2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 09

Room 3-442
Tuesday, March 5, 2:30pm - 4:30pm

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Review of basic concepts:

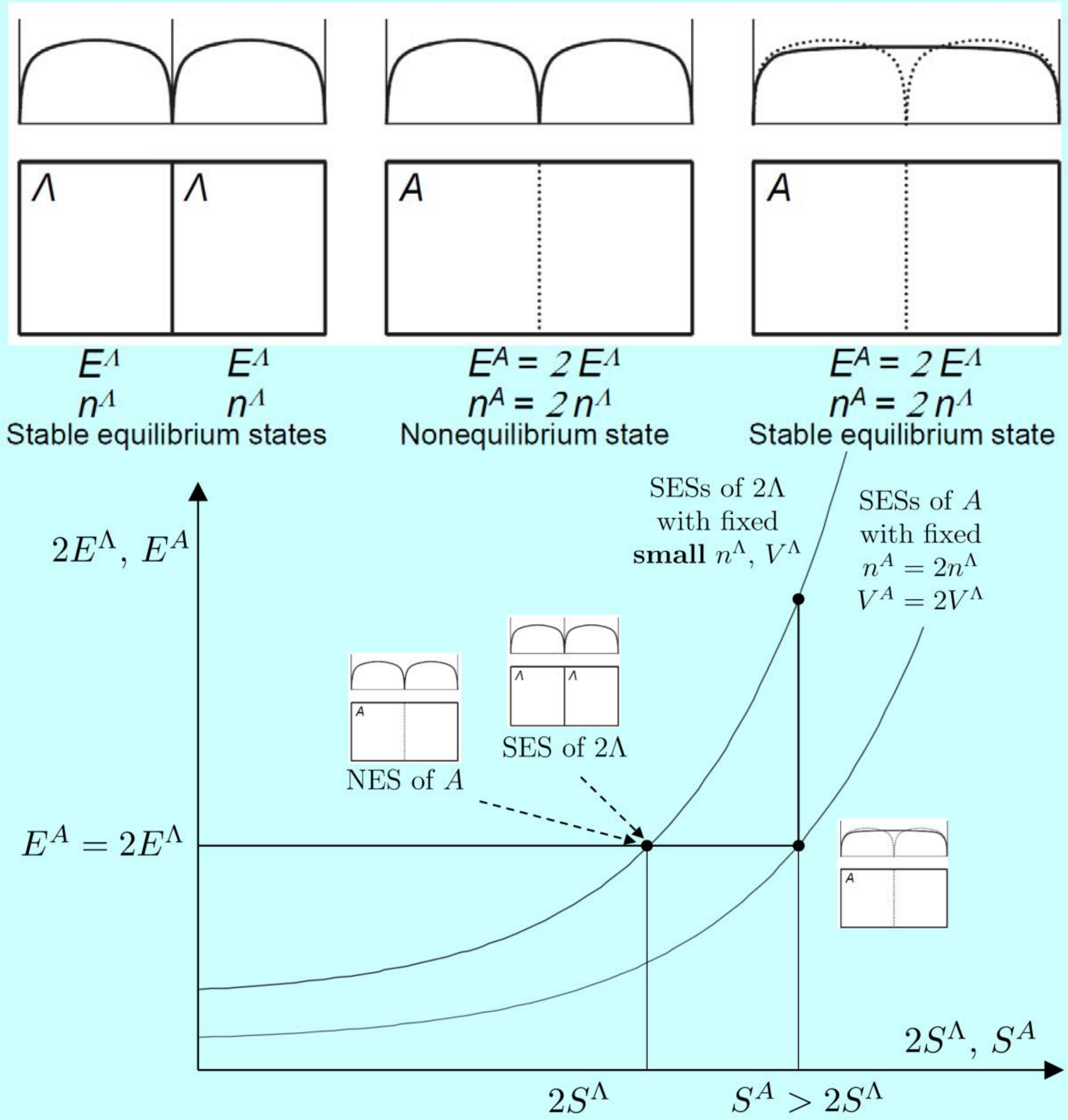
the «Simple System» model
(macroscopic limit)
(many particle limit)

NOTICE:

**all the results reviewed so far
hold for
LARGE as well as SMALL systems**

Review of basic concepts: **micro & meso vs macro**

rarefaction effects near walls at SE



Few particles
per partition:
at SES
(micro or mesoscopic
systems)

$$S^A > 2S^\Lambda$$

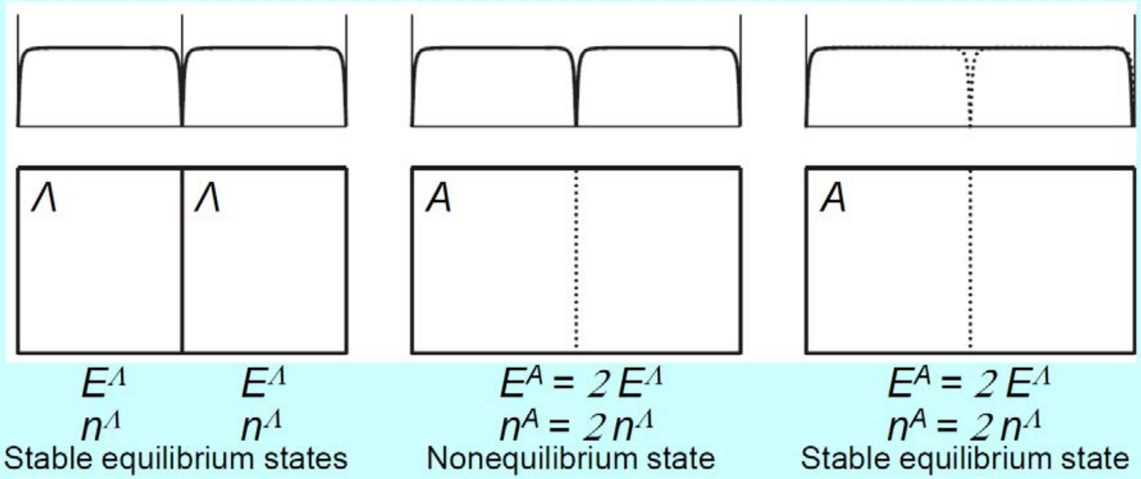
$$S^\Lambda = S_{\text{SES}}(E^\Lambda, n^\Lambda, V^\Lambda)$$

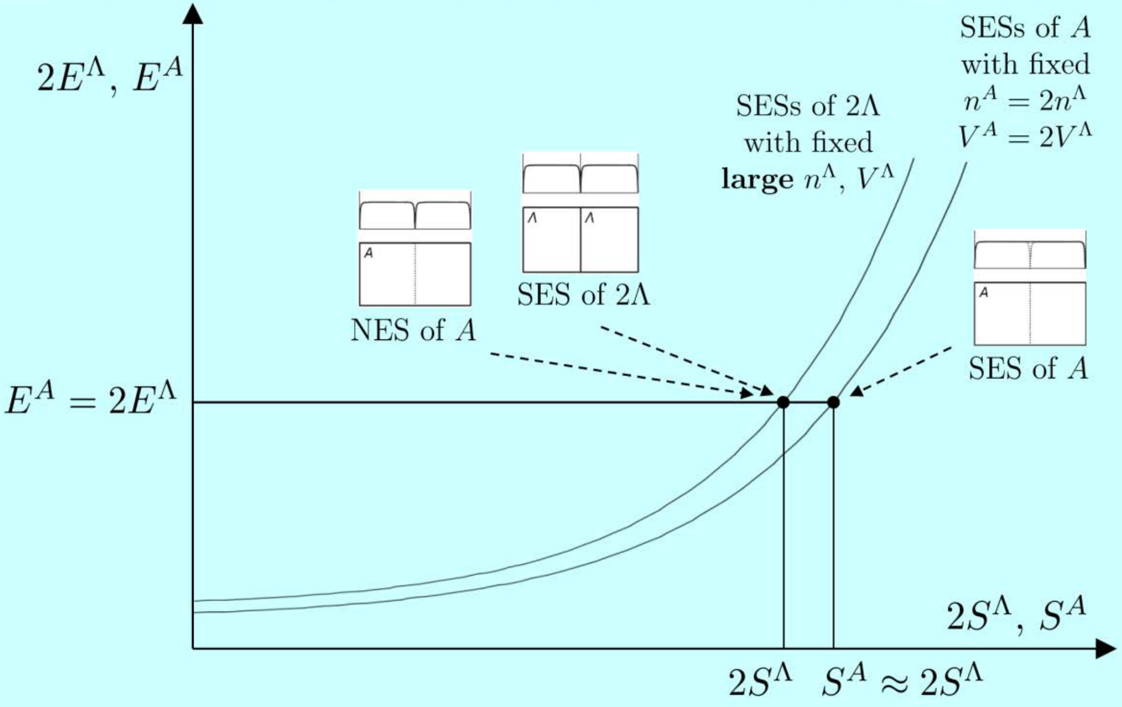
$$S^A = S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda)$$

$$S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) > 2\, S_{\text{SES}}(E^\Lambda, n^\Lambda, V^\Lambda)$$

Review of basic concepts: **micro & meso vs macro**

rarefaction effects near walls at SE





Many particles
per partition:
at SES
(macroscopic
systems)

$$S^A \approx 2S^\Lambda$$

$$S^\Lambda = S_{\rm SES}(E^\Lambda, n^\Lambda, V^\Lambda)$$

$$S^A = S_{\rm SES}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda)$$

$$S_{\rm SES}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) \approx 2\,S_{\rm SES}(E^\Lambda, n^\Lambda, V^\Lambda)$$

