

2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 08

Room 3-442

Friday, March 1, 11:00am - 1:00pm

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Room 3-351d

Review of basic concepts:

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

availability functions

stability conditions

LeChatelier-Braun principle

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

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

$$dA|_{\mathbf{z}} = A_{,x} dx + A_{,y} dy \quad A_{,x} = \left(\frac{\partial A}{\partial x} \right)_{y,\mathbf{z}} = A_{,x}(x, y, \mathbf{z}) \quad A_{,y} = \left(\frac{\partial A}{\partial y} \right)_{x,\mathbf{z}} = A_{,y}(x, y, \mathbf{z})$$

$$d^2 A|_{\mathbf{z}} = [dx \ dy] \begin{bmatrix} A_{,xx} & A_{,xy} \\ A_{,xy} & A_{,yy} \end{bmatrix} \begin{bmatrix} dx \\ dy \end{bmatrix} = A_{,xx} (dx)^2 + 2A_{,xy} dx dy + A_{,yy} (dy)^2$$

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

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

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

$$\begin{aligned} d^2 A|_{\mathbf{z}} &= A_{,xx} \left(dx + \frac{A_{,xy}}{A_{,xx}} dy \right)^2 + \lambda_y (dy)^2 & \text{where} & \quad \lambda_y = A_{,yy} - A_{,xx} \left(\frac{A_{,xy}}{A_{,xx}} \right)^2 \\ &= \lambda_x (dx)^2 + A_{,yy} \left(dy + \frac{A_{,xy}}{A_{,yy}} dx \right)^2 & \text{where} & \quad \lambda_x = A_{,xx} - A_{,yy} \left(\frac{A_{,xy}}{A_{,yy}} \right)^2 \end{aligned}$$

Therefore, since the stability conditions must hold for arbitrary dx and dy ,

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

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

Whether $d^2A|_z$ is positive semidefinite or negative semidefinite

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

$$= \begin{cases} \frac{\partial(A_{,x}, A_{,y})}{\partial(A_{,x}, y)} \frac{\partial(A_{,x}, y)}{\partial(x, y)} = \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \left(\frac{\partial A_{,x}}{\partial x}\right)_y = \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} A_{,xx} \geq 0 \\ \frac{\partial(A_{,x}, A_{,y})}{\partial(x, A_{,y})} \frac{\partial(x, A_{,y})}{\partial(x, y)} = \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \left(\frac{\partial A_{,y}}{\partial y}\right)_x = \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} A_{,yy} \geq 0 \end{cases}$$

Therefore, we can rewrite λ_x and λ_y as

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

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

so that the stability conditions become

$$d^2A|_z \geq 0 \Rightarrow \begin{cases} \left(\frac{\partial A_{,x}}{\partial x}\right)_y \geq \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \geq 0 \\ \left(\frac{\partial A_{,y}}{\partial y}\right)_x \geq \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \geq 0 \end{cases} \quad d^2A|_z \leq 0 \Rightarrow \begin{cases} \left(\frac{\partial A_{,x}}{\partial x}\right)_y \leq \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \leq 0 \\ \left(\frac{\partial A_{,y}}{\partial y}\right)_x \leq \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \leq 0 \end{cases}$$

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

$d^2 A _z \geq 0$	z	x	y	$A_{,x}$	$A_{,y}$	$\left(\frac{\partial A_{,x}}{\partial x}\right)_y \geq \left(\frac{\partial A_{,x}}{\partial x}\right)_{A_{,y}} \geq 0$	$\left(\frac{\partial A_{,y}}{\partial y}\right)_x \geq \left(\frac{\partial A_{,y}}{\partial y}\right)_{A_{,x}} \geq 0$
$d^2 E _n \geq 0$	n	S	V	T	$-p$	$\left(\frac{\partial T}{\partial S}\right)_V \geq \left(\frac{\partial T}{\partial S}\right)_p \geq 0$ $\Rightarrow \frac{T}{C_V} \geq \frac{T}{C_p} \geq 0$ $\Rightarrow C_p \geq C_V \geq 0$	$-\left(\frac{\partial p}{\partial V}\right)_S \geq -\left(\frac{\partial p}{\partial V}\right)_T \geq 0$ $\Rightarrow \frac{1}{V\kappa_S} \geq \frac{1}{V\kappa_T} \geq 0$ $\Rightarrow \kappa_T \geq \kappa_S \geq 0$
$d^2 G _{T,p} \geq 0$	T p	n_1	n_2	μ_1	μ_2	$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{n_2} \geq \left(\frac{\partial \mu_1}{\partial n_1}\right)_{\mu_2} \geq 0$	$\left(\frac{\partial \mu_2}{\partial n_2}\right)_{n_1} \geq \left(\frac{\partial \mu_2}{\partial n_2}\right)_{\mu_1} \geq 0$

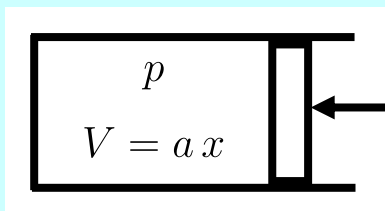
We may interpret these inequalities as follows.

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)

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

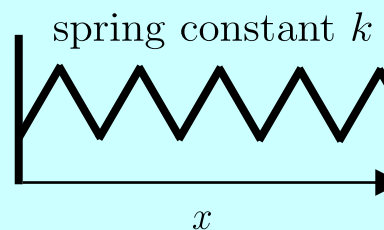


$$F = p a$$

$$dF = a dp$$

$$x = V/a$$

$$dx = dV/a$$



$$F = k(x_0 - x)$$

$$dF = -k dx$$

$$k = -\frac{dF}{dx} = -\frac{a dp}{dV/a} = -a^2 \frac{dp}{dV} = \frac{a^2}{V} \frac{1}{-\frac{1}{V} \frac{\partial V}{\partial p}} = \begin{cases} k_T = \frac{a^2}{V\kappa_T} & \text{slow: } T \text{ constant} \\ k_S = \frac{a^2}{V\kappa_S} & \text{fast: } S \text{ constant} \end{cases}$$

$k_S > k_T \quad \frac{k_S}{k_T} = \frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V}$

Review of basic concepts:

