $\Delta E^A = dE$, and the same values of V and $\boldsymbol{n}$, so that

$$\Delta S^A = S^A(E_R + dE, V, \boldsymbol{n}) - S_R^A = \frac{1}{T_R} dE + \tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}} + \cdots$$

This implies

$$\Delta \Gamma^A = \Delta E^A - T_R \Delta S^A = -\tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 S^A|_{V,\boldsymbol{n}} \leq 0}$$

Stability conditions deriving from the available energy with respect to a
thermal reservoir with fixed volume and amounts

If V and $\boldsymbol{n}$ cannot change for system A, the **partial Hessian of the fundamental relation** $S = S^A(E, \boldsymbol{n}, V)$ is simply the second order derivative

$$\text{partialHessian}(S^A)|_{\boldsymbol{n},V} = \left(\frac{\partial^2 S}{\partial E^2}\right)^A_{\boldsymbol{n},V}$$

The partial second-order differential evaluated at state A_R is

$$d^2 S^A|_{\boldsymbol{n},V} = dE \cdot \text{partialHessian}(S)|_{\boldsymbol{n},V}|_R \cdot dE = \left(\frac{\partial^2 S}{\partial E^2}\right)^A_{\boldsymbol{n},V}\bigg|_R (dE)^2 \leq 0$$

Which, repeated for reservoirs at different T_R's proves an important general concavity feature of the fundamental relation of any system A

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{\boldsymbol{n},V} \leq 0 \quad \Rightarrow \quad -\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_{\boldsymbol{n},V} = -\frac{1}{T^2 C_V} \leq 0 \quad \Rightarrow \quad C_V \geq 0$$

Similarly, from $d^2 E^A|_{\boldsymbol{n},V} \geq 0$ follows that in general, for any system A,

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{\boldsymbol{n},V} \geq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial S}\right)_{\boldsymbol{n},V} \geq 0$$

Stability conditions and
LeChatelier-Braun principle

The inequalities just seen, implied by stability conditions, give body to the general **LeChatelier-Braun theorem** (or **principle**).

So far, we have seen that

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{\boldsymbol{n},V} \leq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial E}\right)_{\boldsymbol{n},V} \geq 0$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{\boldsymbol{n},V}^{A} \geq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial S}\right)_{\boldsymbol{n},V} \geq 0$$

Combined with the idea that T is an escaping tendency for energy, we may interpret this as follows.

If we change a SES to another SES with higher energy (or entropy), the temperature increases, hence enhancing the systems' tendency to give energy (or entropy) away. The increase of temperature can be interpreted as an attemp of the system to counteract the externally imposed increase of energy (or entropy) by enhancing its tendency to give energy (and entropy) away.

If the system is initially in MSE with a reservoir R, an injection (subtraction) of energy pushes its state away from MSE, but the consequent increase (decrease) of its temperature, away from the initial T_R, favors a spontaneous process whereby the system exchanges energy (and entropy) with R so as to return to MSE.

Available energy with respect to a
thermal reservoir with variable volume and fixed amounts
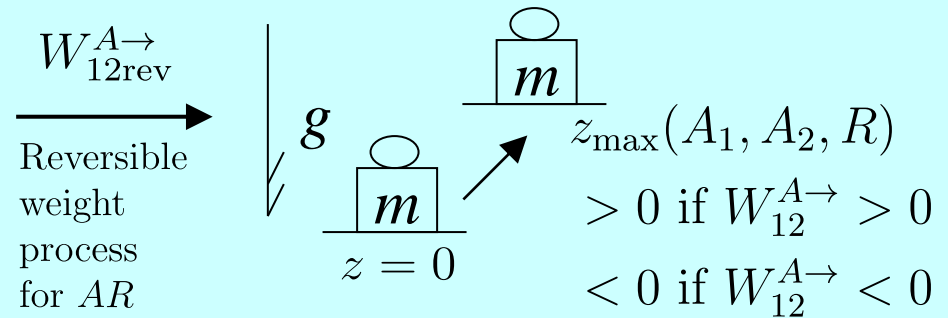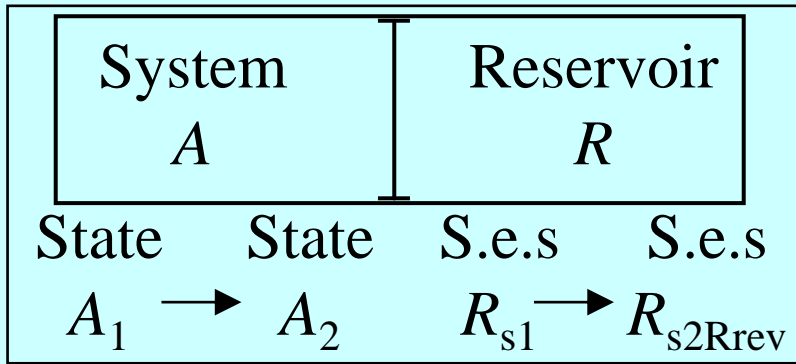
Volume balance: $(V_2^A - V_1^A) + (V_2^R - V_1^R) = 0$

