A Lagrangian Variational Formulation of Nonequilibrium thermodynamics

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Topological and geometrical structures of information

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- Gay-Balmaz F. and Yoshimura H. [2016], A Lagrangian variational formulation for nonequilibrium thermodynamics.
  Part I: discrete systems, *J. Geom. Phys.*, **111**, 169–193;
  Part II: continuum systems, *J. Geom. Phys.*, **111**,194–212.
- Gay-Balmaz F. and Yoshimura H. [2017], Dirac structures in nonequilibrium thermodynamics, `https://arxiv.org/abs/1704.03935`
- Gay-Balmaz F. [2017], Variational derivation of the thermodynamics of a moist atmosphere with irreversible processes, `https://arxiv.org/abs/1701.03921`.

Overview

Variational formulations in mechanics - a powerful tool to study:

(I) Symmetry, conservation laws, reduction;

(II) Inclusion of constraints (holonomic and nonholonomic);

(III) Structure preserving numerical schemes (symplectic, multisymplectic);

(IV) Derivation of new models (e.g., fluid-structure interaction);

(V) ....

Geometric point of view: Configuration manifold Q, Lagrangian $L : TQ \to \mathbb{R}$:

Hamilton's principle:

$$\delta \int_0^T L(q, \dot{q})dt = 0, \quad \text{for arbitrary } \delta q \quad \Rightarrow \quad \text{Euler-Lagrange equations}$$

(I) Symmetries: group action $G \times Q \to Q$ that keeps L invariant $\Rightarrow$ reduction $(TQ)/G$:

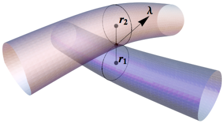
$$\rightsquigarrow \ell : (TQ)/G \to \mathbb{R}, \quad \delta \int_0^T \ell(v)dt = 0, \quad \text{for specific } \delta v \quad \Rightarrow \quad \text{reduced EL equations}$$

Reduction always has a physical reason and meaning:

– Lagrangian-to-Eulerian description (fluids, continuum mechanics, ...)

– Lagrangian-to-body frame description (Cosserat rods, multibody dynamics, ...)

(II) Nonholonomic constraint: $\Delta \subset TQ$ nonintegrable distribution
E.g.: rolling constraint (finite and infinite dimensional examples)



$$\text{Lagrange-d'Alembert principle :} \quad \delta \int_0^T L(q, \dot{q})dt = 0, \quad \text{for } \delta q \in \Delta, \quad \text{where } \dot{q} \in \Delta$$

NOT a Lagrange multiplier approach!

(III) Variational integrators: discretize in time the Hamilton principle

$$\delta \sum_{k=0}^{N-1} L_d(q_k, q_{k+1}) = 0, \quad \text{for arbitrary } \delta q_k \quad \Rightarrow \quad \textit{symplectic numerical integrators}$$

(IV) Geometric modeling: Hamilton's principle is a key tool to derive new models in which a direct application of Newton's laws is impossible: e.g., fluid-structure interactions (fluid conveying flexible pipes).

$\leadsto$ Especially powerful for continuum systems (infinite dim. configuration manifolds)

$$Q = \mathrm{Diff}(\Omega), \quad Q = \mathrm{Emb}(\Omega, \mathbb{R}^3), \quad Q = C^\infty([0, L], SE(3)), \quad \dots$$

$\leadsto$ Has a spacetime version (field theory), naturally related to multisymplectic geometry.

$\leadsto$ *multisymplectic variational numerical integrators.*

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], **many** others.......

• Important works on the geometric formulation of irreversible processes
$\rightsquigarrow$ Bracket formalisms: Kaufman [1984], Morrison [1984], Grmela [1984],....
$\rightsquigarrow$ Contact structures and port Hamiltonian systems: Eberard, Maschke, and van der Schaft [2007], Favache, Dochain, Maschke [2010], Bernard Maschke's talk.

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".

