Advanced thermodynamics / 2011

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Ván Péter : vpet@rmki.kfki.hu

- names: list, email
- conditions: problems/test 12th week : exam | practice: computers || half/half
- apology: english

literature:

Matolcsi T. Ordinary Thermodynamics (2005) Academic Publisers

Kondepudi, D. and Prigogine, I.: Modern Thermodynamics (1998) Wiley

Bejan, A.: Advanced Engineering Thermodynamics
2006, Wiley

Verhás, J. Thermodynamics and rheology, 1997, Academic Publishers

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Intro:

What is thermodynamics?

heat & temperature : NOT only

energy changes : NOT only

→ theory of stability of materials

A general framework of macroscopic physics.

→ foundation of engineering

Modells

System

- Power plant ← steel, concrete
  ← dynamics
- Theory

Validity:

- experiments, observations (reality)
- logic (consistency)

Attitude

- engineer - how?
- scientist - why?
- economist - how much?

mental model:

Truth: - objective - independent of ...

- open mind:
  independent of what you think, and how you think, ...

Global warming:

There is a man(kind) made harmful global warming.

1.) exists?
2.) man made?
3.) harmful?
 - why?
4.) measures?

open mind

- cycles EXP
- CO_2 - ? CONS.
- hockey stick
- H_2O CONS.

Mathematics

→ calculus: partial derivatives (←)

→ ordinary differential equations } math.

→ partial differential equation }

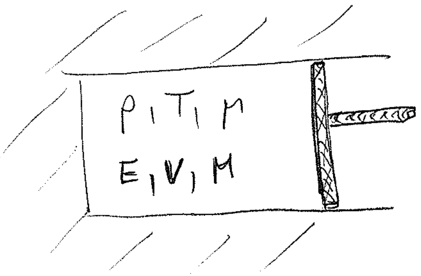
→ Lyapunov stability (←)

→ vector analysis (indices (←)) / Gauss-Ostrogradskii theorem.

I./1. Models – theories – laws

concepts } framework of thinking
relations }

– Example 1.



– discrete
– continuum

Mechanics:

statics — dynamics

discrete — continuum
- point mass
- rigid body

– elastic
– plastic
– viscoelastic
– elastoplastic
– viscoplastic
– viscoelastoplastic

Thermodynamics:

A.) thermostatics – thermodynamics

B.) discrete – continuum

C.) phenomenological – statistical

— model hierarchies, validity conditions

II/1 Extensives, densities, specific quantities (→ continuum thermostatics)

$$\boxed{\begin{array}{l} dE = TdS - pdV + \mu dM \\ E = TS - pV + \mu M \end{array}}$$

$$M = m_0 N$$

a) densities: $(\varepsilon, s\ \rho)$

$$\boxed{d \text{ – differential / Leibnitz rule : } d(fg) = fdg + gdf}$$

$$\left.\begin{array}{l} V\varepsilon = E \\ Vs = S \\ V\rho = M \end{array}\right\}$$

$$\Downarrow$$

$$\varepsilon = Ts - p + \mu\rho$$

$$d(V\varepsilon) = \varepsilon \underset{\sim}{dV} + Vd\varepsilon = Td(Vs) - pdV + \mu d(\rho V) =$$

$$= Ts\underset{\sim}{dV} + VTds - p\underset{\sim}{dV} + \mu Vd\rho + \mu\rho\underset{\sim}{dV} \Rightarrow$$

$$d\varepsilon = \frac{1}{V}\left(\left[-\varepsilon + Ts - p + \mu\rho\right]dV + VTds + \mu Vd\rho\right.$$

$$\boxed{d\varepsilon = Tds + \mu d\rho}$$

b) specific quantities: (e, s, v)

$$\left.\begin{array}{l} Me = E \\ Ms = S \\ Mv = V \end{array}\right\}$$

$$e = Ts - pv + \mu$$

$$d(Me) = edM + Mde = Td(Ms) - pd(Mv) + \mu dM =$$

$$= Ts\underset{\sim}{dM} + TMds - pMdv - vp\underset{\sim}{dM} + \mu\underset{\sim}{dM} \Rightarrow$$

$$de = \frac{1}{M}\left(\left(-e \cancel{+ Ts - pv + \mu}\right)dM + MTds - Mpdv\right]$$

$$\boxed{de = Tds - pdv}$$

Remark:

$$- S(E, V, M) = Ms(e, v) = Ms\left(E/_{M}, V/_{M}\right)$$

0 shape independent → solids

Extensive – intensive:

Def. Euler homogeneity: $f(\lambda x, \lambda y) = \lambda^k f(x, y)$ k-th order

intensives: 0-th order: $T(E, V, M) = T(e, v)$

extensives: 1-th order: $S(E, V, M) = Ms(e, v)$

II/2 Gibbs relation – potentials, variables

$$\boxed{dE = TdS - pdV + \mu dM}$$

$S(E,V,M)$: $\left.\frac{\partial S}{\partial E}\right|_{V,M} = \frac{1}{T}$ $\qquad$ $E(S,V,M)$: $\left.\frac{\partial E}{\partial S}\right|_{V,M} = T$

$\left.\frac{\partial S}{\partial V}\right|_{E,M} = p/T$ $\qquad$ $\left.\frac{\partial E}{\partial V}\right|_{S,M} = -p$

$\left.\frac{\partial S}{\partial M}\right|_{E,V} = -\mu/T$ $\qquad$ $\left.\frac{\partial E}{\partial M}\right|_{E,V} = \mu$

mnemonic for transforming the variables

Potential : $U(F = (x,y,z) = x^i)$

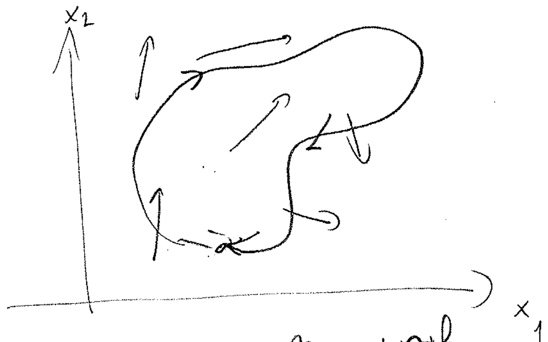
$\bar{F}(\bar{x}) = \left(F_x(x,y,z), F_y(x,y,z), F_z(x,y,z)\right) = F^i(x^i)$ force field

$= -\nabla U = \left(\frac{\partial U}{\partial x}, \frac{\partial U}{\partial y}, \frac{\partial U}{\partial z}\right) = -\partial^i U$

(i) $\exists U(x^i)$ for an $F^i(x^i) \overset{(ii)}{\Longleftrightarrow} \partial^i F^j = \partial^j F^i \quad (\nabla \times F = 0)$

$\overset{(iii)}{\Longleftrightarrow} \oint_G F_j(x^i)\, dx^j = 0$

$\forall G$-re



zero work

Rem: $-\partial^i\partial^j U = -\partial^j\partial^i U$ ✓

- abstract vector field

Ax.: $S(E,V,M)$ is a potential of the vector field: $\left(1/T, p/T, -\mu/T\right)(E,V,M)$

$\Rightarrow$ $s(e,v)$ is a potential of $\left(1/T, p/T\right)$

e.g. $(T, p)(e, v) \longrightarrow$ $\begin{rcases} \partial_e s = 1/T \\ \partial_v s = p/T \end{rcases} \rightarrow \partial_v \frac{1}{T} = \partial_e \, p/T = -\frac{\partial_v T}{T^2} = \frac{\partial_e p}{T} - \frac{p}{T^2}\partial_e T$

$$\boxed{T\partial_e p = p\,\partial_e T - \partial_v T}$$

– Maxwell relations [Theory of Heat 1879 – for skilled workers]

II/3 Legendre transformation – derivatives as variables

+ Math 1 : $f(x) + g(x) = xy \Rightarrow f' = y \;/\; g' = x$

$\mathcal{L}(f) = g$! $\quad g(y) = xy - f(x) = x(y)\,y - f(x(y))$

$f'(x) = y \Rightarrow x(y)$ ~ inverse

a) involutive : $\mathcal{L}(\mathcal{L}f) = f$

$g(y) + h(z) = yz$ $\quad g' = z = x$

$h = \underset{x}{z}y - (xy - f) = f$

b) convexity/concavity is conserved

$g'(y) = \left(x(y)\,y - f(x(y))\right)' = x(y) + y\cancel{x'(y)} - f'\cancel{x'(y)}$

$f'(x) = y$

$g''(y) = x'(y) = \frac{1}{f''(y(x))}$

$\left[\frac{d}{dx}\left[f(\overset{f^{-1}}{\overset{\shortparallel}{g}}(x)) = x\right]\right] = \underset{\underset{f'}{\shortparallel}}{\frac{df}{dg}}(g(x))\;\underset{(f^{-1})'}{\frac{dg}{dx}(x)} = 1$

$\left[\frac{d}{dx} f^{-1}(x) = \frac{1}{\frac{df}{dg}(g(x))}\right]$

Helmholtz free energy :

$F(T,V,M) = \mathcal{L}_S\left[E(S,V,M)\right] \rightarrow F(T,M,V) - E(S,V,M) = -TS$

$\partial_T F(F,V,M) = -S$

$\partial_S E(S,V,M) = T \Rightarrow S(T,V,M)$

$$\left.\frac{\partial F}{\partial T}\right|_{V,M} = -S - T\cancel{\left.\frac{\partial S}{\partial T}\right|_{V,M}} + \underbrace{\left.\frac{\partial E}{\partial S}\right|_{VM}}_{T}\cancel{\left.\frac{\partial S}{\partial T}\right|_{VM}}$$

$$\left.\frac{\partial F}{\partial V}\right|_{T,M} = -T\cancel{\left.\frac{\partial S}{\partial V}\right|_{T,M}} + \underbrace{\left.\frac{\partial E}{\partial V}\right|_{S,M}}_{-p} + \underbrace{\left.\frac{\partial E}{\partial S}\right|_{V,M}}_{T}\cancel{\left.\frac{\partial S}{\partial V}\right|_{T,M}} = -p$$

$$\left.\frac{\partial F}{\partial M}\right|_{T,V} = \dots = +\mu$$

$$dF = d(E - TS) = T\cancel{dS} - pdV + \mu dN - T\cancel{dS} - SdT$$

$$dF = -SdT - pdV + \mu dN$$

- enthalpy, specific enthalpy

$$H - E = pV \rightarrow dH = d(E + pV) = TdS - \cancel{pdV} + \mu dN + Vdp + \cancel{pdV}$$

$$dH = TdS + Vdp + \mu dM$$

$$d(hM) = Td(sM) + vMdp + \mu dM = Mdh + hdM = TsdM + TMds + vMdp + \mu dM$$

$$dh = \cancel{V}\ \frac{1}{M}\left[\cancel{\left(-\underset{-e+pv}{\overset{}{h}} + Ts + \mu\right)} dM + M(Tds + vdp)\right)$$

$$\boxed{dh = Tds + vdp}$$

II

Math 2.

$$\boxed{f(\overset{x}{\overset{\|}{g}}(z,y),y) = \hat{f}(z,y)}$$

1/A $\frac{\partial}{\partial z}$: $\frac{\partial f}{\partial g}\Big|_y \frac{\partial g}{\partial z}\Big|_y = \frac{\partial \hat{f}}{\partial z}\Big|_y \Rightarrow \boxed{\partial_x f\big|_y = \frac{\partial_z \hat{f}|_y}{\partial_z x|_y}}$

$\uparrow$ $x(z,y)$

$$f(f^{-1}(z,y),y) = z$$

1/b $\frac{\partial}{\partial z}$: $\frac{\partial f}{\partial x}\frac{\partial x}{\partial z} = 1 \Rightarrow \boxed{\partial_x f\big|_y = \frac{1}{\partial_f x|_y}}$

2/a $\frac{\partial}{\partial y}$: $\frac{\partial f}{\partial g}\Big|_y \frac{\partial g}{\partial y}\Big|_z + \frac{\partial f}{\partial y}\Big|_g = \frac{\partial \hat{f}}{\partial y}\Big|_z \Rightarrow \boxed{\partial_y f\big|_x = \partial_y \hat{f}\big|_z - \frac{\partial_z \hat{f}|_y}{\partial_z x|_y}\,\partial_y x\big|_z}$

$\uparrow$ $x(z,y)$

$$\hat{f} = z \;/\; g(= f^{-1}) = x$$

2/b $\frac{\partial f}{\partial g}\Big|_y \frac{\partial g}{\partial y}\Big|_z + \frac{\partial f}{\partial y}\Big|_g = 0 \Rightarrow \boxed{\partial_y x\big|_f = -\frac{\partial_y f|_x}{\partial_x f|_y}}$

Ex 1 :

$$c_p - c_v = +T\,\partial_T v|_p\,\partial_T p|_v \qquad c_p = T\,\partial_T s|_p \quad c_v = T\,\partial_T s|_v$$

$$T\,\partial_T s|_p - T\,\partial_T s|_v = +T\,\partial_T v|_p\,\partial_T p|_v$$

$$(T,p) - (T,v)$$

$$\underset{\uparrow\, p(v,T)}{\partial_T s|_p} = \partial_T s|_v - \frac{\partial_v s|_T}{\partial_v p|_T}\,\partial_T p|_v$$

$$\partial_T v|_p = -\frac{\partial_T p|_v}{\partial_v p|_T}$$

$$\cancel{\partial_T s|_v} - \frac{\partial_v s|_T}{\cancel{\partial_v p|_T}}\,\cancel{\partial_T p|_v} - \cancel{\partial_T s|_v} = -\frac{\partial_T p|_v}{\cancel{\partial_v p|_T}}\,\cancel{\partial_T p|_v}$$

$$\boxed{\partial_v s|_T \overset{?}{=} -\partial_T p|_v} \longleftarrow \begin{cases} df = -s\,dT - p\,dv \\ \partial_T f = -s \\ \partial_v f = -p \end{cases}$$

2.

