

[2016-06-09]

## Entropy flow

$$\text{entropy flow} \quad \int_{\mathcal{R}} \rho \dot{\eta} dV = - \int_{\partial \mathcal{R}} \mathbf{j} \cdot \mathbf{n} dA + \int_{\mathcal{R}} \zeta dV$$

entropy flux                  entropy supply (radiation)

$$\rho \dot{\eta} = - \operatorname{div} \mathbf{j} + \zeta \quad \text{rate of entropy exchange}$$

From rate of entropy exchange to power exchange

$$\int_{\mathcal{R}} \rho \theta \dot{\eta} dV = - \int_{\mathcal{R}} \theta \operatorname{div} \mathbf{j} dV + \int_{\mathcal{R}} \theta \zeta dV \quad \forall \theta > 0$$

$$\operatorname{div} \theta \mathbf{j} = \operatorname{tr} \nabla (\theta \mathbf{j}) = \operatorname{tr} (\theta \nabla \mathbf{j} + \nabla \theta \otimes \mathbf{j}) = \theta \operatorname{div} \mathbf{j} + \nabla \theta \cdot \mathbf{j}$$

$$\int_{\mathcal{R}} \rho \theta \dot{\eta} dV = - \int_{\mathcal{R}} \operatorname{div} \theta \mathbf{j} dV + \int_{\mathcal{R}} \mathbf{j} \cdot \nabla \theta dV + \int_{\mathcal{R}} \theta \zeta dV$$

## Entropy power flow

$$\int_{\mathcal{R}} \rho \theta \dot{\eta} dV = - \int_{\partial \mathcal{R}} \theta \mathbf{j} \cdot \mathbf{n} dA + \int_{\mathcal{R}} \mathbf{j} \cdot \nabla \theta dV + \int_{\mathcal{R}} \theta \zeta dV$$

which localizes to

$$\rho \theta \dot{\eta} = - \operatorname{div} (\theta \mathbf{j}) + \mathbf{j} \cdot \nabla \theta + \theta \zeta$$

[Notebook page scanned on 2016/06/30]

Rate of entropy exchange

$$\frac{d}{dt} \int_{\mathcal{R}} \eta \rho \, dV = \frac{d}{dt} \int_{\mathcal{R}_0} \eta \rho \det F_0 \, dV = \frac{d}{dt} \int_{\mathcal{R}_0} \eta \rho_0 \, dV$$

$$= \int_{\mathcal{R}_0} \dot{\eta} \rho_0 \, dV = \int_{\mathcal{R}} \dot{\eta} \rho \, dV$$

Rate of change of internal entropy

$$\frac{d}{dt} \int_{\mathcal{R}} \eta \rho \, dV = \frac{d}{dt} \int_{\mathcal{R}_0} \eta \rho \det F_0 \, dV = \frac{d}{dt} \int_{\mathcal{R}_0} \eta \rho_0 \, dV$$

$$= \int_{\mathcal{R}_0} \dot{\eta} \rho_0 \, dV = \int_{\mathcal{R}} \dot{\eta} \rho \, dV \quad [G. (27.5)]$$

Green & Naghdi (1993) call  $\dot{\eta}$   
"external rate of supply of entropy"

Tadmor, Miller & Elliot (2013) call  $\dot{\eta}$   
"external entropy input"

## Entropy balance

$$\int_{\mathcal{R}} \rho \dot{\eta} dV = \int_{\mathcal{R}} \rho \dot{\eta}_f dV + \int_{\mathcal{R}} \rho \gamma dV$$

rate of change of internal entropy	entropy flow	net entropy production
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## Localizing

$$\rho \dot{\eta} = \rho \dot{\eta}_f + \rho \gamma = -\operatorname{div} j + j + \rho \gamma$$

Entropy power balance (weak form of the entropy balance)

$$\int_{\mathcal{R}} (\rho \theta \dot{\eta} - \rho \theta \dot{\eta}_f) dV = \int_{\mathcal{R}} \rho \theta \gamma dV \quad \forall \theta > 0$$