WARNING: in this talk:
– we only consider the macroscopic description
– we only present the geometric formalism, not the geometric modeling based on it
(see FGB [2017], Variational modelling of moist pseudo-incompressible atmospheric thermodynamics)

PLAN:

1. Thermodynamics of discrete systems

2. Geometric structure of the variational formulation

3. Dirac structures in nonequilibrium thermodynamics

4. Geometry of continuum systems

5. Viscous and heat conducting multicomponent reacting fluid

(**6.** Moist atmosphere thermodynamics)

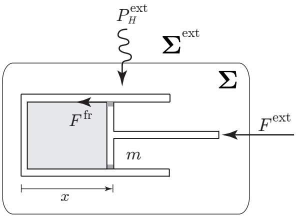
1.1 Simple discrete sytems:

Definition (Stueckelberg):

- A simple system $\boldsymbol{\Sigma}$ 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.
  Second law of thermodynamics $\rightsquigarrow$ we can always choose $\tau = S$.
- A discrete system $\boldsymbol{\Sigma}$ is a collection $\boldsymbol{\Sigma} = \cup_{A=1}^{N} \boldsymbol{\Sigma}_A$ of a finite number of interacting simple systems $\boldsymbol{\Sigma}_A$.

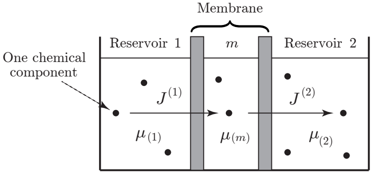
(A) Example of simple discrete systems:

Example 1: piston



ideal gas confined by a piston in a cylinder
state variables: x, $\dot{x}$, S

Example 2: matter transport



Two reservoirs $k = 1, 2$
one membrane $k = m$
Number of moles $N^{(k)}$, $k = 1, 2, m$
state variables: $N^{(1)}$, $N^{(2)}$, $N^{(m)}$, S
$J^{(1)}$ flux "reservoir 1 $\to$ membrane"
$J^{(2)}$ flux "membrane $\to$ reservoir 2"

Example 3: chemical reactions

System of K chemical components $A = 1, ..., K$ undergoing r chemical reactions $a = 1, ..., r$:

$$\sum_A \nu'^a_A A \underset{a_{(2)}}{\overset{a_{(1)}}{\rightleftarrows}} \sum_A \nu''^a_A A, \quad a = 1, ..., r,$$

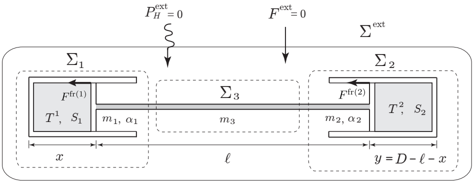
$a_{(1)}$, $a_{(2)}$: forward and backward reactions associated to the reaction a
ν''^a_A, ν'^a_A: forward and backward stoichiometric coefficients for A in reaction a.

e.g., photosynthesis: $6CO_2 + 6H_2O \to C_6H_{12}O_6 + 6O_2$
6 carbon dioxide + 6 water $\to$ 1 glucose + 6 oxygen.

state variables: S and N_A, $A = 1, ...K$.

(B) Example of non-simple discrete systems:

Example 1: the adiabatic piston problem



The adiabatic piston problem:

- Two fixed cylinders, one adiabatic movable piston
- A brake maintains 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

state variables: $x,\ \dot{x},\ S_1,\ S_2$

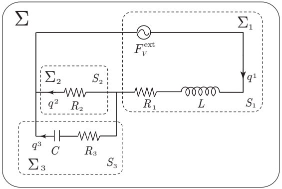
• **the laws of thermostatics cannot predict the final equilibrium state**, Gruber [1999].

$v = 0,\ p_1 A_1 = p_2 A_2,\ U_1(S_1, x) + U_2(S_2, D - \ell - x) = E_0$

Historically relevant problem: various answers for the final temperatures: Callen 1963, Kubo 1969, Landau and Lifshitz 1959, Nozières 1993, Kestin 1979, ...