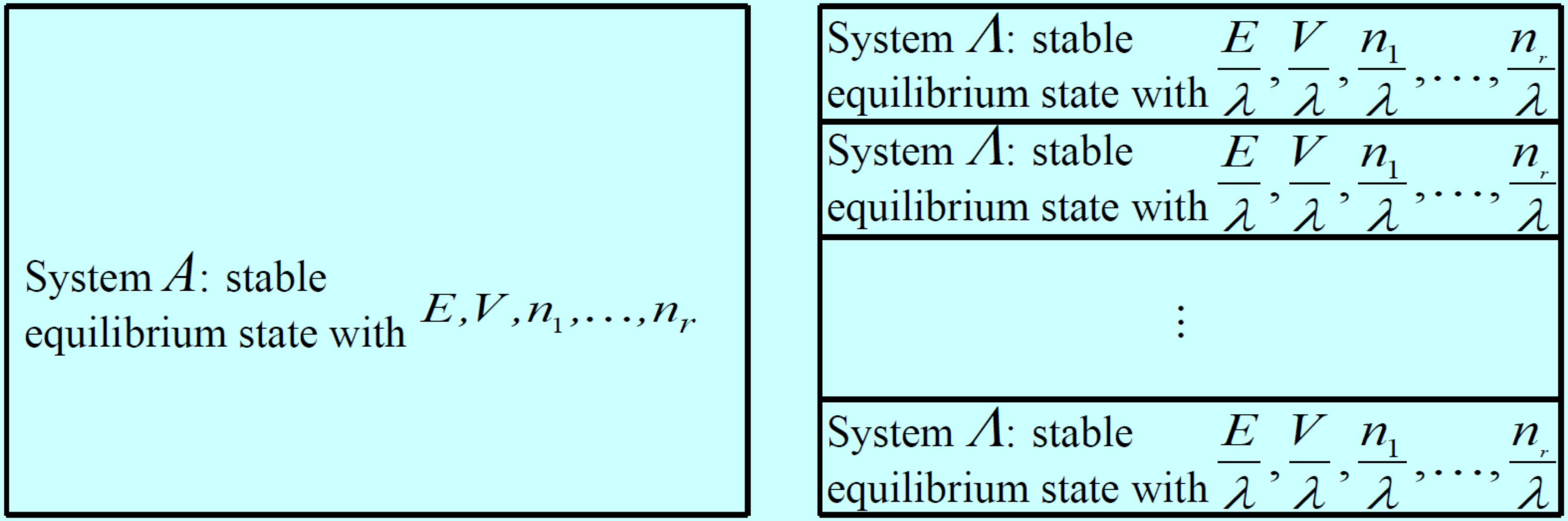
Simple System Model
assumes:

$$S_{\rm SES}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) = 2\,S_{\rm SES}(E^\Lambda, n^\Lambda, V^\Lambda)$$

Review of basic concepts: simple-system model

assumes negligible effect of inserting and removing partitions

Subdivide a system in a s.e.s. in λ contiguous subsystems: subsystem Λ is identical to **system** A (they have the same constituents and are both confined in a region of space by external forces characterized by volume only), hence Λ has the same fundamental relation as A (same functional relation). The **states** of Λ and A are different because different are the values of the volume, the amounts and the energy.



System A: stable equilibrium state with $E, V, n_1, \ldots, n_r$

System Λ: stable equilibrium state with $\frac{E}{\lambda}, \frac{V}{\lambda}, \frac{n_1}{\lambda}, \ldots, \frac{n_r}{\lambda}$

System Λ: stable equilibrium state with $\frac{E}{\lambda}, \frac{V}{\lambda}, \frac{n_1}{\lambda}, \ldots, \frac{n_r}{\lambda}$

$\vdots$

System Λ: stable equilibrium state with $\frac{E}{\lambda}, \frac{V}{\lambda}, \frac{n_1}{\lambda}, \ldots, \frac{n_r}{\lambda}$

$$S^A = S(E, V, \boldsymbol{n})$$

$$S^\Lambda = S(E/\lambda, V/\lambda, \boldsymbol{n}/\lambda)$$

In general $S^A > \lambda\, S^\Lambda$

Simple system model: $S^A \approx \lambda\, S^\Lambda$

Review of basic concepts: simple-system model (macroscopic limit)

limiting assumption about the fundamental SES relation

Simple system model assumption: the fundamental relation is a homogeneous function of first degree in all its variables

$$S(U,V,\mathbf{n}) = \lambda S(U/\lambda, V/\lambda, \mathbf{n}/\lambda) \quad \text{for any real } \lambda$$

$$U(S,V,\mathbf{n}) = \lambda U(S/\lambda, V/\lambda, \mathbf{n}/\lambda) \quad \text{for any real } \lambda$$

We denote the energy with the letter *U* instead of *E* and cal it *internal energy.*

As a consequence of the homogeneity, in addition to the **Gibbs relation**, which holds in general

$$dE = TdS - pdV + \mu_1 dn_1 + \cdots + \mu_r dn_r$$

we have the **Euler relation**

$$U = TS - pV + \mu_1 n_1 + \cdots + \mu_r n_r$$

and the **Gibbs-Duhem relation**

$$0 = SdT - Vdp + n_1 d\mu_1 + \cdots + n_r d\mu_r$$

Review of basic concepts: simple-system model (macroscopic limit)

proof of the Euler relation

The condition of homogeneity of first degree in all variables

$$U(S,V,\boldsymbol{n}) = \lambda\, U\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \text{ for any real } \lambda \qquad (1)$$

implies the Euler relation

$$U = TS - pV + \boldsymbol{\mu}\cdot\boldsymbol{n}$$

It also implies that the potentials conjugated with S, V, $\boldsymbol{n}$ are homogeneous of zero degree in all variables, i.e., for any real λ,

$$T(S,V,\boldsymbol{n}) = T\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad p(S,V,\boldsymbol{n}) = p\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad \boldsymbol{\mu}(S,V,\boldsymbol{n}) = \boldsymbol{\mu}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad (2)$$

Proof of (1): compute the partial derivative of Equation (1) with respect to λ

$$0 = U\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) + \lambda\, T\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{S}{\lambda^2}\Big) - \lambda\, p\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{V}{\lambda^2}\Big) + \lambda\,\boldsymbol{\mu}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\Big(-\frac{\boldsymbol{n}}{\lambda^2}\Big)$$

and let $\lambda = 1$ to get $0 = U(S,V,\boldsymbol{n}) - T(S,V,\boldsymbol{n})\,S + p(S,V,\boldsymbol{n})\,V - \boldsymbol{\mu}(S,V,\boldsymbol{n})\cdot\boldsymbol{n}$.

Proof of (2): compute the partial derivatives of Equation (1) with respect to S, V, and $\boldsymbol{n}$, respectively.

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Review of basic concepts: simple-system model (macroscopic limit)

main consequence of the Euler relation

A main practical feature is that for a simple system the fundamental relation can be written in the form

$$U = U(S, V, \boldsymbol{n}) = n\,u(s, v, \boldsymbol{y})$$

Proof:

$$u = \frac{1}{n} U(S, V, \mathbf{n}) = \frac{1}{n} U(ns, nv, ny_1, \cdots, ny_r)$$

$$\frac{\partial u}{\partial n} = -\frac{U}{n^2} + \frac{1}{n}\frac{\partial U}{\partial S}\frac{\partial ns}{\partial n} + \frac{1}{n}\frac{\partial U}{\partial V}\frac{\partial nv}{\partial n} + \frac{1}{n}\sum_{i=1}^{r}\frac{\partial U}{\partial n_i}\frac{\partial ny_i}{\partial n}$$

$$= -\frac{U}{n^2} + \frac{1}{n}Ts - \frac{1}{n}pv + \frac{1}{n}\sum_{i=1}^{r}\mu_i y_i = -\frac{1}{n^2}\left(U - TS + pV - \sum_{i=1}^{r}\mu_i n_i \right) = 0$$

It means that if we double the overall number of particles keeping fixed relative composition and equal specific volume and specific entropy, the energy doubles.