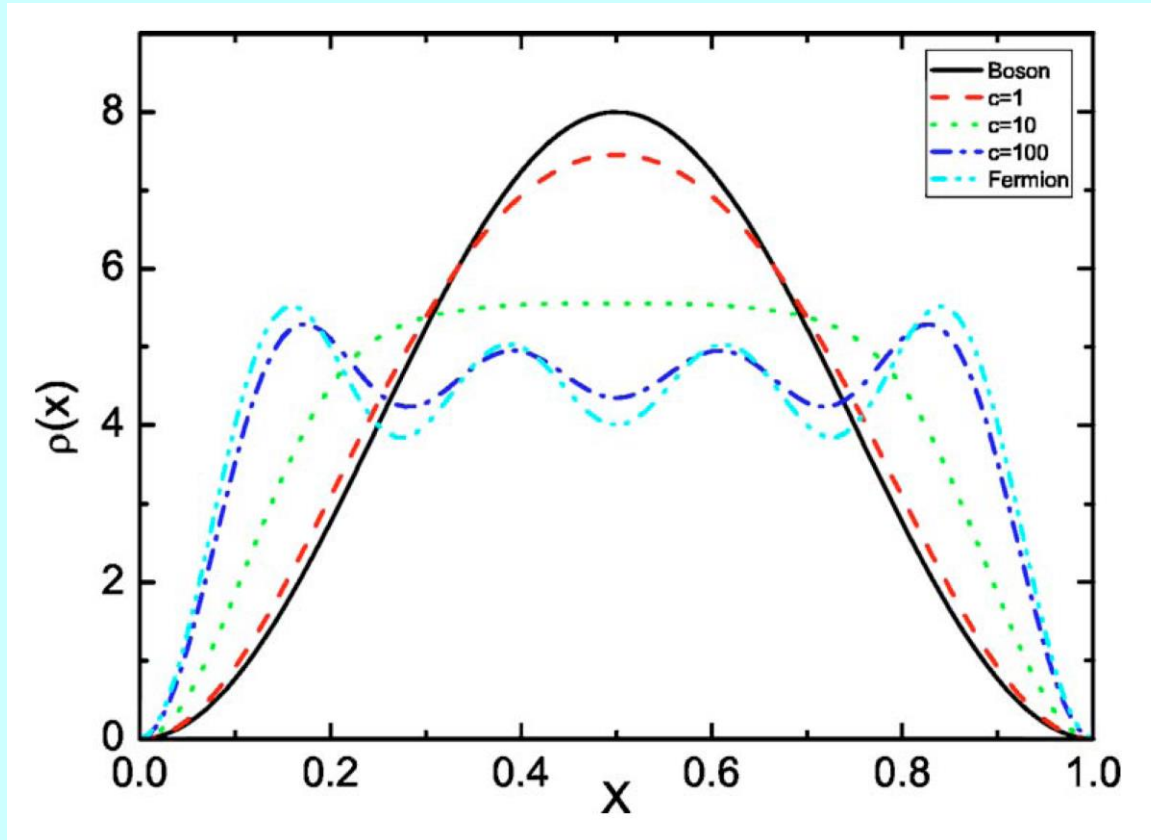
**the «Simple System» model
(macroscopic limit)
(many particle limit)**

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

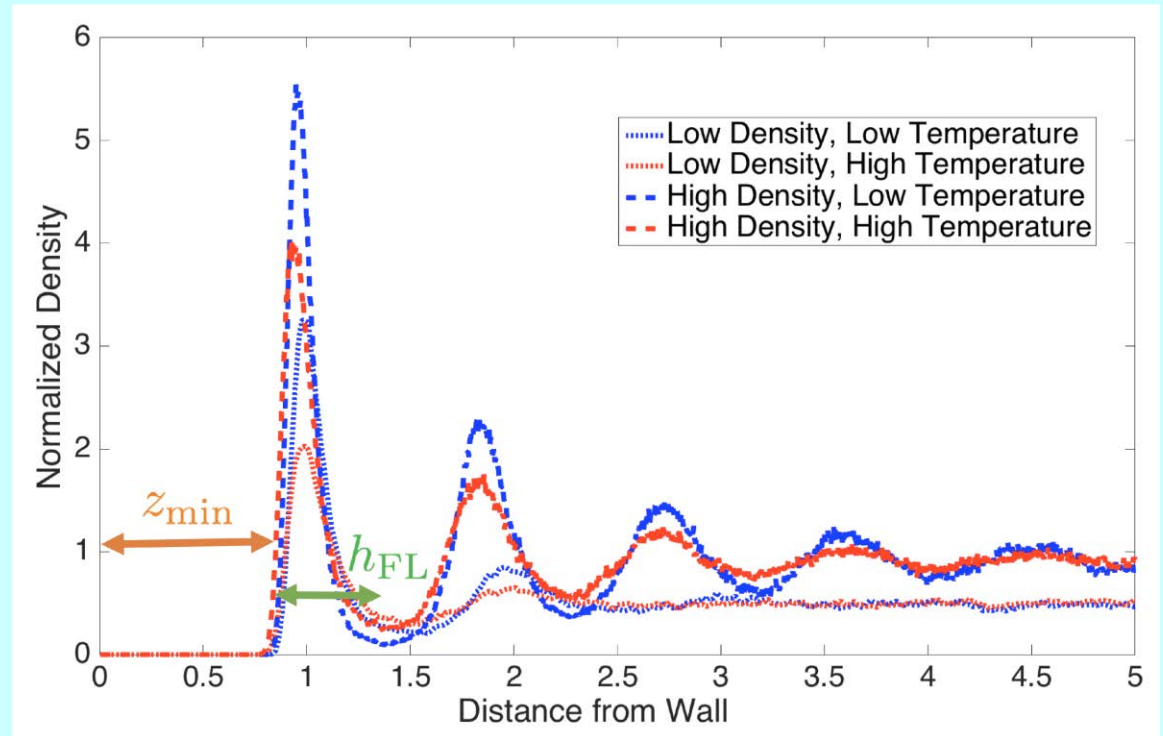
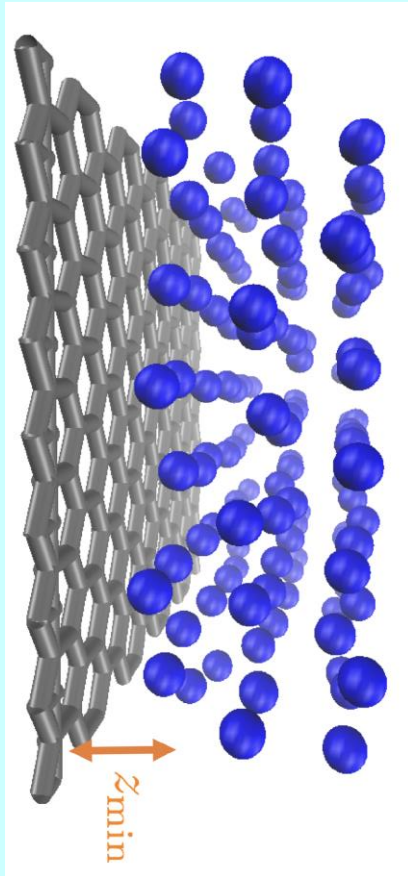


4 particles confined in a one-dimensional hard-wall trap. Density profiles of the ground state for different repulsive interaction constants.

From: Hao, Yajiang, et al., Phys. Rev. A, 73, 063617 (2006)