(dissipation)  $\rho \theta \gamma \geq 0$  basic assumption

$$\rho \theta \dot{\eta} = -\operatorname{div}(\theta j) + j \cdot \nabla \theta + \theta j + \rho \theta \gamma$$

heat flux  $q \equiv \theta j$

radiation  $\rho r \equiv \theta j$

[Notebook page scanned on 2016/06/30]

## Thermoelasticity

rate of change of internal energy

$$\rho \dot{\epsilon} = T \cdot L - \operatorname{div} q + \rho r \quad [\text{C. \& N. (2.4)}]$$

Replacing  $(-\operatorname{div}(\theta j) + \theta r)$  in the entropy power balance we get

$$\rho \theta \dot{\eta} = \rho \dot{\epsilon} - T \cdot L + j \cdot \nabla \theta + \rho \theta r$$

$$\rho \theta \dot{\eta} - \rho \dot{\epsilon} + T \cdot L - j \cdot \nabla \theta = \rho \theta r \geq 0 \quad [\text{C. \& N. (4.5)}]$$

Introducing the Helmholtz free energy

$$\psi = \epsilon - \theta \eta$$

$$\text{since } \dot{\psi} = \dot{\epsilon} - \dot{\theta} \eta - \theta \dot{\eta}$$

$$-\rho \dot{\epsilon} + \rho \theta \dot{\eta} = -\rho \dot{\theta} \eta - \rho \dot{\psi} \quad \text{we get}$$

$$T \cdot L - \rho \dot{\theta} \eta - \rho \dot{\psi} - j \cdot \nabla \theta = \rho \theta r \geq 0$$

$$T \cdot L - \left( \frac{q}{\theta} \cdot \nabla \theta + \rho \eta \dot{\theta} \right) - \rho \dot{\psi} = \rho \theta r \geq 0$$

The entropy is not a form of energy.

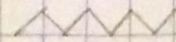
Nevertheless  $\theta \eta$  is the energy related to entropy, called "heat density per unit mass" [Green & Naghdi]

## Power balance laws

$$\int_{\mathcal{R}} b \cdot v \, dV + \int_{\partial \mathcal{R}} t \cdot v \, dA - \int_{\mathcal{R}} T \cdot \nabla v \, dV = 0 \quad \forall v$$



$$\int_{\mathcal{R}} \rho \theta \dot{\eta} \, dV = - \int_{\partial \mathcal{R}} \theta j \cdot n \, dA + \int_{\mathcal{R}} j \cdot \nabla \theta \, dV + \int_{\mathcal{R}} \theta \gamma \, dV \quad \forall \theta \geq 0$$



“external power expenditure” [G. p548]

## Free energy imbalance laws

$$\int_{\mathcal{R}} \rho \dot{\epsilon} \, dV = \int_{\mathcal{R}} T \cdot \dot{F} F^{-1} \, dV + \int_{\mathcal{R}} \rho \theta \dot{\eta} \, dV - \int_{\mathcal{R}} j \cdot \nabla \theta \, dV - \int_{\mathcal{R}} \rho \delta \, dV$$

$$\delta \geq 0$$

$$\int_{\mathcal{R}} \rho \theta \dot{\eta} \, dV = \int_{\mathcal{R}} \rho \theta \dot{\eta} \, dV + \int_{\mathcal{R}} \rho \theta \gamma \, dV \quad \gamma \geq 0$$

$$\rho \dot{\epsilon} - \rho \theta \dot{\eta} = T \cdot \dot{F} F^{-1} - j \cdot \nabla \theta - \rho (\delta + \theta \gamma)$$

$$- \rho \dot{\theta} \eta$$

$$- \rho \dot{\theta} \eta$$

[Notebook page scanned on 2016/06/30]