Review of basic concepts: (small systems)

specific properties depend on the total amount of constituents

$$\mathit{Eu} = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} \qquad \mathrm{d}\mathit{Eu} = -S\,\mathrm{d}T + V\,\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu} \qquad n_i = -\left(\frac{\partial \mathit{Eu}}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}'_i}$$

$\mathit{Eu} = \mathit{Eu}(T,p,\boldsymbol{\mu})$ $\quad T,p,\boldsymbol{\mu}$ for a small system are all independent

$$\mathit{eu} = e - Ts + pv - \boldsymbol{\mu}\cdot\boldsymbol{y} \qquad \mathrm{d}\mathit{eu} = -s\,\mathrm{d}T + v\,\mathrm{d}p - \boldsymbol{y}\cdot\mathrm{d}\boldsymbol{\mu} \qquad \sum_{i=1}^{r} y_i = 1 \qquad \sum_{i=1}^{r}\mathrm{d}y_i = 0$$

$\mathit{eu} = \mathit{eu}(T,p,\boldsymbol{\mu})$ $\quad T,p,\boldsymbol{\mu}$ for a small system are all independent

$$s = \frac{S}{n} = \frac{1}{n}S(nu,nv,n\boldsymbol{y}) = s(u,v,\boldsymbol{y},n) \qquad \left(\frac{\partial s}{\partial n}\right)_{u,v,\boldsymbol{y}} = \frac{1}{n^2}\frac{\mathit{Eu}}{T} = \frac{1}{n}\frac{\mathit{eu}}{T}$$

$$e = \frac{E}{n} = \frac{1}{n}E(ns,nv,n\boldsymbol{y}) = e(s,v,\boldsymbol{y},n) \qquad \left(\frac{\partial e}{\partial n}\right)_{s,v,\boldsymbol{y}} = -\frac{1}{n^2}\mathit{Eu} = -\frac{1}{n}\mathit{eu}$$

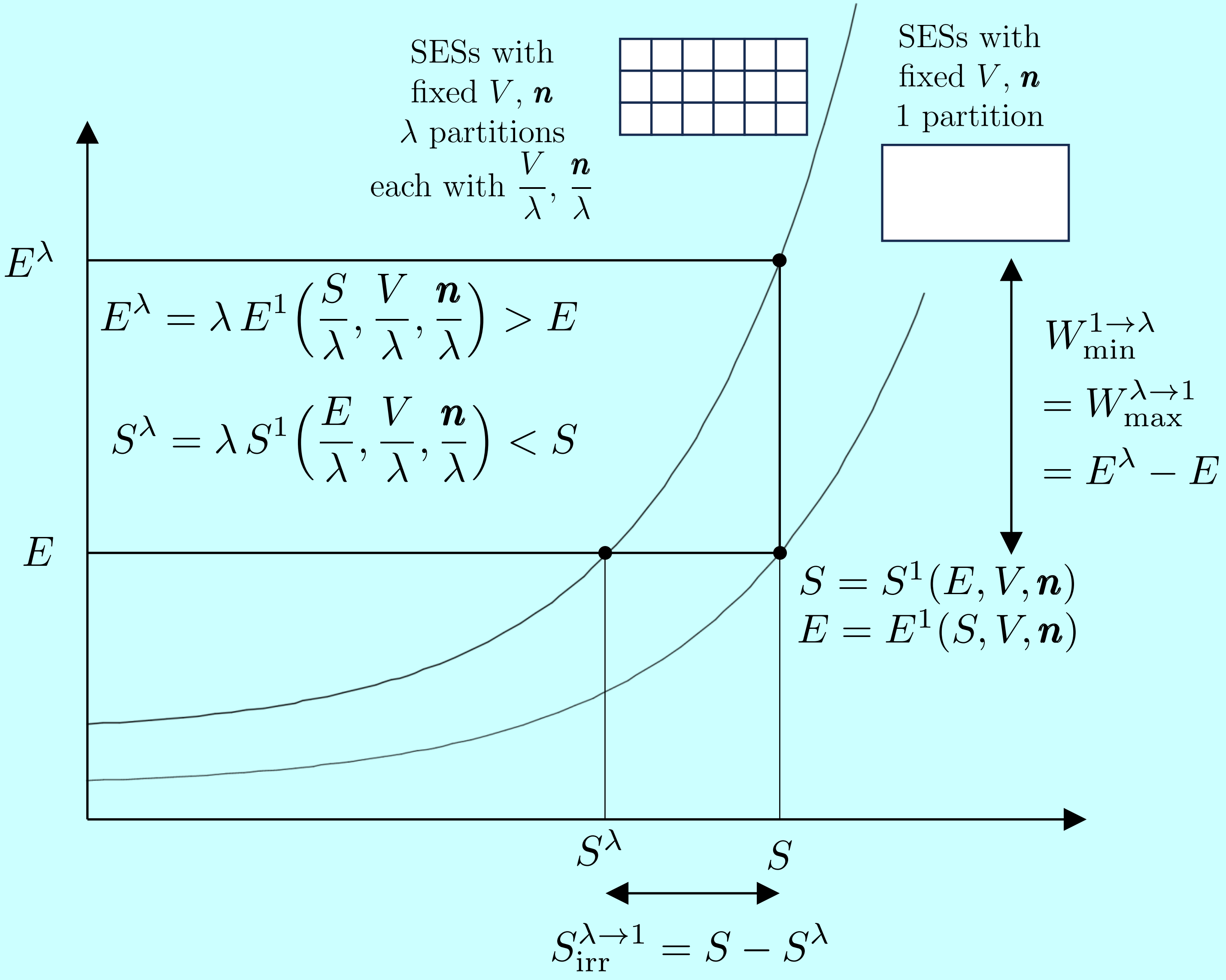
$$h = \frac{H}{n} = \frac{1}{n}H(ns,p,n\boldsymbol{y}) = h(s,p,\boldsymbol{y},n) \qquad \left(\frac{\partial h}{\partial n}\right)_{s,p,\boldsymbol{y}} = -\frac{1}{n^2}\mathit{Eu} = -\frac{1}{n}\mathit{eu}$$

$$f = \frac{F}{n} = \frac{1}{n}F(T,nv,n\boldsymbol{y}) = f(T,v,\boldsymbol{y},n) \qquad \left(\frac{\partial f}{\partial n}\right)_{T,v,\boldsymbol{y}} = -\frac{1}{n^2}\mathit{Eu} = -\frac{1}{n}\mathit{eu}$$

$$g = \frac{G}{n} = \frac{1}{n}G(T,p,n\boldsymbol{y}) = g(T,p,\boldsymbol{y},n) \qquad \left(\frac{\partial g}{\partial n}\right)_{T,p,\boldsymbol{y}} = -\frac{1}{n^2}\mathit{Eu} = -\frac{1}{n}\mathit{eu}$$

Review of basic concepts: (small systems)

minimum work of partitioning



SESs with
fixed V, $\boldsymbol{n}$
λ partitions
each with $\frac{V}{\lambda}, \frac{\boldsymbol{n}}{\lambda}$

SESs with
fixed V, $\boldsymbol{n}$
1 partition

$$E^\lambda = \lambda\, E^1\left(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{\boldsymbol{n}}{\lambda}\right) > E$$

$$S^\lambda = \lambda\, S^1\left(\frac{E}{\lambda}, \frac{V}{\lambda}, \frac{\boldsymbol{n}}{\lambda}\right) < S$$

$$W_{\text{min}}^{1\to\lambda} = W_{\text{max}}^{\lambda\to 1} = E^\lambda - E$$

$$S = S^1(E, V, \boldsymbol{n})$$
$$E = E^1(S, V, \boldsymbol{n})$$

$$S_{\text{irr}}^{\lambda\to 1} = S - S^\lambda$$

Review of basic concepts: **(small systems)**

minimum work of partitioning

Minimum work of partitioning into λ identical compartments in identical SES:

$$W_{\min}^{1\to\lambda} = W_{\max}^{\lambda\to 1} = E^{\lambda} - E = \lambda\, E^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - E^{1}(S,V,\boldsymbol{n})$$

Minimum work to increment or decrement λ by one:

$$W_{\min}^{\lambda\to\lambda+1} = \frac{W_{\min}^{1\to\lambda+1} - W_{\min}^{1\to\lambda}}{(\lambda+1)-\lambda} = \frac{W_{\min}^{1\to\lambda} - W_{\min}^{1\to\lambda-1}}{\lambda-(\lambda-1)} = \frac{\partial W_{\min}^{1\to\lambda}}{\partial\lambda}$$

$$= E^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) + \lambda\, T^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{S}{\lambda^2}\Big)$$

$$-\lambda\, p^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{V}{\lambda^2}\Big) + \lambda\,\boldsymbol{\mu}^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\Big(-\frac{\boldsymbol{n}}{\lambda^2}\Big)$$

$$= E^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - \frac{S}{\lambda}\, T^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)$$

$$+\frac{V}{\lambda}\, p^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - \boldsymbol{\mu}^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\frac{\boldsymbol{n}}{\lambda}$$

$$= \mathit{Eu}^{1}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)$$

where we recall that we defined the Euler free energy

$$\mathit{Eu} = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n}$$

So we see that its value for one of the λ partitions equals the minimum work to increase or decrease by one the number of partitions.

Basic simple-system models of stable-equilibrium properties of (macroscopic amounts of) PURE SUBSTANCES:

Extensive, intensive, and specific properties
Homogeneous vs heterogoneous SESs
Phases
Gibbs' phase rule
Phase diagrams (u-s-v, T-p, h-s, T-s)

Ideal solid
Incompressible fluid
Ideal gas

SES relations valid within the simple system model:

Extensive properties (definition)

For SES properties of simple systems, we adopt the following definitions.

A property P_e is ***extensive*** if the value of the SES function $P_e(U,V,\mathbf{n})$ changes by a factor λ when the independent variables U, V, $\mathbf{n}$, change by the same factor λ

$$P_e(U,V,\mathbf{n}) = \lambda P_e(U/\lambda, V/\lambda, \mathbf{n}/\lambda) \quad \text{for any real } \lambda$$

Examples of extensive properties:

$$S, U, V, n_1, \ldots, n_r, n = \sum_{i=1}^{r} n_i\,, H, m_i = n_i M_i, m = \sum_{i=1}^{r} m_i\,, C_V, C_p$$

where n is the total number of moles, M_i the *molar mass* of constituent i, m_i the mass of constituent i and m the overall mass of the system.

SES relations valid within the simple system model:

Specific properties (definition)

A ***specific property*** is defined by the ratio between the extensive properties.

