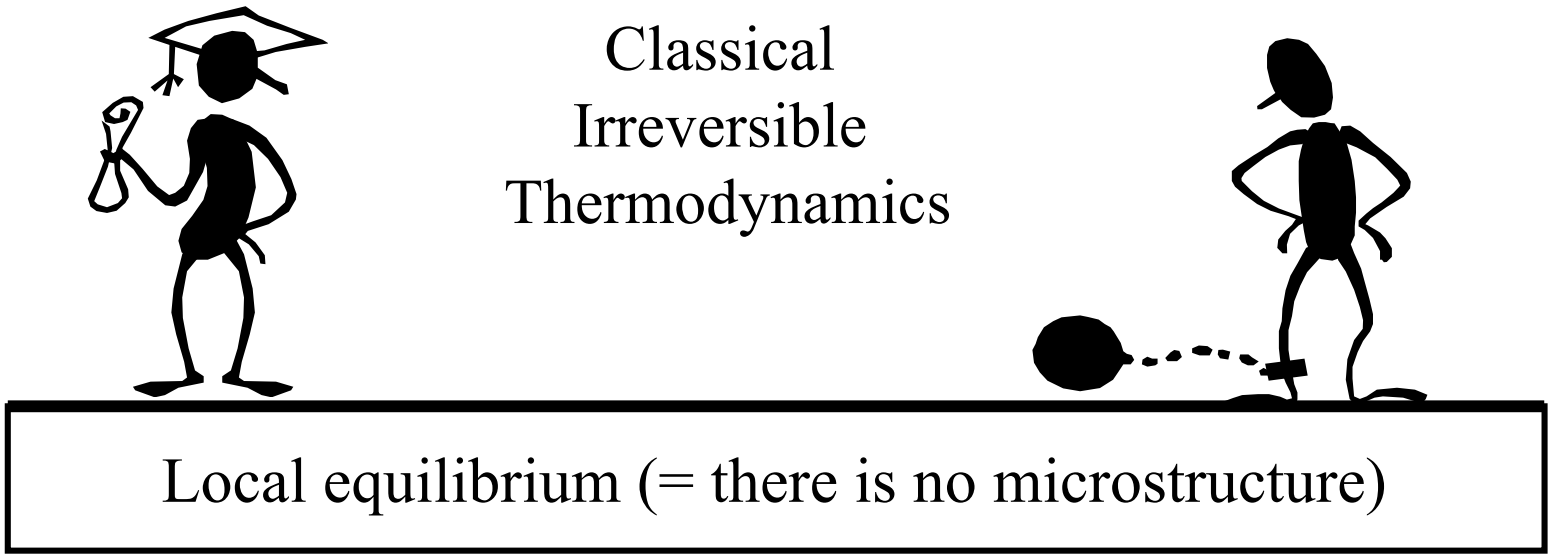
Classical and nonlocal theories of nonequilibrium thermodynamics

Peter Ván
BUTE, Department of Chemical Physics

- Beyond local equilibrium
- Relocalizable theories

  Extended irreversible thermodynamics
- Non relocalizable theories

  Once again on the Ginzburg-Landau equation



Violations (nonlocality):

- in time (memory effects) ⟶ dynamic variables
- in space (structure effects) ⟶ current multipliers + ??

Nonlocalities:

	Space	Time
Strongly nonlocal	Space integrals	Memory functionals
Weakly nonlocal	Gradient dependent constitutive functions	Rate dependent constitutive functions
Relocalized	Current multipliers	Internal variables

Weakly nonlocal extended thermodynamics

$$\partial_t u + \nabla \cdot \mathbf{q} = 0$$
$$\partial_t \mathbf{q} + G = 0$$
$$\partial_t s + \nabla \cdot \mathbf{j}_s \geq 0$$

$(u, \nabla u, \mathbf{q}, \nabla \mathbf{q}, \nabla^2 \mathbf{q})$ state space

$(G, s, \mathbf{j_s})$ constitutive functions

Liu procedure (Farkas's lemma)

$s(u, \mathbf{q})$ $\qquad$ $j_s(u, \mathbf{q}, \nabla \mathbf{q})$

$$\sigma_s = \nabla \cdot \mathbf{j}_s - \partial_1 s \nabla \cdot \mathbf{q} - \partial_3 s G \geq 0$$