[2016-06-15]

$$\psi := \epsilon - \theta \eta$$

$$\rho \dot{\psi} = T \cdot \dot{F} F^{-1} - \rho \dot{\theta} \eta - j \cdot \nabla \theta - \underbrace{\rho(\delta + \theta \gamma)}_{\geq 0}$$

$$T \cdot \dot{F} F^{-1} - \rho \dot{\theta} \eta - j \cdot \nabla \theta - \rho \dot{\psi} = \rho(\delta + \theta \gamma) \geq 0$$

If  $\psi = \hat{\psi}(F, \theta)$

and  $\rho \dot{\psi} = T \cdot \dot{F} F^{-1} - \rho \eta \dot{\theta}$

then the inequality above reduces to

$$-j \cdot \nabla \theta \geq 0$$

which leads to the following characterization of the heat flux

$$j = -K \nabla \theta \quad \text{Fourier's law}$$

with  $K$  a positive definite tensor

$$K \nabla \theta \cdot \nabla \theta \geq 0$$

[Notebook page scanned on 2016/06/30]

## Densities

any density  $\rho$  can be moved backward/forward

$$\int_{\mathcal{R}} \rho \, dV = \int_{\mathcal{R}_0} \underbrace{\rho \det \nabla \phi}_{\rho_0} \, dV$$

$T \cdot \nabla v$  is a power density per unit current volume  
because  $T$  is a density

$c\rho$  is a molar density like  $\rho$   
while  $c$  is not a density

$h$  is a molar density per unit current  
area and per unit time

$c$  transforms a lattice site molar density,  
per unit (current or reference) volume,  
into a thin molar density

What is a measure?

What is detectable?

$\eta$  is a measure  $\int_{\mathcal{B}} d\eta = \int_{\mathcal{R}} \eta dV$

$\Theta$  is not a measure even though it is detectable

$\Theta\eta$  is an energy  $\int_{\mathcal{B}} \Theta d\eta = \int_{\mathcal{R}} \Theta\eta dV$

We write a balance of the entropy, not a balance of  $\Theta$ ;  
as we write a balance of the moles, not a balance of  $\mu$ .

$c_p$  and  $\eta$  are densities per unit volume

$\hat{\mu}(c_p)$  and  $\hat{\Theta}(\eta)$  are "energy"

$\tilde{\mu}(c_p)$  and  $\tilde{\Theta}(\eta)$  are "power"

At a microscopic level  $\eta$  is a measure of  
"fluctuation",

while  $\Theta$  is just an amplitude



[Larché & Cahn, 1984] "The interaction of dislocations and stress in crystalline solids"

Whenever we encounter new restrictions or constraints, it is necessary to return to the two basic laws to find new conditions for equilibrium that are general, subject only to the restrictions or constraints.

[...] (p.470)

The derivation often identifies the useful free energy. It is dangerous to assert conditions for equilibrium under new restrictions (some type of free energy to be minimized or some potential to be constant) without a derivation that begins with the basic two laws.

There are various derivations in the literature.

[...] They differ on whether they begin with the basic two laws, or with some derived law.

It is not difficult to start with the basic

laws used by Gibbs:

Gibbs:

"For the equilibrium of any isolated system, it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive".

[111] (p.471)

A variational statement of the first and second laws of thermodynamics for the multi-component network solid has been carried out [Larché & Cahn, 1973]



Larché, F.C. and Cahn J.W., 1973. A linear theory of thermochemical equilibrium of solids under stress.  
Acta Metallurgica 21, 1051-1063

[Gurtin - Fried - Anand, 2010, Cambridge UP]  $\equiv$  [G.]