For example, the following specific properties are important for applications:

$$s=\frac{S}{n},u=\frac{U}{n},v=\frac{V}{n},h=\frac{H}{n},c_v=\frac{C_V}{n},c_p=\frac{C_p}{n},y_i=\frac{n_i}{n},c_p=\frac{C_p}{n}$$

$$s^*=\frac{S}{m},u^*=\frac{U}{m},v^*=\frac{V}{m},h^*=\frac{H}{m},c_v^*=\frac{C_V}{m},c_p^*=\frac{C_p}{m},x_i=\frac{m_i}{m}$$

$$\rho s=\frac{S}{V},\rho u=\frac{U}{V},\rho=\frac{m}{V},\rho h=\frac{H}{V},\rho c_v=\frac{C_V}{V},\rho c_p=\frac{C_p}{V},c_i=[N_i]=\frac{n_i}{V}$$

Where the asterisk (*) serves to distinguish mass specific properties from molar ones, if necessary. The asterisks are often omitted if the context and/or the dimensional homogeneity of the relationships make it clear that whether they refer to mass quantities..

SES relations valid within the simple system model:

Intensive properties and intensive state (definition)

Property P_i is ***intensive*** if the value of the SES function $P_i(U,V,\mathbf{n})$ remains unchanged when the values of the independent variables U, V, $\mathbf{n}$, are all changed by the same factor λ

$$P_i(U,V,\mathbf{n}) = P_i(U/\lambda, V/\lambda, \mathbf{n}/\lambda) \quad \text{per ogni } \lambda \text{ reale}$$

Examples of intensive properties:

$$T, p, \mu_1, \ldots, \mu_r, \rho = \frac{m}{V}, y_i = \frac{n_i}{n}, x_i = \frac{m_i}{m}$$

Moreover, *all specific properties are intensive properties, according to our definition*. Please notice: this definition may differ from other more restrictive ones used in the literature.

We call ***intensive state*** *the set of the values of all intensive SES properties*

$$\{y_1, \ldots, y_r, v, u, s, h, T, p, \mu_1, \ldots, \mu_r, \rho, \ldots\}$$

It is easy to show that the state, i.e., the set of values of all properties, is known if, in addition to the intensive state, the value of at least one extensive property (e.g., mass m) is known.

SES relations valid within the simple system model:

Homogeneous vs heterogeneous SES, phases (definitions)

Consider a simple system in a SES divided into many subsystems (approaching infinitesimally small) all in MSE: the various subsystems must have the same values for $T, p, \mu_1, \ldots, \mu_r$ but they can have different intensive states.

- If, regardless of the subdivision, all partitions share the same intensive state, the state is called a **homogeneous SES**.
- If it is possible to subdivide the system in a way that not all partitions share the same intensive state, the state is called a **heterogeneous SES**, and each set, composed of all subsystems sharing the same intensive state, is called a **phase**.

System A: SES with

$$
\begin{aligned}
E &= E^{(1)} + E^{(2)} + \cdots + E^{(q)} \\
V &= V^{(1)} + V^{(2)} + \cdots + V^{(q)} \\
n_1 &= n_1^{(1)} + n_1^{(2)} + \cdots + n_1^{(q)} \\
&\vdots \\
n_r &= n_r^{(1)} + n_r^{(2)} + \cdots + n_r^{(q)}
\end{aligned}
$$

Phase (1):	$E^{(1)}, V^{(1)}, n_1^{(1)}, \ldots, n_r^{(1)}$
Phase (2):	$E^{(2)}, V^{(2)}, n_1^{(2)}, \ldots, n_r^{(2)}$
	$\vdots$
Phase (q):	$E^{(q)}, V^{(q)}, n_1^{(q)}, \ldots, n_r^{(q)}$

SES relations valid within the simple system model:

Gibbs' phase rule (proof)

The **Gibbs' phase rule** asserts that of the 2+*rq* variables

$$T, p, \mathbf{y}^{(1)}, \mathbf{y}^{(2)}, \ldots, \mathbf{y}^{(q)}$$

which determine the intensive states of all phases, only a subset of *r*+2-*q* is independent, i.e., can be varied independently when the simple system must transition from an initial SES with *q* phases to an adjacent SES with the same *q* phases. The number ***F=r+2-q*** of independently variable intensive properties in the above set is called **variance**.

Indeed, not only the following *q* trivial conditions must hold

$$\sum_{i=1}^{r} y_i^{(j)} = 1 \quad \text{for } j = 1, \ldots, q$$

but also the *(q*-1*) r* equalities

$$\mu_i^{(1)}(T, p, \mathbf{y}^{(1)}) = \mu_i^{(2)}(T, p, \mathbf{y}^{(2)}) = \ldots = \mu_i^{(q)}(T, p, \mathbf{y}^{(q)})$$

that represent the necessary conditions for MSE between the *q* different phases.

Note = This holds true if no chemical reactions are allowed within the system. If reactions are allowed, the variance is ***F=r+2-q-z*** where *z* is the number of independent chemical equilibrium conditions (see later).

SES relations valid within the simple system model:

Gibbs' phase rule (possible cases for a pure substance)

For a pure substance $r = 1$: $F = 3 - q$

The variables are 2+q : $T, p, y_1^{(1)}, y_1^{(2)}, \ldots, y_1^{(q)}$ $\Rightarrow$ only 2 variables T, p

But we have the q trivial conditions: $y_1^{(j)} = 1 \quad \text{for } j = 1, \ldots, q$

and the q-1 MSE conditions : $\mu_1^{(1)}(T,p) = \mu_1^{(2)}(T,p) = \ldots = \mu_1^{(q)}(T,p)$

Single-phase (homogeneous) SES: $q = 1 \Rightarrow F = 2$
To change the SES to a neighboring single-phase SESs we may vary T and p independently, and we have $\mu = \mu(T,p)$.

Two-phase (heterogeneous) SES: $q = 2 \Rightarrow F = 1$
To change the SES to a neighboring two-phase SESs we may vary only either T or p independently, not both: their variations must be related by $\mu_1^{(1)}(T,p) = \mu_1^{(2)}(T,p)$ from which follow the relations $p = p_{\text{sat}}(T)$ or $T = T_{\text{sat}}(p)$.

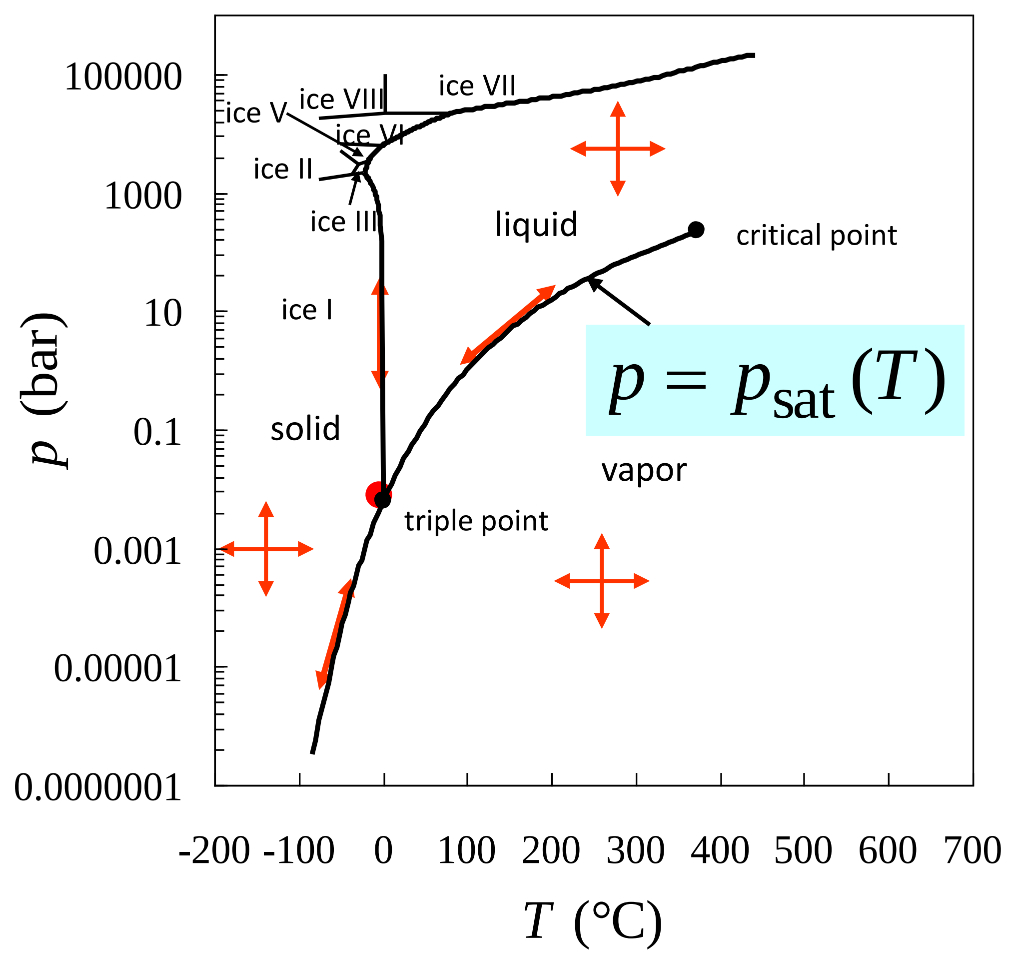
Three-phase (heterogeneous) SES: $q = 3 \Rightarrow F = 0$
There exist no neighboring SES with different values of T and p, and we have

$$\mu_1^{(1)}(T,p) = \mu_1^{(2)}(T,p) = \mu_1^{(3)}(T,p).$$

There cannot be SES of a pure substance with four or more phases.