Energy balance: $(E_2^A - E_1^A) + (E_2^R - E_1^R) = -W_{12}^{A\rightarrow}$

Entropy balance: $(S_2^A - S_1^A) + (S_2^R - S_1^R) = S_{\text{gen}}$

Fund.rel. for R: $E_2^R - E_1^R = T_R(S_2^R - S_1^R) - p_R(V_2^R - V_1^R)$

Eliminate $(V_2^R - V_1^R)$, $(E_2^R - E_1^R)$ and $(S_2^R - S_1^R)$ from the above to yield:

$W_{12}^{A\rightarrow} = E_1^A - E_2^A - T_R(S_1^A - S_2^A) + p_R(V_1^A - V_2^A) - T_R S_{\text{gen}} = W_{12\text{rev}}^{A\rightarrow} - T_R S_{\text{gen}}$

$W_{12\text{rev}}^{A\rightarrow} = \left(\Omega^{R_V}\right)_1^A - \left(\Omega^{R_V}\right)_2^A = \Phi_1^A - \Phi_2^A$

where $\left(\Omega^{R_V}\right)^A = E^A - E_R^A - T_R(S^A - S_R^A) + p_R(V^A - V_R^A) = \Phi^A - \Phi_R^A$

we define the **availability function** $\Phi = E - T_R S + p_R V$

Φ is **minimum at state** A_R with $T_R^A = T_R$, $p_R^A = p_R$, where $\Phi_R = G_R$

Stability conditions deriving from the available energy with respect to

changes in volume at fixed amounts

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta\Phi^A = \Phi_1^A - \Phi_R^A > 0 \qquad \text{where} \quad \Phi^A = E^A - T_R S^A + p_R V^A$$

For example, choose A_1 to be the neighbouring SES with $\Delta S^A = dS$, $\Delta V^A = dV$ and the same values of $\boldsymbol{n}$, so that

$$\Delta E^A = E^A(S_R + dS, V_R + dV, \boldsymbol{n}) - E_R^A = T_R\,dS - p_R\,dV + \tfrac{1}{2}d^2 E^A\big|_{\boldsymbol{n}} + \cdots$$

This implies

$$\Delta\Phi^A = \Delta E^A - T_R\Delta S^A + p_R\Delta V^A = \tfrac{1}{2}d^2 E^A\big|_{\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 E^A\big|_{\boldsymbol{n}} \geq 0}$$
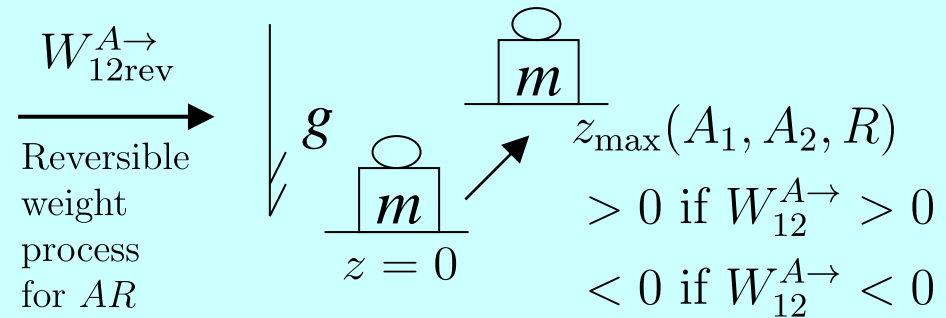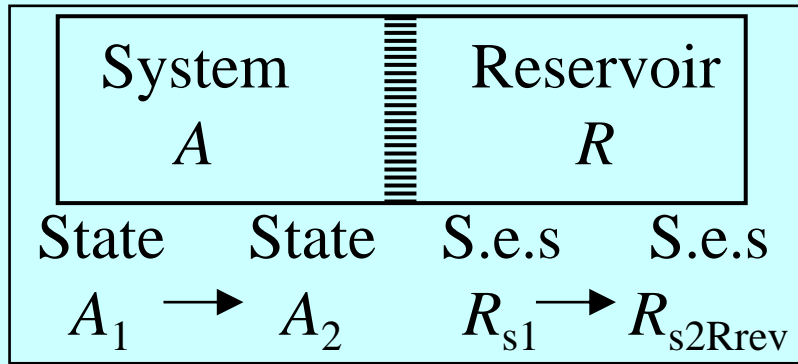
Again, choose instead A_1 to be the neighbouring SES with $\Delta E^A = dE$, $\Delta V^A = dV$ and the same values of $\boldsymbol{n}$, so that

$$\Delta S^A = S^A(E_R + dE, V, \boldsymbol{n}) - S_R^A = \frac{1}{T_R}dE + \frac{p_R}{T_R}dV + \tfrac{1}{2}d^2 S^A\big|_{\boldsymbol{n}} + \cdots$$