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

rarefaction effects near walls at SE

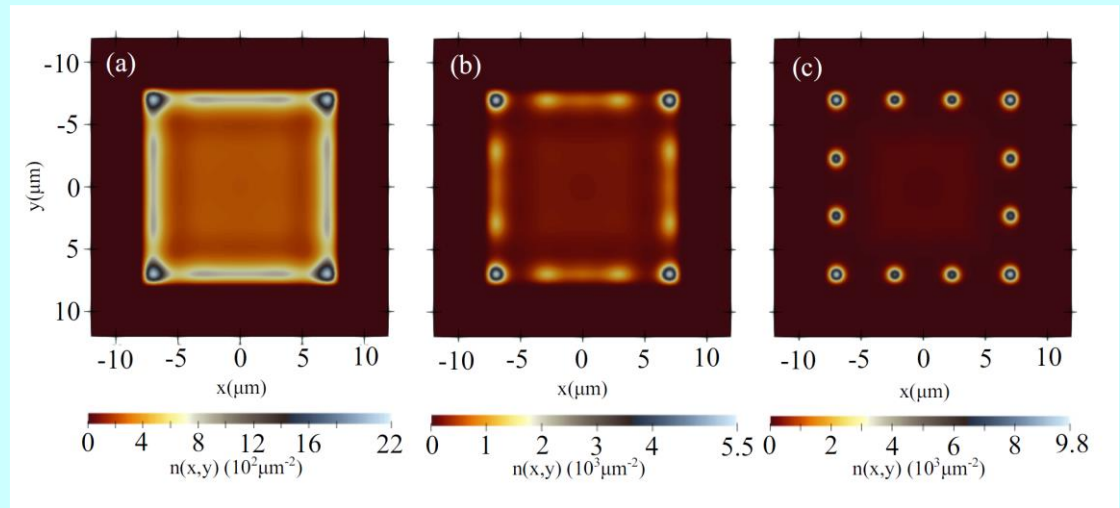
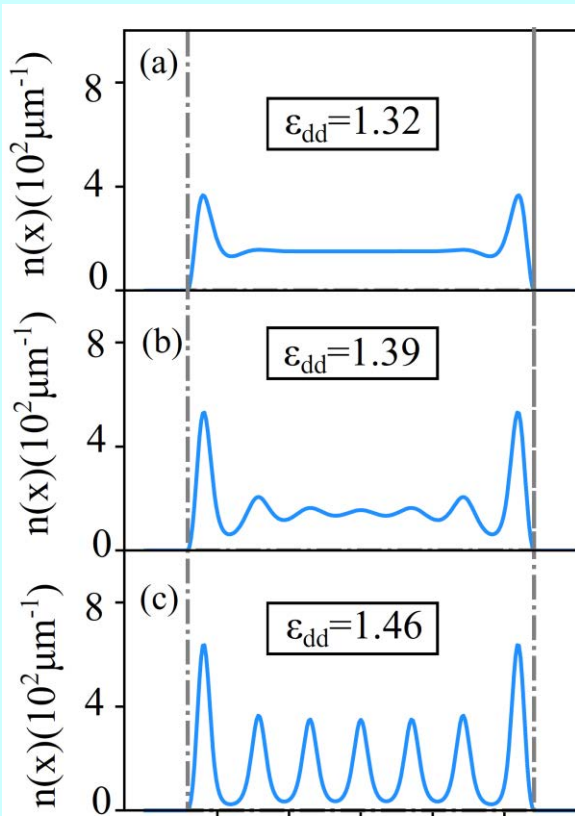


Highly non-uniform spatial density profile in a fluid near a solid confining wall at the molecular scale (MD simulations).

From: Wang and Hadjiconstantinou, Phys. Rev. Fluids, 2, 094201 (2017)

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

rarefaction effects near walls at SE

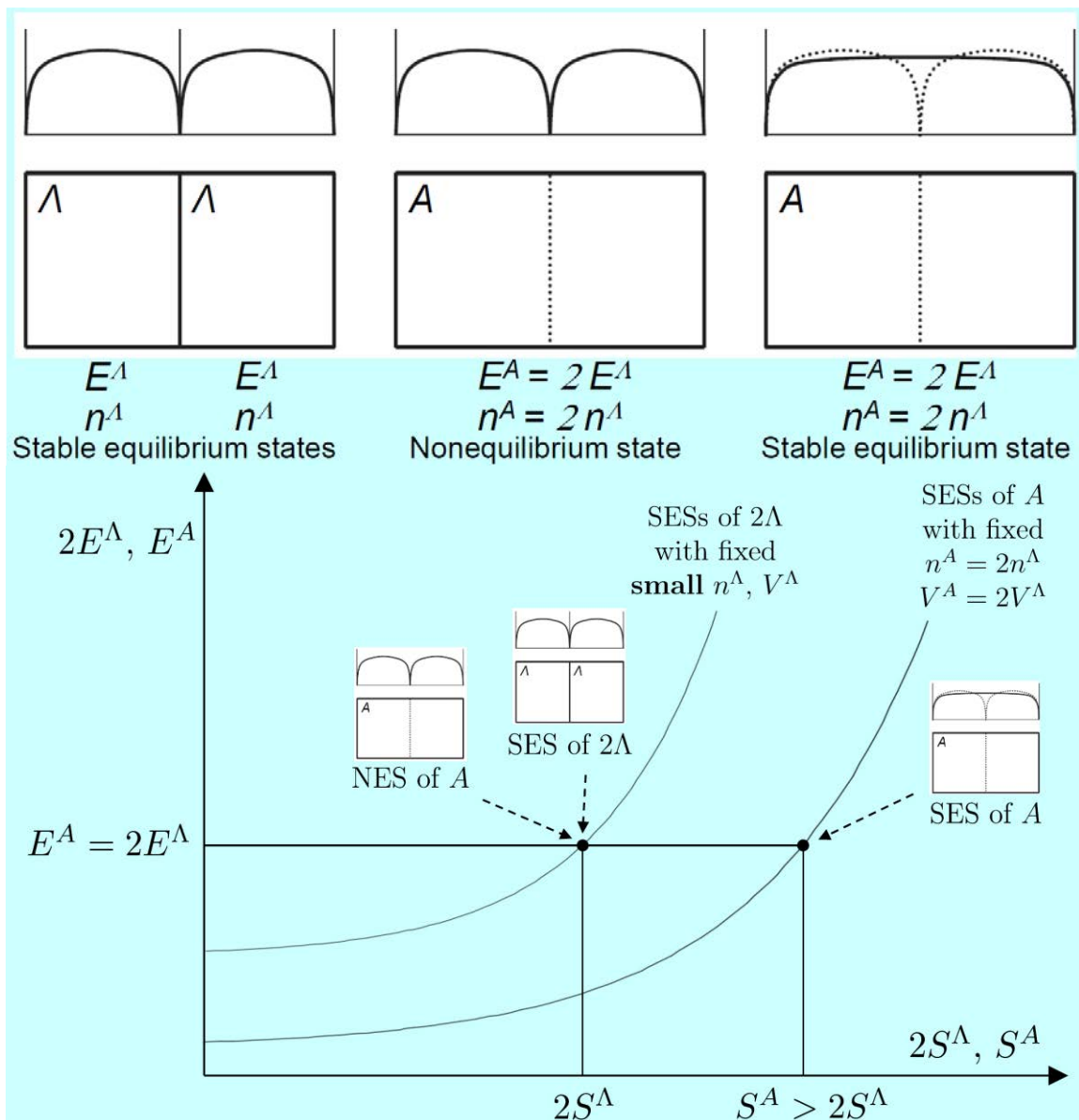


Density distributions of a dipolar condensed gas (10^5 atoms of dysprosium 164) confined in a box potential reveal a strong depletion in the bulk region and an accumulation of atoms near the walls, well separated from the bulk, as a consequence of the competition between the attractive and the repulsive nature of the dipolar force.