SES relations valid within the simple system model:

Gibbs' phase rule (possible cases for a pure substance)



$$p = p_{\text{sat}}(T)$$

Fig. 9.2 in Beretta, Termodinamica, Editrice Snoopy, Brescia, 2002.

***p*-*T* diagram for H_2O** (extended to high pressures and different forms of ice)

✛ *F*=2 (single-phase SES)

↗ *F*=1 (two-phase SES)

● *F*=0 (three-phase SES)

Construction of the fundamental relation of a pure substance, within the simple system model, from $T, p, \alpha_p, \kappa_T, C_p$

Recall these general SES relations, valid for SESs of any system:

$$(dE)_{\boldsymbol{n}} = \left(C_p - pV\alpha_p\right)dT + \left(p\kappa_T - T\alpha_p\right) V dp$$

$$(dS)_{\boldsymbol{n}} = \frac{C_p}{T} dT - \alpha_p V dp$$

$$(dH)_{\boldsymbol{n}} = C_p dT + \left(1 - T\alpha_p\right) V dp$$

For a pure substance may rewrite them in terms of **mass specific properties**

$$(du)_{\mathrm{n}} = \left(c_p - pv\alpha_p\right)dT + \left(p\kappa_T - T\alpha_p\right) v dp$$

$$(ds)_{\mathrm{n}} = \frac{c_p}{T} dT - \alpha_p v dp$$

$$(dh)_{\mathrm{n}} = c_p dT + \left(1 - T\alpha_p\right) v dp$$

SES relations valid within the simple system model:

Ideal (perfect) incompressible solid or fluid model

It is based on the assumption that the specific volume (v) is approximately constant, leading to

$$\kappa_T = 0, \alpha_p = 0, c_p = c_v = c = c(T)$$

The constitutive equations then become:

$$\begin{cases} du = c(T)\ dT \\ ds = c(T)\dfrac{dT}{T} \\ dh = c(T)\ dT + v\ dp \end{cases}$$

$$\begin{aligned} u &= u(T) \\ s &= s(T) \\ h &= h(T,p) \end{aligned}$$

«Perfect» if $c(T)$ is constant:

$$\begin{cases} u(T) - u(T_0) = c\ (T - T_0) \\ s(T) - s(T_0) = c\ \ln\dfrac{T}{T_0} \\ h(T,p) - h(T_0,p_0) = c\ (T - T_0) + v\ (p - p_0) \end{cases}$$

$$\begin{cases} u(T) - u(T_0) = \displaystyle\int_{T_0}^{T} c(T)\, dT \\ s(T) - s(T_0) = \displaystyle\int_{T_0}^{T} c(T)\frac{dT}{T} \\ h(T,p) - h(T_0,p_0) = \displaystyle\int_{T_0}^{T} c(T)\, dT + v\ (p - p_0) \end{cases}$$

SES relations valid within the simple system model:

Ideal (perfect) gas model

It is based on the assumption that the equation of state is $pV = nRT$ with $R = N_{\text{Avogadro}} k_{\text{Boltzmann}} = 8.314 \frac{\text{kJ}}{\text{kmol K}}$ so that

$$\kappa_T = 1/p, \alpha_p = 1/T, c_p(T) = c_v(T) + R$$

The constitutive equations then become:

$$\begin{cases} du = c_v(T) dT \\ ds = c_p(T) \dfrac{dT}{T} - R \dfrac{dp}{p} \\ \quad = c_v(T) \dfrac{dT}{T} + R \dfrac{dv}{v} \\ \quad = c_p(T) \dfrac{dv}{v} + c_v(T) \dfrac{dp}{p} \\ dh = c_p(T) dT \end{cases}$$

$$u = u(T)$$
$$s = s(T,p)$$
$$h = h(T)$$

«Perfect» if $c_v(T)$ is constant:

$$\begin{cases} u(T) - u(T_0) = c_v(T - T_0) \\ s(T,p) - s(T_0,p_0) = c_p \ln \dfrac{T}{T_0} - R \ln \dfrac{p}{p_0} \\ s(T,v) - s(T_0,v_0) = c_v \ln \dfrac{T}{T_0} + R \ln \dfrac{v}{v_0} \\ s(v,p) - s(v_0,p_0) = c_p \ln \dfrac{v}{v_0} + c_v \ln \dfrac{p}{p_0} \\ h(T) - h(T_0) = c_p(T - T_0) \end{cases}$$

SES relations valid within the simple system model:

Ideal (perfect) gas model

in a broad range of relatively low temperatures, where the vibrational and electronic degrees of freedom are not activated, the following approximations are reasonable, depending on the structure of the gas molecules:

Monoatomic gas

$$c_v = \frac{3}{2}R \quad \left(c_p = \frac{5}{2}R, \quad \gamma = \frac{c_p}{c_v} = \frac{5}{3} = 1.67\right)$$

Biatomic or aligned polyatomic molecules

$$c_v = \frac{5}{2}R \quad \left(c_p = \frac{7}{2}R, \quad \gamma = \frac{c_p}{c_v} = \frac{7}{5} = 1.4\right)$$

Polyatomic non-aligned molecules

$$c_v = 3R \quad \left(c_p = 4R, \quad \gamma = \frac{c_p}{c_v} = \frac{4}{3} = 1.33\right)$$

For perfect gas behavior, it is possible to derive relationships that link temperatures, pressures, and specific volumes in the case of an isentropic transformation (i.e., where the entropy does not change):

$$c_p \ln\frac{T_2}{T_1} = R\ln\frac{p_2}{p_1} \quad \Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$c_v \ln\frac{T_2}{T_1} = -R\ln\frac{v_2}{v_1} \quad \Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

$$c_p \ln\frac{v_2}{v_1} = -c_v\ln\frac{p_2}{p_1} \quad \Rightarrow \quad \frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}$$

Therefore, along an isentropic process of an ideal gas, we have:

$$p^{\frac{\gamma-1}{\gamma}}/T = \text{const}; \quad Tv^{\gamma-1} = \text{const}; \quad pv^{\gamma} = \text{const}$$

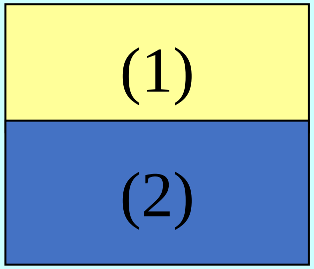
SES relations valid within the simple system model:

Clausius-Clapeyron relation (two-phase states of a pure substance)

Two Gibbs-Duhem relations, one for each phase:

$$
\begin{aligned}
0 &= S^{(1)}dT - V^{(1)}dp + n^{(1)}d\mu^{(1)} \quad \Rightarrow \quad 0 = s^{(1)}dT - v^{(1)}dp + d\mu^{(1)} \\
0 &= S^{(2)}dT - V^{(2)}dp + n^{(2)}d\mu^{(2)} \quad \Rightarrow \quad 0 = s^{(2)}dT - v^{(2)}dp + d\mu^{(2)}
\end{aligned}
$$

To change a two-phase SES at T and p, and therefore with $\mu^{(1)}(T,p) = \mu^{(2)}(T,p)$ to a neighboring two-phase SES with the same two phases, we must tune the changes in T and p to so as to keep the MSE condition $\mu^{(1)}(T+dT,p+dp) = \mu^{(2)}(T+dT,p+dp)$ satisfied. Therefore, we need that $d\mu^{(1)} = d\mu^{(2)}$, which yields



$$
\frac{dp_{\mathrm{sat}}}{dT} = \frac{s^{(2)} - s^{(1)}}{v^{(2)} - v^{(1)}} = \frac{h^{(2)} - h^{(1)}}{T\left(v^{(2)} - v^{(1)}\right)}
$$

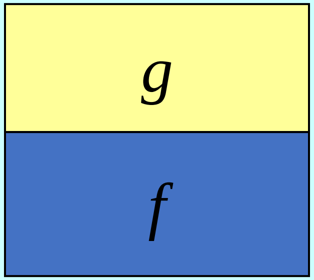
where we recall that for a pure substance $\mu = g = h - Ts$, so the MSE condition of the initial state, $\mu^{(1)} = \mu^{(2)}$ gives $\mu^{(1)} = h^{(1)} - Ts^{(1)} = \mu^{(2)} = h^{(2)} - Ts^{(2)}$ and

$$
T = \frac{h^{(2)} - h^{(1)}}{s^{(2)} - s^{(1)}}
$$

SES relations valid within the simple system model:

properties of two-phase liquid-vapor states of a pure substance

For example, consider two-phase SES with liquid and vapor coexisting in MSE. Adopt the symbol x to denote the *vapor mass fraction* (*steam quality*)



$$x = \frac{n_g}{n} = \frac{m_g}{m} \qquad \begin{aligned} n_g &= xn \\ m_g &= xm \end{aligned} \qquad \begin{aligned} n_f &= (1-x)n \\ m_f &= (1-x)m \end{aligned}$$

The specific volume, energy, enthalpy, and entropy of vaporization are

$$v_{fg} = v_g - v_f, \quad u_{fg} = u_g - u_f, \quad h_{fg} = h_g - h_f, \quad s_{fg} = s_g - s_f$$