Ex 2 : $\left(p + a/v^2\right)(v-b) = RT$ $a=0$ $b=0 \Rightarrow$ id. gas.

$$e = cT - a/v$$

a) Entropie:

$$\partial_v \frac{1}{T} = \partial_v \frac{c}{e + a/v} = \frac{c}{(e+a/v)^2}\,\frac{a}{v^2}$$

$$\| \quad \checkmark$$

$$\partial_e\,p/T = \partial_e\left[\frac{R}{v-b} - \frac{ac}{v^2(e+a/v)}\right] = +\frac{ac}{v^2(e+a/v)^2}$$

b) Entropy:

$$s(e,v) = \int \frac{1}{T}(e,v)\,de = \int \frac{cv}{ev+a}\,de = \frac{c\cancel{v}}{\cancel{v}}\ln(ev+a) + K_1(v)$$

$$s(e,v) = \int \frac{p}{T}(e,v)\,dv = \int\left(\frac{R}{v-b} - \frac{ac}{v(ev+a)}\right)dv = R\ln(v-b) - \int\left(\frac{c}{v} - \frac{ec}{ev+a}\right)dv =$$

$$\frac{1}{v(ev+a)} = \frac{A}{v} + \frac{B}{ev+a} = \frac{Aev + Aa + Bv}{v(ev+a)} \qquad A = 1/a \quad B = -e/a$$

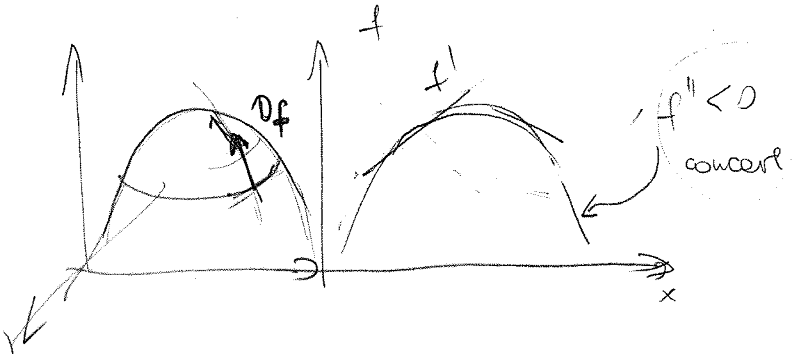
$$= R\ln(v-b) - c\ln v + \underline{c\ln(ev+a)} + K_2(e)$$

$$s(e,v) = c\ln(ev+a) + \ln\left[(v-b)^{R}v^{-c}\right] + S_0$$

$$\underline{s(e,v) = \ln\left[\left(e+\frac{a}{v}\right)^{-c}(v-b)^{R}\right] + S_0}$$

Thermodynamic stability –

– concave ⇔ maximal models mix!



$$s(e,v)$$

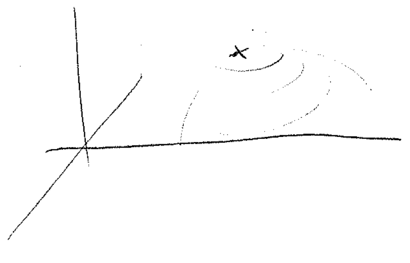
$$Ds = \left(\frac{\partial s}{\partial e}\Big|_v , \frac{\partial s}{\partial v}\Big|_e\right) = \left(\frac{1}{T} , p/T\right)$$

$$D^2 s = \begin{pmatrix} \frac{\partial^2 s}{\partial e^2}\Big|_v & \frac{\partial^2 s}{\partial e \partial v} \\ \frac{\partial^2 s}{\partial e \partial v} & \frac{\partial^2 s}{\partial v^2}\Big|_e \end{pmatrix} = \begin{pmatrix} \partial_e \frac{1}{T} & \partial_v 1/T \\ \partial_e p/T & \partial_v p/T \end{pmatrix} = \begin{pmatrix} -\frac{\partial_e T}{T^2} & -\frac{\partial_v T}{T^2} \\ \frac{\partial_e p}{T} - \frac{p}{T^2}\partial_e T & \frac{\partial_v p}{T} - p/T^2\,\partial_v T \end{pmatrix}$$

$$= -\frac{1}{T^2}\begin{pmatrix} \partial_e T & \partial_v T \\ -T\partial_e p + p\,\partial_e T & -T\partial_v p + p\,\partial_v T \end{pmatrix}$$

$D^2 s$ negative definite ($\Leftrightarrow D^2 s$ positive definite)

$$x^i A^{ij} x^j < 0 \qquad \forall x^i, x^j$$



Sylvester criteria: A symmetric matrix is + definite ⟺

$\boxed{\text{Det}\,\Delta_i > 0}$ $\forall_i$

$$\begin{array}{cccc} \Delta_1 & \Delta_2 & \Delta_3 & \\ a_{11} & a_{12} & a_{13} & \cdots \\ a_{12} & a_{22} & a_{23} & \cdots \\ a_{13} & a_{23} & a_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{array}$$

$D^2_s =$ a) $\boxed{\partial_e T > 0}$ ⟺ isochor spec. heat $c_V > 0$

$$c_V = T\,\partial_T s|_v = T\,\frac{\partial_e s|_v}{\partial_e T|_v} = \frac{1}{\partial_e T|_v}$$

b) $$-\partial_e T\left(T\partial_v p - p\,\partial_v T\right) = -\partial_v T\left(T\partial_e p - p\,\partial_e T\right)$$

$$T\partial_e T\left(\partial_v p - \frac{\partial_v T}{\partial_e T}\partial_e p\right) = -T\,\partial_e T|_v\,\partial_v p|_T > 0$$

$\boxed{\partial_v p|_V < 0}$ κ_T - isothermal compressibility > 0

$$\kappa_T = -\frac{1}{v}\,\partial_p v|_T$$

sensible: $\left.\frac{\Delta T}{\Delta E}\right|_V > 0$ $E\uparrow \Rightarrow T\uparrow$

$E\downarrow \Rightarrow T\downarrow$

$\left.\frac{\Delta p}{\Delta V}\right|_V > 0$ $p\uparrow \Rightarrow v\downarrow$

$p\downarrow \Rightarrow v\uparrow$

} Le Châtelier-Braun principle

- chemistry
- economy

3

VdW gas +

van der Waals gas

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$T = \frac{e}{c} + \frac{a}{vc}$$

Exc: – $p(v,T) \Rightarrow e(v,T)$

– $s(v,T)$

– $\mu(p,T)$

– thd stab.

Critical state parametrization:

$$(1) \quad \partial_v p|_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = \frac{2a(v-b)^2 - RTv^3}{v^3(v-b)} < 0$$

$$(2) \quad \partial_{w} p|_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

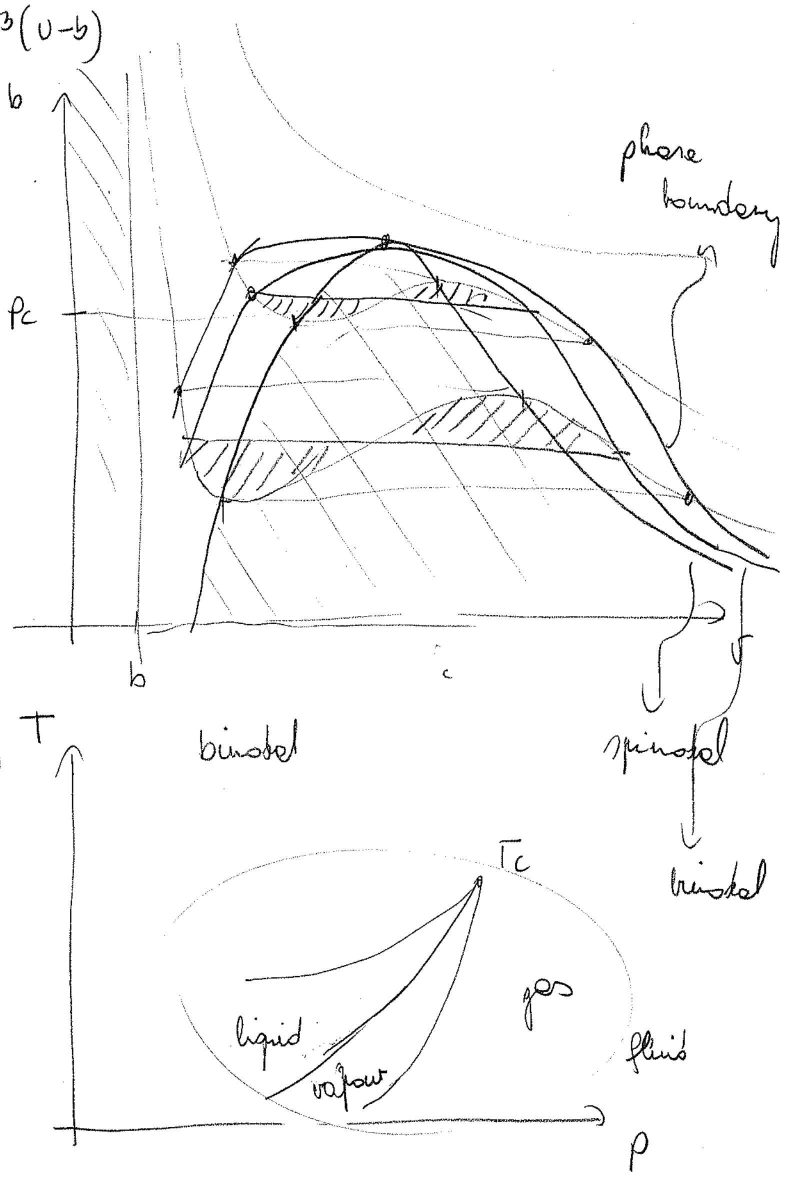
$$\left.\begin{aligned} (1) \quad \frac{RT}{(v-b)^2} &= \frac{2a}{v^3} \\ (2) \quad \frac{RT}{(v-b)^3} &= \frac{3a}{v^4} \end{aligned}\right\} \quad \frac{RT\,v^3}{(v-b)^2 a} = 2 \overset{!}{=} \frac{3(v-b)}{v}$$

$$\cancel{2}v = \cancel{3}v - 3b$$

$$\boxed{v_c = 3b}$$

$$T_c = \frac{2a}{(3b)^3}\frac{(2b)^2}{R} = \frac{8ab^{\cancel{2}}}{27Rb^{\cancel{3}}} = \boxed{\frac{8a}{27bR} = T_c}$$

$$p_c = \frac{\cancel{R}\,8a}{27bR\,2b} - \frac{a}{9b^2} = \left(\frac{\cancel{8}4}{3\cdot\cancel{2}} - 1\right)\frac{a}{9b^2} = \boxed{\frac{a}{27b^2} = p_c}$$