• **Dynamical equations of nonequilibrium thermodynamics** $\rightsquigarrow$ the final equilibrium state can be uniquely predicted. (The similar problem with a diathermic piston is straightforward)

Example 2: a non-simple electric circuit.



R resistor, C capacitor,

L inductor, V voltage source

state variables: $q_i,\ \dot{q}_i,\ S_i,\ i = 1, 2, 3.$

1.2 Variational formulation for simple discrete systems:

Theorem (Simple systems, friction only)

Consider a simple closed system: $L : TQ \times \mathbb{R} \to \mathbb{R}$, $F^{\rm ext}, F^{\rm fr} : TQ \times \mathbb{R} \to T^*Q$, $P_H^{\rm ext}$.

- *Suppose* $(q(t), S(t))$ *satisfies*

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

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 δq *and* δS *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 the evolution equations*

$$\left\{\begin{array}{l} \dfrac{d}{dt}\dfrac{\partial L}{\partial \dot{q}} - \dfrac{\partial L}{\partial q} = F^{\rm ext}(q, \dot{q}, S) + F^{\rm fr}(q, \dot{q}, S), \\[2mm] \dfrac{\partial L}{\partial S}\dot{S} = \left\langle F^{\rm fr}(q, \dot{q}, S), \dot{q} \right\rangle - P_H^{\rm ext}. \end{array}\right.$$

- **Inclusion of matter transport**

Thermodynamic affinity (force) for matter transport:

$$\mu_{(k)} = \frac{\partial U}{\partial N_k} : \quad \text{chemical potential of substance in reservoir } k$$

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

- **Inclusion of chemical reactions**

Thermodynamic affinity (force) for chemical reactions:

$$\mathcal{A}^a := -\sum_{A=1}^{R} \nu_A^a \mu^A : \quad \text{chemical affinity of reaction } a, \;\; \nu_A^a := \nu''^a_A - \nu'^a_A$$

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

Theorem (Simple systems with friction, matter transfer, & chemical reactions)

Consider a simple closed system with - *Lagrangian* $L : TQ \times \mathbb{R} \times \mathbb{R}^{K \times r} \to \mathbb{R}$
- *External force and heat power* $F^{\rm ext} : TQ \times \mathbb{R} \times \mathbb{R}^{K \times r} \to T^*Q$, $P_H^{\rm ext}$
- *Fluxes* $F^{\rm fr} : TQ \times \mathbb{R} \times \mathbb{R}^{K \times r} \to T^*Q$ *and* $J_A^{(k)}, J_a^{{\rm fr}(k)} : TQ \times \mathbb{R} \times \mathbb{R}^{K \times r} \to \mathbb{R}$.

Suppose $(q(t), S(t), N_A^{(k)}(t), W_{(k)}^A(t), \nu_{(k)}^a(t))$ *satisfies*

$$\delta \int_{t_1}^{t_2} \Big(L(q, \dot q, S, \{N_A^{(k)}\}) + \sum_{I,k} \dot W_{(k)}^A N_A^{(k)} \Big) dt + \int_{t_1}^{t_2} \big\langle F^{\rm ext}, \delta q \big\rangle = 0,$$

VARIATIONAL CONDITION

with nonlinear nonholonomic constraint:

PHENOMENOLOGICAL & CHEMICAL CONSTRAINTS

$$\frac{\partial L}{\partial S}\dot S = \underbrace{\big\langle F^{\rm fr}, \dot q \big\rangle}_{\textit{friction}} + \underbrace{\sum_A \Big(J_A^{(1)}(\dot W_{(1)}^A - \dot W_{(m)}^I) + J_A^{(2)}(\dot W_{(m)}^A - \dot W_{(2)}^A) \Big)}_{\textit{matter transfer}} + \underbrace{\sum_{k,a} J_a^{{\rm fr}\,(k)} \dot \nu_{(k)}^a}_{\textit{chemical reaction}} - P_H^{\rm ext}, \quad \underbrace{\dot\nu_{(k)}^a = \sum_I \nu_A^a \dot W_{(k)}^I}_{\textit{chemical constraint}},$$

and with respect to variations δq, δS, $\delta N_A^{(k)}$, $\delta W_{(k)}^A$, $\delta \nu_{(k)}^a$ *subject to*