This implies

$$\Delta\Phi^A = \Delta E^A - T_R\Delta S^A + p_R\Delta V^A = -\tfrac{1}{2}d^2 S^A\big|_{\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 S^A\big|_{\boldsymbol{n}} \leq 0}$$

Available energy with respect to a
thermal reservoir with fixed volume and variable amount of "i"

Amount balance: $(n_{i2}^A - n_{i1}^A) + (n_{i2}^R - n_{i1}^R) = 0$

Energy balance: $(E_2^A - E_1^A) + (E_2^R - E_1^R) = -W_{12}^{A\rightarrow}$

Entropy balance: $(S_2^A - S_1^A) + (S_2^R - S_1^R) = S_{\text{gen}}$

Fund.rel. for R: $E_2^R - E_1^R = T_R(S_2^R - S_1^R) + \mu_{iR}(n_{i2}^R - n_{i1}^R)$

Eliminate $(n_{i2}^R - n_{i1}^R)$, $(E_2^R - E_1^R)$ and $(S_2^R - S_1^R)$ from the above to yield:

$W_{12}^{A\rightarrow} = E_1^A - E_2^A - T_R(S_1^A - S_2^A) + \mu_{iR}(n_{i1}^A - n_{i2}^A) - T_R S_{\text{gen}} = W_{12\text{rev}}^{A\rightarrow} - T_R S_{\text{gen}}$

$W_{12\text{rev}}^{A\rightarrow} = \left(\Omega^{R_{n_i}}\right)_1^A - \left(\Omega^{R_{n_i}}\right)_2^A = \Upsilon_1^A - \Upsilon_2^A$

where $\left(\Omega^{R_{n_i}}\right)^A = E^A - E_R^A - T_R(S^A - S_R^A) + \mu_{iR}(n_i^A - n_{iR}^A) = \Upsilon^A - \Upsilon_R^A$

we define the **osmotic availability function** $\Upsilon = E - T_R S - \mu_{iR} n_i$

and note that Υ is **minimum at state** A_R with $T_R^A = T_R$ and $\mu_{iR}^A = \mu_{iR}$.

Stability conditions deriving from the available energy with respect to
changes in variable amount of "i" at fixed volume

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta \Upsilon^A = \Upsilon_1^A - \Upsilon_R^A > 0 \qquad \text{where} \quad \Upsilon^A = E^A - T_R S^A - \mu_{iR} n_i^A$$

For example, choose A_1 to be the neighbouring SES with $\Delta S^A = dS$, $\Delta n_i^A = dn_i$ and the same values of V and the other $\boldsymbol{n}'_i$, so that

$$\Delta E^A = E^A(S_R + dS, V, n_{iR} + dn_i, \boldsymbol{n}'_i) - E_R^A = T_R\, dS + \mu_{iR}\, dn_i + \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}'_i} + \cdots$$