From: Rocuzzo, Stringari, and Recati, Phys. Rev. Research, 4, 013086 (2022)

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

rarefaction effects near walls at SE



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

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

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

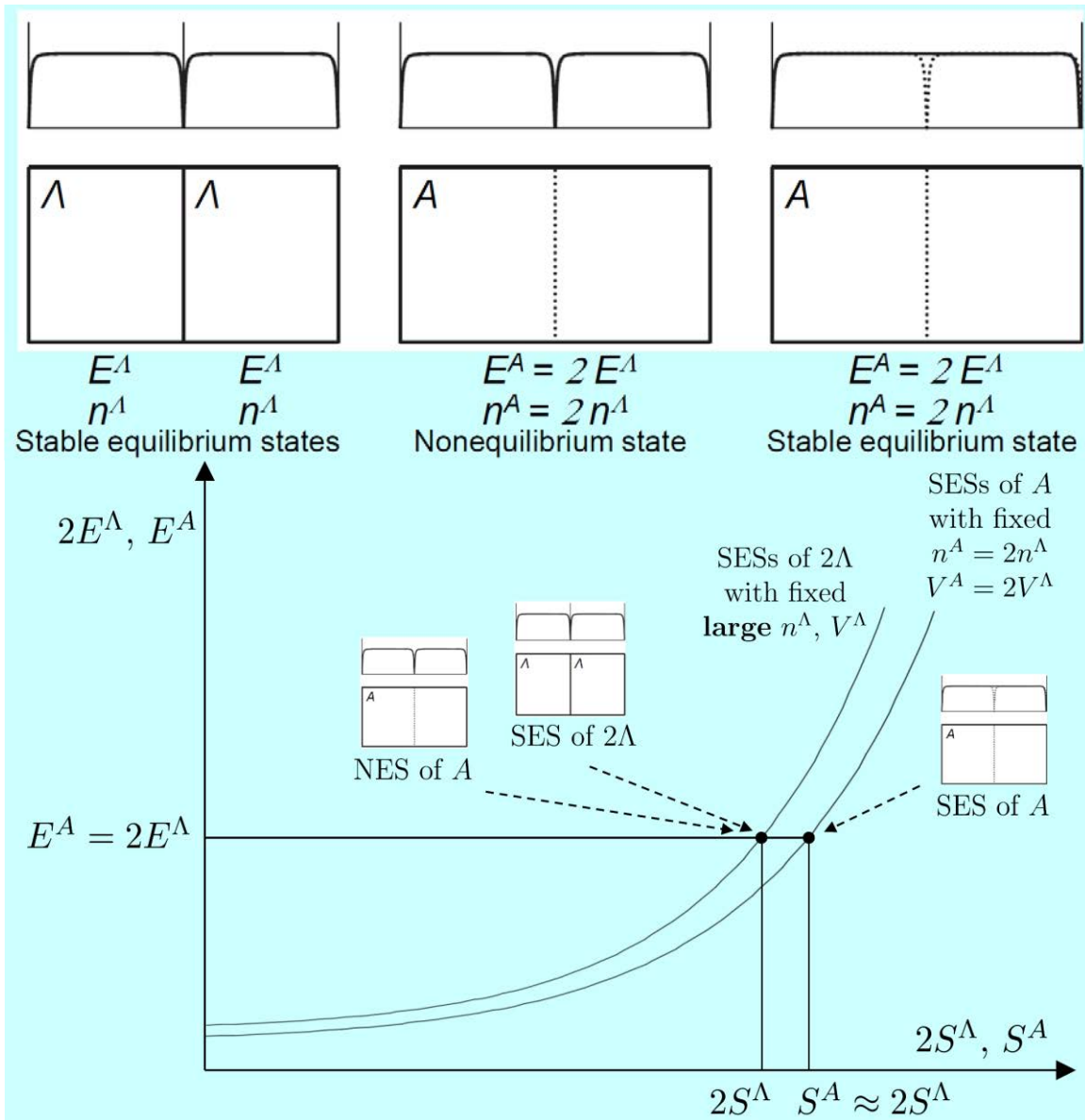
$$S^A = S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda)$$

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

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

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

rarefaction effects near walls at SE



Many particles
per partition:
at SES
(macroscopic
systems)

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

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

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

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

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

Simple System Model
assumes:

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

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

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, \dots, n_r

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

In general $S^A > \lambda S^{\Lambda}$

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

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

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

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 call 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**

proof of the Euler relation

The condition of homogeneity of first degree in all variables

$$U(S, V, \mathbf{n}) = \lambda U\left(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{\mathbf{n}}{\lambda}\right) \text{ for any real } \lambda \quad (1)$$

implies the Euler relation

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

It also implies that the potentials conjugated with S , V , \mathbf{n} are homogeneous of zero degree in all variables, i.e.,

$$T(S, V, \mathbf{n}) = T\left(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{\mathbf{n}}{\lambda}\right) \text{ for any real } \lambda \quad (2)$$

$$p(S, V, \mathbf{n}) = p\left(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{\mathbf{n}}{\lambda}\right) \text{ for any real } \lambda \quad (3)$$

$$\boldsymbol{\mu}(S, V, \mathbf{n}) = \boldsymbol{\mu}\left(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{\mathbf{n}}{\lambda}\right) \text{ for any real } \lambda \quad (4)$$

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

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

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

Proof of (2), (3), (4): compute the partial derivative of Equation (1) with respect to S , V , and \mathbf{n} , respectively.

Review of basic concepts: **simple-system model**
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

$$U = U(S, V, \mathbf{n}) = nu(s, v, \mathbf{y})$$

Proof:

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

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

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

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:

Local equilibrium approximation

Continuum approximation

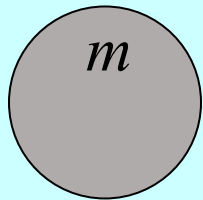
Bulk flow states

Bulk flow interactions

Review of basic concepts: the **simple-system model** is the basis also for the **bulk-flow local-equilibrium state model**

Bulk flow state or local equilibrium model: an only-apparently non-equilibrium state for which there is a reference frame in which it is a stable equilibrium state

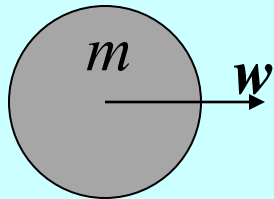
Consider a fluid element in a s.e.s. with respect to a given reference frame and assume the simple system model



$$U = m u(s, v, \mathbf{y})$$

$$S = m s$$

View it from a reference frame moving with velocity $-\mathbf{w}$



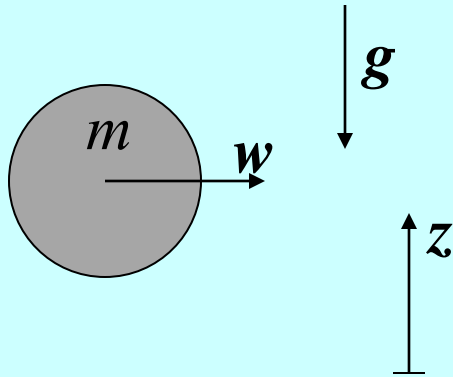
A kinetic energy is added w.r.to this frame

$$E = m u(s, v, \mathbf{y}) + \frac{1}{2} m w^2 \quad \text{where } w \text{ is the modulus of } \mathbf{w}$$

$$S = m s$$

Review of basic concepts: the **simple-system model** is the basis also for the **bulk-flow local-equilibrium state model**

