A variational Lagrangian formulation for nonequilibrium thermodynamics

François Gay-Balmaz

CNRS-LMD-IPSL - Ecole Normale Supérieure de Paris

Joint work with H. Yoshimura, Waseda University, Tokyo

XXV IFWGP, Madrid, 31 August 2016

F. Gay-Balmaz and H. Yoshimura [2016], A Lagrangian variational formulation for nonequilibrium thermodynamics. Part I: discrete systems, Part II: continuum system, to appear in JGP.

Supported by ANR project GEOMFLUID.



Overview

Variational formulations in mechanics - a powerful tool to study:

- Symmetry and conservation laws;
- Reduction;
- Inclusion of constraints;
- Structure preserving numerical schemes;
- Derivation of new models;

-

Question: how can we extend these variational formulations to nonequilibrium thermodynamics?

Various variational principles related to nonequilibrium thermodynamics: Principle of least dissipation Onsager [1931], Onsager, Machlup [1953]; Principle of minimum entropy production Prigogine [1947], Glansdorff, Prigogine [1971] And others: Gyarmati [1970], Ichiyanagi [1994], Biot [1975], Fukagawa, Fujitani [2012].

Our goal: develop a variational formulation that:

- Produces the complete set of evolution equations of the thermodynamical system
- Recovers the Hamilton principle "in absence of irreversible processes"

PLAN:

- 1. What is nonequilibrium thermodynamics?
- 2. The two laws of thermodynamics
- 3. Variational principles in mechanics

4. Variational formulation for the nonequilibrium thermodynamics of simple discrete systems

5. Geometric structure of the variational formulation

6. Variational formulation for the nonequilibrium thermodynamics of discrete systems

7. Variational formulation for the nonequilibrium thermodynamics of continuum systems

・ 同 ト ・ ヨ ト ・ ヨ ト

1. What is nonequilibrium thermodynamics?

1.1 Thermodynamics:

> A PARIS, CHEX BACHELIER, LIBRAIRE

In a classical historical sense: not a dynamical theory!!

- Started during the industrialisation period;
- Closely related to the need to improve the efficiency of steam engines, i.e., the efficiency of the conversion heat \rightarrow work;
- Foundational work of Carnot in is book 1824:



Nicolas Léonard Sadi Carnot (1796-1832)

A famous movie from 1926

– Provides an upper limit on the efficiency η that any classical thermodynamic engine can achieve during the conversion heat \rightarrow work

$$\eta = \frac{\text{Work done by the system}}{\text{heat put into the system}} \le 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

$$- \text{ The famous Carnot cycle has } \eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \text{ (because of its reversibility)}. \quad \text{ If } \eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \text{ (because of its reversibility)}. \quad \text{ If } \eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \text{ (because of its reversibility)}.$$

Many contributors to the field of thermodynamics: Carnot (1796-1832), Mayer (1814-1878), Joule (1818-1899), Clausius (1822-1888), Kelvin (1824-1907), Maxwell (1831-1879), Rayleigh (1842-1919),

- Since these foundational works until 1960, thermodynamics has been a phenomenological theory mainly restricted to the description of either:

- equilibrium states
- quasi-static processes: processes that happen slowly enough for the system to remain in internal equilibrium.

 \rightsquigarrow does not aim to describe the dynamic evolution of the system.

- Such a classical theory can be developed in a well established setting (Gibbs [1902]), governed by the well-known first and second laws.

- Main quantities:
 - The energy [J] of the system: the ability of the system to do work;

 The entropy [J/K] of the system: a measure of its disorder and of the unavailability of its energy to do work. (Clausius, based on Carnot) - The two laws of thermodynamics (more precise later):

First law: For any system: $\Delta U = \Delta W^{\text{ext}} + \Delta Q^{\text{ext}} + \Delta M^{\text{ext}}$

Second law: For an adiabatically closed system ($\Delta Q^{\text{ext}} = 0 = \Delta M^{\text{ext}}$): $\Delta S \ge 0$.

- Usual quantities in thermodynamics (e.g., case of a fluid with one component):
- \rightarrow Extensive variables:

Energy *U*, Entropy *S*, Number of moles *N*, Volume *V* Fundamental relation: U = U(S, V, N) (energy representation) homogeneous of degree one; S = S(U, V, N) (entropy representation) homogeneous of degree one.

 \rightarrow Intensive variables: in the energy representation:

Temperature $T = \frac{\partial U}{\partial S}$, Pressure $p = -\frac{\partial U}{\partial V}$, Chemical potential $\mu = \frac{\partial U}{\partial N}$ - Extensive VS intensive variables: V + U = VT + T + U = V

1.2 Nonequilibrium thermodynamics:

Goal: describe the macroscopic evolution of thermodynamical systems out of equilibrium.

- Also useful to predict final equilibrium states!
- There are systems, e.g., the controversial adiabatic piston problem, for which classical thermodynamics cannot predict the final equilibrium state, Gruber [1999].



- Importance of the transport phenomena:

The adiabatic piston problem:

- Two fixed cylinders, one adiabatic movable piston
- A brake maintain first the piston at rest
- Each two fluids are in equilibrium with $p_1(0), T_1(0), V_1(0)$ and $p_2(0), T_2(0), V_2(0)$
- The brake is released:
- \rightsquigarrow find the final equilibrium state

matter (e.g., diffusion), heat (e.g., conduction), momentum (e.g., viscosity)

- Importance of the expression of the associated entropy production involving possible cross-effects (Onsager's relations).

- Deep impact in all branches of engineering and sciences
- E.g., successfully applied to biological processes such as protein folding and transport through membranes;
 - fundamental for atmospheric circulation and weather prediction;
 - fundamental for the dynamics of thermal, multiphase, multicomponent, or viscoelastic, fluids.

Big names in non-equilibrium thermodynamics include: Onsager (1903-1976) Nobel prize in chemistry, Stueckelberg (1905-1984), Meixner (1908-1994), Prigogine (1917-2003) Nobel prize in chemistry.



Non-equilibrium thermodynamics is a work in progress, not an established edifice.

Since 1960 Stueckelberg has consistently presented thermodynamics in a way similar to mechanics, i.e. as a phenomenological theory with time evolution described by first order differential equations \rightsquigarrow new point of view on macroscopic physical theories



Our variational formulations will reflect these inclusions.

2. The two laws of nonequilibrium thermodynamics (Stueckelberg's formulation)

- $\pmb{\Sigma}$ a physical system, $\pmb{\Sigma}^{\mathrm{ext}}$ its exterior;
- The state of the system is defined by a set of state variables (usually a set of mechanical variables and thermal variables);
- State functions are functions of these variables.

First law:

For every system Σ , there exists an extensive scalar state function *E*, called the **energy**, which satisfies

$$rac{d}{dt}E(t)=P_W^{
m ext}(t)+P_H^{
m ext}(t)+P_M^{
m ext}(t), \quad {
m where:}$$

 $P_W^{\text{ext}}(t)$: power due to external forces acting on the mechanical variables of Σ ; $P_H^{\text{ext}}(t)$: power due to heat transfer from the exterior to Σ ; $P_M^{\text{ext}}(t)$: power due to matter transfer from the exterior to Σ .

- Sometimes not possible to clearly distinguish between these three forms of power (pour hot water into cold water...)