This implies

$$\Delta \Upsilon^A = \Delta E^A - T_R \Delta S^A + \mu_{iR} \Delta n_i^A = \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}'_i} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 E^A|_{V,\boldsymbol{n}'_i} \geq 0}$$
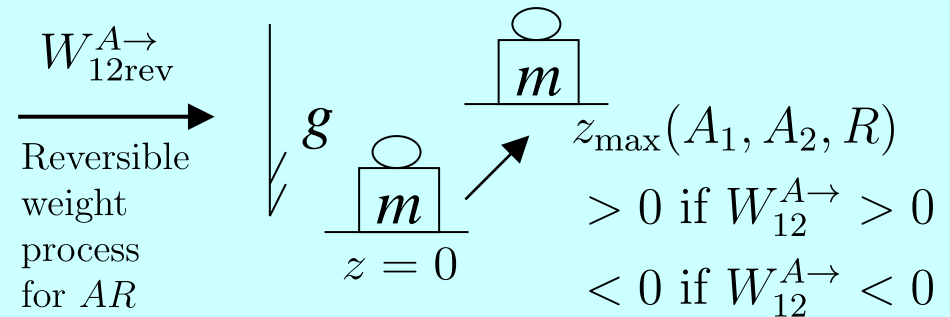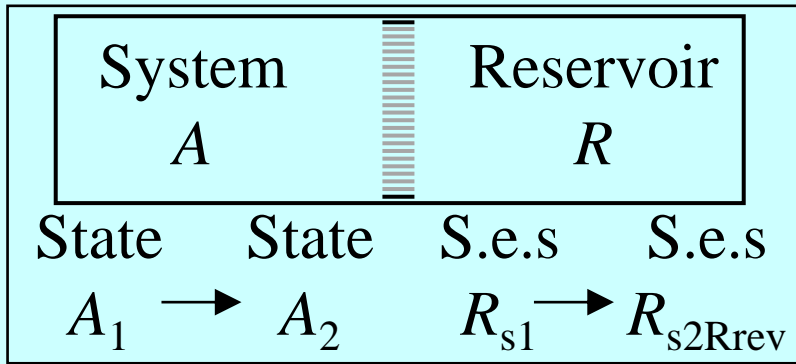
Again, choose instead A_1 to be the neighbouring SES with $\Delta E^A = dE$, $\Delta n_i^A = dn_i$ and the same values of V and the other $\boldsymbol{n}'_i$, so that

$$\Delta S^A = S^A(E_R + dE, V, n_{iR} + dn_i, \boldsymbol{n}'_i) - S_R^A = \frac{1}{T_R} dE - \frac{\mu_{iR}}{T_R} dn_i + \tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}'_i} + \cdots$$

This implies

$$\Delta \Upsilon^A = \Delta E^A - T_R \Delta S^A + \mu_{iR} \Delta n_i^A = -\tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}'_i} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 S^A|_{V,\boldsymbol{n}'_i} \leq 0}$$

Available energy with respect to a
thermal reservoir with variable volume and all amounts

System A — Reservoir R

State $A_1 \to$ State A_2 — S.e.s $R_{s1} \to$ S.e.s R_{s2Rrev}

$W^{A\to}_{12rev}$ — Reversible weight process for AR

g — m at $z=0$, m at $z_{max}(A_1, A_2, R)$
> 0 if $W^{A\to}_{12} > 0$
< 0 if $W^{A\to}_{12} < 0$

V and n_i's balances: $(V_2^A - V_1^A) + (V_2^R - V_1^R) = 0 \quad (n_{i2}^A - n_{i1}^A) + (n_{i2}^R - n_{i1}^R) = 0 \, \forall i$

Energy balance: $(E_2^A - E_1^A) + (E_2^R - E_1^R) = -W^{A\to}_{12}$

Entropy balance: $(S_2^A - S_1^A) + (S_2^R - S_1^R) = S_{gen}$

Fund.rel. for R: $E_2^R - E_1^R = T_R(S_2^R - S_1^R) - p_R(V_2^R - V_1^R) + \sum_i \mu_{iR}(n_{i2}^R - n_{i1}^R)$

Eliminate $(V_2^R - V_1^R)$, $(E_2^R - E_1^R)$, $(S_2^R - S_1^R)$ and all $(n_{i2}^R - n_{i1}^R)$'s from the above to yield:

$W^{A\to}_{12} = E_1^A - E_2^A - T_R(S_1^A - S_2^A) + p_R(V_1^A - V_2^A) + \sum_i \mu_{iR}(n_{i1}^A - n_{i2}^A) - T_R S_{gen}$

$W^{A\to}_{12rev} = \left(\Omega^{R_V,\boldsymbol{n}}\right)_1^A - \left(\Omega^{R_V,\boldsymbol{n}}\right)_2^A = \Xi_1^A - \Xi_2^A$

where $\left(\Omega^{R_V,\boldsymbol{n}}\right)^A = E^A - E_R^A - T_R(S^A - S_R^A) + p_R(V^A - V_R^A) - \sum_i \mu_{iR}(n_i^A - n_{iR}^A)$

we define the **Euler availability function** $\Xi = E - T_R S + p_R V - \sum_i \mu_{iR} n_i$

Ξ is **minimum at** A_R with $T_R^A = T_R$, $p_R^A = p_R$, $\mu_{iR}^A = \mu_{iR} \, \forall i$, where $\Xi_R = Eu_R$

Stability conditions deriving from the available energy with respect to
changes in volume and amounts

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta \Xi^A = \Xi_1^A - \Xi_R^A > 0 \qquad \text{where} \quad \Xi^A = E^A - T_R S^A + p_R V^A - \boldsymbol{\mu}_R \cdot \boldsymbol{n}^A$$