The MSE equality of chemical potentials of the two phases, yields

$$h_{fg} = u_{fg} + p v_{fg}, \quad h_{fg} = T s_{fg}$$

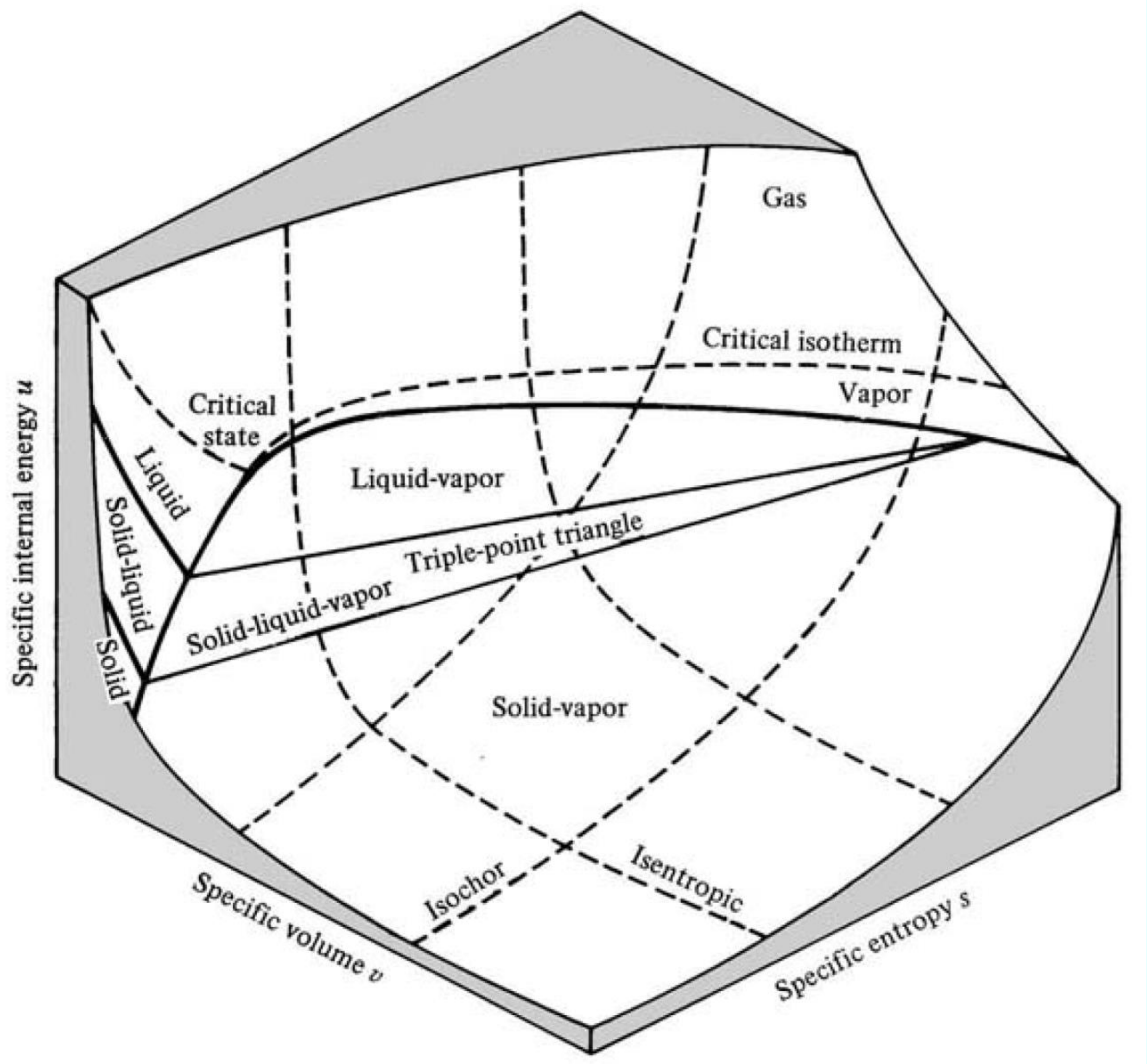
The additivity of volume, energy, entropy, and enthalpy (additive in this case because the two phases are at the same p), allows to write

$$\begin{aligned} V &= V_f + V_g \\ U &= U_f + U_g \\ H &= H_f + H_g \\ S &= S_f + S_g \end{aligned} \qquad \begin{aligned} v &= x v_g + (1-x) v_f = v_f + x v_{fg} \\ u &= x u_g + (1-x) u_f = u_f + x u_{fg} \\ h &= x h_g + (1-x) h_f = h_f + x h_{fg} \\ s &= x s_g + (1-x) s_f = s_f + x s_{fg} \end{aligned}$$

$$x = \frac{v - v_f}{v_{fg}} = \frac{u - u_f}{u_{fg}} = \frac{h - h_f}{h_{fg}} = \frac{s - s_f}{s_{fg}}$$

graphical representation of the SES fundamental relation valid within the simple system model:

the *u-s-v* fundamental surface

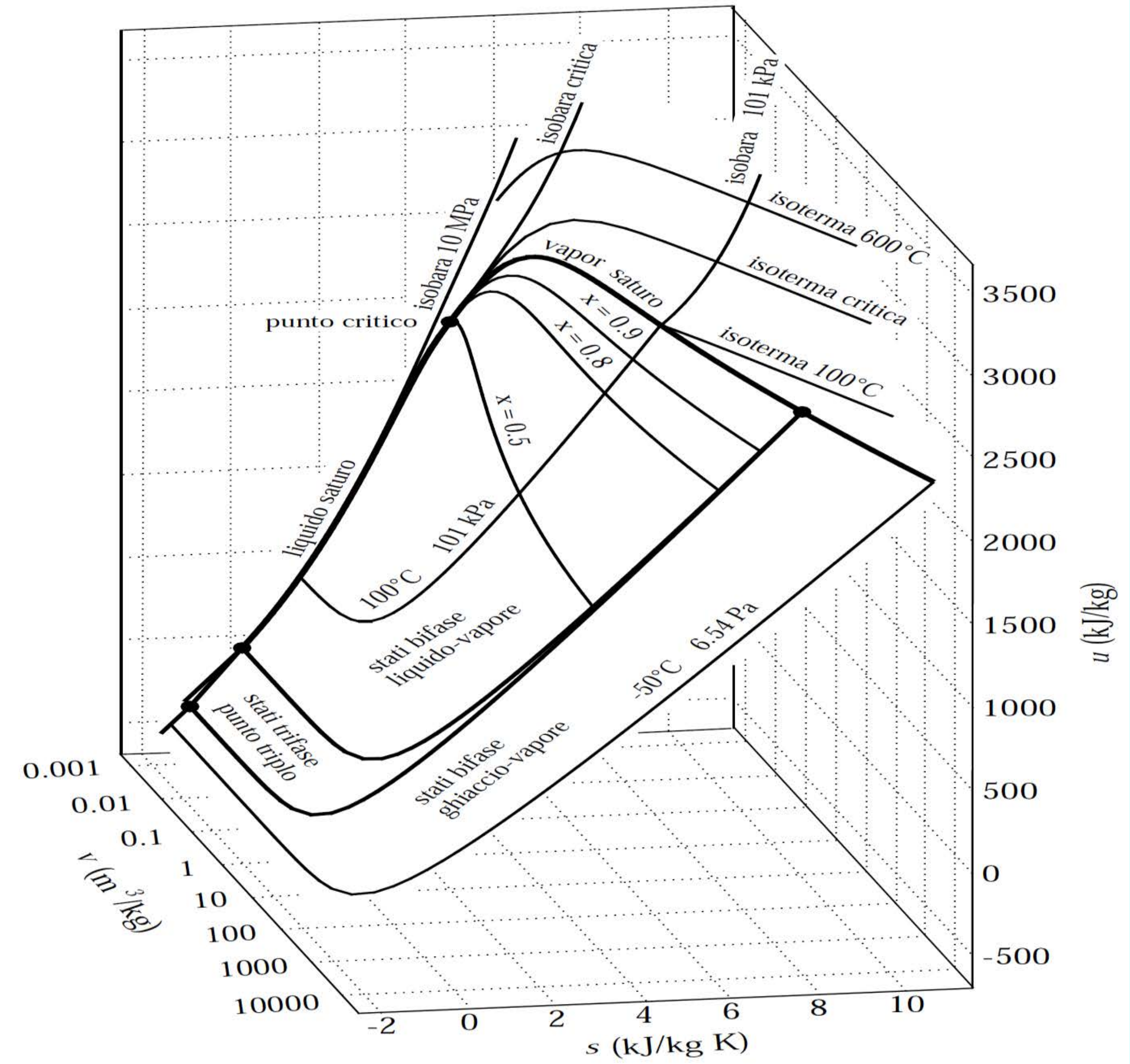


Pictorial representation of the $u = u(s, v)$ surface for a pure substance.