Definitions:

- A system is said to be closed if there is no exchange of matter, i.e., $P_M^{\text{ext}}(t) = 0.$
- A system is said to be adiabatically closed if it is closed and there is no heat exchanges, i.e., $P_M^{\text{ext}}(t) = P_H^{\text{ext}}(t) = 0$.
- A system is said to be isolated if it is adiabatically closed and there is no mechanical power exchange, i.e., $P_M^{\text{ext}}(t) = P_H^{\text{ext}}(t) = P_W^{\text{ext}}(t) = 0$.

- From the first law, it follows that the energy of an isolated system is constant.

Second law:

For every system Σ , there exists an extensive scalar state function *S*, called **entropy**, which obeys the following two conditions

(a) Evolution part:

If the system is adiabatically closed, the entropy S is a non-decreasing function with respect to time, i.e.,

$$\frac{d}{dt}S(t)=I(t)\geq 0,$$

where I(t) is the entropy production rate of the system accounting for the irreversibility of internal processes.

(b) Equilibrium part:

If the system is isolated, as time tends to infinity the entropy tends towards a finite local maximum of the function S over all the thermodynamic states ρ compatible with the system, i.e.,

$$\lim_{t \to +\infty} S(t) = \max_{\rho \text{ compatible}} S[\rho].$$

(日) (周) (三) (三)

Definition:

- The evolution of an isolated system is said to be reversible if I(t) = 0, namely, the entropy is constant.
- The evolution of a system Σ is said to be reversible, if the evolution of the total isolated system with which Σ interacts is reversible.

- Cyclic engines ($\Delta S_{\rm Eng} = 0$). The isolate system is $\Sigma_{\rm Eng} \cup \Sigma_h \cup \Sigma_c$. Carnot is reversible $\Delta S_{\rm tot} = 0$, Rankine is irreversible $\Delta S_{\rm tot} > 0$

Definition (Stueckelberg):

- A simple system Σ is a macroscopic system for which one (scalar) thermal variable τ and a finite set of mechanical variables are sufficient to describe entirely the state of the system.
 From the second law of thermodynamics, we can always choose τ = S.
- A discrete system Σ is a collection Σ = ∪^N_{A=1}Σ_A of a finite number of interacting simple systems Σ_A.

- The adiabatic piston is not a simple system $(S_1 \text{ and } S_2)$

3

ヘロト 人間 ト くほ ト くほ トー

INTERMEDIATE SUMMARY

- Classical thermodynamics: field created during the industrialisation period; study of equilibrium states and quasi-static processes.
- Main concepts: energy and entropy; the two laws; usual variables: U, S, V, N, T, p, μ.
- A controversial problem: the adiabatic piston problem cannot be solved in the setting of classical thermodynamics. One needs the evolution equations.
- Nonequilibrium thermodynamics: a field containing macroscopic disciplines: classical mechanics, electromagnetism, fluid mechanics,

 $\rightsquigarrow~$ Our variational formulation has to reflect this

- Stueckelberg's formulation of the two laws
- Properties of a system: closed, adiabatically closed, isolate, reversible, simple, or discrete.

- 4 同 6 4 日 6 4 日 6

3. Variational principles in mechanics

3.1 Mechanical systems

 Σ a mechanical system. Q configuration manifold; state space: the tangent bundle $TQ \ni (q, v)$;

- Examples of configuration spaces:
- Material point $Q = \mathbb{R}^3 \ni \mathbf{x}$
- Rigid body $Q = SO(3) \ni A$

Fluid mechanics $Q = \mathsf{Diff}(\mathcal{D}) \ni \varphi$, $X \in \mathcal{D} \mapsto \varphi(t, X) \in \mathcal{D}$

Continuum mechanics $Q = \text{Emb}(\mathcal{D}, \mathbb{R}^3)$

Electrically charged fluids $Q = \underbrace{\text{Diff}(\mathcal{D})}_{\text{fluid motion}} \otimes \underbrace{\mathcal{C}^{\infty}(\mathcal{D}, U(1))}_{\text{charge}}$ Liquid crystals $Q = \underbrace{\text{Diff}(\mathcal{D})}_{\text{fluid}} \otimes \underbrace{\mathcal{C}^{\infty}(\mathcal{D}, SO(3))}_{\text{charge}}$

fluid motion

François Gay-Balmaz (CNRS-ENS-PARIS)

microstructure

・ロト ・四ト ・ヨト ・ヨトー

- Equations of motions for mechanical systems

Naturally described and studied by using the Lagrangian and Hamiltonian formalisms

Underlying abstract structures: variational principles, symplectic and Poisson structures

3.2 Hamilton's principle:

- Lagrangian function

 $L = L(q, \dot{q}) : TQ \rightarrow \mathbb{R}$ L = kinetic energy – potential energy

- Equations of motion: q(t) critical curve of the action functional

$$\mathcal{A}(q()) := \int_0^T L(q(t), \dot{q}(t)) dt$$

among curves in Q with fixed endpoints: $q(0) = q_0$, $q(T) = q_T$.

 \sim Hamilton's principle:

$$0 = \delta \int_0^T L(q(t), \dot{q}(t)) dt = \int_0^T \underbrace{\left(\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}}\right)}_{\text{Euler-Lagrange equations}} \delta q \, dt + \underbrace{\frac{\partial L}{\partial \dot{q}}\delta q}_{\text{Lagrangian 1-form on } TQ}$$

イロン イヨン イヨン イヨン

3.3 Forced mechanical systems

System not isolated in mechanics $\rightsquigarrow P_W^{\text{ext}}$.

External force $F^{\mathrm{ext}}: TQ \to T^*Q$ can be easily included in the variational principle

- Hamilton's principle with force

$$\delta \int_0^T L(q(t), \dot{q}(t)) dt + \int_0^T \left\langle F^{\mathrm{ext}}(q(t), \dot{q}(t)), \delta q(t) \right\rangle dt = 0$$

- Equations of motion

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = F^{\text{ext}}$$

- Energy

$$E(q,\dot{q}) = \left\langle \frac{\partial L}{\partial \dot{q}}, \dot{q} \right\rangle - L(q,\dot{q})$$

 $\frac{d}{dt}E = \langle F^{\text{ext}}, \dot{q} \rangle = P_W^{\text{ext}}$: first law in mechanics

3.4 Nonholonomic mechanical systems:

Rolling constraint: rolling ball, bike, cars,...





Electrical network:



Infinite dimensional example:



(Kirchhoff current law: constraint distribution on the configuration charge space)

\rightsquigarrow constraint distribution $\Delta \subset TQ$.