View it from a reference frame which is also accelerated with acceleration $-g$



Also a potential energy is added w.r.to this frame

$$E = m u(s, v, y) + \frac{1}{2} m w^2 + m g z$$

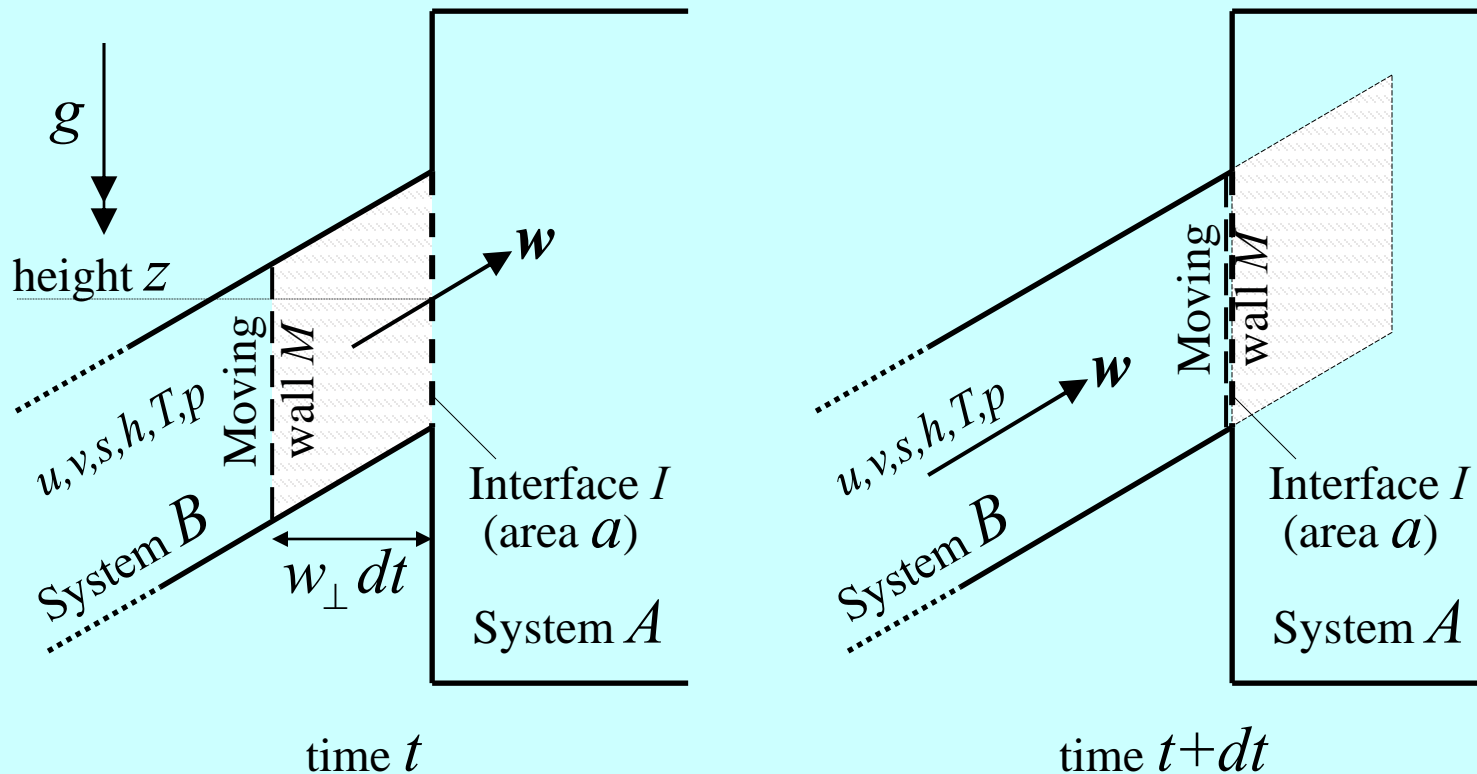
$$S = m s$$

Note1: the two added contributions are purely mechanical and therefore introduce no entropy

Note2: with respect to the moving and accelerated reference frame, the state is not stable equilibrium, and therefore no temperature, no pressure, and no chemical potentials are defined. However, we may still attribute to this state the temperature, pressure, and chemical potentials that it has with respect to the reference frame in which it is a stable equilibrium state.

Review of basic concepts: the **simple-system model** is the basis also for the model of **bulk flow interactions**

Inlet bulk flow interaction model:

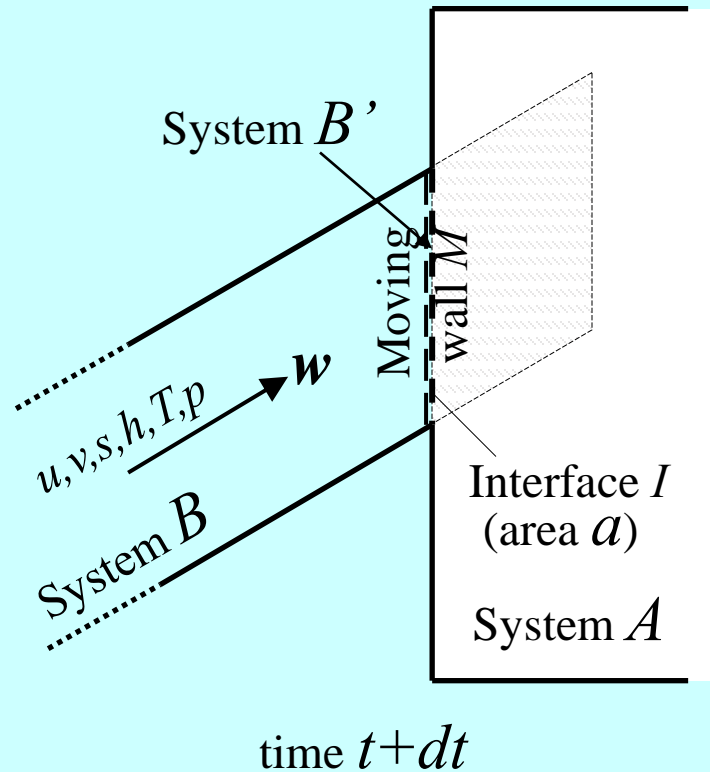
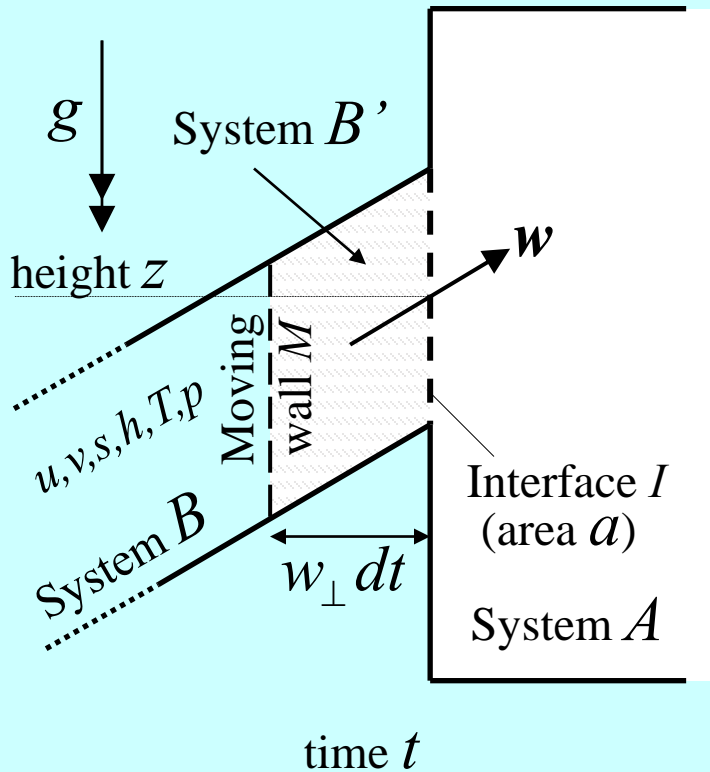


pulsion work (and how enthalpy gets in)

$$E_{t+dt}^{AB'} - E_t^{AB'} = \delta W^{AB'\leftarrow} \Rightarrow E_{t+dt}^A - E_t^A + E_{t+dt}^{B'} - E_t^{B'} = \delta W^{AB'\leftarrow}$$