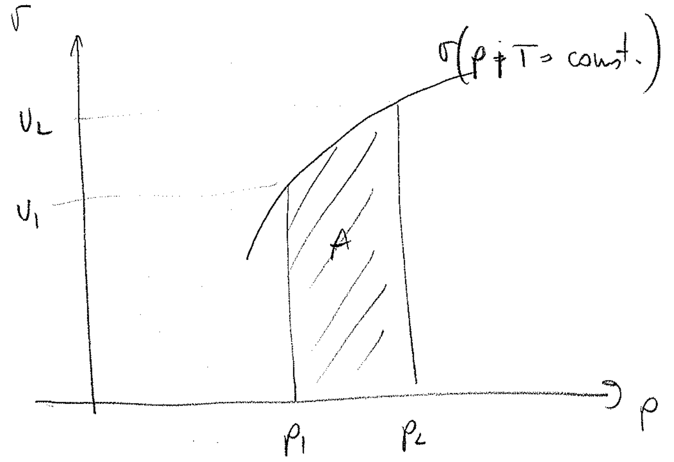
$v_c = 1 \Rightarrow b = 1/3$

$p_c = 1 \Rightarrow a = 27 \cdot \frac{1}{9} = 3,$

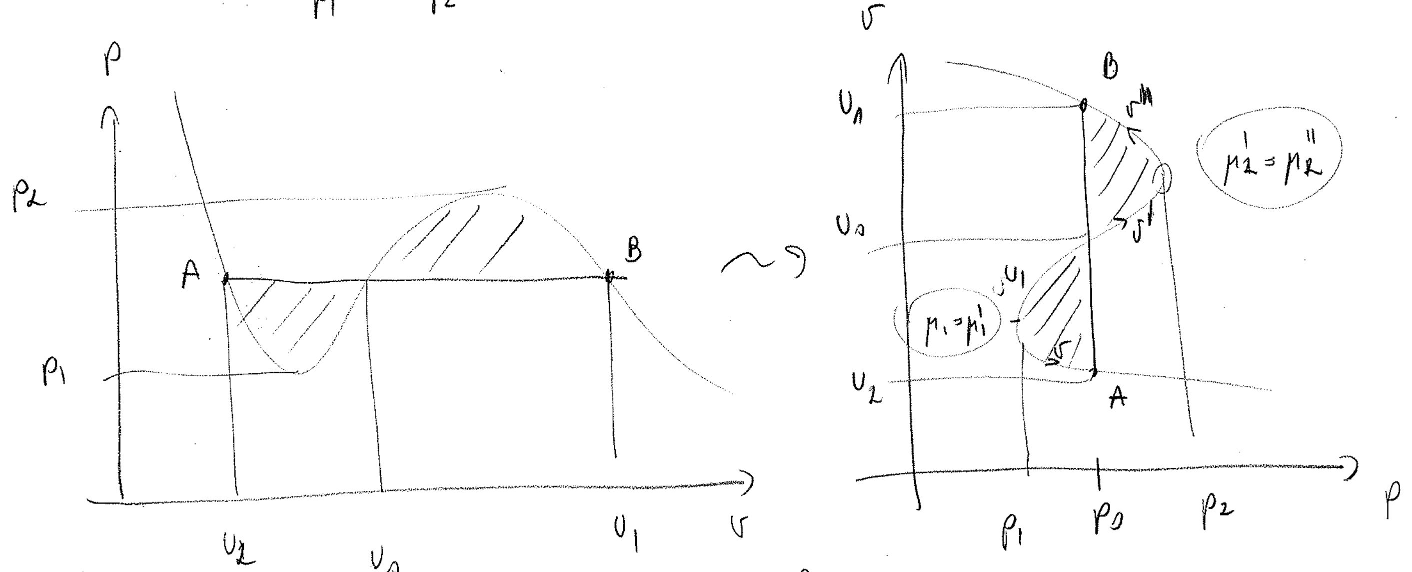
$T_c = 1 \Rightarrow R = \frac{8 \cdot \cancel{3}3}{\cancel{27}\,3} = 8/3$

Binodal – coexistence

$$\left.\begin{aligned} de &= T\,ds - p\,dv \\ e &= Ts - pv + \mu \end{aligned}\right\} \quad \begin{aligned} d\mu &= -s\,dT + v\,dp \\ &\mu(T,p) \end{aligned}$$



$$A = \int_{p_1}^{p_2} v(p)\,dp = \mu(p_2,T) - \mu(p_1,T)$$

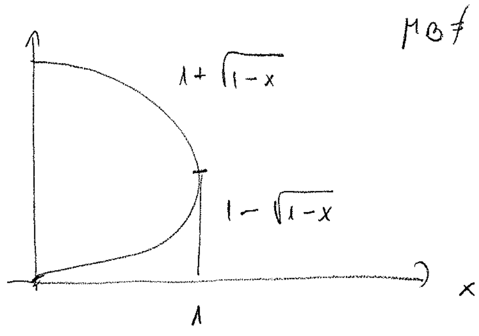


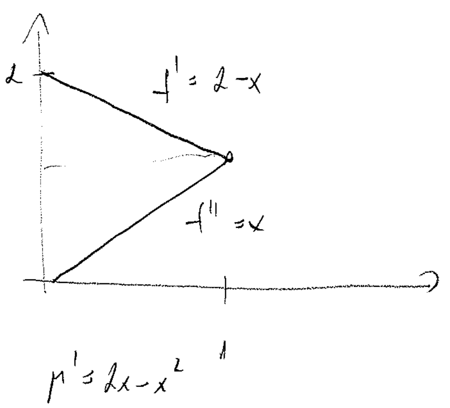
$$\int_A^B v\,dp = +\int_{p_0}^{p_1} v\,dp + \int_{p_1}^{p_0} v'\,dp + \int_{p_0}^{p_2} v'\,dp + \int_{p_2}^{p_0} v'''\,dp = \cancel{\mu_1} - \mu_0 + \cancel{\mu_0'} - \cancel{\mu_1'} + \cancel{\mu_2'} - \cancel{\mu_0'} +$$

$$+ \mu_0'' - \cancel{\mu_2''} = \mu_0'' - \mu_0 = -\mu(T,v_2) + \mu(T,v_1)$$

$\mu_B \neq \mu_A$ is not a trivial fact.

Rem:





$\mu' = 2x - x^2$

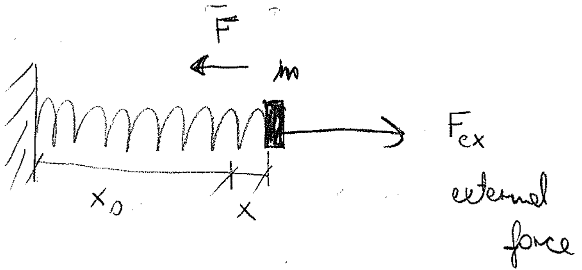
$\mu'' = x^2$

Def: PHASE : coexistence - different phase

$(p,T)(e,v)$ is invertible and maximal with that property

$Ph \subset Dom(p,T)[e,v]$

Spring – total and internal energies



$F_e = -Dx$
$E_e = D\frac{x^2}{2}$ } statics

$\dot{E}_e = Dx\,x'$

$K = \frac{m x'^2}{2}$

$K' = m u \dot{u}$

$u = x'$

! $m\dot{u} = F_{ex} - F$

$W = F_{ex}x$

$P_{ex} = F_{ex}u$

$E_T = E_e + K + E_i$

$$\frac{dE_T}{dt} = \dot{Q} + P_k = Q + F_e u = E_e' + K' + E_i' = Dxu + m u u' + \dot{E}_i$$

$$\dot{E}_i = Q + \cancel{F_{ex}}u - (\cancel{F}_{ex} - F)u - Dxu$$

$$\dot{E}_i = Q + (F - Dx)u \quad \rightsquigarrow \quad \boxed{dE_i = T d\hat{S} + (F - Dx)\,dx}$$

$E_i = E_T - E_e - K$

E_T – total
K – kinetic
E_{el} – elastic
E_i – internal_1

F_{ex} – external
$F_{el} = Dx$ – elastic
F – actual
$F - Dx$ – dissipative

$u = E_i + E_{el} = \text{internal}_2$

$$du = d\left(E_i + \frac{Dx^2}{2}\right) = TdS + Fdx \qquad \boxed{du = TdS + Fdx}$$

$u = E_T - K$

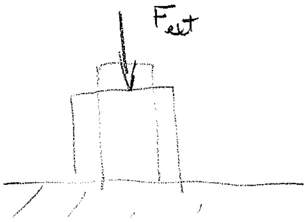
$$S(u, x) = S\left(E_i + \frac{Dx^2}{2}, x\right) = \hat{S}(E_i, x)$$

necessary $m \sim 0$

Remarks:

(i) phases

gas – no equilibrium [external force]
liquid – eq. volume
solid – e.q. shape

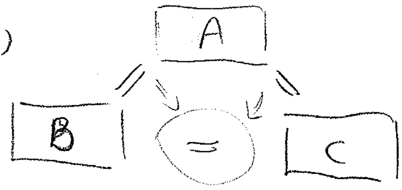


(ii) extensivity ⇒ solids: shape dependence

ε^{ij} – deformation / $\sigma^{ij} = -p^{ij}$ stress = – pressure $\frac{\text{shear}}{\text{volume}}$

Laws of thermodynamics

0 0th → equilibrium a)

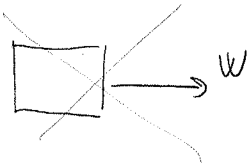


b) intensives are equal:

1th energy conservation (heat and work)

0

$$\dot E = Q + W + G \qquad (\delta Q / \delta W / \delta G)$$



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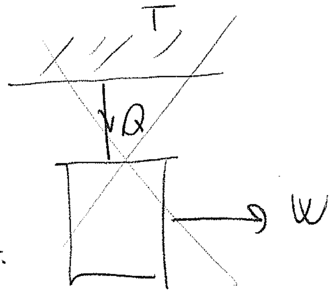
2nd a) „It is impossible to construct a machine working periodically and produce no effect except performing work and cooling a heat-reservoir." (Kelvin-Planck)



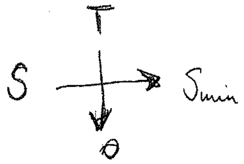
b) Clausius
$\dot S \geq 0$ in isolated systems

c) Heat can flow from the hotter to the colder.

d) Prigogine:

$$dS = d_T S + d_i S \qquad \begin{cases} d_T S = Q/T & \text{(open!)} \\ d_i S \geq 0 \end{cases}$$

0 3rd



(T=0 is not attainable.)

* * *

- Statistical physics ⟺ universal.
- $\dot E = \underbrace{Q + W + G}_{\text{environment}} = \underbrace{T\dot S - p\dot V}_{\text{body}} + \mu \dot N \quad \Longleftrightarrow \quad \underset{\text{body}}{\dot p} = \underset{\text{environment}}{F}$

?

Story:

1th: J. R. von Meyer (physician) (1842 May)

J. P. Joule (amateur) (1842 Aug.)

2nd: Sadi Carnot (military engineer) 1824.

father: Lazare Carnot (military engineer)
(Great Carnot / Organizer of the Victory)
one of the leaders of the Revolution / minister of war of Napoleon

brother: (Lazare) Hippolyte Carnot – senator for life

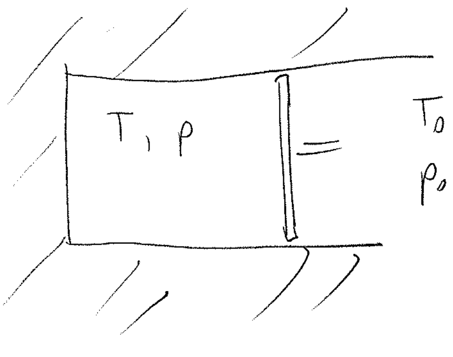
cousin: Sadi – president of the Third Republic (1887 – 94, assassination)

engineers: Carnot / Clapeyron / Rankine
physicians: Meyer / Helmholtz
public servants: Fourier / Lazare Carnot
amateur: Joule

} fight with physicists

↓ natural philosophy → general reasons

$$\left.\begin{aligned} \frac{de}{dt} &= \dot q + \dot w = \dot q(e,v) + \dot w(e,d) \\ \frac{dv}{dt} &= f(e,v) \quad \text{(?)} \end{aligned}\right\} \text{differential equation}$$