- Q configuration manifold, $L: TQ \rightarrow \mathbb{R}$ Lagrangian.
- Nonholonomic linear constraint $\Delta \subset TQ$, vector subbundle.
- Lagrange-d'Alembert principle

$$\frac{d}{d\varepsilon}\bigg|_{\varepsilon=0}\int_0^T L(q_\varepsilon,\dot{q}_\varepsilon)dt=0, \quad \text{where } \delta q=\left.\frac{d}{d\varepsilon}\right|_{\varepsilon=0}q_\varepsilon\in\Delta \text{ and } \dot{q}_{\varepsilon=0}\in\Delta$$

- Equations of motion

$$rac{d}{dt}rac{\partial L}{\partial \dot{q}} - rac{\partial L}{\partial q} \in \Delta^\circ, \quad \dot{q} \in \Delta$$

Can be written with a Lagrange multiplier: $\Delta=\ker\omega$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = \lambda \cdot \omega(q), \quad \omega(q) \cdot \dot{q} = 0$$

This is **NOT** a Lagrange multiplier variational principle! ("vakonomic mechanics", useful in control problems)

Variational principles in Lagrangian mechanics:

- A systematic and efficient way to recover equations or propose new models in classical mechanics
- Naturally extend to include external forces and linear nonholonomic constraints
- A natural setting to study the symmetries of the system and deduce the corresponding conservation laws via Noether's theorem
- Admits a temporal discretization useful to derive numerical schemes (variational integrators)

4. Variational formulation for the nonequilibrium thermodynamics of simple discrete systems

0

4.1 From mechanics to nonequilibrium thermodynamics: why do we need the entropy?

Mass-spring system with friction: mass m, spring constant k, friction force

$$\begin{cases} F^{\rm fr}(x,\dot{x}) = -\lambda \frac{\dot{x}}{|\dot{x}|} & \text{if } \dot{x} \neq 0, \quad \lambda > \\ |F^{\rm fr}| \leq F^{\rm fr}_{\rm max} & \text{if } \dot{x} = 0 \end{cases}$$



 $E_{\rm mec} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$ Equations of motion: $m\ddot{x} = -kx + F^{\rm fr}$

Experiment in two steps: (1) $0 \rightarrow 1$: Relaxation to an equilibrium Initial mechanical state: $x_0 \neq 0$, $\dot{x}_0 = 0$. Damped oscillations until it reaches equilibrium state: $x_1 = 0$, $\dot{x}_1 = 0$. Computation $\frac{d}{dt}E_{mech} = \dot{x}F^{fr} = -\lambda|\dot{x}|$ Isolate system: First Law $\Rightarrow \frac{d}{dt}E = 0$, where *E* is state function \Rightarrow there exists some state function *U*, called internal energy, such that $E = E_{mech} + U$

(II) $1 \rightarrow 2$: Back to initial position by applying an external force F^{ext} First Law: $\frac{d}{dt}E = P^{\text{ext}}_W = F^{\text{ext}}\dot{x}$

$$\Rightarrow 0 < W^{\text{ext}} = \int_{t_1}^{t_2} P_W^{\text{ext}} dt = E_2 - E_1 \stackrel{(I)}{=} E_2 - E_0 = U_2 - U_0$$

Original and final mechanical states are identical & E is a state function & $U_2 > U_1$

 \Rightarrow there exists an additional state variable; Second Law \Rightarrow this variable is the entropy.

First and Second Laws force us to introduce a new non-mechanical state variable, the entropy, to distinguish the final state from the original one.

- Energy:

$$E(x, \dot{x}, S) = \frac{1}{2}m\dot{x}^{2} + \frac{1}{2}kx^{2} + U(S)$$

- Lagrangian: a function L = L(q, v, S) : $TQ imes \mathbb{R} o \mathbb{R}$

- Equation for S: If the system is isolate

$$0 = \frac{d}{dt}E = F^{\rm fr}\dot{x} + T\dot{S}, \quad T := \frac{\partial U}{\partial S} \text{ the temperature.}$$

 \rightsquigarrow Complete system of evolution equations

$$\begin{cases} m\ddot{x} = -kx + F^{\rm fr} & \text{mechanical equation} \\ \dot{S} = -\frac{1}{T}F^{\rm fr}\dot{x} = \frac{\lambda}{T}|\dot{x}| & \text{thermal equation} \end{cases}$$

4.2 The variational formulation (FGB & Yoshimura [2016])

Theorem

Consider a simple closed system: $L : TQ \times \mathbb{R} \to \mathbb{R}$, $F^{ext}, F^{fr} : TQ \times \mathbb{R} \to T^*Q$, P_H^{ext} . Suppose (q(t), S(t)) satisfies

$$\delta \int_{t_1}^{t_2} L(q, \dot{q}, S) dt + \int_{t_1}^{t_2} \left\langle F^{\text{ext}}(q, \dot{q}, S), \delta q \right\rangle = 0, \quad \text{VARIATIONAL CONDITION}$$

with nonlinear nonholonomic constraint

$$\frac{\partial L}{\partial S}(q,\dot{q},S)\dot{S} = \left\langle F^{\rm fr}(q,\dot{q},S),\dot{q}\right\rangle - P_{H}^{\rm ext}, \quad \text{Phenomenological Constraint}$$

and with respect to variations $\delta \textbf{q}$ and $\delta \textbf{S}$ subject to

$$\frac{\partial L}{\partial S}(q, \dot{q}, S)\delta S = \left\langle F^{\rm fr}(q, \dot{q}, S), \delta q \right\rangle, \qquad \text{VARIATIONAL CONSTRAINT}$$

with $\delta q(t_1) = \delta q(t_2) = 0$. Then, the curve (q(t), S(t)) satisfies

$$\left(\begin{array}{c} \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = F^{\text{ext}}(q, \dot{q}, S) + F^{\text{fr}}(q, \dot{q}, S), \\ \frac{\partial L}{\partial S} \dot{S} = \left\langle F^{\text{fr}}(q, \dot{q}, S), \dot{q} \right\rangle - P_{H}^{\text{ext}}.$$

François Gay-Balmaz (CNRS-ENS-PARIS)

- Roughly speaking: we include thermodynamics by imposing the Second Law as a nonholonomic nonlinear constraint;
- Pass from the phenomenological constraint to the variational constraint in a "similar way" with nonholonomic mechanics: (more later...)

 $\dot{q} \in \Delta \quad \rightsquigarrow \quad \delta q \in \Delta.$

 Assume Σ is isolate. In this case the evolution of the system is reversible if and only if (*F*^{fr}(*q*(*t*), *q*(*t*)), *q*(*t*)) = 0. The system is reversible if and only if *F*^{fr} = 0.

Proof. Applying

$$\delta \int_{t_1}^{t_2} L(q, \dot{q}, S) dt + \int_{t_1}^{t_2} \langle F^{\text{ext}}(q, \dot{q}, S), \delta q \rangle = 0$$

and using $\delta q(t_1) = \delta q(t_2) = 0$, we get

$$\int_{t_1}^{t_2} \left(\left\langle \frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} + F^{\text{ext}}, \delta q \right\rangle + \frac{\partial L}{\partial S} \delta S \right) dt = 0.$$

Variational constraint \rightsquigarrow replace $\frac{\partial L}{\partial S}\delta S$ by the virtual work of the friction force $\langle F^{\rm fr}(q,\dot{q},S), \delta q \rangle$.

François Gay-Balmaz (CNRS-ENS-PARIS)

Example 1: piston

System



ideal gas confined by a piston in a cylinder closed system: $P_M^{\text{ext}} = 0$ state variables (x, \dot{x}, S) derived in Gruber [1999] from Stueckelberg's two laws

Lagrangian and forces

$$L(x, \dot{x}, S) = \frac{1}{2}m\dot{x}^2 - \mathcal{U}(x, S), \quad \mathcal{U}(x, S) := U(S, V = Ax, N_0)$$
$$U(S, N, V) = U_0 e^{\frac{1}{cR}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)} \left(\frac{N}{N_0}\right)^{\frac{1}{c}+1} \left(\frac{V_0}{V}\right)^{\frac{1}{c}}: \quad \text{internal energy of the gas}$$

deduced from U = cNRT and pV = NRT, c the gas constant (e.g. $c = \frac{3}{2}$ for monoatomic gas, $c = \frac{5}{2}$ for diatomic gas), R the universal gas constant.