For example, choose A_1 to be the neighbouring SES with $\Delta S^A = dS$, $\Delta V^A = dV$, and $\Delta n_i^A = dn_i \ \forall i$, so that

$$\Delta E^A = E^A(S_R + dS, V_R + dV, \boldsymbol{n}_R + d\boldsymbol{n}) - E_R^A = T_R \, dS - p_R \, dV + \boldsymbol{\mu}_R \cdot d\boldsymbol{n} + \tfrac{1}{2} d^2 E^A + \cdots$$

This implies

$$\Delta \Xi^A = \Delta E^A - T_R \Delta S^A + p_R \Delta V^A - \boldsymbol{\mu}_R \cdot \Delta \boldsymbol{n}^A = \tfrac{1}{2} d^2 E^A + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 E^A \geq 0}$$

Again, choose instead A_1 to be the neighbouring SES with $\Delta E^A = dE$, $\Delta V^A = dV$, and $\Delta n_i^A = dn_i \ \forall i$, so that

$$\Delta S^A = S^A(E_R + dE, V_R + dV, \boldsymbol{n}_R + d\boldsymbol{n}) - S_R^A = \frac{1}{T_R} dE + \frac{p_R}{T_R} dV - \frac{1}{T_R} \boldsymbol{\mu}_R \cdot d\boldsymbol{n} + \tfrac{1}{2} d^2 S^A + \cdots$$

This implies

$$\Delta \Xi^A = \Delta E^A - T_R \Delta S^A + p_R \Delta V^A - \boldsymbol{\mu}_R \cdot \Delta \boldsymbol{n}^A = -\tfrac{1}{2} d^2 S^A + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 S^A \leq 0}$$

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

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

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.

Stability conditions deriving from the available energy with respect to
changes in the amounts at fixed temperature and pressure

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta \Xi^A = \Xi_1^A - \Xi_R^A > 0 \qquad \text{where} \quad \Xi^A = E^A - T_R S^A + p_R V^A - \boldsymbol{\mu}_R \cdot \boldsymbol{n}^A$$

For example, choose A_1 to be the neighbouring SES with same temperature $T_1^A = T_R$ and pressure $p_1^A = p_R$, and $\Delta n_i^A = dn_i \; \forall i$, so that

$$\Delta E^A = E^A(T_R, p_R, \boldsymbol{n}_R + d\boldsymbol{n}) - E_R^A$$

$$\Delta S^A = S^A(T_R, p_R, \boldsymbol{n}_R + d\boldsymbol{n}) - S_R^A$$

$$\Delta V^A = V^A(T_R, p_R, \boldsymbol{n}_R + d\boldsymbol{n}) - V_R^A$$

and therefore also $\Delta E^A - T_R \Delta S^A + p_R \Delta V^A$

$$= \Delta G^A = G^A(T_R, p_R, \boldsymbol{n}_R + d\boldsymbol{n}) - G_R^A = \boldsymbol{\mu}_R \cdot d\boldsymbol{n} + \tfrac{1}{2} d^2 G^A\big|_{T,p} + \cdots$$

This implies

$$\Delta \Xi^A = \Delta G^A - \boldsymbol{\mu}_R \cdot \Delta \boldsymbol{n}^A = \tfrac{1}{2} d^2 G^A\big|_{T,p} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 G^A\big|_{T,p} \geq 0}$$

Stability conditions deriving from the available energy with respect to
changes in volume and amounts at fixed temperature

If A is in state A_R (MSE with the thermal reservoir R), any possible variation to another state A_1 is such that

$$\Delta \Xi^A = \Xi_1^A - \Xi_R^A > 0 \qquad \text{where} \quad \Xi^A = E^A - T_R S^A + p_R V^A - \boldsymbol{\mu}_R \cdot \boldsymbol{n}^A$$

For example, choose A_1 to be the neighbouring SES with same temperature $T_1^A = T_R$, $\Delta V^A = dV$, and $\Delta n_i^A = dn_i$ $\forall i$, so that

$$\Delta E^A = E^A(T_R, V_R + dV, , \boldsymbol{n}_R + d\boldsymbol{n}) - E_R^A$$

$$\Delta S^A = S^A(T_R, V_R + dV, , \boldsymbol{n}_R + d\boldsymbol{n}) - S_R^A$$

and therefore also $\Delta E^A - T_R \Delta S^A$

$$= \Delta F^A = F^A(T_R, V_R + dV, \boldsymbol{n}_R + d\boldsymbol{n}) - F_R^A = -p_R \, dV + \boldsymbol{\mu}_R \cdot d\boldsymbol{n} + \tfrac{1}{2} d^2 F^A\big|_T + \cdots$$

This implies

$$\Delta \Xi^A = \Delta F^A + p_R \Delta V^A - \boldsymbol{\mu}_R \cdot \Delta \boldsymbol{n}^A = \tfrac{1}{2} d^2 F^A\big|_T + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 F^A\big|_T \geq 0}$$

Stability conditions and
LeChatelier-Braun principle

The inequalities just seen, implied by stability conditions, give body to the general **LeChatelier-Braun theorem** (or **principle**).