VARIATIONAL CONSTRAINTS

$$\frac{\partial L}{\partial S}\delta S = \underbrace{\big\langle F^{\rm fr}, \delta q \big\rangle}_{\textit{virtual friction}} + \underbrace{\sum_{A=1}^R \Big(J_A^{(1)}(\delta W_{(1)}^I - \delta W_{(m)}^I) + J_A^{(2)}(\delta W_{(m)}^A - \delta W_{(2)}^A) \Big)}_{\textit{virtual matter transfer}} + \underbrace{\sum_{k,a} J_a^{{\rm fr}\,(k)} \delta \nu_{(k)}^a}_{\substack{\textit{virtual}\\ \textit{chemical reactions}}}, \quad \underbrace{\delta\nu_{(k)}^a = \sum_A \nu_A^a \delta W_{(k)}^A}_{\substack{\textit{virtual}\\ \textit{chemical constraint}}}.$$

Then,...

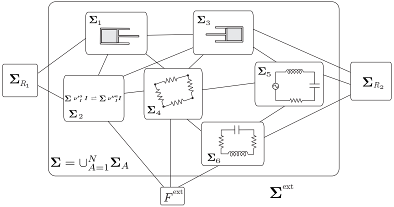
....

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

$$\begin{cases} \dfrac{d}{dt}\dfrac{\partial L}{\partial \dot q} - \dfrac{\partial L}{\partial q} = F^{\rm ext} + F^{\rm fr} & \text{mechanical equation} \\ \dot N_A^{(1)} = J_A^{(1)} + J_a^{\mathrm{fr}\,(1)}\nu_A^a, \qquad A = 1, \dots, K & \\ \dot N_A^{(m)} = -J_A^{(1)} + J_A^{(2)} + J_a^{\mathrm{fr}\,(m)}\nu_A^a, \qquad A = 1, \dots, R & \text{reaction-diffusion equations} \\ \dot N_A^{(2)} = -J_A^{(2)} + J_a^{\mathrm{fr}\,(2)}\nu_A^a, \qquad A = 1, \dots, K. & \\ -T\dot S = -\left\langle F^{\rm fr}, \dot q \right\rangle + J_A^{(1)}\left(\mu_{(1)}^A - \mu_{(m)}^A\right) + J_A^{(2)}\left(\mu_{(m)}^A - \mu_{(2)}^A\right) - J_a^{\mathrm{fr}\,(k)}\mathcal{A}_{(k)}^a - P_H^{\rm ext} & \text{thermal equation.} \end{cases}$$

1.3 Variational formulation for (non-simple) discrete systems:

Recall: closed discrete system $\mathbf{\Sigma} = \cup_{A=1}^{N} \mathbf{\Sigma}_A$, $\mathbf{\Sigma}_A$ simple systems, entropy variables S_A.



- Internal heat power exchange

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

$\kappa_{AB} = \kappa_{BA} \geq 0$ heat transfer phenomenological coefficient.
- Mechanical analogy: $\rightsquigarrow$ 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].
- Introduction of $\Gamma_A \rightsquigarrow$ introduction of Σ_A: in entropy units (clarified in the continuum case), $\dot{\Sigma}_A$ entropy source.

Theorem (Discrete systems - friction & heat conduction only)

Consider a closed discrete system with L, $F^{\mathrm{ext}\to\mathrm{A}}$, $F^{\mathrm{fr(A)}}$, $P_H^{R\to A}$, *and* κ_{AB}.