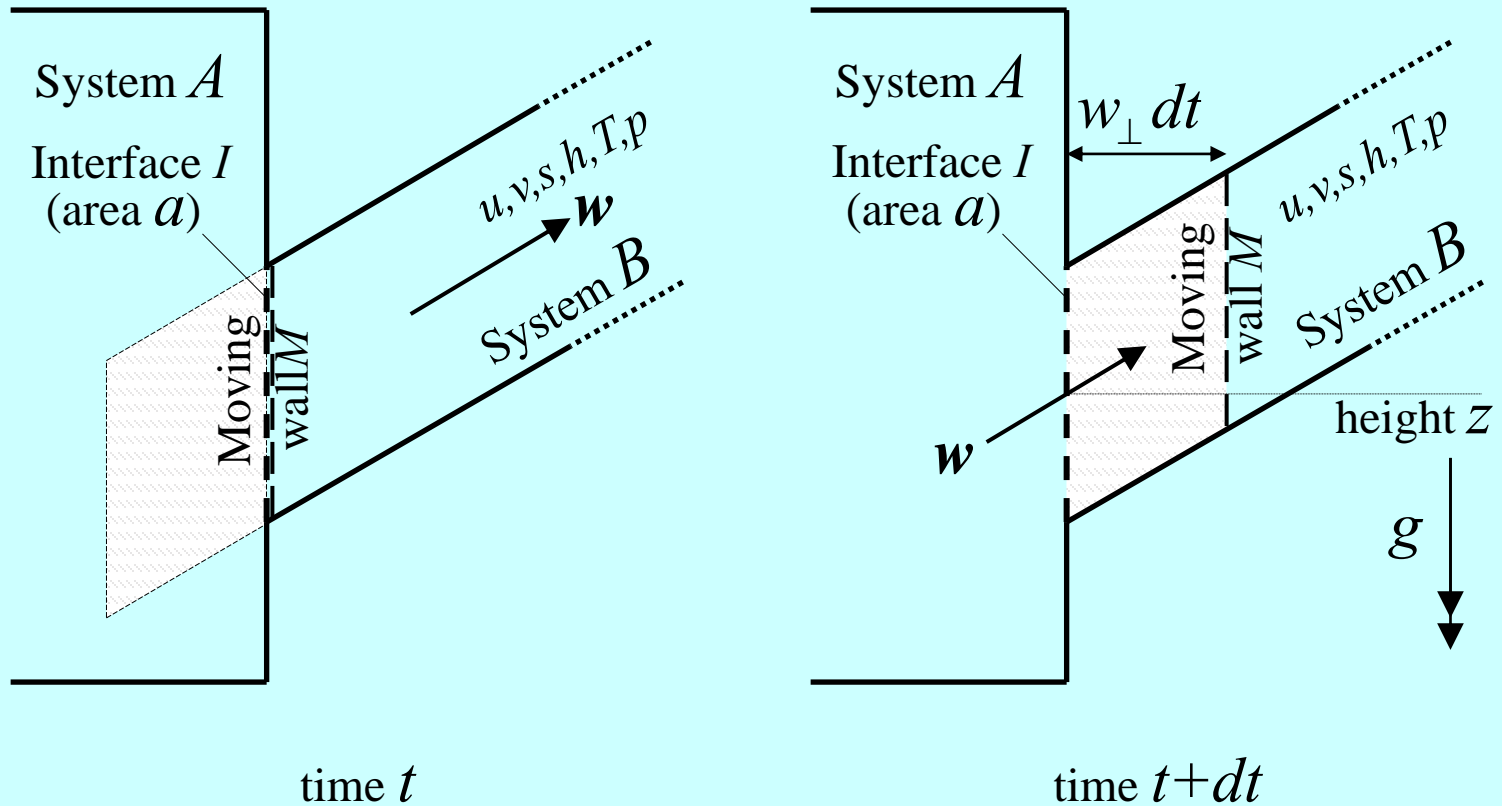
$$E_{t+dt}^{B'} = 0 \quad E_t^{B'} = (u + w^2/2 + gz)\delta m^{A\leftarrow} \quad \delta W^{AB'\leftarrow} = p a w_{\perp} dt = p v \delta m^{A\leftarrow}$$

$$\Rightarrow E_{t+dt}^A - E_t^A = (u + w^2/2 + gz)\delta m^{A\leftarrow} + p v \delta m^{A\leftarrow} = (h + w^2/2 + gz)\delta m^{A\leftarrow}$$



Review of basic concepts: the **simple-system model** is the basis also for the model of **bulk flow interactions**

Outlet bulk flow interaction model:



Review of basic concepts: the **simple-system model** is the basis also for the model of **bulk flow interactions**

For an inlet bulk flow interaction

$$\delta m^{B \rightarrow A} = \rho w_{\perp \text{in}} a dt$$

$$\delta E^{B \rightarrow A} = \delta m^{B \rightarrow A} (h + w^2/2 + gz)$$

$$\delta S^{B \rightarrow A} = \delta m^{B \rightarrow A} s$$

where $w_{\perp \text{in}}$ is the component of \mathbf{w} orthogonal to the inlet interface a in the inward direction.

For an outlet bulk flow interaction

$$\delta m^{A \rightarrow B} = \rho w_{\perp \text{out}} a dt$$

$$\delta E^{A \rightarrow B} = \delta m^{A \rightarrow B} (h + w^2/2 + gz)$$

$$\delta S^{A \rightarrow B} = \delta m^{A \rightarrow B} s$$

where $w_{\perp \text{out}}$ is the component of \mathbf{w} orthogonal to the outlet interface of area a in the outward direction.

Review of basic concepts: the **simple-system model** is the basis also for the model of **bulk flow interactions**

For continuous flow, we define the (bulk) mass flow rate

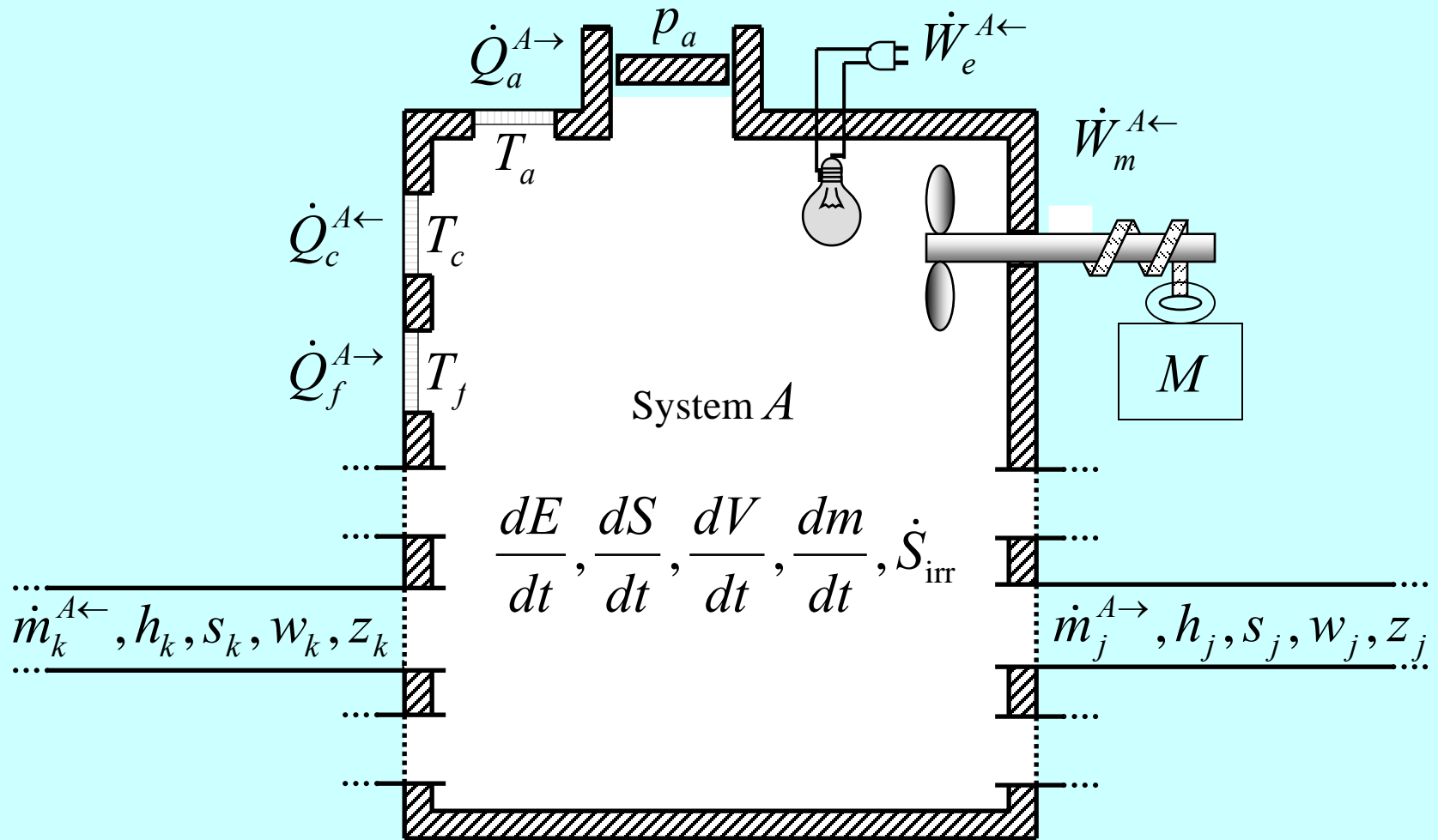
$$\dot{m}^{B \rightarrow A} = \frac{\delta m^{B \rightarrow A}}{dt} = \rho w_{\perp \text{in}} a$$