So far, we have seen that

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{\boldsymbol{n},V} \leq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial E}\right)_{\boldsymbol{n},V} \geq 0$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{\boldsymbol{n},V}^{A} \geq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial S}\right)_{\boldsymbol{n},V} \geq 0$$

Combined with the idea that T is an escaping tendency for energy, we may interpret this as follows.

If we change a SES to another SES with higher energy (or entropy), the temperature increases, hence enhancing the systems' tendency to give energy (or entropy) away. The increase of temperature can be interpreted as an attemp of the system to counteract the externally imposed increase of energy (or entropy) by enhancing its tendency to give energy (and entropy) away.

If the system is initially in MSE with a reservoir R, an injection (subtraction) of energy pushes its state away from MSE, but the consequent increase (decrease) of its temperature, away from the initial T_R, favors a spontaneous process whereby the system exchanges energy (and entropy) with R so as to return to MSE.

Stability conditions and
LeChatelier-Braun principle (more general statement)

Given a function $A(x, y, \boldsymbol{z})$, write its first and second differentials with this notation

$$\mathrm{d}A|_{\boldsymbol{z}} = A_{,x}\,\mathrm{d}x + A_{,y}\,\mathrm{d}y \qquad A_{,x} = \left(\frac{\partial A}{\partial x}\right)_{y,\boldsymbol{z}} = A_{,x}(x, y, \boldsymbol{z}) \qquad A_{,y} = \left(\frac{\partial A}{\partial y}\right)_{x,\boldsymbol{z}} = A_{,y}(x, y, \boldsymbol{z})$$

$$\mathrm{d}^2 A|_{\boldsymbol{z}} = [\mathrm{d}x\ \mathrm{d}y] \begin{bmatrix} A_{,xx} & A_{,xy} \\ A_{,xy} & A_{,yy} \end{bmatrix} \begin{bmatrix} \mathrm{d}x \\ \mathrm{d}y \end{bmatrix} = A_{,xx}\,(\mathrm{d}x)^2 + 2A_{,xy}\,\mathrm{d}x\,\mathrm{d}y + A_{,yy}\,(\mathrm{d}y)^2$$

$$A_{,xx} = \left(\frac{\partial^2 A}{\partial x^2}\right)_{y,\boldsymbol{z}} = \left(\frac{\partial A_{,x}}{\partial x}\right)_{y,\boldsymbol{z}} \qquad A_{,yy} = \left(\frac{\partial^2 A}{\partial y^2}\right)_{x,\boldsymbol{z}} = \left(\frac{\partial A_{,y}}{\partial y}\right)_{x,\boldsymbol{z}}$$

$$A_{,xy} = \left(\frac{\partial^2 A}{\partial x \partial y}\right)_{\boldsymbol{z}} = \left(\frac{\partial A_{,y}}{\partial x}\right)_{y,\boldsymbol{z}} = \left(\frac{\partial A_{,x}}{\partial y}\right)_{x,\boldsymbol{z}} = \left(\frac{\partial^2 A}{\partial y \partial x}\right)_{\boldsymbol{z}} = A_{,yx}$$

The quadratic form can be rewritten (check by substitution) in the two canonical forms

$$\mathrm{d}^2 A|_{\boldsymbol{z}} = A_{,xx}\left(\mathrm{d}x + \frac{A_{,xy}}{A_{,xx}}\,\mathrm{d}y\right)^2 + \lambda_y\,(\mathrm{d}y)^2 \qquad \text{where} \qquad \lambda_y = A_{,yy} - A_{,xx}\left(\frac{A_{,xy}}{A_{,xx}}\right)^2$$

$$= \lambda_x\,(\mathrm{d}x)^2 + A_{,yy}\left(\mathrm{d}y + \frac{A_{,xy}}{A_{,yy}}\,\mathrm{d}x\right)^2 \qquad \text{where} \qquad \lambda_x = A_{,xx} - A_{,yy}\left(\frac{A_{,xy}}{A_{,yy}}\right)^2$$