0th: a) $\dot q(T, p, T_0\, p_0)$

$\dot w(T, p, T_0\, p_0)$

$f(T, p, T_0\, p_0)$

b) $(q, w, f)(T_0, p_0, T_0\, p_0) = (0, 0, 0)$

Example 1

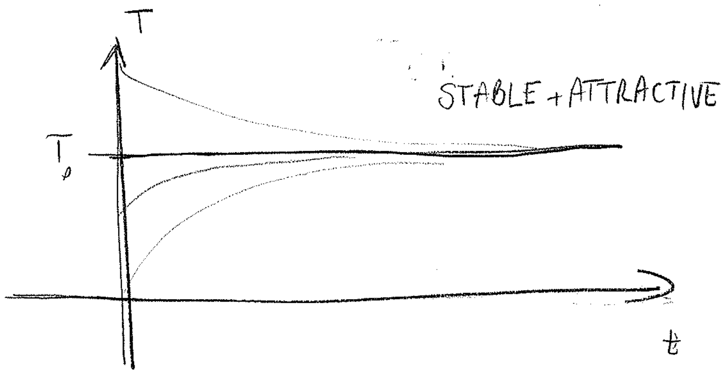
$$\left.\begin{array}{l} \hat{q} = -\alpha(T-T_0) \\ \hat{\dot{\omega}} = -pf \\ f = \beta(p-p_0) \end{array}\right\} \quad \begin{array}{l} \dot{e} = -\alpha(T-T_0) - p\dot{v} \\ \dot{v} = \beta(p-p_0) \\ p = \frac{RT}{v} \quad cT = e \Rightarrow T = e/c \quad p = \frac{Re}{cv} \end{array}$$

$$\dot{e} = -\alpha\left(e/c - T_0\right) + \frac{R}{c}\frac{e}{v}\beta\left(\frac{Re}{cv} - p_0\right)$$

$$\dot{v} = -\beta\left(\frac{Re}{cv} - p_0\right)$$

$$\beta = 0 \qquad \dot{e} = -\alpha\left(\frac{e}{c} - T_0\right) \rightarrow c\dot{T} = -\alpha(T-T_0)$$

$$\left.\begin{array}{l} T(t) = T_0 + ke^{-\alpha/c\,t} \\ T(0) = T_i = T_0 + k \end{array}\right\} \quad T(t) = T_i + T_0\left(1 - e^{-\alpha/c\,t}\right)$$



Second Law

a) $\exists S$ (thermodynamic potentials)

b) S is concave (—"— stability)

} asymptotic stability

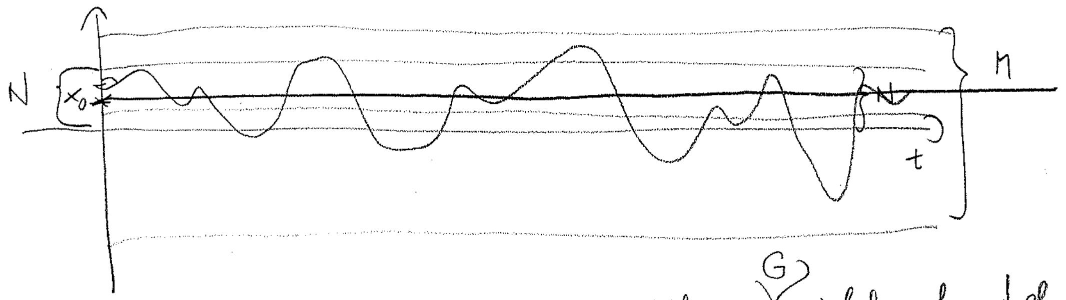
c) $\dot{S} \geq 0$

3 Math. interplay – Lyapunov stability

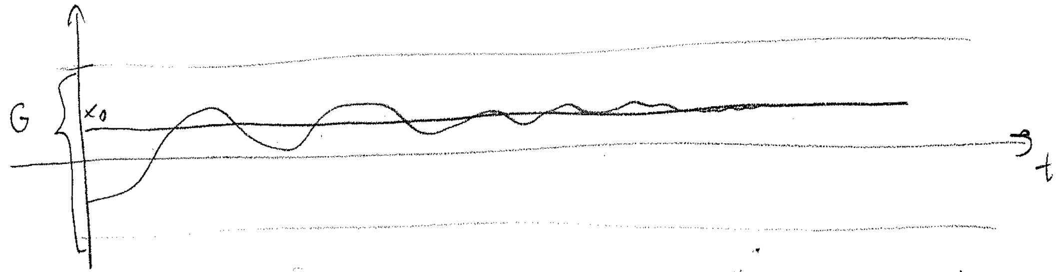
(*) $\frac{d}{dt} x^i = \cancel{f^i(x^j)} = f^i(x^1, \dots, x^n)$ autonomous differential equation $x^i : \mathbb{R} \to \mathbb{R}^n$; $t \mapsto x^i(t)$, $f^i : \mathbb{R}^n \to \mathbb{R}^n$

Def 1 $x_0^i \in \mathbb{R}^n$ is an <u>equilibrium</u> of (*) if $x_0^i \in \mathrm{Dom}\, f^i$ and $f^i(x_0^j) = 0^i$

Def 2 x_0^i equilibrium of (*) is <u>stable</u> if $\forall N$ neighbourhood of x_0^i there is a neighbourhood M (of x_0^i) so that $\forall\, x^i(t)$ starting from N ($x^i(0) \in N$) $x^i(t)$ proceeds in M ($x^i(t) \in M \;\; \forall\, t \in [0, \infty)$)



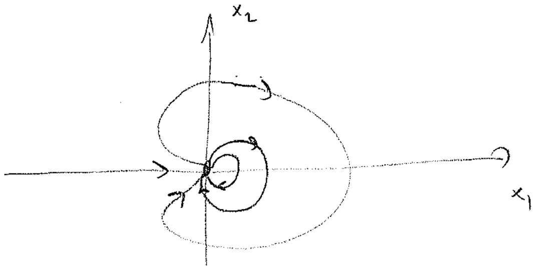
Def 3 x_0^i equilibrium of (*) is <u>attractive</u> if exists a neighbourhood (G) of x_0^i so that $x^i(t)$ starting from G tends to x_0^i ($x^i(t) \xrightarrow[\infty]{t} x_0^i \quad x^i(0) \in G$).



Def 4 x_0^i equilibrium is <u>asymptotically stable</u> if stable and attractive.

stable $\not\Rightarrow$ attractive

attractive $\not\Rightarrow$ stable



Def 5 <u>Derivative along (*)</u>:

$L : \mathbb{R}^n \to \mathbb{R}$ $\qquad L^\square := DL \cdot f : \mathbb{R}^n \to \mathbb{R}$

$$\frac{d}{dt} L(x^1, \dots, x^n) = \left(\underset{\partial_1 L}{\underset{\shortparallel}{\frac{\partial L}{\partial x_1}}}, \partial_2 L, \dots \partial_n L \right) \left(\dot{x}^1, \dot{x}^2, \dots \dot{x}^n \right) = \sum_{i=1}^{n} \partial_i L f^i = \partial^i L f^i (x^j(t)) = L^\square (x^j(t))$$

<u>Def 6</u> $L: \mathbb{R}^n \to \mathbb{R}$ is a <u>Lyapunov-function</u> of an x_0^i equilibrium of (*) if

(i) L has a strict maximum at x_0^i $\left(L(x_0^i) \geq L(x^i) \right)$

(ii) $L^{\Box}$ has a strict minimum at x_0^i. $\left(L^{\Box}(x_0^i) \leq \overset{\Box}{L}(x^i) \right)$ ~~decreasing~~ increasing along (*)

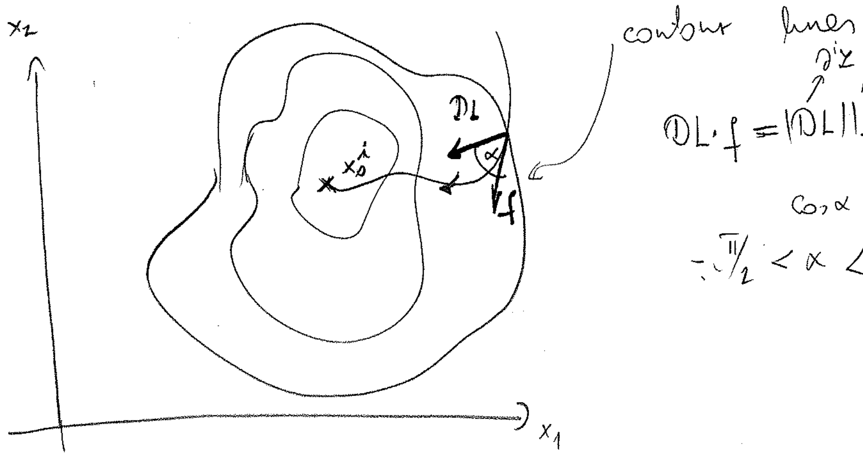
<u>Def 7</u> L has a <u>strict maximum</u>, if $L(x_0^i) \geq L(x^i)$ $\forall x^i \in N(x_0^i)$ and equality is valid iff $x_0^i = x^i$.

<u>Rem:</u> - $L(x_0^i) = 0$ is not a restriction $0 \geq L(x^i)$ / $0 \leq \overset{\Box}{L}(x^i)$

- max. ⟷ min.

<u>Theorem</u> (Lyapunov): If an equilibrium solution x_0^i of (*) has a ~~Lyapunov~~ Lyapunov function, then x_0^i is asymptotically stable.

<u>proof</u>:



$$\mathbb{D}L \cdot f = |\overset{\partial^i L}{\mathbb{D}L}||\overset{f^i}{f}| \cos\alpha \geq 0$$

$$\cos\alpha > 0$$

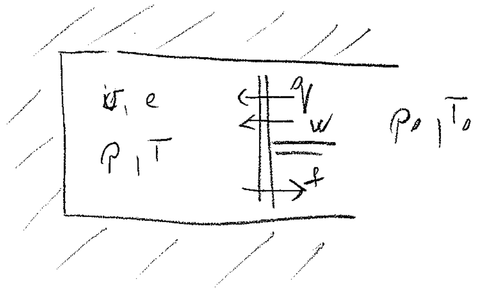
$$-\pi/2 < \alpha < \pi/2$$

<u>Example</u> $\dot{T} = -\alpha(T - T_0)$

$L(T) = -(T - T_0)^2$ $L'(T) = -2(T - T_0)$

$$L^{\Box} = L' \cdot f = -2(T - T_0)^2(-\alpha) = 2\alpha(T - T_0)^2 > 0$$

(*) $$\boxed{\begin{aligned} \frac{\partial e}{dt} &= q(e,v) + w(e,v) \\ \frac{dv}{dt} &= f(e,v) \end{aligned}}$$



properties:

static eos: $p(e,v)$, $T(e,v)$

(i) $\underline{\exists s(e,v)}$ $\Leftrightarrow$ $\partial_v \frac{1}{T} = \partial_e p/T$ (2nd law/A)

(ii) $\underline{s \text{ is concave}}$ $\Rightarrow$ $D^2 s$ neg. def. (thd. stability)

$\partial_e T|_v > 0$ $\partial_v p|_T < 0$

interaction q, w, f

(i) $\underline{\exists \text{ equilibrium}}$ $T = T_0$, $p = p_0$ (0th law)

$(q,w,f)(T, T_0, p, p_0)$

$(q,w,f)(T_0, T_0, p, T_0) \equiv (0, 0, p)$

(ii) dissipation

$$-q\frac{(T-T_0)}{T} - \overset{-f}{\overset{\shortparallel}{\frac{w}{p}}}(p - p_0) \geq 0$$ (2nd law/2)

[(iii) classical work: $w = -pf$

a) $p > p_0 \Rightarrow f > 0$ / $T > T_0 \Rightarrow q < 0$

b) $p < p_0 \Rightarrow f < 0$ / $T < T_0 \Rightarrow q > 0$

Theorem: $L(e,v) = s(e,v) - e/T_0 - \frac{p_0}{T_0} v$ is a Lyapunov f. of eq. (1)

Proof: $DL = \left(\frac{1}{T} - \frac{1}{T_0}, p/T - p_0/T_0\right)$

$D^2 L = D^2 s \Rightarrow$ concave $\Rightarrow$ (e_0, v_0) is a max.

$$D^{\square} L = \left(\frac{1}{T} - \frac{1}{T_0}\right)(q - pf) + \left(p/T - \frac{p_0}{T_0}\right)f = q\left(\frac{1}{T} - \frac{1}{T_0}\right) - \cancel{\frac{pf}{T}} + \frac{pf}{T_0} + \cancel{\frac{pf}{T}} - \frac{p_0 f}{T_0}$$

$$= q\left(\frac{1}{T} - \frac{1}{T_0}\right) + \left(\frac{p}{T_0} - \frac{p_0}{T_0}\right)f = \frac{1}{T}\left[-q\frac{(T-T_0)}{T} + (p - p_0)f\right] \geq 0$$

QED

Corr 1. Entropy of the environment.

$$\frac{\partial s_A}{\partial e_A} = \frac{1}{T_0} \qquad \frac{\partial s_A}{\partial v_A} = \frac{p_0}{T_0} \Rightarrow s_A(e_A, v_A) = \frac{e_A}{T_0} + \frac{p_A}{T_0} v_0 + S$$

$$\left.\begin{aligned} e_T &= e + e_A \\ v_T &= v + v_A \end{aligned}\right\} \quad s_A(e_T - e, v_T - v) = -\frac{e}{T_0} - \frac{p_0}{T_0} v + \underbrace{\frac{e_T}{T_0} + \frac{p_0}{T_0} v_T + S}_{K = const =}$$

$$L = s(e,v) - \frac{e}{T_0} - \frac{p_0}{T_0} v + \cancel{K}$$

$T_0 L = T_0 s - e - p_0 v \quad \rightarrow$ exergy / max. available work

Rem 1 No need of entropy (!).