Fig. 19.14 in Gyftopoulos, Beretta, Thermodynamics. Foundations and Applications, Dover 2005.

graphical representation of the SES fundamental relation valid within the simple system model:

the *u-s-v* fundamental surface (water)

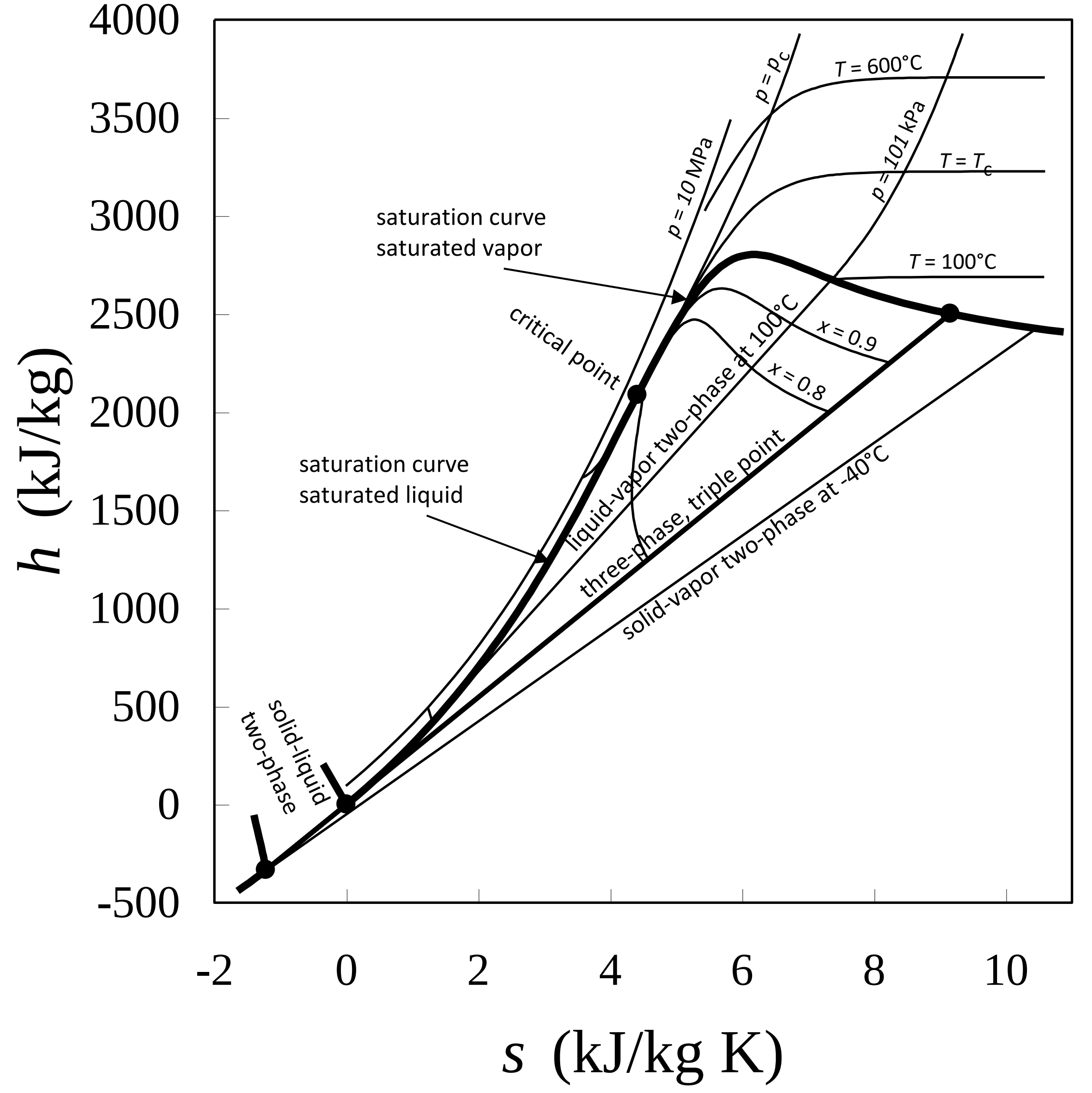


u-s-v diagram for H_2O

Fig. 9.1 in Beretta, Termodinamica, Editrice Snoopy, Brescia, 2002.

graphical representation of the SES fundamental relation valid within the simple system model:

the Mollier *h-s* diagram (water)



***h-s* diagram for H_2O**
(Mollier diagram)

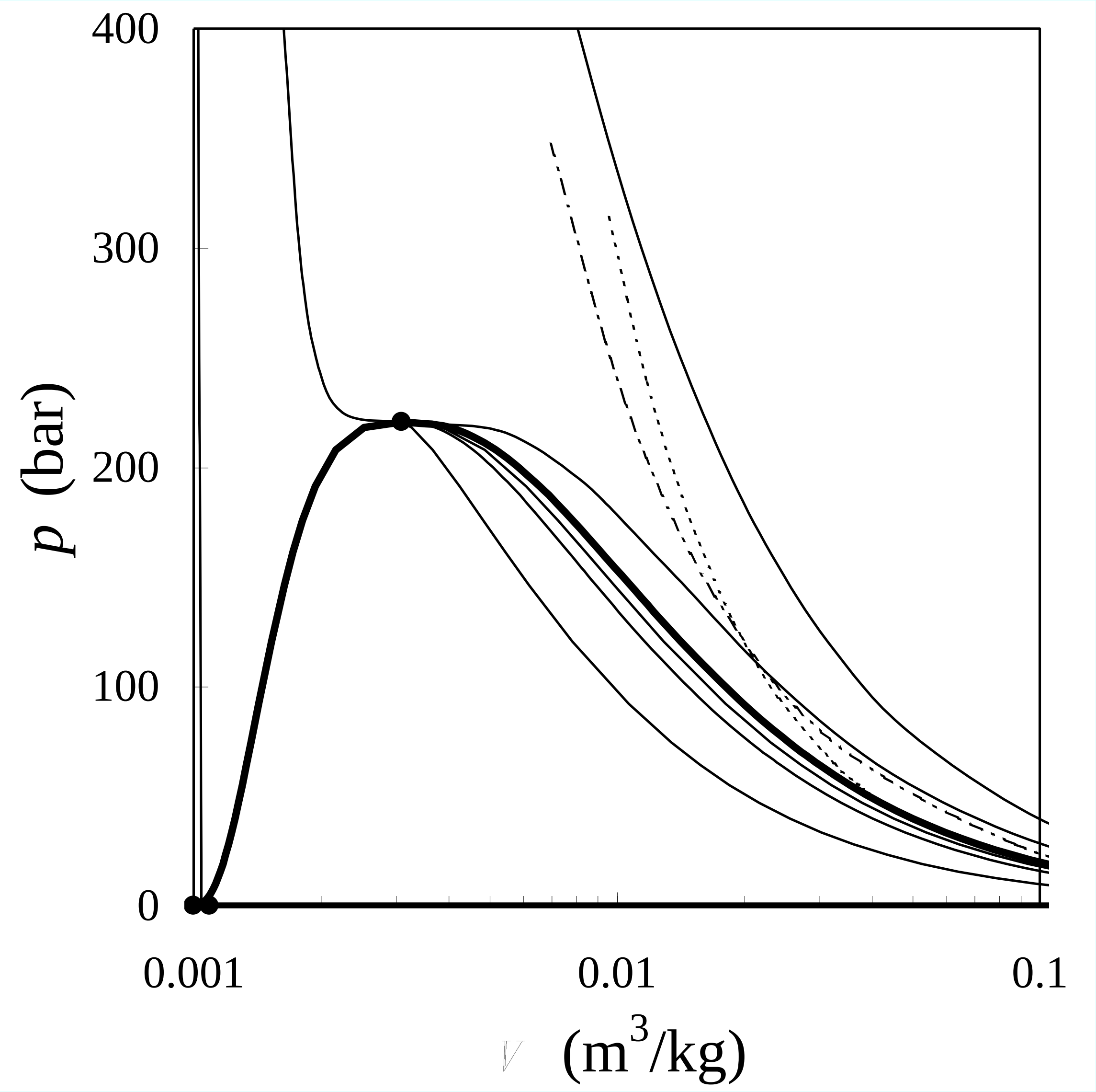
$$\begin{cases} p_{\mathrm{tp}} = 0.61166\ \mathrm{kPa} \\ T_{\mathrm{tp}} = 0.01°\mathrm{C} \end{cases}$$

$$\begin{cases} p_{\mathrm{c}} = 22.064\ \mathrm{MPa} \\ T_{\mathrm{c}} = 373.95°\mathrm{C} \end{cases}$$

Fig. 9.3 in Beretta, Termodinamica, Editrice Snoopy, Brescia, 2002.