Therefore, since the stability conditions must hold for arbitrary $\mathrm{d}x$ and $\mathrm{d}y$,

$$\mathrm{d}^2 A|_{\boldsymbol{z}} \geq 0 \implies \begin{cases} A_{,xx} \geq \lambda_x \geq 0 \\ A_{,yy} \geq \lambda_y \geq 0 \end{cases} \quad \text{whereas} \quad \mathrm{d}^2 A|_{\boldsymbol{z}} \leq 0 \implies \begin{cases} A_{,xx} \leq \lambda_x \leq 0 \\ A_{,yy} \leq \lambda_y \leq 0 \end{cases}$$

Stability conditions and
LeChatelier-Braun principle (more general statement)

Whether $\mathrm{d}^2A|_{\boldsymbol{z}}$ is positive semidefinite or negative semidefinite

$$0 \le \det(\mathrm{Hess}(A)) = \begin{vmatrix} A_{,xx} & A_{,xy} \\ A_{,xy} & A_{,yy} \end{vmatrix} = \frac{\partial(A_{,x}, A_{,y})}{\partial(x, y)} = \frac{\partial(A_{,x}, A_{,y})}{\partial(x, y)}$$

$$= \begin{cases} \dfrac{\partial(A_{,x}, A_{,y})}{\partial(A_{,x}, y)} \dfrac{\partial(A_{,x}, y)}{\partial(x, y)} = \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \left(\dfrac{\partial A_{,x}}{\partial x}\right)_y = \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} A_{,xx} \ge 0 \\[3em] \dfrac{\partial(A_{,x}, A_{,y})}{\partial(x, A_{,y})} \dfrac{\partial(x, A_{,y})}{\partial(x, y)} = \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \left(\dfrac{\partial A_{,y}}{\partial y}\right)_x = \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} A_{,yy} \ge 0 \end{cases}$$

Therefore, we can rewrite λ_x and λ_y as

$$\lambda_x = A_{,xx} - A_{,yy}\left(\frac{A_{,xy}}{A_{,yy}}\right)^2 = \frac{\det(\mathrm{Hess}(A))}{A_{,yy}} = \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}}$$

$$\lambda_y = A_{,yy} - A_{,xx}\left(\frac{A_{,xy}}{A_{,xx}}\right)^2 = \frac{\det(\mathrm{Hess}(A))}{A_{,xx}} = \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}}$$

so that the stability conditions become

$$\mathrm{d}^2A|_{\boldsymbol{z}} \ge 0 \Rightarrow \begin{cases} \left(\dfrac{\partial A_{,x}}{\partial x}\right)_y \ge \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \ge 0 \\[1.5em] \left(\dfrac{\partial A_{,y}}{\partial y}\right)_x \ge \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \ge 0 \end{cases} \qquad \mathrm{d}^2A|_{\boldsymbol{z}} \le 0 \Rightarrow \begin{cases} \left(\dfrac{\partial A_{,x}}{\partial x}\right)_y \le \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \le 0 \\[1.5em] \left(\dfrac{\partial A_{,y}}{\partial y}\right)_x \le \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \le 0 \end{cases}$$

Stability conditions and
LeChatelier-Braun principle (more general statement)

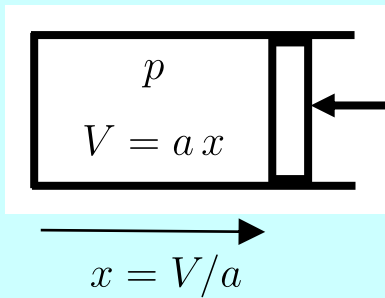| $\mathrm{d}^2 A\vert_{\boldsymbol{z}} \gtreqless 0$	$\boldsymbol{z}$	x	y	$A_{,x}$	$A_{,y}$	$\left(\dfrac{\partial A_{,x}}{\partial x}\right)_y \gtreqless \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \gtreqless 0$	$\left(\dfrac{\partial A_{,y}}{\partial y}\right)_x \gtreqless \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \gtreqless 0$
$\mathrm{d}^2 E\vert_{\boldsymbol{n}} \geq 0$	$\boldsymbol{n}$	S	V	T	$-p$	$\left(\dfrac{\partial T}{\partial S}\right)_V \geq \left(\dfrac{\partial T}{\partial S}\right)_p \geq 0$ $\Rightarrow \quad \dfrac{T}{C_V} \geq \dfrac{T}{C_p} \geq 0$ $\Rightarrow \quad C_p \geq C_V \geq 0$	$-\left(\dfrac{\partial p}{\partial V}\right)_S \geq -\left(\dfrac{\partial p}{\partial V}\right)_T \geq 0$ $\Rightarrow \quad \dfrac{1}{V\kappa_S} \geq \dfrac{1}{V\kappa_T} \geq 0$ $\Rightarrow \quad \kappa_T \geq \kappa_S \geq 0$
$\mathrm{d}^2 G\vert_{T,p} \geq 0$	$\begin{matrix}T\\p\end{matrix}$	n_1	n_2	μ_1	μ_2	$\left(\dfrac{\partial \mu_1}{\partial n_1}\right)_{n_2} \geq \left(\dfrac{\partial \mu_1}{\partial n_1}\right)_{\mu_2} \geq 0$	$\left(\dfrac{\partial \mu_2}{\partial n_2}\right)_{n_1} \geq \left(\dfrac{\partial \mu_2}{\partial n_2}\right)_{\mu_1} \geq 0$