and the rates of energy and entropy transfer

$$\dot{E}^{B \rightarrow A} = \frac{\delta E^{B \rightarrow A}}{dt} = \dot{m}^{B \rightarrow A} (h + w^2/2 + gz)$$

$$\dot{S}^{B \rightarrow A} = \frac{\delta S^{B \rightarrow A}}{dt} = \dot{m}^{B \rightarrow A} s$$

Review of basic concepts: **mass, energy and entropy balances** for a system open to **bulk flow, heat, and work interactions**



Review of basic concepts: **mass, energy and entropy balances**
for a system open to **bulk flow, heat, and work interactions**

$$\frac{dm^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow}$$

$$\frac{dE^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow} \left(h_i + \frac{w_i^2}{2} + gz_i \right) + \sum_k \dot{Q}_k^{A\leftarrow} - \sum_j \dot{W}_j^{A\rightarrow} - p_a \frac{dV^A}{dt}$$

$$\frac{dS^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow} s_i + \sum_k \frac{\dot{Q}_k^{A\leftarrow}}{T_k} + \dot{S}_{\text{irr}}$$

Note: $\dot{m}_i^{A\leftarrow}$ is positive if the flow is inward, negative is outward: $\dot{m}_i^{A\leftarrow} = -\dot{m}_i^{A\rightarrow}$

These balance equations are the basis for the analysis of energy systems, as well as for exergy analysis.

**Exergies
and
first and second law
efficiencies**

**in
energy conversion
technologies**

Review of basic concepts: **exergy balance**

for a system open to bulk flow, heat, and work interactions

$$\frac{dm^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow}$$

$$\frac{dE^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow} \left(h_i + \frac{w_i^2}{2} + gz_i \right) + \sum_k \dot{Q}_k^{A\leftarrow} - \sum_j \dot{W}_j^{A\rightarrow} - p_a \frac{dV^A}{dt}$$

$$\frac{dS^A}{dt} = \sum_i \dot{m}_i^{A\leftarrow} s_i + \sum_k \frac{\dot{Q}_k^{A\leftarrow}}{T_k} - \dot{S}_{\text{irr}}$$

Note: $\dot{m}_i^{A\leftarrow}$ is positive if the flow is inward, negative is outward: $\dot{m}_i^{A\leftarrow} = -\dot{m}_i^{A\rightarrow}$

These balance equations are the basis for the analysis of energy systems, as well as for exergy analysis. For example, to get the exergy balance equation with respect to a thermal reservoir (environment) at temperature T_0 multiply the entropy balance equation by T_0 , and subtract the result from the energy balance

$$\begin{aligned} \frac{d(E^A - T_0 S^A + p_a V^A)}{dt} &= \sum_i \dot{m}_i^{A\leftarrow} \left(h_i - T_0 s_i + \frac{w_i^2}{2} + gz_i \right) \\ &+ \sum_k \dot{Q}_k^{A\leftarrow} \left(1 - \frac{T_0}{T_k} \right) - \sum_j \dot{W}_j^{A\rightarrow} - T_0 \dot{S}_{\text{irr}} \end{aligned}$$

First-law vs second-law efficiencies

$$\eta_{\text{heat engine}} = \frac{W^{\rightarrow}}{Q_A^{\leftarrow}}$$

$$\eta_{\text{II}} \Big|_{\text{heat engine}} = \frac{W^{\rightarrow}}{W_{\text{rev}}^{\rightarrow}} \Big|_{Q_A^{\leftarrow}} = \frac{W^{\rightarrow}}{Q_A^{\leftarrow} \left(1 - \frac{T_B}{T_A}\right)}$$

$$\text{COP} \Big|_{\text{refrigerator}} = \frac{Q_B^{\leftarrow}}{W^{\leftarrow}}$$

$$\eta_{\text{II}} \Big|_{\text{refrigerator}} = \frac{Q_B^{\leftarrow}}{Q_{B,\text{rev}}^{\leftarrow}} \Big|_{W^{\leftarrow}} = \frac{Q_B^{\leftarrow} \left(\frac{T_A}{T_B} - 1\right)}{W^{\leftarrow}}$$

$$\text{COP} \Big|_{\text{heat pump}} = \frac{Q_A^{\rightarrow}}{W^{\leftarrow}}$$

$$\eta_{\text{II}} \Big|_{\text{heat pump}} = \frac{Q_A^{\rightarrow}}{Q_{A,\text{rev}}^{\rightarrow}} \Big|_{W^{\leftarrow}} = \frac{Q_A^{\rightarrow} \left(1 - \frac{T_B}{T_A}\right)}{W^{\leftarrow}}$$

First law efficiency or COP (definition)

One way to assess the operation of a machine (or a component) is to compare the energy that it produces as a useful effect with the energy which it takes from the source. The ratio between the produced useful effect and the associated energy used from the source is called **first law efficiency**. In the particular case of refrigeration equipment and heat pumps this ratio is called **COP (coefficient of performance)**.

$$\eta_{I(o COP)} = \frac{\text{energy associated with produced useful effect}}{\text{energy associated with the source used}}$$

- The first law efficiency can take values between 0 and 1
- The *COP* instead takes the values which are greater than 1

N.B. = The first law efficiency compares the energies, without taking into account the different types of energy and regardless of their "useless" energy content. Therefore it does not allow to understand how much "useful" energy becomes "useless" (and is therefore lost) during the conversion made by the machine.