Corr 2 Gibbs relation:

$$de = T ds - p dv \longleftrightarrow \frac{de}{dt} = q + w = T s^{\square} - p \frac{dv}{dt} \quad !$$

$$s^{\square} = \frac{1}{T}(q - \cancel{pf}) + \cancel{f} f = q/T = \boxed{d_q s} \quad \text{(reversible change)}$$

- variable transformations (differentials)
- existence (definition) of entropy
- energy conservation

Corr 3 Onsagerian interaction

$$0 \leq -q\frac{(T-T_0)}{T} + f(p-p_0) \qquad q, f = \bigcirc ?$$

$$q = -\alpha_1(T-T_0) - \alpha_2(p-p_0)$$

$$f = \beta_1(T-T_0) + \beta_2(p-p_0)$$

$$0 \leq -q\frac{(T-T_0)}{T} + f(p-p_0) = \frac{\alpha_1}{T}(T-T_0)^2 + \frac{\alpha_2}{T}(T-T_0)(p-p_0) + \beta_1(T-T_0)(p-p_0)$$

$$+\beta_2(p-p_0)^2 = \frac{\alpha_1}{T}(T-T_0)^2 + \left(\frac{\alpha_2}{T} + \beta_1\right)(T-T_0)(p-p_0) + \beta_2(p-p_0)^2 \geq 0$$

⑱

$$= (T-T_0, \rho-\rho_0) \underbrace{\begin{pmatrix} \frac{\alpha_1}{T} & \frac{1}{2}\left(\frac{\alpha_2}{T}+\beta_1\right) \\ \frac{1}{2}\left(\frac{\alpha_2}{T}+\beta_1\right) & \beta_2 \end{pmatrix}}_{+\text{ def.}} \begin{pmatrix} T-T_0 \\ \rho-\rho_0 \end{pmatrix} \geq 0$$

$$\boxed{\begin{matrix} \frac{\alpha_1}{T} > 0 & \beta_2 > 0 \\ \alpha_1\beta_2 - \alpha_2\beta_1 > 0 & \end{matrix}}$$

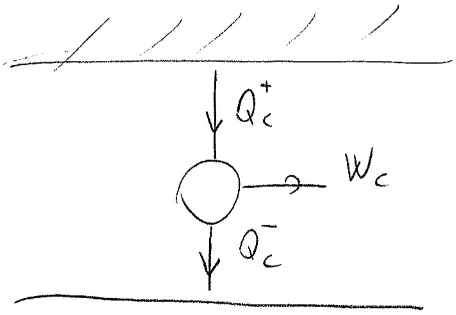
$$\frac{\alpha_1\beta_2}{T} - \frac{1}{4}\left(\frac{\alpha_2}{T}+\beta_1\right)^2 =$$

$$\frac{\alpha_1\beta_2}{T} - \frac{\alpha_2^2}{4T^2} - \frac{1}{2}\frac{\alpha_2\beta_1}{T} - \frac{\beta_1^2}{4} =$$

$$\Rightarrow \alpha_1\beta_2 - \alpha_2\beta_1 = T\left(\frac{\alpha_2^2}{4T} - \frac{\alpha_2\beta_1}{2} + \beta_1^2/4\right)$$

$$= \frac{T}{4}\left(\frac{\alpha_2}{T} - \beta_1\right)^2 \geq 0$$

Heat engines - Carnot cycle



periodic: $[t_1, t_2]$

$Q_c^+ - Q_c^- = W_c$ 1st law

$Q(t) = M_q\left(T(t), T_0(t), \rho(t), \rho_0(t)\right)$

$W(t) = M_w(\qquad)$

$J^+ = \{t \in [t_1, t_2] \mid Q(t) > 0\}$ absorption

$J^- = \{t \in [t_1, t_2] \mid Q(t) < 0\}$ emission

$$Q_c^+ = \int_{J^+} Q(t)\,dt \qquad Q_c^- = -\int_{J^-} Q(t)\,dt$$

$$\dot{S}(t) = \frac{Q(t)}{T(t)} \qquad S(t_1) = S(t_2) \Rightarrow 0 = \int_{t_1}^{t_2} \frac{Q(t)}{T(t)}\,dt = \int_{J^+} \frac{Q}{T}\,dt + \int_{J^-} \frac{Q}{T}\,dt$$

$T^{+\uparrow} = \max\{T(t) \mid t \in J^+\}$ max absorption temperature

$T^{+\downarrow} = \min\{T(t) \mid t \in J^-\}$ min absorption temperature

$T^{-\uparrow} = \max\{T(t) \mid t \in \mathcal{J}^-\}$ max. emission temperature

$T^{-\downarrow} = \min\{T(t) \mid t \in \mathcal{J}^-\}$ min. emission temperature

$$\frac{Q_c^+}{T^{+\uparrow}} = \int_{\mathcal{J}^+} \frac{Q}{T^{+\uparrow}}\,dt \le \int_{\mathcal{J}^+} \frac{Q}{T}\,dt = -\int_{\mathcal{J}^-} \frac{Q}{T}\,dt \le -\int \frac{Q}{T^{-\downarrow}}\,dt = \frac{Q_c^-}{T^{-\downarrow}} \Rightarrow \boxed{\frac{Q_c^+}{T^{+\uparrow}} \le \frac{Q_c^-}{T^{-\downarrow}}}$$

$$\frac{Q_c^+}{T^{+\downarrow}} = \int_{\mathcal{J}^+} \frac{Q}{T^{+\downarrow}}\,dt \ge \qquad \ge -\int \frac{Q}{T^{-\uparrow}}\,dt = \frac{Q_c^-}{T^{-\uparrow}} \Rightarrow \boxed{\frac{Q_c^+}{T^{+\downarrow}} \ge \frac{Q_c^-}{T^{-\uparrow}}}$$

Corr. 1, $Q_c^+ = 0 \; \substack{\Rightarrow \\ \Leftarrow} \; Q_c^- = 0$ Kelvin - Planck

Cor. 2, $\eta_c = \frac{W}{Q_c^+} = 1 - \frac{Q_c^-}{Q_c^+} = 1 - \frac{T^-}{T^+}$ Carnot efficiency

$T^+ = T^{+\downarrow} = T^{+\uparrow}$

$T^- = T^{-\downarrow} = T^{-\uparrow}$

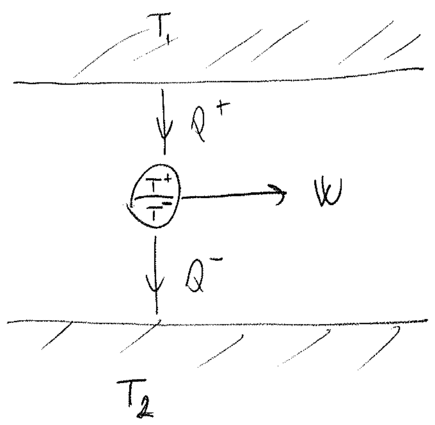
T^+/T^- → temperature of the <u>machine</u>

<u>Corr</u> 3 Kelvin - Planck $\substack{\not\Rightarrow \\ \not\Leftarrow}$ Clausius

<u>Corr</u> 4! $T(t) = \text{const} \Lleftarrow T_a(t)/p_a(t)$

$\eta \neq 0$

Curzon - Ahlborn machine



T^+ / T^- const.

$$\left.\begin{aligned} Q^+ &= \alpha(T_1 - T^+) = \alpha x \\ Q^- &= \beta(T^- - T_2) = \beta y \end{aligned}\right\} \quad \begin{aligned} T^+ &= T_1 - x \\ T^- &= T_2 + y \end{aligned}$$

$$\left.\begin{aligned} Q_c^+ &= J^+ Q^+ \\ Q_c^- &= J^- Q^- \end{aligned}\right\} \frac{J^+}{J^-} = \frac{Q_c^+}{Q_c^-}\frac{Q^-}{Q^+} = \frac{T^+}{T^-}\frac{\beta y}{\alpha x} =$$

$$\frac{Q_c^+}{Q_c^-} = \frac{T^+}{T^-} \quad \text{Carnot}$$

$$\gamma := \frac{t_2 - t_1}{J^+ + J^-} \quad (= \text{const})$$

Maximal average power:

$$\overline{\Pi} = \frac{W_c}{t_2 - t_1} = \frac{Q_c^+ - Q_c^-}{\gamma(J^+ + J^-)} = \frac{J^+ \alpha x - J^- \beta y}{\gamma(J^+ + J^-)} = \frac{\alpha x \dfrac{T^+ \beta y}{T^- \alpha x} - \beta y}{\gamma\left(\dfrac{T^+ \beta y}{T^- \alpha x} + 1\right)} =$$

$$= \frac{\alpha\beta xy\,(T^+ - T^-)}{\gamma(T^+\beta y + T^-\alpha x)} = \frac{\alpha\beta}{\gamma}\frac{xy(T_1 - x - T_2 - y)}{((T_1 - x)\beta y + (T_2 + y)\alpha x)}$$

$$\hat{\Pi} \left| \boxed{\frac{\gamma}{\alpha\beta}\overline{\Pi} = \frac{xy\,(T_1 - T_2 - x - y)}{(\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y}} \right. = \frac{N}{D} \quad \text{MAX?} \quad \Rightarrow \quad N'D = ND'$$

$$\frac{\partial\hat{\Pi}}{\partial x} = 0 \Rightarrow \left[\cancel{y}(T_1 - T_2 - 2x - y) - \cancel{xy}\right]\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right) = x\cancel{y}\cancel{(T_1 - T_2 - x - y)((\alpha - \beta)y + \alpha T_2)}$$

$$= x\cancel{(T_1 - T_2 - x - y)((\alpha - \beta)y} + \alpha T_2) + (T_1 - T_2 - x - y)\beta T_1 y - x\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right) \Rightarrow$$

$$\beta T_1 y\,(T_1 - T_2 - x - y) = x\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right)$$

$$\frac{\partial\hat{\Pi}}{\partial y} = 0 \Rightarrow \left[\cancel{x}(T_1 - T_2 - x - 2y) - \cancel{xy}\right]\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right) = \cancel{x}y\cancel{(T_1 - T_2 - x - y)((\alpha - \beta)x} + \beta T_1)$$

$$= (T_1 - T_2 \cancel{- x - y)\,y((\alpha - \beta)x} + \beta T_1) + (T_1 - T_2 - x - y)\alpha T_2 x - y\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right)$$

$$\alpha T_2 x(T_1 - T_2 - x - y) = y\left((\alpha - \beta)xy + \alpha T_2 x + \beta T_1 y\right) \rightsquigarrow \frac{\beta T_1 y}{x} = \frac{\alpha T_2 x}{y}$$

$$\boxed{x = y\sqrt{\frac{\beta T_1}{\alpha T_2}}}$$

$$\cancel{\beta T_1}\cancel{y}\left(T_1 - T_2 - y - y\sqrt{\ }\right) = \cancel{y}\sqrt{\ }\left((\alpha-\beta)\, y^2 \sqrt{\ } + \alpha T_2 \sqrt{\ }\, y + \beta T_1 y\right)$$

$$= (\alpha-\beta)\, y^2 \frac{\cancel{\beta T_1}}{\alpha T_2} + \cancel{\beta T_1}\, y + \cancel{\beta T_1}\sqrt{\frac{\beta T_1}{\alpha T_2}}\, y$$

$$\boxed{\frac{(\alpha-\beta)}{\alpha T_2}\, y^2 + 2\left(1 + \sqrt{\frac{\beta T_1}{\alpha T_2}}\right) y + T_2 - T_1 = 0}$$

$$y_{12} = \frac{\alpha T_2}{\cancel{2}(\alpha-\beta)}\left(-\cancel{2}\left(1+\sqrt{\frac{\beta}{\alpha}\frac{T_1}{T_2}}\right) \pm \sqrt{\cancel{4}\left(\cancel{1} + 2\sqrt{\frac{\beta}{\alpha}\frac{T_1}{T_2}} + \cancel{\frac{\beta}{\alpha}\frac{T_1}{T_2}}\right) - \cancel{4}\,\frac{(\alpha-\beta)}{\alpha T_2}(T_2 - T_1)}\right)$$