Friction force

$$F^{\mathrm{fr}}(x,\dot{x},S) = -\lambda(x,S)\dot{x}$$

 $\lambda(x, S) \ge 0$ phenomenological coefficient.

Phenomenological constraint

$$\frac{\partial \mathcal{U}}{\partial S}\dot{S} = \lambda(x,S)\dot{x}^2 + P_H^{\mathrm{ext}}$$

Variational formulation

$$\delta \int_{t_1}^{t_2} \left[\frac{1}{2} m \dot{x}^2 - \mathcal{U}(x, S) \right] dt + \int_{t_1}^{t_2} \left\langle F^{\text{ext}}(q, \dot{q}, S), \delta q \right\rangle dt = 0,$$

subject to the variational constraint

$$\frac{\partial \mathcal{U}}{\partial S}\delta S = \lambda(x,S)\dot{x}\delta x.$$

Evolution equations

 $\begin{cases} m\ddot{x} = p(x,S)A + F^{\text{ext}} - \lambda(x,S)\dot{x} & \text{mechanical equation} \\ T\dot{S} = \lambda(x,S)\dot{x}^2 + P_H^{\text{ext}} & \text{thermal equation} \end{cases}$

where $T = \frac{\partial U}{\partial S}$ and $p := -\frac{\partial U}{\partial V}$.

Example 2: including matter transport





Two reservoirs k = 1, 2one membrane k = mNumber of moles $N^{(k)}$, k = 1, 2, mState variables $(N^{(1)}, N^{(2)}, N^{(m)}, S)$ $J^{(1)}$ flux "reservoir 1 \rightarrow membrane" $J^{(2)}$ flux "membrane \rightarrow reservoir 2" internal energy $U(S, N^{(1)}, N^{(2)}, N^{(m)})$ chemical potentials $\mu_{(k)} = \frac{\partial U}{\partial N^{(k)}}$

Entropy production:

$$\dot{S} = -rac{1}{T} \left(J^{(1)}(\mu_{(1)} - \mu_{(m)}) + J^{(2)}(\mu_{(m)} - \mu_{(2)})
ight)$$

see, e.g., Oster, Perelson, Katchalsky [1973]. The fluxes are determined phenomenologically.

How to interpret this as a phenomenological constraint to which is naturally associated a variational constraint?

Define the thermodynamic displacements $W_{(k)}$ such that $\dot{W}_{(k)} = \mu_{(k)}$.

Lagrangian

$$L(S, N^{(1)}, N^{(2)}, N^{(m)}) = -U(S, N^{(1)}, N^{(2)}, N^{(m)})$$

Phenomenological constraint

Using the thermodynamic displacements $W_{(k)}$

$$\frac{\partial L}{\partial S}\dot{S} = J^{(1)}(\dot{W}_{(1)} - \dot{W}_{(m)}) + J^{(2)}(\dot{W}_{(m)} - \dot{W}_{(2)})$$

Other constraint mass conservation

$$\dot{N}^{(1)} + \dot{N}^{(2)} + \dot{N}^{(m)} = 0$$

Variational formulation

We need equations of evolution + thermodynamic displacements \rightsquigarrow

$$\delta \int_{t_1}^{t_2} \left(L(S, N^{(1)}, N^{(2)}, N^{(m)}) + \dot{W}_{(k)} N^{(k)} \right) dt = 0,$$

subject to the variational constraints

 $\frac{\partial L}{\partial S}\delta S = J^{(1)}(\delta W_{(1)} - \delta W_{(m)}) + J^{(2)}(\delta W_{(m)} - \delta W_{(2)}), \quad \delta N^{(1)} + \delta N^{(2)} + \delta N^{(m)} = 0$ with $\delta W_{(k)}(t_i) = 0$, for k = 1, 2, m and i = 1, 2

Evolution equations

$$\begin{cases} \dot{N}^{(1)} = J^{(1)}, & \dot{N}^{(m)} = -J^{(1)} + J^{(2)}, & \dot{N}^{(2)} = -J^{(2)} & \text{matter diffusion equation} \\ T\dot{S} = -J^{(1)}(\mu_{(1)} - \mu_{(m)}) - J^{(2)}(\mu_{(m)} - \mu_{(2)}) & \text{thermal equation} \end{cases}$$

where $T = \frac{\partial U}{\partial S}$ and $p := -\frac{\partial U}{\partial V}$.

3

イロト イ理ト イヨト イヨト

Example 3: chemical reactions

System

System of *R* chemical components I = 1, ..., R undergoing *r* chemical reactions a = 1, ..., r:

$$\sum_{I} \nu'_{I}^{a} I \stackrel{a_{(1)}}{\underset{a_{(2)}}{\rightleftharpoons}} \sum_{I} \nu''_{I}^{a} I, \quad a = 1, ..., r,$$

 $a_{(1)}, a_{(2)}$: forward and backward reactions associated to the reaction $a_{\nu''_{I}}^{a}, \nu'_{I}^{a}$: forward and backward stoichiometric coefficients for I in reaction a.

e.g., photosynthesis:
$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

6 carbon dioxide + 6 water $\rightarrow 1$ glucose + 6 oxygen

- Number of moles of the component $I: N_I$.

- Internal energy of a multicomponent gas: $U = U(S, N_1, ..., N_R, V)$
- Affinity of reaction a: $\mathcal{A}^a := -\sum_{l=1}^R \nu_l^a \mu_l^l$, a = 1, ..., r.
- Mass conservation during each reaction: Lavoisier law "rien ne se perd, rien ne se crée, tout se transforme":

$$\sum_{I} m_{I} \nu_{I}^{a} = 0, \quad \forall a, \quad \nu_{I}^{a} := \nu_{I}^{\prime \prime a} - \nu_{I}^{\prime a}, \quad m_{I} \text{ molecular weight of } I$$

- Entropy production

$$T\dot{S} = J_a^{\rm fr} \mathcal{A}^a + P_H^{\rm ext},$$

where J_a^{fr} is the friction rate of reaction *a*, determined phenomenologically. As before: associated variational constraint?

Define the thermodynamic displacements ν_a such that $\dot{\nu}_a = \mathcal{A}^a$.

Lagrangian

$$L(N_1, ..., N_R, S) := -U(N_1, ..., N_R, S, V_0),$$
 (isochoric)

Phenomenological constraint Using thermodynamic displacements ν^a :

$$\frac{\partial L}{\partial S}\dot{S} = \sum_{a=1}^{r} J_{a}^{\rm fr} \dot{\nu}^{a} - P_{H}^{\rm ext}$$

Other constraint Chemical constraint

$$\dot{\nu}^a = \sum_{I=1}^R \nu_I^a \dot{W}^I$$

通 ト イヨ ト イヨト

Variational formulation

We need equations of evolution + thermodynamic displacements \rightsquigarrow

$$\delta \int_{t_1}^{t_2} \left(L(N_1, ..., N_R, S) + \sum_{I=1}^R \dot{W}^I N_I \right) dt = 0,$$

subject to the variational constraints

$$\frac{\partial L}{\partial S}\delta S = \sum_{a=1}^{r} J_{a}^{\rm fr} \delta \nu^{a} \text{ and } \delta \nu^{a} = \sum_{l=1}^{R} \nu_{l}^{a} \delta W^{l},$$

Evolution equations

$$\begin{cases} \dot{N}_{I} = J_{a}^{\rm fr} \nu_{I}^{a} & \text{matter reaction equation} \\ T \dot{S} = J_{a}^{\rm fr} \mathcal{A}^{a} + P_{H}^{\rm ext} & \text{thermal equation} \end{cases}$$

where $T = \frac{\partial U}{\partial S}$.