?

$$s(u,\mathbf{q}) = s_0(u) - \frac{1}{2}\mathbf{q}\cdot\mathbf{m}(u,\mathbf{q})\cdot\mathbf{q}$$ extended (Gyarmati) entropy

$$\mathbf{j}_s(u,\mathbf{q},\nabla\mathbf{q}) = \mathbf{B}(u,\mathbf{q},\nabla\mathbf{q})\cdot\mathbf{q}$$ entropy current (Nyíri)

(**B** – *current multiplier*)

$$\sigma_s = (\mathbf{B} - \partial_1 s\mathbf{I}) : \nabla\mathbf{q} + (\nabla\cdot\mathbf{B} + G\cdot\hat{\mathbf{m}})\cdot\mathbf{q} \geq 0$$

$$\mathbf{B} - \partial_1 s\mathbf{I} = L_{11}\nabla\mathbf{q} + L_{12}\mathbf{q}$$

$$\nabla\cdot\mathbf{B} + G\cdot\hat{\mathbf{m}} = L_{21}\nabla\mathbf{q} + L_{22}\mathbf{q}$$

$$\hat{\mathbf{m}}\cdot\partial_t\mathbf{q} + \nabla\cdot(L_{11}\nabla\mathbf{q} + L_{12}\mathbf{q} + \partial_1 s\mathbf{I}) = L_{21}\nabla\mathbf{q} + L_{22}\mathbf{q}$$

Ginzburg-Landau (variational)

$$F(\xi)=\int\left(f(\xi)+\frac{\lambda}{2}(\nabla\xi)^2\right)dV \quad \Longrightarrow \quad \delta_\xi F = f'(\xi)-\lambda\Delta\xi$$

$$\dot{\xi}=-l\delta_\xi F$$

$$\dot{\xi}=-l\left(f'(\xi)-\lambda\Delta\xi\right)$$

– Second Law
– Variational (!)
– $+\,k\Delta\dot{\xi}$

Ginzburg-Landau (thermodynamic, relocalized)

$$\partial_t \xi + F = 0$$
$$\partial_t s + \nabla \cdot \mathbf{j}_s \geq 0$$

$(\xi, \nabla\xi, \nabla^2\xi)$ state space

$(F, s, \mathbf{j_s})$ constitutive functions

Liu procedure (Farkas's lemma)

$s(\xi)$ $\quad$ $\mathbf{j}_s(\xi, \nabla\xi)$

$$\sigma_s = \nabla \cdot \mathbf{j}_s - \partial_1 sF \geq 0$$

?

$$\mathbf{j}_s(\xi, \nabla\xi) = \mathbf{B}(\xi, \nabla\xi)\partial_1 s$$ current multiplier

$$\sigma_s = \mathbf{B}\cdot\nabla\partial_1 s + (\nabla\cdot\mathbf{B} - F)\partial_1 s \geq 0$$

$$\mathbf{B} = L_{11}\partial_1 s + L_{12}\nabla\partial_1 s$$

$$\nabla\cdot\mathbf{B} - F = L_{21}\nabla\partial_1 s + L_{22}\partial_1 s$$

isotropy

$$\partial_t\xi = L_{11}\partial_1 s - \nabla\cdot(L_{22}\nabla\partial_1 s)$$

$$\dot{\xi} = -l(f'(\xi) - \lambda\Delta\xi)$$

Ginzburg-Landau (thermodynamic, non relocalizable)

$$\partial_t \xi + F = 0$$

$$\partial_t \nabla \xi + \nabla F = 0$$

$$\partial_t s + \nabla \cdot \mathbf{j}_s \geq 0$$

$(\xi, \nabla\xi, \nabla^2\xi)$ state space

$(F, s, \mathbf{j_s})$ constitutive functions

Liu procedure (Farkas's lemma)

$s(\xi, \nabla\xi)$ $\qquad$ $j_s(.) = j_0(\xi, \nabla\xi) - \partial_1 s\, F(.)$

$$\sigma_s = -(\partial_1 s - \nabla \cdot \partial_2 s) F \geq 0$$

$$\partial_t \xi = -L(\partial_1 s - \nabla \cdot \partial_2 s)$$

Conclusions

- Not everything is a balance
- Internal variables are not omnipotent