$$-\left(\cancel{1} - \frac{\beta}{\alpha} - \frac{T_1}{T_2} + \cancel{\frac{\beta T_1}{\alpha T_2}}\right)$$

$$\frac{\beta}{\alpha} + \frac{T_1}{T_2} + 2\sqrt{\frac{\beta}{\alpha}\frac{T_1}{T_2}} = \left(\sqrt{\frac{\beta}{\alpha}} + \sqrt{\frac{T_1}{T_2}}\right)^2$$

$$y_{12} = \frac{T_2}{1 - \beta/\alpha}\left(-1 - \sqrt{\frac{\beta}{\alpha}\frac{T_1}{T_2}} \pm \sqrt{\beta/\alpha} \pm \sqrt{\frac{T_1}{T_2}}\right) = -T_2\,\frac{\left(1 \mp \sqrt{\beta/\alpha}\right)\left(1 \mp \sqrt{\frac{T_1}{T_2}}\right)}{\left(1 + \sqrt{\beta/\alpha}\right)\left(1 - \sqrt{\beta/\alpha}\right)}$$

$$\boxed{y_{12} = -T_2\left(\frac{1 \mp \sqrt{\frac{T_1}{T_2}}}{1 \pm \sqrt{\beta/\alpha}}\right)}$$

$$\Rightarrow 1 \mp \sqrt{\frac{T_1}{T_2}} = -\frac{y}{T_2}\left(1 \pm \sqrt{\beta/\alpha}\right) = -\frac{y}{T_2}\left(1 \pm \frac{x}{y}\sqrt{\frac{T_2}{T_1}}\right)$$

$$\cancel{1 \mp \sqrt{\frac{T_1}{T_2}}} = -\frac{1}{T_2}\left(T^- - T_2 \pm \sqrt{\frac{T_2}{T_1}}\left(T_1 - T^+\right)\right) = -\frac{T^-}{T_2} + \cancel{1} \mp \cancel{\sqrt{\frac{T_1}{T_2}}} \pm \frac{T^+}{\sqrt{T_2 T_1}}$$

$$\frac{T^+}{T^-} = \pm\sqrt{\frac{T_2}{T_1}} \Rightarrow \boxed{\eta_{CA} = 1 - \sqrt{\frac{T_1}{T_2}}} < \eta_C$$

$\oplus$ $\uparrow$

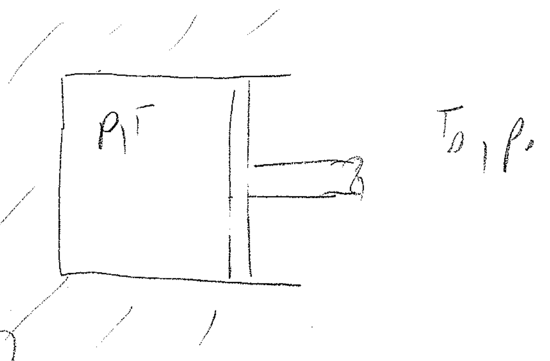
y_1	y_2	$T_1 > T_2$	$\beta > \alpha$
$-\left(\frac{-}{+}\right) \oplus$	$-\left(\frac{+}{-}\right) \oplus$	i	i
$-\left(\frac{-}{+}\right) \oplus$	$-\left(\frac{+}{+}\right) \ominus$	i	h
$-\left(\frac{+}{+}\right) \ominus$	$-\left(\frac{+}{-}\right) \oplus$	h	i
$-\left(\frac{+}{+}\right) \ominus$	$-\left(\frac{+}{+}\right) \ominus$	h	h

$$y = -T_2\,\frac{1 - \sqrt{\frac{T_1}{T_2}}}{1 + \sqrt{\beta/\alpha}}$$

előrébb ←

Sources of irreversibility

$$-\frac{q}{T_1}\left(T_1 - T_0\right) + f\left(p - p_0\right) \geq 0$$



Reducing irreversibility:

q - thermal insulation

$T_1 - T_0$ - ~~heat transfer reduction~~ temperature homogenization

$\alpha(T - T_0)$ $\downarrow$ $\downarrow$

f - slow volume change

$p_1 - p_0$ - ~~work reduction~~ pressure homogenization

Model:

1.) $\dot{v}(p - p_0) > 0$ oscillation ?

2.) $dS = d_t S + d_i S = Q/T + \underset{\substack{\vee|\\ 0}}{d_i S}$

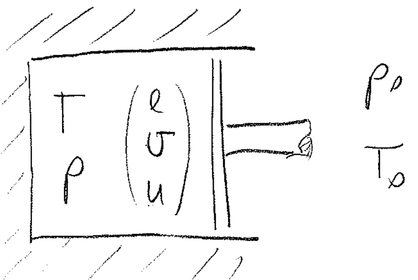
3.) internal irreversibilities ??

$$m\ddot{x} = A(p - p_0) \quad (?)$$

Generalization - extended simple system

$$\boxed{\begin{aligned} \frac{de}{dt} &= \tilde{q} - \tilde{p}u \\ \frac{dv}{dt} &= u \\ \frac{du}{dt} &= \frac{1}{\gamma}\left(\tilde{p} - p_a\right) \end{aligned}}$$

γ - const.



$$e_T = e + \gamma\frac{u^2}{2}$$

$s(e, v)$ $\quad de = Tds - pdv$

Dynamic pressure – extended state space :

$$\left.\begin{aligned} \tilde{p}(e,v,u) &= p(e,v) + \hat{p}(e,v,u) \\ p(e,v) &:= \tilde{p}(e,v,0) \end{aligned}\right\} \quad \hat{p}(e,v,0) = 0$$

Equilibrium :

$$\tilde{q}(T, T_0, p, p_0, u) \qquad \tilde{q}(T_0, T_0, p_0, p_0, 0) = 0$$

Stability :

$$L(e,v,u) = s(e,v) - \frac{1}{T_0}\left(e + \gamma\frac{u^2}{2}\right) - \frac{p_0}{T_0}v$$

$$\left(e + e_a + \gamma\frac{u^2}{2} = \text{const}\right)$$

$$DL = \left(\frac{1}{T} - \frac{1}{T_0}, \; p/T - \frac{p_0}{T_0}, \; -\frac{\gamma u}{T_0}\right) \qquad DL(e_0, v_0, 0) = (0, 0, 0)$$

$$D^2L = \begin{pmatrix} \partial_e \frac{1}{T} & \partial_e p/T & 0 \\ \partial_v 1/T & \partial_v p/T & 0 \\ 0 & 0 & -\gamma/T_0 \end{pmatrix} = -\begin{pmatrix} \frac{\partial_e T}{T^2} & -\partial_e p/T & 0 \\ \frac{\partial_v T}{T^2} & -\partial_v p/T & 0 \\ 0 & 0 & \gamma/T_0 \end{pmatrix} = \begin{pmatrix} D^2 s & 0 \\ 0 & -\gamma/T_0 \end{pmatrix}$$

Δ_1, Δ_2

$$+\;\Delta_1 = \frac{1}{T^2}\partial_e T > 0$$

$$\Delta_2 = \frac{-1}{T^2}\left(\partial_e T \, \partial_v p/T - \partial_v T \, \partial_e p/T\right) = \dots = -\frac{1}{T^3}\, \overset{\overset{0}{\wedge}}{\partial_e T} \; \overset{\overset{0}{\vee}}{\partial_v p|_T} \geq 0$$

$$\Delta_3 = \Delta_2 \, \gamma/T_0 \longrightarrow \boxed{\gamma > 0}$$

$$L^{\square} = \left(\frac{1}{T} - \frac{1}{T_0}\right)\left(\tilde{q} - \tilde{p}u\right) + \left(p/T - p_0/T_0\right)u - \frac{\cancel{\gamma} u}{T_0}\frac{1}{\cancel{\gamma}}\left(\tilde{p} - p_0\right)$$

$$= \left(\frac{1}{T} - \frac{1}{T_0}\right)\tilde{q} - \tilde{p}u\left(\frac{1}{T} - \cancel{\frac{1}{T_0}}\right) + \frac{pu}{T} - \cancel{\frac{p_0 u}{T_0}} - \cancel{\frac{\tilde{p} u}{T_0}} + \cancel{\frac{p_0 u}{T_0}}$$

$$= \underset{\checkmark}{\boxed{\frac{1}{T}\left(\tilde{q}\frac{(T_0 - T)}{T_0} - \hat{p}u\right) \geq 0}}$$

$$\left.\begin{matrix} u > 0 & \hat{p} < 0 \\ u < 0 & \hat{p} > 0 \end{matrix}\right\} \quad \begin{matrix} \boxed{\hat{p} = -ku} \\ k > 0 \end{matrix}$$

Cor 1: Entropy

$$s^{\square} = \frac{e'}{T} + \frac{p}{T} v' = \frac{1}{T}(q - \tilde{p}\dot{v}) + \frac{p}{T} v' = q/T - \underset{\overset{\wedge}{0}}{\frac{\hat{p}u}{T}} = d_t s + \underset{\overset{\vee}{\rho}}{d_i s}$$

Cor 2 Reversible - irreversible — ~~time reversal~~

$$\frac{de}{dt} = q - pf \qquad\qquad \frac{de}{dt} = \tilde{q} - \hat{p}u$$

$$\frac{dv}{dt} = f \qquad\qquad \frac{dv}{dt} = u$$

$$\frac{du}{dt} = \tilde{f} = \frac{1}{\gamma}(\tilde{p} - p_0)$$

can be stopped

$T = T_a$ / $p = p_a$

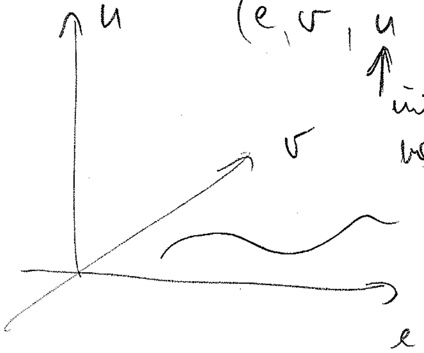
external control

cannot be stopped

e.g. state space

(e, v, u)

↑ internal variable

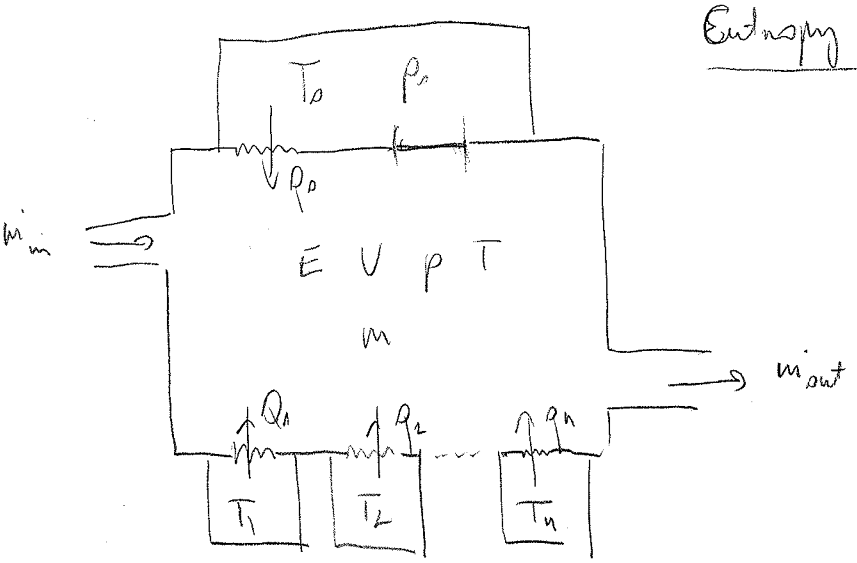


quasistatic ~~process~~ body/model

irreversible

Cor 3 Optimization → ㉕

Entropy generation minimization



⇒ kiterjesztett modellel!

$Q_i = m q_i \leftarrow (!) \quad \dot m q_i \neq Q_i$

$E = m\cancel{E}e$

$S = m s$

$s_i^{\square} = \frac{q_i}{T_i} \qquad i = 0, 1 \dots n)$

$\dot e = \sum_{i=0}^{n} q_i - p\dot v$

$$\dot E = \dot m e + \dot e m = \dot m e + m\left(\sum_0 q_i - p\dot v\right)$$

$$\left(\frac{V}{m}\right)^{\cdot} = \frac{\dot V - v\dot m}{m}$$

(1) $$\boxed{\dot E = Q_0 + \sum_{i=1}^{n} Q_i - p\dot V + \underbrace{(e + pv)}_{h}\dot m}$$

$$m s_T^{\square} = m\left(\frac{S_T}{m}\right)^{\square} = S_T^{\square} - s_T \dot m$$

$$s_T = s + s_0 + \sum_{i=1}^{n} s_i \Rightarrow s_T^{\square} = s^{\square} - \frac{q_0}{T_0} - \sum_{i=1}^{n} \frac{q_i}{T_i}$$

$m\sum q^i = Q$

2!