3

Example 4: coupling of matter transfer and chemical reactions Membrane transfer with several chemical components:



R chemical components that can - diffuse through the membrane - undergo *r* chemical reactions Number of moles $N_I^{(1)}$, $N_I^{(2)}$, $N_I^{(m)}$, I = 1, ..., R $J_I^{(1)}$ flux "reservoir 1 \rightarrow membrane", for component *I* $J_I^{(2)}$ flux "membrane \rightarrow reservoir 2", for component *I*

$$U(S, \{N_{I}^{(1)}, N_{I}^{(2)}, N_{I}^{(m)}\}), \quad \mu_{(k)}^{I} = \frac{\partial U}{\partial N_{I}^{(k)}}, \quad \mathcal{A}_{(k)}^{a} := -\sum_{I=1}^{\kappa} \nu_{I}^{a} \mu_{(k)}^{I}, \quad a = 1, ..., r$$

Thermodynamic displacements $\nu_{(k)}^a$, $W_{(k)}^l$ with $\dot{\nu}^a = \mathcal{A}_{(k)}^a$ and $W_{(k)}^l = \mu_{(k)}^l$.

4.3 Variational formulation for the coupling of mechanics, matter transfer and chemical reactions (FGB & Yoshimura [2016])

Theorem

$$\begin{aligned} & \text{Consider a simple closed system with } - \text{Lagrangian } L : TQ \times \mathbb{R} \times \mathbb{R}^{R \times r} \to \mathbb{R} \\ & - \text{External force and heat power } F^{\text{ext}} : TQ \times \mathbb{R} \times \mathbb{R}^{R \times r} \to T^*Q, P_H^{\text{ext}} \\ & - \text{Fluxes } F^{\text{fr}} : TQ \times \mathbb{R} \times \mathbb{R}^{R \times r} \to T^*Q \text{ and } J_1^{(k)}, J_3^{\text{fr}(k)} : TQ \times \mathbb{R} \times \mathbb{R}^{R \times r} \to \mathbb{R}. \end{aligned}$$

$$& \text{Suppose } (q(t), S(t), N_1^{(k)}(t), w_{(k)}^{(t)}(t), u_{(k)}^{(t)}(t)) \text{ satisfies} \\ & \delta \int_{t_1}^{t_2} \left(L(q, \dot{q}, S, \{N_l^{(k)}\}) + \sum_{l,k} \dot{W}_{(k)}^{(l)} N_1^{(k)} \right) dt + \int_{t_1}^{t_2} \left\langle F^{\text{ext}}, \delta q \right\rangle = 0, \qquad \text{VARIATIONAL CONSTRAINTS} \\ & \text{with nonlinear nonholonomic constraint: PHENOMENOLOGICAL & CHEMICAL CONSTRAINTS} \\ & \frac{\partial L}{\partial S} \dot{S} = \left\langle F^{\text{fr}}, \dot{q} \right\rangle + \underbrace{\sum_{l=1}^{l} \left(J_1^{(1)} (\dot{W}_{(1)}^{l} - \dot{W}_{(m)}^{l}) + J_1^{(2)} (\dot{W}_{(m)}^{l} - \dot{W}_{(2)}^{l}) \right)}_{\text{matter transfer}} + \underbrace{\sum_{k,a}^{l} J_a^{\text{fr}(k)} \dot{\nu}_{(a)}^{k} - P_H^{\text{ext}}}_{\text{chemical constraint}}, \qquad \underbrace{\psi_{(k)}^{l} = \sum_{l=1}^{l} \nu_l^a \dot{W}_{(k)}^{l}, \\ & \frac{\partial L}{\partial S} \dot{S} = \left\langle F^{\text{fr}}, \delta q \right\rangle + \underbrace{\sum_{l=1}^{R} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} + \underbrace{\sum_{l=1}^{R} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} + \underbrace{\sum_{l=1}^{R} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} + \underbrace{\sum_{l=1}^{R} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} + \underbrace{\sum_{k=1}^{R} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} \underbrace{\sum_{k=1}^{l} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} \underbrace{\sum_{k=1}^{l} \int_{l=1}^{l} \left(J_1^{(1)} (\delta W_{(1)}^{l} - \delta W_{(m)}^{l}) + J_1^{(2)} (\delta W_{(m)}^{l} - \delta W_{(2)}^{l}) \right)}_{\text{virtual friction}} \underbrace{\sum_{k=1}^{l} \int_{l=1}$$

....

Then, the curve $(q(t), S(t), N_l^{(k)}(t))$ satisfies

$$\begin{cases} \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = F^{\text{ext}} + F^{\text{fr}} & \text{mechanical equation} \\ \dot{N}_{l}^{(1)} = J_{l}^{(1)} + J_{a}^{\text{fr}(1)} \nu_{l}^{a}, & l = 1, ..., R \\ \dot{N}_{l}^{(m)} = -J_{l}^{(1)} + J_{l}^{(2)} + J_{a}^{\text{fr}(m)} \nu_{l}^{a}, & l = 1, ..., R \\ \dot{N}_{l}^{(2)} = -J_{l}^{(2)} + J_{a}^{\text{fr}(2)} \nu_{l}^{a}, & l = 1, ..., R \\ -T\dot{S} = -\langle F^{\text{fr}}, \dot{q} \rangle + J_{l}^{(1)} (\mu_{l1}^{l} - \mu_{m}^{l}) + J_{l}^{(2)} (\mu_{lm}^{l} - \mu_{l2}^{l}) - J_{a}^{\text{fr}(k)} \mathcal{A}_{(k)}^{a} - P_{H}^{\text{ext}} & \text{thermal equation.} \end{cases}$$

2

イロト イ団ト イヨト イヨト

INTERMEDIATE SUMMARY

• From mechanics to nonequilibrium thermodynamics: illustrated, from a basic example, the need of introducing a new non-mechanical state variable: the entropy.

• Variational formulation (first look):

regard the second law as a nonlinear constraint: called "phenomenological"; construct the associated variational constraint "virtual second law".

• Various examples:

First: strict application of the theorem to the piston; Then: does the same ideas apply to matter transfer and chemical reactions? Yes!!: define the corresponding "thermodynamic displacements".

• Variational formulation for simple systems:

Systems with friction, matter transfer, chemical reaction. Unifying idea:

$$\dot{q}, \dot{\Gamma}, \dot{
u} \rightarrow \delta q, \delta \Gamma, \delta
u$$

5. Geometric structure of the variational formulation

- The phenomenological constraint in thermodynamics is nonlinear. Example: given by

$$C := \left\{ (q, \dot{q}, S, \dot{S}) \in T(Q \times \mathbb{R}) \mid \frac{\partial L}{\partial S}(q, \dot{q}, S) \dot{S} = \left\langle F^{\mathrm{fr}}(q, \dot{q}, S), \dot{q} \right\rangle \right\} \subset T(Q \times \mathbb{R})$$

- In thermodynamics: natural definition of the virtual constraint:

$$\delta m{q}, \delta m{S}$$
 such that $rac{\partial L}{\partial S}(m{q}, \dot{m{q}}, m{S}) \delta m{S} = \left\langle m{F}^{ ext{fr}}(m{q}, \dot{m{q}}, m{S}), \delta m{q}
ight
angle$

- In mechanics, nonlinear constraints $C \subset TQ$ have been considered: Appell [1911], Chetaev [1934]. Lagrange-d'Alembert principle?