We may interpret these inequalities as follows.

Assertion 1. If a system is initially in MSE with a thermal reservoir R and we perturb it to another SES with higher (lower) value of an additive property x, the system responds by increasing (decreasing) the conjugate potential $A_{,x}$ that measures the escaping tendency of that property. As a result, the system moderates/contrasts the effect of the imposed exchange of x by favoring a spontaneous exchange with R with an opposite effect in an attempt to reestablish MSE.

Assertion 2. The system's response is stronger when a higher number of equilibrium conditions are disrupted by the perturbation. A perturbation that constrains the system to maintain a fixed value of another additive property y produces a stronger counter reaction. In other words, it results in a larger change in the potential $A_{,x}$, which is conjugate to x, than a perturbation that also induces a tuned change in y, designed to maintain the conjugate potential $A_{,y}$ unaltered at its MSE value.
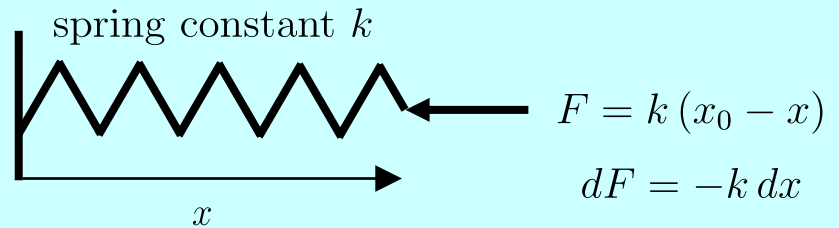
Stability conditions and
LeChatelier-Braun principle (example: air springs)

$d^2 A\|_{\boldsymbol{z}} \gtrless 0$	$\boldsymbol{z}$	x	y	$A_{,x}$	$A_{,y}$	$\left(\dfrac{\partial A_{,x}}{\partial x}\right)_y \gtrless \left(\dfrac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \gtrless 0$	$\left(\dfrac{\partial A_{,y}}{\partial y}\right)_x \gtrless \left(\dfrac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \gtrless 0$
$d^2 E\|_{\boldsymbol{n}} \geq 0$	$\boldsymbol{n}$	S	V	T	$-p$	$\left(\dfrac{\partial T}{\partial S}\right)_V \geq \left(\dfrac{\partial T}{\partial S}\right)_p \geq 0$ $\Rightarrow \quad \dfrac{T}{C_V} \geq \dfrac{T}{C_p} \geq 0$ $\Rightarrow \quad C_p \geq C_V \geq 0$	$-\left(\dfrac{\partial p}{\partial V}\right)_S \geq -\left(\dfrac{\partial p}{\partial V}\right)_T \geq 0$ $\Rightarrow \quad \dfrac{1}{V\kappa_S} \geq \dfrac{1}{V\kappa_T} \geq 0$ $\Rightarrow \quad \kappa_T \geq \kappa_S \geq 0$

$$p, \quad V = a\,x \qquad F = p\,a \qquad dF = a\,dp$$

$$\text{spring constant } k \qquad F = k\,(x_0 - x) \qquad dF = -k\,dx$$

$$x = V/a$$
$$dx = dV/a$$

$$k = -\frac{dF}{dx} = -\frac{a\,dp}{dV/a} = -a^2 \frac{dp}{dV} = \frac{a^2}{V}\frac{1}{-\dfrac{1}{V}\dfrac{\partial V}{\partial p}} = \begin{cases} k_T = \dfrac{a^2}{V\kappa_T} & \text{slow: } T \text{ constant} \\[2ex] & k_S > k_T \qquad \dfrac{k_S}{k_T} = \dfrac{\kappa_T}{\kappa_S} = \dfrac{C_p}{C_V} \\[2ex] k_S = \dfrac{a^2}{V\kappa_S} & \text{fast: } S \text{ constant} \end{cases}$$

2.43 Advanced Thermodynamics
Spring 2024