(2) $$0 \le T_0 m s_T^{\square} = -\dot m T_0 s_T + T_0\overbrace{(m s_T)^{\cdot}}^{\dot S} - \left(q_0 + \sum_{1}^{n} q_i \frac{T_0}{T_i}\right)$$

$$= -T_0 s_T \dot m + \overset{\dot S}{\cancel{\frac{Q}{T}}}\, T_0 - \sum Q_i \frac{T_0}{T_i} - \left(\dot E - \sum_{i=1}^{n} Q_i + p\dot V - h\dot m\right) + p_0\dot V - p_0\dot V$$

$$= \underbrace{-\underbrace{\left(\dot E + p_0\dot V - T_0 \underset{\dot S\,(2)}{\frac{Q}{T}}\right)}_{\dot E_x \text{ – exergiaváltozás}} + \sum_{i=1}^{n} Q_i\left(1 - \frac{T_0}{T_i}\right) + (h - T_0 s_T)\dot m}_{\dot W_{rev}} - \underbrace{(p - p_0)\dot V}_{\dot W}$$

előjel?? javít!!

$$0 \le T_0 S_T^{\square} = \dot W_{rev} - \dot W = \dot W_{lost}$$

Gouy–Stodola theorem

Spec.: $\left.\begin{array}{l}\dot m = 0 \\ Q_i = 0\end{array}\right\} \Rightarrow$ exergy analysis

Új: reverzibilis/homogénes és kiterjesztett rendszerre is!!

Continuum thermodynamics – fluids

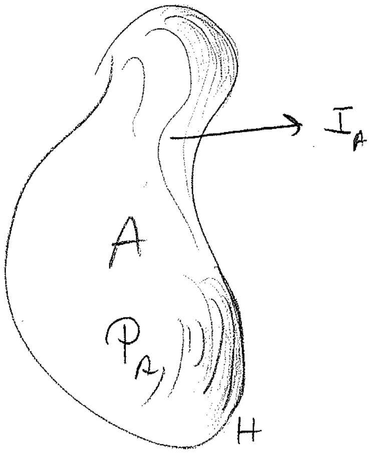
- Second Law
- Material symmetries – isotropy
- objectivity – material frame indifference

$\}\rightarrow$ Balances

homogeneous $\xrightarrow[\text{equilibrium}]{\text{local}}$ Second Law $\longrightarrow$ material / constitutive models $\rightarrow$ Balances

Fields : $a(t, x^i)$ time and space dependence

extensives : density / specific



homogeneous : $\rho_A = A/V$

$a = A/M$

spec. $\rho = M/V$ $v = V/M$ $\rho_A = \rho a$

inhomogeneous : $A(t) = \int_H \rho_A(t, x^i)\, dV$

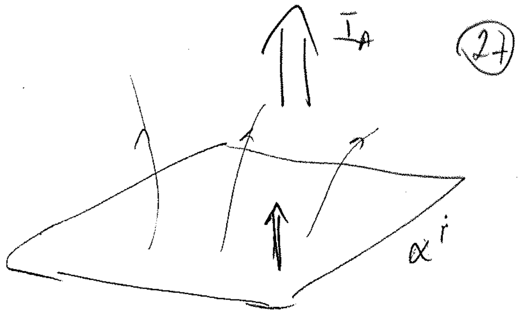
Balances :

$$\boxed{\frac{dA}{dt} = -I_A + P_A}$$

P_A production

I_A flux

Surface densities:



homogeneous:

$$j_A^i = \frac{I_A}{|\alpha^i|} \Leftarrow I_A = \alpha^i \cdot j_A^i$$

inhomogeneous:

$$I_A^i(t) = \int j_A^i(t, x^i)\, d\alpha^i$$

$$\frac{dA}{dt} + I_A = P_A = \boxed{\frac{d}{dt}\int_H \rho_A(t,x^i)\,dV + \oint_{\partial H} j_A^i(t,x)\,d\alpha^i = \underbrace{\int_H \sigma_A(t,x^i)\,dV}_{P_A(t)}}$$

global (integral) balances

σ_A - production density

$$\oint_{\partial H} a^i d\alpha^i = \int_H \partial^i a^i\, dV$$

Gauss - Ostrogradskii theorem

∀H subsets !

(i) $$\int_H \left(\frac{\partial}{\partial t}\rho_A + \partial^i j_A^i - \sigma_A\right) dV = 0 \longrightarrow \boxed{\frac{\partial}{\partial t}\rho_A + \partial^i j_A^i = \sigma_A}$$

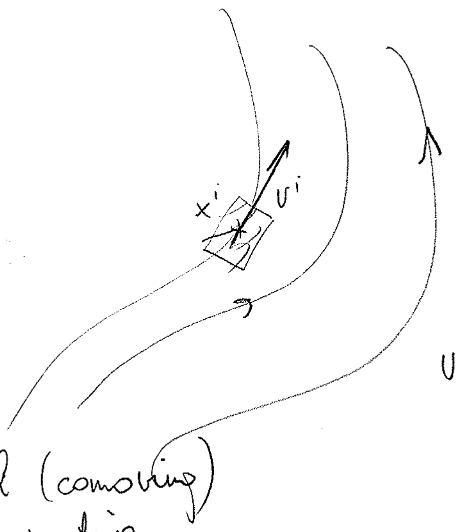
local balance

$$j_A^i \begin{cases} \rho_A v^i & \text{- convective} \\ j_A^i & \text{- conductive} \end{cases}$$

stream lines

(ii) $$\frac{d}{dt} a(t, x^i(t)) = \frac{\partial a}{\partial t} + \partial^i a \underset{\overset{\shortparallel}{v^i}}{\frac{\partial x^i}{\partial t}} =$$

$$\boxed{\dot{a} = \frac{\partial a}{\partial t} + v^i \partial^i a}$$



stream lines

$v^i(t, x^i)$ velocity field

substantial (comoving) derivative

㉘

<u>Mass</u>: $\rho_A = \rho \;/\; a = 1$

$$\boxed{0 = \frac{\partial \rho}{\partial t} + \partial^i(\rho v^i)} = \frac{\partial \rho}{\partial t} + v^i \partial^i \rho + \rho \partial^i v^i = \boxed{\dot{\rho} + \rho \partial^i v^i = 0}$$

local

substantial balance of mass.

$$\frac{\partial \rho a}{\partial t} + \partial^i\left(\rho a v^i + j_A^i\right) = \sigma_A = \rho \frac{\partial a}{\partial t} + \cancel{a \frac{\partial \rho}{\partial t}} + \rho v^i \partial^i a + \cancel{a \partial^i(\rho v^i)} + \partial^i j_A^i =$$

$$= \boxed{\rho \dot{a} + \partial^i j_A^i = \sigma_A}$$

substantial balance of A.

<u>Mathematical interplay h</u> – index notation

(bookkeeping of tensor derivatives)

$$x^i = \bar{x} = \begin{pmatrix} x^1 \\ x^2 \\ x^3 \end{pmatrix} \quad \text{vector}$$

row column

$$B^{ij} = \begin{pmatrix} B^{11} & B^{12} & B^{13} \\ B^{21} & B^{22} & B^{23} \\ B^{31} & B^{32} & B^{33} \end{pmatrix} \quad \text{– tensor } (\Leftrightarrow \text{matrix})$$

independent of coordinates – abstract indices

transpose: $A^{T} = (A^{ij})^{T} = A^{ji}$

<u>Scalar product</u>:

$$\bar{x} \cdot \bar{y} = (x^1 \; x^2 \; x^3)\begin{pmatrix} y^1 \\ y^2 \\ y^3 \end{pmatrix} = x^1 y^1 + x^2 y^2 + x^3 y^3 = \sum_{i=1}^{3} x^i y^i = x^i y^i \quad \text{(Einstein convention)}$$

<u>indices</u>: free
contracted

trace: $\mathrm{tr}\, A = A^{ii} = \sum_{i=1}^{3} A^{ii} = A^{11} + A^{22} + A^{33}$

<u>Derivatives of fields</u>. $a(t, x^i)$

$$\frac{\partial a}{\partial t} = \left.\frac{\partial a}{\partial t}\right|_{x^i} \qquad \partial^i a = \left(\frac{\partial a}{\partial x^1}, \frac{\partial a}{\partial x^2}, \frac{\partial a}{\partial x^3}\right)$$

∂^i – vector AND derivative

$$\partial^i A^{ij} = \begin{pmatrix} \partial^1 & \partial^2 & \partial^3 \end{pmatrix} \begin{pmatrix} A^{11} & A^{12} & A^{13} \\ A^{21} & A^{22} & A^{23} \\ A^{31} & A^{32} & A^{33} \end{pmatrix} = \begin{pmatrix} \partial^1 A^{11} + \partial^2 A^{21} + \partial^3 A^{31} \\ \partial^1 A^{12} + \partial^2 A^{22} + \partial^3 A^{32} \\ \partial^1 A^{13} + \partial^2 A^{23} + \partial^3 A^{33} \end{pmatrix}$$

Identity tensor:

$$\delta^{ij} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad v^i \delta^{ij} = v^j$$

Nabla – index:

$$\nabla \cdot (a \cdot b) = a \cdot \nabla b + b \cdot \nabla a$$

$$\partial^i (a^j b^j) = a^j (\partial^i b^j) + b^j (\partial^i a^j)$$

Examples:

- $\partial^i x^j = \delta^{ji}$
- $\partial^i x^i = 3$
- $\partial^i r = x^i / r \qquad r = \sqrt{x^i x^i}$
- $\partial^i 1/r = - x^i / r$
- $\partial^i (v^j p^{ij}) = (\partial^i v^j) p^{ij} + v^j \partial^i p^{ij}$
- $\partial^i (\rho v^i) = \rho \partial^i v^i + v^i \partial^i \rho$

$$\partial^j \left(x^i / r \right) = -\frac{2}{r^3} x^j$$

Local and substantial forms of the basic balances

$(a = 1 \; ; \; j_A^i = 0)$

$$\frac{\partial \rho}{\partial t} + \partial^i (\rho v^i) = 0 \quad / \quad \boxed{\dot{\rho} + \rho \partial^i v^i = 0} \qquad \text{balances of mass}$$

$$\frac{\partial}{\partial t}(\rho a) + \partial^i (\rho a v^i + j_A^i) = \sigma_A \quad / \quad \rho \dot{a} + \partial^i j_A^i = \sigma_A \qquad \text{balances of A}$$

Balance of momentum – Cauchy equation

$$a = v^i \; / \; j_{Mom}^{ij} = p^{ij} \; / \; \sigma_{Mom}^i = \rho f^i$$

$$\frac{\partial \rho v^i}{\partial t} + \partial^j (\rho v^i v^j + p^{ij}) = \rho f^i \quad / \quad \boxed{\rho \dot{v}^i + \partial^j p^{ij} = \rho f^i}$$

Energies

Total energy: $\sigma_T = 0$ conserved

$$\partial_t(\rho e_T) + \partial^i(\rho e_T v^i + j_T^i) = 0 \qquad \rho\dot{e}_T + \partial_i j^i = 0$$

Kinetic energy: $e_K = v^2/2 \;/\; f^i = 0$

$$v^i(\rho\dot{v}^i + \partial^j p^{ij}) = \rho v^i\dot{v}^i + v^i\partial^j p^{ij} \Rightarrow \rho\left(\frac{v^2}{2}\right)^{\cdot} + \partial^j(p^{ij}v^i) = p^{ij}\partial_i v_j$$

$$\frac{\partial}{\partial t}(\rho v^2/2) + \partial^i\left(\rho \frac{v^2}{2} v^i + v^j p^{ji}\right) = p^{ij}\partial^i v^j$$

Internal energy $e = e_T - e_K$

$$\rho\dot{e} = \rho\dot{e}_T + \rho\left(v^2/2\right)^{\cdot} = -\left(\partial^i j_T^i\right) - \left(\partial^i(v^j p^{ij}\right) + p^{ij}\partial^i v^j$$

$$\boxed{\rho\dot{e} + \partial^i(\underbrace{j_T^i + v^j p^{ij}}_{q^i}) = -p^{ij}\partial^j v^i}$$

$$\frac{\partial \rho e}{\partial t} + \partial^i(\rho e v^i + q^i) = -p^{ij}\partial^j v^i$$

Entropy – the concept of local equilibrium

$$dE = TdS - pdV + \mu dN \rightarrow de = Tds - pdv \qquad v = 1/\rho$$

$$de = Tds + \frac{p}{\rho^2}d\rho \Rightarrow \boxed{\dot{e} = T\dot{s} + p/\rho^2\,\dot{\rho}}$$

Locally: same EOS and same variables. — ordinary thd.

$$\boxed{\rho\dot{s} + \partial^i J_s^i = \sigma_s}$$ — calculated!

$$J_s^i = q^i/T \quad \sim \quad TdS = Q$$

?!