- For Chetaev: if $C = \{(q, v) \in TQ \mid R(q, v) = 0\}$, then

$$\delta q$$
 such that $rac{\partial R}{\partial v}(q,v)\cdot\delta q=0$

- Simple examples show that Chetaev's rule cannot be used in general (e.g., for some systems in Appell [1911] obtained as limits of linear constraints, already observed in Delassus [1911]).

François Gay-Balmaz (CNRS-ENS-PARIS)

- Marle [1998] considers the kinematic constraint C_K and the virtual constraint C_V as independent objects.

- Geometric setting in Cendra, Ibort, de León, Martín de Diego [2004], Cendra, Grillo [2009]:

kinematic constraint $C_K \subset TQ$: a submanifod variational constraint $C_V \subset TQ \times_Q TQ$ such that

 $C_V(q, v) := C_V \cap (\{(q, v)\} imes T_q Q)$ are vector subspace of same dimensions

- Principe of virtual work

$$\frac{d}{d\varepsilon}\bigg|_{\varepsilon=0}\int_0^T L(q_\varepsilon,\dot{q}_\varepsilon)dt=0, \quad \text{where } \delta q=\left.\frac{d}{d\varepsilon}\right|_{\varepsilon=0}q_\varepsilon\in C_V(q,\dot{q}) \text{ and } (q,\dot{q})_{\varepsilon=0}\in C_K$$

- Equations of motion

$$rac{d}{dt}rac{\partial L}{\partial \dot{q}} - rac{\partial L}{\partial q} \in C_V(q,\dot{q})^\circ, \quad (q,\dot{q}) \in C_K$$

3

(1) Mechanics with linear nonholonomic constraints

 $C_{K} = \Delta \rightsquigarrow C_{V} = TQ \times_{Q} \Delta$ i.e. $C_{V}(q, v) = \Delta(q)$

 \sim Energy preserving

(2) Chetaev's approach:

 $C_{\mathcal{K}} = \{(q, v) \in TQ \mid R_{\mathcal{K}}(q, \dot{q}) = 0\} \rightsquigarrow C_{V} = \{(q, v, \delta q) \mid \frac{\partial R}{\partial v}(q, v) \cdot \delta q = 0\}$

Recovers (1) if $C_{\mathcal{K}}$ linear \sim Not energy preserving in general

(3) Thermodynamics of simple and isolated systems without matter transfer and without chemical reactions: $Q \rightsquigarrow Q \times \mathbb{R}$,

 $C_V \subset T(Q imes \mathbb{R}) imes_{Q imes \mathbb{R}} T(Q imes \mathbb{R}) \rightsquigarrow C_K \subset T(Q imes \mathbb{R})$

Also mathematically recovers (1) (with $Q \to Q \times \mathbb{R}$) if C_V does not depend on v (forbidden by the Second Law!!).

 \sim Energy preserving (First Law).

▲ロト ▲圖ト ▲画ト ▲画ト 三直 - のへで

6. Variational formulation for the nonequilibrium thermodynamics of discrete systems

6.1 Discrete systems

Recall: closed discrete system $\boldsymbol{\Sigma} = \cup_{A=1}^{N} \boldsymbol{\Sigma}_{A}$, $\boldsymbol{\Sigma}_{A}$ simple systems



- State variables $q \in Q_{\Sigma}$ (not q_A), S_A , A = 1, ..., N.
- External forces: $P_W^{\text{ext}} = \sum_A P_W^{\text{ext} \to A} = \sum_A \langle F^{\text{ext} \to A}, \dot{q} \rangle$, $F^{\text{ext} \to A} : TQ_{\Sigma} \times \mathbb{R}^N \to T^*Q_{\Sigma}$
- External heat power: $P_H^{\text{ext}} = \sum_{A,R} P_H^{R \to A}$, Σ_R heat sources: system with $U_R(S_R)$
- Friction forces $F^{\mathrm{fr}(\mathrm{A})}: TQ_{\Sigma} imes \mathbb{R}^{N} o T^{*}Q_{\Sigma}$
- Internal heat power exchange $P_H^{B \to A}$.

6.2 Internal heat power as a "friction force"

- From the first and second law

$$P_{H}^{B \to A} = \kappa_{AB}(q, S^{A}, S^{B})(T^{B} - T^{A}),$$

 $\kappa_{AB} = \kappa_{BA} \geq 0$ heat transfer phenomenological coefficient. We write

$$\sum_{B=1}^{N} P_{H}^{B o A} = -\sum_{B=1}^{N} J_{B}^{ ext{fr}(A)}(m{q}, m{S}^{A}, m{S}^{B}) T^{B}, \quad J_{B}^{ ext{fr}(A)} := -\left(\kappa_{AB} - \delta_{AB} \sum_{C=1}^{N} \kappa_{AC}
ight)$$

 \rightsquigarrow suggests to write $T_B = \dot{\Gamma}_B$.

Define the thermodynamic displacement Γ_B such that $\dot{\Gamma}_B = T_B$.

- Such a variable has been considered!! Green and Naghdi [1991] (non classical heat conduction theory): the thermal displacement.

- Introduction of $\Gamma_A \sim introduction$ of Σ_A (in entropy units, clarified in the continuum case)

6.3 Variational formulation (FGB & Yoshimura [2016])

Theorem

Consider a closed discrete system with L, $F^{ext \rightarrow A}$, $F^{fr(A)}$, $P_{H}^{R \rightarrow A}$, and $J_{B}^{fr(B)}$. Suppose $(q(t), S_{A}(t), \Gamma^{A}(t), \Sigma_{A}(t))$ satisfies

$$\delta\int_{t_1}^{t_2} \left(L(q,\dot{q},S_1,...,S_N) + \sum_A (S_A - \Sigma_A)\dot{\Gamma}^A\right) dt + \int_{t_1}^{t_2} \left\langle F^{\mathrm{ext}},\delta q
ight
angle = 0,$$

VARIATIONAL CONDITION

with nonlinear nonholonomic constraint:

$$\frac{\partial L}{\partial S_{A}} \dot{\Sigma}_{A} = \left\langle F^{\text{fr}(A)}, \dot{q} \right\rangle + \sum_{B=1}^{N} J_{B}^{\text{fr}(A)} \dot{\Gamma}^{B} - P_{H}^{\text{ext} \to A}, \quad \forall A, \qquad \begin{array}{c} \text{Phenomenological}\\ \text{Constraint} \end{array}$$

and with respect to variations δq , δS_A , $\delta \Gamma^A$, $\delta \Sigma_A$, $\delta \nu^a_{(k)}$ subject to

$$\frac{\partial L}{\partial S_A} \delta \Sigma_A = \left\langle F^{\text{fr}(A)}(...), \delta q \right\rangle + \sum_{B=1}^N J_B^{\text{fr}(A)}(...) \delta \Gamma^B, \quad \forall A, \qquad \begin{array}{c} \text{VARIATIONAL} \\ \text{CONSTRAINT} \end{array}$$