- *Suppose* $(q(t), S_A(t), \Gamma^A(t), \Sigma_A(t))$ *satisfies*

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

VARIATIONAL CONDITION

with nonlinear nonholonomic constraint:

$$\frac{\partial L}{\partial S_A}\dot\Sigma_A=\Big\langle F^{\mathrm{fr}(A)},\dot q\Big\rangle-\sum_{B=1}^N\kappa_{AB}(\dot\Gamma^B-\dot\Gamma^A)-P_H^{\mathrm{ext}\to\mathrm{A}},\ \ \forall\ A,$$

PHENOMENOLOICAL CONSTRAINT

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

$$\frac{\partial L}{\partial S_A}\delta\Sigma_A=\Big\langle F^{\mathrm{fr}(A)}(...),\delta q\Big\rangle-\sum_{B=1}^N\kappa_{AB}(\delta\Gamma^B-\delta\Gamma^A),\ \ \forall\ A,$$

VARIATIONAL CONSTRAINT

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

$$\begin{cases}\dfrac{d}{dt}\dfrac{\partial L}{\partial\dot q}-\dfrac{\partial L}{\partial q}=\displaystyle\sum_{A=1}^N F^{\mathrm{fr}(A)}+F^{\mathrm{ext}}, \qquad \delta\Gamma^A:\ \dot S_A=\dot\Sigma_A+0, \qquad \delta S_A:\ \dot\Gamma^A=-\dfrac{\partial L}{\partial S_A}\\[2ex] \dfrac{\partial L}{\partial S_A}\dot S_A=\Big\langle F^{\mathrm{fr}(A)},\dot q\Big\rangle+\displaystyle\sum_{B=1}^N\kappa_{AB}\left(\dfrac{\partial L}{\partial S_B}-\dfrac{\partial L}{\partial S_A}\right)-P_H^{\mathrm{ext}\to\mathrm{A}},\ \ \forall\ A,\end{cases}$$

2. Geometric structure of the variational formulation

• In thermodynamics the phenomenological constraint is nonlinear.

Example: for simple systems given by

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

with associated variational constraint:

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

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

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

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

- 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]).

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

- Variational 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

$$C_V(q,v) := C_V \cap (\{(q,v)\} \times T_qQ) \quad \text{are vector subspace of same dimensions}$$

- Principe of virtual work

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

- Equations of motion

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

(1) Mechanics with linear nonholonomic constraints

$$C_K = \Delta \quad \rightsquigarrow \quad C_V = TQ \times_Q \Delta \quad \text{i.e.} \quad C_V(q,v) = \Delta(q)$$

$\rightsquigarrow$ Energy preserving

(2) Chetaev's approach:

$$C_K = \Big\{(q,v) \in TQ \mid R_K(q,\dot{q}) = 0\Big\} \;\; \rightsquigarrow \;\; C_V = \Big\{(q,v,\delta q) \mid \frac{\partial R}{\partial v}(q,v) \cdot \delta q = 0\Big\}$$

Recovers (1) if C_K linear

$\rightsquigarrow$ Not energy preserving in general

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

$$C_V \subset T(Q \times \mathbb{R}) \times_{Q \times \mathbb{R}} T(Q \times \mathbb{R}) \;\; \rightsquigarrow \;\; C_K \subset T(Q \times \mathbb{R})$$

Converse to Chetaev!!

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

$\rightsquigarrow$ Energy preserving (First Law).

3. Dirac structures in nonequilibrium thermodynamics

3.1 Dirac structures Dorfman [1987], Courant and Weinstein [1988], Courant [1990]

An (almost) Dirac structure on a manifold M is a vector subbundle $D \subset TM \oplus T^*M$ such that $D = D^\perp$, where $D^\perp$ is the orthogonal of D relative to the natural pairing

$$\langle\langle (u, \alpha), (v, \beta) \rangle\rangle = \langle \beta, u \rangle + \langle \alpha, v \rangle$$

Standard examples: graph of a 2-form ω or a 2-vector field Λ:

$$D_\omega = \{(X, \mathbf{i}_X \omega) \mid X \in TM\} \quad \text{and} \quad D_\Lambda = \{(\mathbf{i}_\alpha \Lambda, \alpha) \mid \alpha \in T^*M\}.$$

Integrability: Courant [1990], Dorfman [1993]