As the theory under consideration is mechanical, we take as our basic thermodynamical law the free-energy imbalance

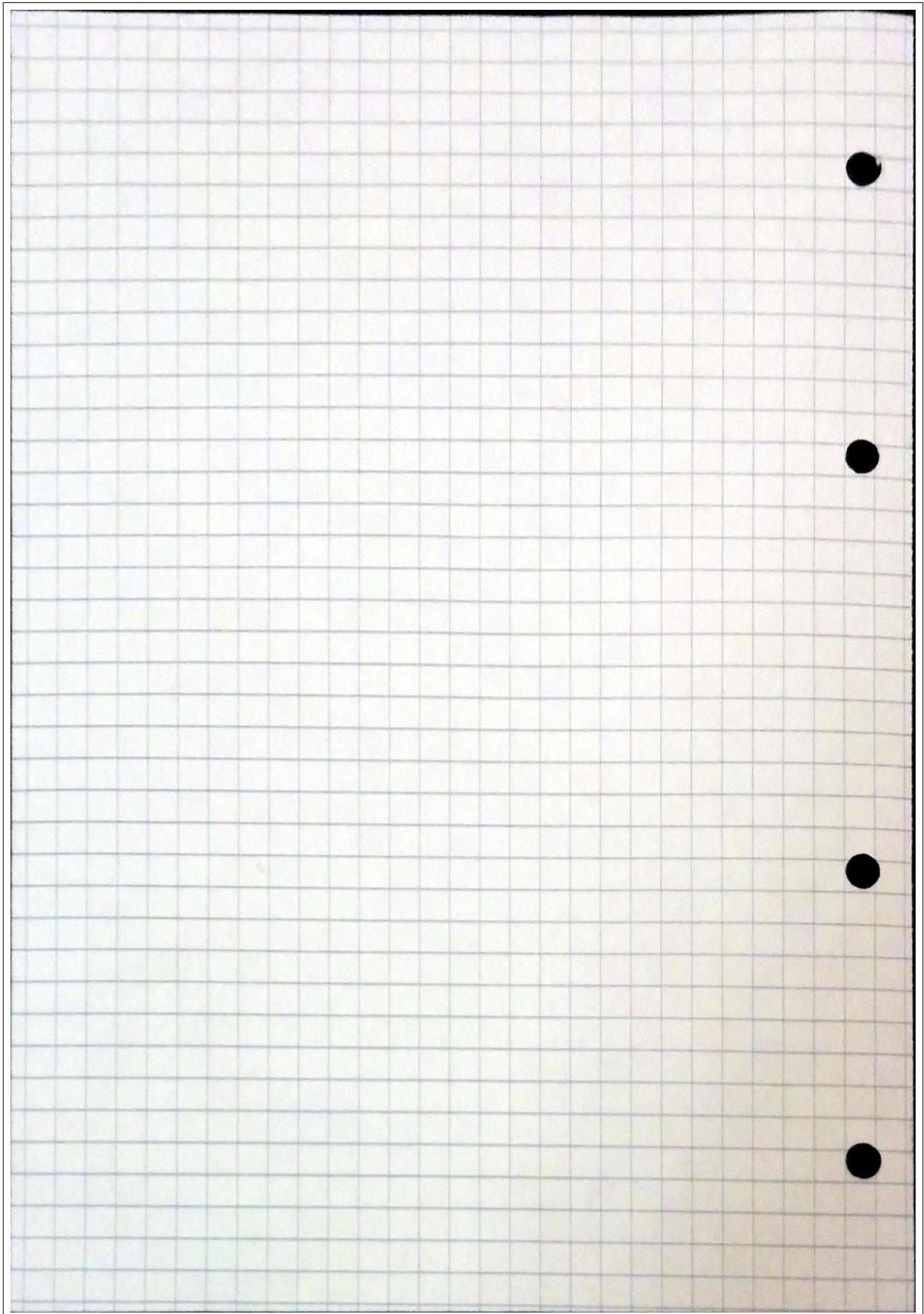
$$\rho \dot{\psi} - T \cdot D = -\delta \leq 0 \quad [G. (43.6)]$$

External power expenditure [G. p 548]

Free energy imbalance [G. p 553]

"for any spatial region  $P_t$  convecting with the body, the temporal increase in free-energy of  $P_t$  be less than or equal to the power expended on  $P_t$  minus the dissipation within  $P_t$ "

$$\int_{\mathcal{R}_0} \dot{\psi} dV - \int_{\mathcal{R}} T \cdot D dV \leq 0 \quad [G. (93.2)]$$



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