Reminder: - extended
- spring

$$\rho \dot{s}(e,\rho) + \partial^i\left(\frac{q^i}{T}\right) = \rho \underset{=\,1/T}{\frac{\partial s}{\partial e}}\dot{e} + \rho \underset{=\,p/\rho^2 T}{\frac{\partial s}{\partial \rho}}\dot{\rho} + \partial^i \frac{q^i}{T} =$$

$$= \frac{1}{T}(\rho\dot{e}) - \frac{p}{T\rho^2}\dot{\rho} + \partial^i\left(\frac{q^i}{T}\right) = -\frac{1}{T}\left(\cancel{\partial^i q^i} + P^{ij}\partial^i v^j\right) + \frac{p}{T\cancel{\rho}}\rho\,\partial_i v^i + \cancel{\frac{1}{T}\partial^i q^i} + q^i\partial^i \frac{1}{T}$$

$$= \boxed{q^i\partial^i \frac{1}{T} - \frac{1}{T}\left(P^{ij} - p\delta^{ij}\right)\partial^i v^j \geq 0}$$

A) No dissipation: $q^i = 0$ / $P^{ij} = p\delta^{ij}$ Pascal

$$\left\|\begin{array}{l} \rho\dot{e} = p\partial_i v^i \\ \rho\dot{v}^i + \partial_i p = 0 \end{array}\right.$$ Euler equation

B) Constitutive theory

q^i	$\partial^i \frac{1}{T}$	Thermal
$P_v^{ij} = P^{ij} - p\delta^{ij}$	$\partial^i v^j$	Mechanical
FLUX	FORCE	

- $q^i\left(\partial^i \frac{1}{T}, \partial^i v^j\right) = \hat{\lambda}\partial^i \frac{1}{T} = -\frac{\hat{\lambda}}{T^2}\partial^i T = -\lambda\partial^i T$

λ - Fourier's heat conduction coefficient

- $P_v^{ij}\left(\partial^i \frac{1}{T}, \partial^i v^j\right) = -\underbrace{\eta_v}_{\text{volume}}\partial^k v^k \delta^{ij} - \underbrace{\eta}_{\text{shear viscosity}}\left(\partial^i v^j + \partial^j v^i\right)$

$$\bar{P} = p\bar{I} - \eta_v \nabla\cdot\bar{v}\,\bar{I} + 2\eta(\nabla\circ\bar{v})^s$$ Newton's ~~stress~~ pressure

General entropy production

$$\sigma_S = \sum_{i=1}^{n} J^i X_i \geq 0$$

J^i fluxes – not determined

X^i forces

$$J^i(X^i) = L^{ik} X^k \Longrightarrow \quad \sigma_S = \sum X^i L^{ik} X^k \geq 0 \qquad \forall X^i, X^k$$

+ def. symmetric

Homogeneous $\quad (\tilde{p} - p_0) v^i$

$$q^i\left(\tfrac{1}{T} - \tfrac{1}{T_0}\right) - \frac{1}{T}\overset{\shortparallel}{\hat{p}} u \geq 0 \quad \longleftrightarrow \quad q\,\partial_i \frac{1}{T} - \frac{1}{T}(P^v)^{ij}\,\partial^i v^j \geq 0$$

$$\rho = \frac{1}{v} \qquad \dot{\rho} + \rho\,\partial_i v^i = 0 \longrightarrow \partial^i v^i = -\dot{\rho}/\rho = -v\left(\frac{1}{v}\right)^{\cdot} = \dot{v}/v$$

$$\begin{cases} \dot{q} \sim \alpha(T - T_0) \\ \hat{p} \sim ku \end{cases}$$

constitutive theory

– Differential equations

Euler, Navier–Stokes, Fourier, ...

Isotropy – direction independence

$$\boxed{q^i}\Big(\underset{\substack{\uparrow \\ \text{fluid (?)}}}{\rho}, T, v^i, \partial^i\rho, \partial^i T, \partial^i v^i, \underset{\substack{\uparrow \\ \text{solid (?)}}}{\Sigma^{ij}}, \ldots\Big)$$

— ? constitutive theory

scalar : $\phi(a, b^i, c^{ij})$

rotation : orthogonal tensor $\quad O^{ij} O^{kj} = \delta^{ik} / \det O = 1$

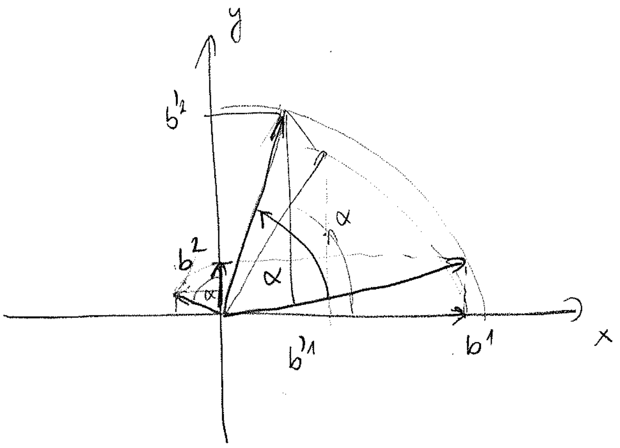
$$\begin{pmatrix} O^{11} & 12 & 13 \\ & & \\ & & \end{pmatrix}\begin{pmatrix} 11 & 21 & 23 \\ 12 & & \\ 13 & & \end{pmatrix}$$

Example:

$$b^i = \begin{pmatrix} b^1 \\ b^2 \end{pmatrix}$$

$$b'^i = \begin{pmatrix} b'^1 \\ b'^2 \end{pmatrix} = \overbrace{\begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix}}^{O^{ij}} \begin{pmatrix} b^1 \\ b^2 \end{pmatrix}$$

$$= \begin{pmatrix} \cos\alpha\, b^1 - \sin\alpha\, b^2 \\ \sin\alpha\, b^1 + \cos\alpha\, b^2 \end{pmatrix}$$



Check:

$$\begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} \cos\alpha & +\sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad / \quad \det O = 1$$

Def: If $\phi(a, b^i, c^{ij}) = \phi(a, O^{ij} b^j, O^{ik} O^{jl} c^{kl})$, than ϕ is isotropic.

Isotropic invariants:

		iso. inv.
scalar	a	a
vector	b^i	$b^i b^i$
symmetric tensor	c^{ij}	c^{ii} (= tr c) ; $c^{ij}c^{ji}$ (= tr$(\bar{\bar{c}}\cdot\bar{\bar{c}})$) ; $c^{ij}c^{jk}c^{ki}$ = tr(c^3)

Theorem (representation)

$\phi(a, b^i, c^{ij})$ is isotropic function if and only if it depends on an irreducible set of isotropic invariants of its variables.

$$\phi(a, b^i, \overset{\overset{c^{ji}}{\shortparallel}}{c^{ij}}) = f(a, b^i b^i, c^{ii}, c^{ij}c^{ji}, c^{ij}c^{jk}c^{ki}, b^i c^{ij} c^{j}, b^i c^{ij} c^{jk} b^k)$$

$$\phi(a, \bar{b}, \bar{\bar{c}}) = f(a, \bar{b}^2, \mathrm{tr}\,\bar{\bar{c}}, \mathrm{tr}(\bar{\bar{c}}\cdot\bar{\bar{c}}), \mathrm{tr}\,\bar{\bar{c}}^3, \bar{b}\cdot\bar{\bar{c}}\cdot\bar{b}, \bar{b}\cdot\bar{\bar{c}}\cdot\bar{\bar{c}}\cdot\bar{b})$$

Example: Entropy production:

$$\sigma_s = q^i \underbrace{\partial^i 1/T}_{X_1^i} - \underbrace{\frac{1}{T}\left(p^{ij} - p\delta^{ij}\right)}_{\Pi^{ij}(X^{ij})} \underbrace{\partial^i v^j}_{X_2^{ij}} \geq 0$$

σ_s – isotropic

– quadratic

$$\left.\begin{array}{l} q^i(X_1^i, X_2^{ij}) \\ \Pi^{ij}(X_1^i; X_2^{ij}) \end{array}\right\} \text{linear}$$

$$\sigma_s(X_1^i, X_2^{ij}) = \lambda X_1^i X_1^i - \eta_v (X_2^{ii})^2 - 2\eta X_2^{ij} X_2^{ji} =$$

$$= q^i X_1^i - \Pi^{ij}(X_1^i, X_2^{ij}) X_2^{ij}$$

$\det A = \frac{1}{6}(\mathrm{tr} A)^3 - (3\,\mathrm{tr}A\,\mathrm{tr}A^2 + 2\,\mathrm{tr}A^3)$

$$\Rightarrow \quad q^i = \lambda X_1^i = \lambda \partial^i 1/T = -\frac{\lambda}{T^2}\partial^i T$$

$$\Pi^{ij} = p^{ij} - p\delta^{ij} = -\eta_v X_2^{kk}\delta^{ij} - 2\eta (X_2^{ij} -$$

$$\boxed{p^{ij} - p\delta^{ij} = \Pi^{ij} = -\eta_v \partial^k v^k \delta^{ij} - \eta\left(\partial^i v^j + \partial^j v^i\right)}$$

Beyond local equilibrium

$$\rho\dot{e} + \partial_i q^i = 0$$

$$s(e, q^i) = s\left(e - l\,q^2/2\right)$$

$$\rho\dot{s} + \partial_i q^i/T = \frac{1}{T}\left(\rho\dot{e} - \rho l\, q^i \dot{q}^i\right) + \partial_i q^i/T = \cancel{-\frac{\partial_i q^i}{T}} - \frac{\rho l}{T} q^i \dot{q}^i + q^i \partial_i 1/T$$

$$\cancel{+ 1/T\,\partial_i q^i} = q^i\left(-\frac{\rho l}{T}\dot{q}^i + \partial_i 1/T\right) \geq 0$$

state: e, q^i

constitutive function: q^i

$$q^i = -\underbrace{\lambda\frac{\rho l}{T}}_{\tau}\dot{q}^i - \underbrace{\lambda/T^2}_{\hat{\lambda}}\partial_i T \Longrightarrow \boxed{\tau\dot{q}^i + q^i + \hat{\lambda}\partial^i T = 0}$$

Cattaneo – Vernotte

$e = cT$

$$\rho c \ddot{T} + \partial^i \dot{q}^i = 0$$

$$\tau \partial_i \dot{q}^i + \partial^i q^i + \hat{\lambda} \partial^{ii} T = 0$$

$$\rho c \ddot{T} - \frac{1}{\tau} \underset{\overset{\parallel}{-\rho c \dot{T}}}{\partial^i q^i} - \frac{\hat{\lambda}}{\tau} \partial^{ii} T = \rho c \ddot{T} + \frac{\rho c}{\tau} \dot{T} - \frac{\hat{\lambda}}{\tau} \partial^{ii} T = 0$$

$$\boxed{\tau \ddot{T} + \dot{T} - \frac{\hat{\lambda}}{\rho c} \partial^{ii} T = 0}$$

telegraph equation

- → finite speed
- → internal variables

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Summary

– universality / stability

Theories:

D.) discrete (t)

C.) continuum (t, x^i)

state

D) – ordinary (quasistatic) : $(e, v(=1/\rho))$

– extended (non-equilibrium) : $(e, v, u = v')$

static eos : (p, T) – body

dynamic eos: (q, W, f) – body + environment

II nd Law: – stability $\underbrace{(s, D^2 s, s^{\square}}_{\text{Liapunov}})$

C) local equilibrium – e, ρ fluid

– e, ε^{ij} solid

static e.o.s : p, T – local

dynamic e.o.s : q^i, p^{ij} – weakly nonlocal (∇)
(constitutive)

non-equilibrium : (e, ρ, q^i) Cattaneo-Vernotte

2nd Law : stability of homogeneous equilibrium

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