Then $(q(t), S_A(t))$ satisfies

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = \sum_{A=1}^{N} F^{\text{fr}(A)} + F^{\text{ext}},$$

$$\frac{\partial L}{\partial S_{A}}\dot{S}_{A} = \left\langle F^{\text{fr}(A)}, \dot{q} \right\rangle + \sum_{B=1}^{N} J_{B}^{\text{fr}(A)}\dot{\Gamma}^{B} - P_{H}^{\text{ext} \to A}, \quad \forall A,$$

and $\dot{S}_{A} = \dot{\Sigma}_{A}, \quad \dot{\Gamma}^{A} = -\frac{\partial L}{\partial S_{A}}$

7. Variational formulation for the nonequilibrium thermodynamics of continuum systems

7.1 Geometry of continuum mechanics

- Configuration space: $Q = \text{Emb}(\mathcal{B}, \mathcal{S})$, \mathcal{B} compact with smooth boundary; dim $\mathcal{S} = \dim \mathcal{B}$, often $\mathcal{S} = \mathcal{B}$ or $\mathcal{S} = \mathbb{R}^n$.
- Motion: $\varphi(t) \in \mathsf{Emb}(\mathcal{B},\mathcal{S})$

 $x = \varphi(t, X), \quad X^{A}$: material coordinates; x^{a} spatial coordinates

- Reference fields: $ho_{
 m ref}(X)$, $S_{
 m ref}(X)$, $G_{
 m ref}(X)$, others
- Spatial fields: g(x),
- Lagrangian: $L: T \operatorname{Emb}(\mathcal{B}, \mathcal{S}) \to \mathbb{R}$, general form

$$egin{aligned} \mathcal{L}(arphi,\dot{arphi}) &= \int_{\mathcal{B}} \mathfrak{L}(X,arphi(X),\dot{arphi}(X),\mathcal{T}_{X}arphi)\mu_{G_{ ext{ref}}}(X) \ &= \int_{\mathcal{B}} \left[rac{1}{2}
ho_{ ext{ref}}|\dot{arphi}|_{g}^{2}\mu_{G_{ ext{ref}}} - \mathfrak{E}(\mathcal{T}_{X}arphi,..., ext{ref})\mu_{G_{ ext{ref}}} -
ho_{ ext{ref}}\mathcal{V}(arphi)
ight]\mu_{G_{ ext{ref}}} \end{aligned}$$

- Boundary conditions:

I) free boundary II) fixed boundary: e.g., S = B - no slip: $\varphi|_{\partial B} = id \rightsquigarrow Q = \text{Diff}_0(S)$ - tangential: Q = Diff(S)

7.2 Hamilton's principle in reversible continuum mechanics

- Equations of motion

$$\delta \int_{t_1}^{t_2} L(\varphi, \dot{\varphi}) dt = 0, \quad \delta \varphi(0) = \delta \varphi(T) = 0, \quad \delta \varphi|_{\partial \mathcal{B}} = \dots$$

$$\sim \rho_{\rm ref} \frac{D\dot{\varphi}}{Dt} = {\sf DIV} \, {\bf P}^{\rm cons} + \rho_{\rm ref} {\bf B}^{\rm cons},$$

$$\begin{split} \mathbf{P}^{\mathrm{cons}} &:= \left(\frac{\partial \mathfrak{E}}{\partial T_X \varphi}\right)^{\sharp_g} : \mathsf{Piola-Kirchhoff stress tensor} \\ \mathbf{B}^{\mathrm{cons}} &:= -(\mathbf{d}\mathcal{V} \circ \varphi)^{\sharp_g} : \mathsf{material body forces} \end{split}$$

- $\mathbf{P}(X)$: $T_X^*\mathcal{B} imes T_x^*\mathcal{S} o \mathbb{R}$ a two-point tensor field;

- DIV $P^a = P^{aA}_{|A} = P^A_{a,A} + P^L_a \Gamma^A_{LA} P^A_I \gamma^I_{an} \varphi^n_{,A}$, relative to G_{ref} and g
- D/Dt relative to g.
- Boundary conditions:

 $\textit{I)} \ \mathbf{P}^{\mathrm{cons}}(\mathbf{N}^{\flat_{\mathcal{G}}}, _) = 0 \ \text{on} \ \partial \mathcal{B} \qquad \textit{II}) \ \text{nothing or} \ \mathbf{P}^{\mathrm{cons}}(\mathbf{N}^{\flat_{\mathcal{G}}}, _)|_{\mathcal{T}\partial \mathcal{B}} = 0 \ \text{on} \ \partial \mathcal{B}$

イロン イヨン イヨン イヨン

- Spatial representation:

Assume right invariance w.r.t. isotropy subgroup of the reference fields. Define the spatial fields

$$\begin{split} \rho &:= \varphi_* \rho_{\rm ref} \;\; \text{mass density} \\ b &:= \varphi_* (G_{\rm ref}^{\sharp}) \;\; \text{Finger deformation} \\ s &:= \varphi_* S_{\rm ref} \;\; \text{spatial entropy} \end{split}$$

 \rightsquigarrow spatial Lagrangian

$$\ell(\mathbf{v},\rho,s,b) = \int_{\mathcal{S}} \left[\frac{1}{2} \rho |\mathbf{v}|_{g}^{2} - \epsilon(\rho,s,b) - \rho \mathcal{V} \right] \mu_{g}$$

- Equations of motion

 $\begin{cases} \rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = \operatorname{div} \boldsymbol{\sigma}^{\operatorname{cons}} + \rho \mathbf{b}^{\operatorname{cons}}, & \text{balance of momenta} \\ \partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0, \quad \partial_t s + \operatorname{div}(s \mathbf{v}) = 0, \quad \partial_t b + \mathcal{L}_{\mathbf{v}} b = 0, & \text{continuity equations} \end{cases}$

$$\boldsymbol{\sigma}^{\mathrm{cons}} = -\boldsymbol{p}\boldsymbol{g}^{\sharp} + \boldsymbol{\sigma}^{\mathrm{cons}}_{\mathrm{el}}, \quad \boldsymbol{p} = \epsilon - \rho \frac{\partial \epsilon}{\partial \rho} - \boldsymbol{s} \frac{\partial \epsilon}{\partial \boldsymbol{s}}, \quad \boldsymbol{\sigma}^{\mathrm{cons}}_{\mathrm{el}} = 2\left(\frac{\partial \epsilon}{\partial \boldsymbol{b}} \cdot \boldsymbol{b}\right)^{\sharp_{\boldsymbol{g}}}$$

< □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □ > < □

7.2 Heat conducting viscous fluid (Navier-Stokes-Fourier)

Recall the variational formulation for the thermodynamics of discrete systems:

- need Γ_A and Σ_A ;
- entropy is a dynamic variable:

 $L(\varphi, \dot{\varphi}; S_{\mathrm{ref}}), S_{\mathrm{ref}}(X) \longrightarrow L(\varphi, \dot{\varphi}, S), S(t, X)$

- Friction force \rightsquigarrow friction stress:

$$\left\langle \mathcal{F}^{\mathrm{fr}},\dot{q}
ight
angle \qquad \rightsquigarrow \qquad (\mathbf{P}^{\mathrm{fr}})^{\flat_g}:
abla^g\dot{arphi}$$

- Heat conduction:

 $\kappa_{AB}(T^B - T^A), \quad T^A = \dot{\Gamma}^A \qquad \rightsquigarrow \qquad \mathbf{J}_S \cdot \mathbf{d}\mathfrak{T}, \quad \mathfrak{T} = \dot{\Gamma},$

 $J_{5}(t, X)$: entropy flux density; $\Gamma(t, X)$: temperature displacement; $\mathfrak{T}(t, X)$: temperature; all in material representation.