Second law efficiency (definition)

Another way to evaluate the operation of a machine (or a component) is to compare the exergy associated with the produced useful effect with the associated exergy of the energy drawn from the source. In this way it carries out a comparison of equivalent terms, the "mechanical equivalents" of various energies. The ratio between the exergy associated with the produced useful effect and the one associated with the utilized source is called **second law efficiency**.

$$\eta_{II} = \frac{\text{exergy associated with the produced useful effect}}{\text{exergy associated with the source used}}$$

- The second law efficiency can take values between 0 and 1 and the maximum value (machine which operates reversibly) is always 1
- N.B.** = the second law efficiency allows us to understand how much "useful" energy becomes "useless" (and is therefore lost) during the conversion made by the machine itself.

Exergy (generic definition of the concept)

Exergy: is the optimal equivalent work, i.e., the part of the energy of a system or the fraction of a given energy transfer that can be converted into ("useful") work.

We have already seen several exergies:

Exergy associated with the energy of an adiabatic system (can undergo only weight processes): it is the adiabatic availability

$$E_{X\Psi} = \Psi^A = E^A - E_S^A$$

Exergies associated with the energy of a system in combination with a thermal reservoir (we defined it with respect to various types of reservoirs)

$$E_{X\Omega^R} = (\Omega^R)^A = E^A - E_R^A - T_R (S^A - S_R^A)$$

$$E_{X\Omega^{RV}} = (\Omega^{RV})^A = E^A - E_R^A - T_R (S^A - S_R^A) + p_R (V^A - V_R^A)$$

$$E_{X\Omega^{Rn_i}} = (\Omega^{Rn_i})^A = E^A - E_R^A - T_R (S^A - S_R^A) + \mu_{iR} (n_i^A - n_{iR}^A)$$

$$E_{X\Omega^{RV,n}} = (\Omega^{RV,n})^A = E^A - E_R^A - T_R (S^A - S_R^A) + p_R (V^A - V_R^A) - \sum_i \mu_{iR} (n_i^A - n_{iR}^A)$$

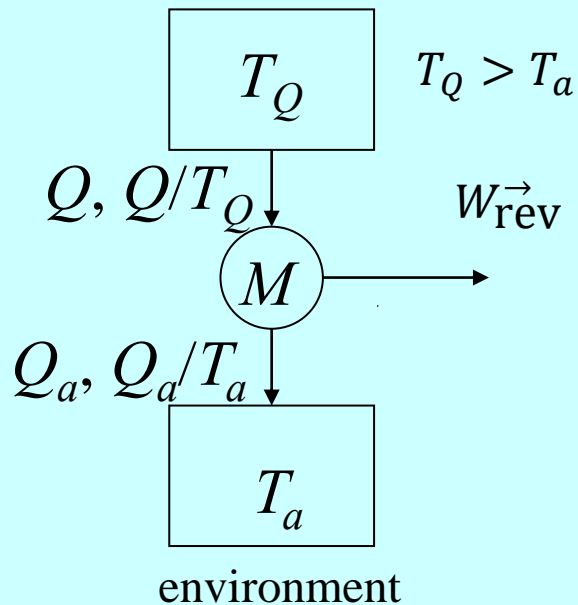
Exergy associated with the work interaction W : is the work itself

$$E_{XW} = W$$

Exergy associated with heat exchange

Exergy associated with the heat Q at temperature T_Q : the heat convertible into work is equal to the amount of heat multiplied by the Carnot coefficient

From the energy and entropy balances for M one can determine the optimal equivalent work W_{rev} of heat Q , which is therefore the exergy associated with the heat Q



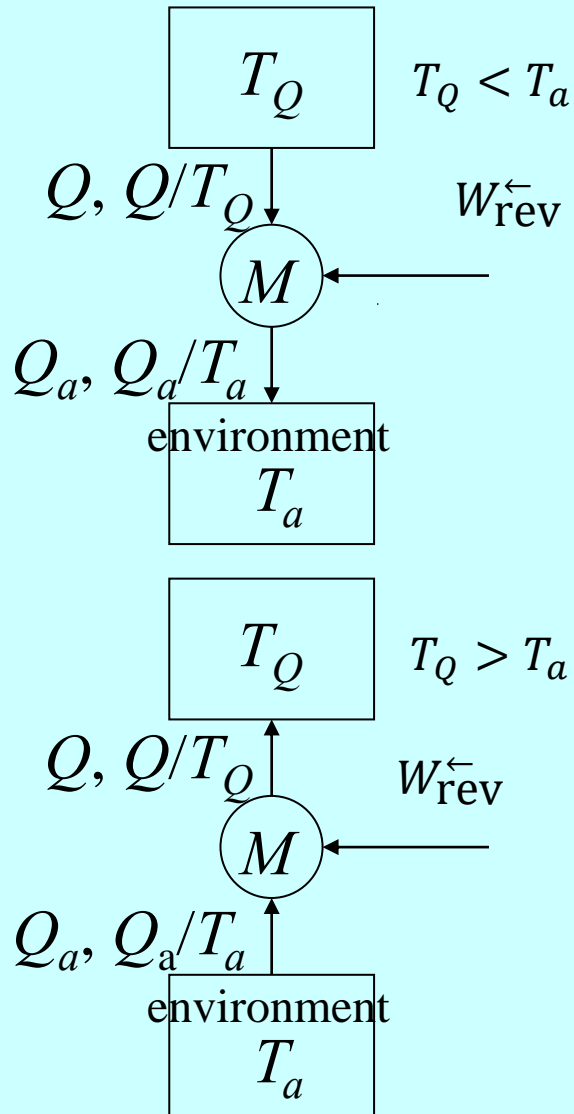
Maximum work by heating (heat engine)

$$W_{\text{rev}}^{\rightarrow} = Ex_Q = Q^{\leftarrow} \left(1 - \frac{T_a}{T_Q} \right)$$

Exergy associated with heat exchange

Exergy associated with the heat Q at temperature

T_Q : the heat convertible into work is equal to the amount of heat itself multiplied by the Carnot coefficient



Minimum work for a cooling (chiller)

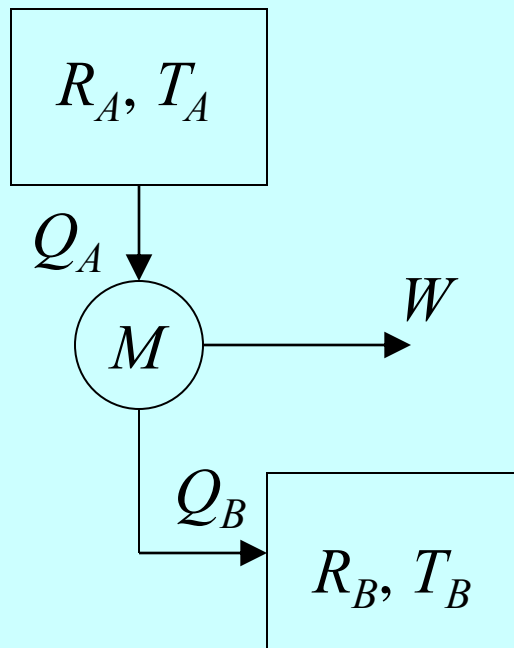
$$W_{\text{rev}}^{\leftarrow} = Ex_Q = Q^{\leftarrow} \left(\frac{T_a}{T_Q} - 1 \right)$$

Minimum work for a heating (heat pump)

$$W_{\text{rev}}^{\leftarrow} = Ex_Q = Q^{\rightarrow} \left(1 - \frac{T_a}{T_Q} \right)$$

Exergy and 2nd law efficiency in simple cogeneration

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



$$\eta_I = \frac{W + Q_B}{Q_A} = 1$$

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

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

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