graphical representation of the SES fundamental relation valid within the simple system model:

the *p*-*v* diagram (water)



p-v diagram for H_2O

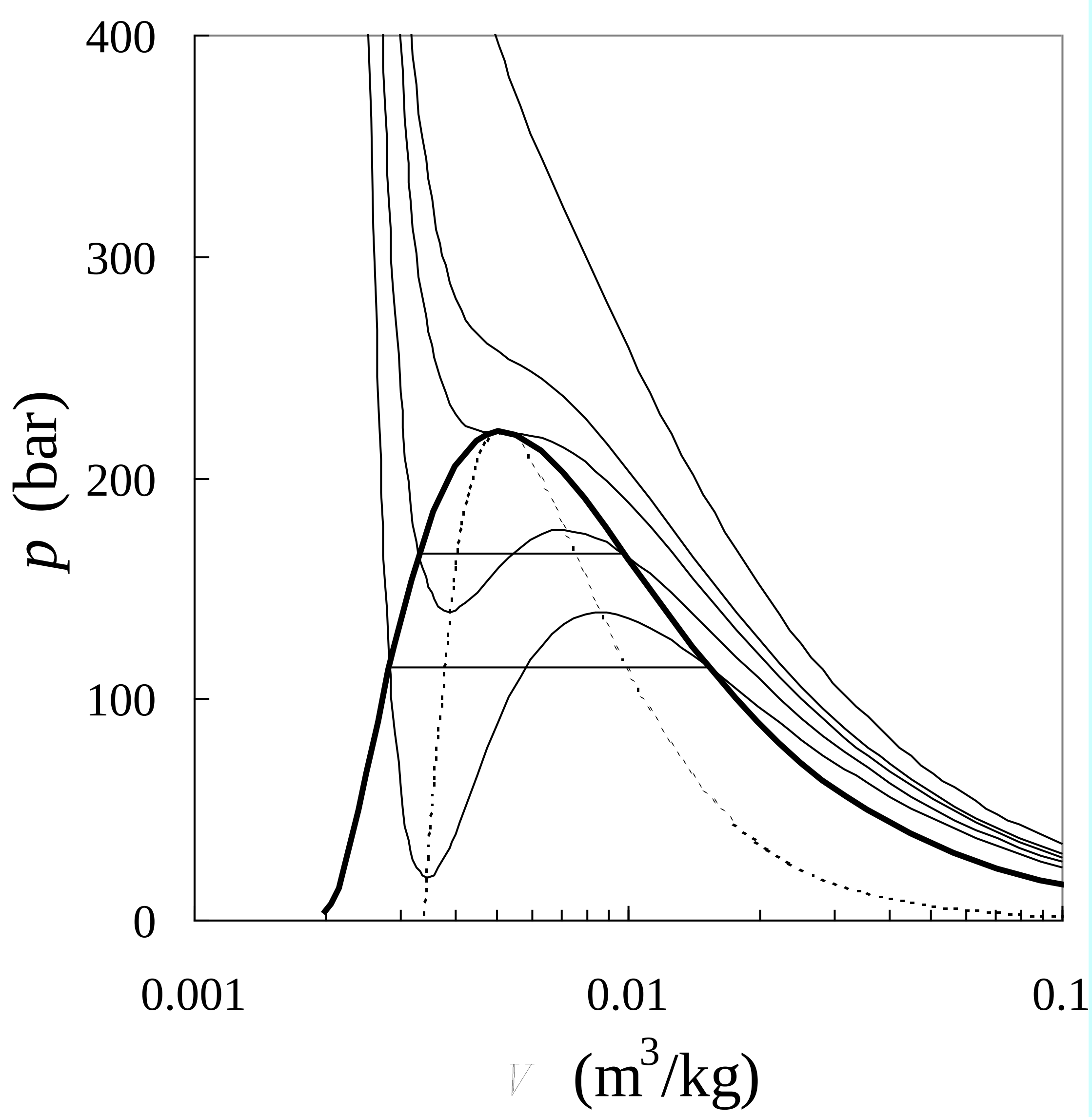
$$\begin{cases} p_{\mathrm{tp}} = 0.61166\ \mathrm{kPa} \\ T_{\mathrm{tp}} = 0.01°\mathrm{C} \end{cases}$$

$$\begin{cases} p_{\mathrm{c}} = 22.064\ \mathrm{MPa} \\ T_{\mathrm{c}} = 373.95°\mathrm{C} \end{cases}$$

From Fig. 9.4 in Beretta, Termodinamica, Editrice Snoopy, Brescia, 2002.

graphical representation of the SES fundamental relation valid within the simple system model:

the *p-v* diagram according to the van der Waals model (water)



Approximate *p-v* diagram for H_2O based on the **van der Waals equation of state**

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

where $v = V/n$ and the values of a and b are obtained from

$$\begin{cases} p_\mathrm{c} = \dfrac{a}{27b^2} = 22.064\ \mathrm{MPa} \\ T_\mathrm{c} = \dfrac{8a}{27Rb} = 373.95°\mathrm{C} \end{cases}$$

From Fig. 9.5 in Beretta, Termodinamica, Editrice Snoopy, Brescia, 2002.

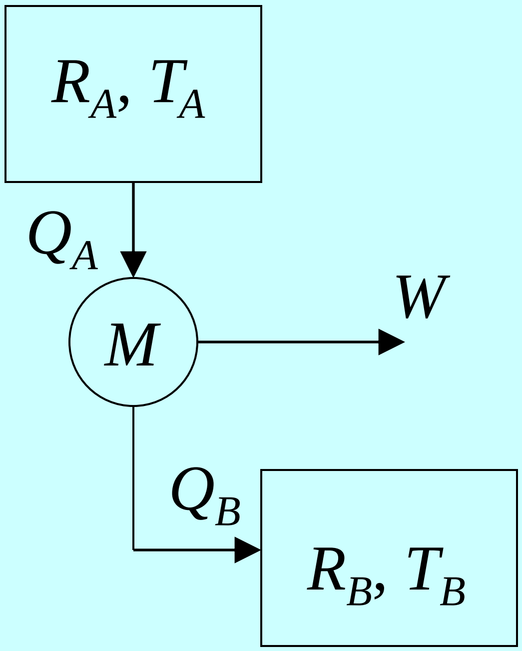
Review of basic concepts:

Exergies
and
first and second law efficiencies

in
energy conversion technologies

Review of basic concepts: **Exergy and 2nd law efficiency in simple cogeneration**

Combined production of heat and mechanical energy (cogeneration, CHP)



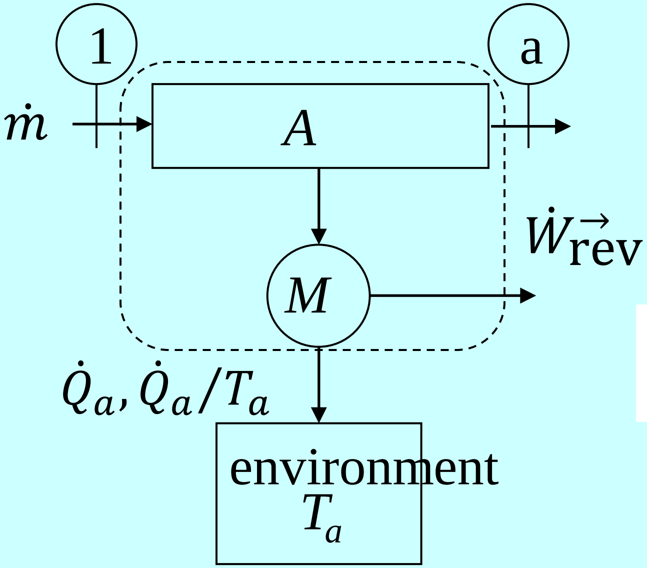
$$\eta_{\mathrm{I}} = \frac{W + Q_B}{Q_A} = 1$$

$$\eta_{\mathrm{II}} = \frac{W + Q_B\left(1 - \frac{T_o}{T_B}\right)}{Q_A\left(1 - \frac{T_o}{T_A}\right)}$$

N.B. : $\eta_{\mathrm{I}} = 1$, even though the heat energy is less valuable (not all useful) and regardless of its temperature T_B; $\eta_{\mathrm{II}} < 1$, and varies with changes in temperature T_B

Review of basic concepts: **Exergy of bulk flow interactions**

Exergy associated with an interaction of mass flow in conditions 1



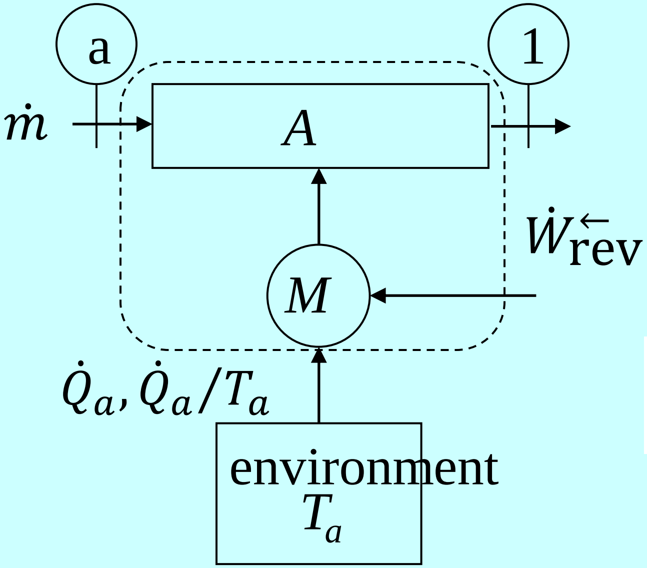
- To obtain the maximum power from the flow in conditions 1, the flow must be taken in a position 'a' in mutual equilibrium with the environment

$$\dot{W}^{\rightarrow}_{\text{rev}} = \dot{E}x_1 = \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)]$$

From the balance of energy and entropy (per unit time) for AM, the optimal equivalent mechanical power of flow in conditions 1 can be determined; which is therefore the exergy per unit time associated with the flow in conditions 1

Review of basic concepts: Exergy of bulk flow interactions

Exergy associated with an interaction of mass flow in conditions 1



- The lowest power that is necessary to use in order to produce the flow conditions in 1 starting from the condition 'a' in mutual equilibrium with the environment

$$\dot{W}^{\leftarrow}_{\text{rev}} = \dot{E}x_1 = \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)]$$

From energy and entropy balances (per unit time) for AM the optimal equivalent mechanical power of flow in conditions 1 can be determined, which is therefore the exergy per unit time associated with the flow in conditions 1

Image Credits

Slide 26:

Pictorial representation of the specific internal energy courtesy of Elias P. Gyftopoulos and Gian Paolo Beretta.

2.43 Advanced Thermodynamics
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