1

- Heat power supply:

$$\mathcal{P}_Q^{ ext{ext}} \quad \rightsquigarrow \quad \mathcal{P}_Q^{ ext{ext}} = \int_{\mathcal{B}}
ho_{ ext{ref}} \mathcal{R} \mu_{\mathcal{G}_{ ext{ref}}}.$$

イロト イ理ト イヨト イヨト 二日

Theorem (Variational formulation of Navier-Stokes-Fourier equations)

The variational formulation

$$\delta \int_{t_1}^{t_2} \left(L(\varphi, \dot{\varphi}, S) + \int_{\mathcal{B}} (S - \Sigma) \dot{\Gamma} \mu_{G_{\text{ref}}} \right) dt = 0, \quad \text{Variational Condition}$$

with no-slip boundary conditions $\varphi|_{\partial \mathcal{B}} = \operatorname{id}$,

$$\begin{split} &\frac{\partial \mathfrak{L}}{\partial S} \dot{\Sigma} = -(\mathbf{P}^{\mathrm{fr}})^{\flat_g} : \nabla^g \dot{\varphi} + \mathbf{J}_S \cdot \mathbf{d} \dot{\Gamma} - \rho_{\mathrm{ref}} R, \quad \text{Phenomenological Constraint} \\ &\frac{\partial \mathfrak{L}}{\partial S} \delta \Sigma = -(\mathbf{P}^{\mathrm{fr}})^{\flat_g} : \nabla^g \delta \varphi + \mathbf{J}_S \cdot \mathbf{d} \delta \Gamma, \quad \text{Variational Constraint} \end{split}$$

and $\delta \Gamma|_{\partial \mathcal{B}} = 0$, yields the Navier-Stokes-Fourier system

$$\begin{cases} \rho_{\rm ref} \frac{D\mathbf{V}}{Dt} = \mathsf{DIV}(\mathbf{P}^{\rm cons} + \mathbf{P}^{\rm fr}) + \rho_{\rm ref} \mathbf{B}^{\rm cons}, \quad \mathbf{V} = \dot{\varphi} \\ \mathfrak{T}(\dot{S} + \mathsf{DIV} \mathbf{J}_{S}) = (\mathbf{P}^{\rm fr})^{\flat_{g}} : \nabla^{g} \mathbf{V} - \mathbf{J}_{S} \cdot \mathbf{d}\mathfrak{T} + \rho_{\rm ref} R, \end{cases} \text{ with } \dot{\Sigma} = \dot{S} + \mathsf{DIV} \mathbf{J}_{S}!!!$$

Moreover: $\delta \Gamma|_{\partial \mathcal{B}}$ free $\Rightarrow \mathbf{J}_{S} \cdot \mathbf{N}^{\flat_{G}}|_{\partial \mathcal{B}} = 0$. If in addition $\rho_{\mathrm{ref}}R = 0$, then the fluid is adiabatically closed.

- Spatial representation:

Check that L and the constraints are right-invariant

 \rightsquigarrow Similar variational formulation in spatial variable yields:

$$\begin{aligned} \rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) &= -\operatorname{grad} p + \operatorname{div} \boldsymbol{\sigma}^{\mathrm{fr}}, \quad p = \frac{\partial \varepsilon}{\partial \rho} \rho + \frac{\partial \varepsilon}{\partial s} s - \varepsilon, \\ \partial_t \rho + \operatorname{div}(\rho \mathbf{v}) &= 0, \\ T(\partial_t s + \operatorname{div}(s \mathbf{v}) + \operatorname{div} \mathbf{j}_S) &= (\boldsymbol{\sigma}^{\mathrm{fr}})^{\flat_s} : \nabla \mathbf{v} - \mathbf{j}_S \cdot \mathbf{d}T + \rho r, \quad T = \frac{\partial \varepsilon}{\partial s} \end{aligned}$$

(familiar form of Navier-Stokes-Fourier, e.g., Landau & Lifshitz [1987])

- Thermodynamic phenomenology:

Phenomenological expressions for the "fluxes" σ^{fr} and \mathbf{j}_S in terms of the "affinities" Def **v** and **d***T* compatible with the Second Law.

Well-known relations

$$\boldsymbol{\sigma}^{\mathrm{fr}} = 2\mu (\mathsf{Def}\,\mathbf{v})^{\sharp_g} + \left(\zeta - \frac{2}{3}\mu\right) (\mathsf{div}\,\mathbf{v})g^{\sharp} \quad \mathsf{and} \quad T\mathbf{j}_S^{\flat_g} = -\kappa \mathbf{d}\,T \ \text{(Fourier law)},$$

 $\mu \geq 0$ shear viscosity, $\zeta \geq 0$ bulk viscosity, $\kappa \geq 0$ thermal conductivity. $_{=}$,

7.3 Multicomponent reacting viscous fluid

Works by collecting all the previous examples

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\operatorname{grad} p + \operatorname{div} \boldsymbol{\sigma}^{\operatorname{fr}}, \quad p = \frac{\partial \varepsilon}{\partial n_A} n_A + \frac{\partial \varepsilon}{\partial s} s - \varepsilon,$$

$$\partial_t n_A + \operatorname{div}(n_A \mathbf{v}) + \operatorname{div} \mathbf{j}_A = j_a \nu_A^a,$$

$$T(\partial_t s + \operatorname{div}(s \mathbf{v}) + \operatorname{div} \mathbf{j}_S) = (\boldsymbol{\sigma}^{\operatorname{fr}})^{\flat_g} : \operatorname{Def} \mathbf{v} - \mathbf{j}_S \cdot \mathbf{d}T - \mathbf{j}_A \cdot \mathbf{d}\mu^A + j_a \mathcal{A}^a + \rho r,$$

- Thermodynamic phenomenology:

$$-\begin{bmatrix}\mathbf{j}_{S}\\\mathbf{j}_{A}\end{bmatrix} = \begin{bmatrix}\mathcal{L}_{SS} & \mathcal{L}_{SB}\\\mathcal{L}_{AS} & \mathcal{L}_{AB}\end{bmatrix} \begin{bmatrix}\mathbf{d} T\\\mathbf{d}\mu^{B}\end{bmatrix}, \begin{bmatrix}\operatorname{Tr} \boldsymbol{\sigma}^{\mathrm{fr}}\\j_{a}\end{bmatrix} = \begin{bmatrix}\mathcal{L}_{00} & \mathcal{L}_{0b}\\\mathcal{L}_{a0} & \mathcal{L}_{ab}\end{bmatrix} \begin{bmatrix}\frac{1}{3}\operatorname{div} \mathbf{v}\\\mathcal{A}^{b}\end{bmatrix}, \ (\boldsymbol{\sigma}^{\mathrm{fr}})^{(0)} = 2\mu(\operatorname{Def} \mathbf{v}^{\sharp_{g}})^{(0)},$$

Positive quadratic forms & satisfy Onsager's reciprocal relations.

- Important application: atmospheric entry



Current works:

- Reduction
- Dirac structures
- Discretizations
-

2

イロト イヨト イヨト イヨト

Thank you

2

メロト メポト メヨト メヨト