$\Leftrightarrow$ D satisfies the condition

$$[\Gamma(D), \Gamma(D)] \subset \Gamma(D).$$

relative to the bracket on $\Gamma(TM \oplus T^*M)$:

$$[(X_1, \alpha_1), (X_2, \alpha_2)] := ([X_1, X_2], \mathcal{L}_{X_1}\alpha_2 - \mathcal{L}_{X_2}\alpha_1 + \mathbf{d}\langle \alpha_1, X_2 \rangle) \quad (\Rightarrow \omega \text{ closed}, \Lambda \text{ Poisson})$$

$\Leftrightarrow$ D satisfies the condition

$$\langle \mathcal{L}_{X_1}\alpha_2, X_3 \rangle + \langle \mathcal{L}_{X_2}\alpha_3, X_1 \rangle + \langle \mathcal{L}_{X_3}\alpha_1, X_2 \rangle = 0, \quad \text{for all} \quad (X_i, \alpha_i) \in \Gamma(D)$$

$\Leftrightarrow$ $(D, \mathrm{pr}_1|_D, [\,,\,])$ is a Lie algebroid $\Rightarrow$ $\mathrm{pr}_1(D)$ generates a presymplectic singular foliation.

3.2 Dirac structures in nonholonomic mechanics

- Application to nonholonomic systems and circuits from a Hamiltonian point of view: van der Schaft and Maschke [1995]; Bloch and Crouch [1997]
- Lagrangian side and relation with variational structures: Yoshimura Marsden [2006]

Nonholonomic mechanics: distribution $\Delta_Q \subset TQ$ (e.g. rolling constraint).

$\rightsquigarrow$ need a Dirac structure on T^*Q $\rightsquigarrow$ lifted distribution on T^*Q:

$$\Delta_{T^*Q} := (T\pi_Q)^{-1}(\Delta_Q) \subset T(T^*Q), \quad \pi_Q : T^*Q \to Q$$

Locally: $\Delta_{T^*Q} \cong \left\{ v_{(q,p)} = (q, p, \dot{q}, \dot{p}) \mid \dot{q} \in \Delta(q) \right\}$

$\rightsquigarrow$ induced Dirac structure D_{Δ_Q} on T^*Q:

$$D_{\Delta_Q}(p_q) = \{(v_{p_q}, \alpha_{p_q}) \in T_{p_q}T^*Q \times T^*_{p_q}T^*Q \mid v_{p_q} \in \Delta_{T^*Q}(p_q), \text{ and } \alpha_{p_q}(w_{p_q}) = \Omega_{T^*Q}(p_q)(v_{p_q}, w_{p_q}) \text{ for all } w_{p_q} \in \Delta_{T^*Q}(p_q)\}.$$

Locally:
$D_{\Delta_Q}(q,p) = \{((q,p,\dot{q},\dot{p}),(q,p,\alpha,u)) \mid \dot{q} \in \Delta(q),\ u = \dot{q}, \text{ and } \alpha + \dot{p} \in \Delta(q)^\circ\}$.

Integrability: D_{Δ_Q} integrable if and only if Δ_Q is holonomic.

3.3 Dirac dynamical systems

Yoshimura & Marsden [2006]

Q configuration manifold of the mechanical system; $\Delta_Q \subset TQ$ distribution constraint;

– $L : TQ \to \mathbb{R}$ Lagrangian;

– $E : P = TQ \oplus T^*Q \to \mathbb{R}$ generalized energy; $E(q,v,p) := \langle p, v\rangle - L(q,v)$

– If L hyperregular: $H : T^*Q \to \mathbb{R}$; $H(q,p) = \langle p, v(q,p)\rangle - L(q, v(q,p))$

$$\Delta_Q \quad \rightsquigarrow \quad D_{\Delta_{T^*Q}} \subset T(T^*Q) \oplus T^*(T^*Q) \quad \text{and} \quad D_{\Delta_P} \subset TP \oplus T^*P$$

■ Lagrange-Dirac system: $((\dot q(t), \dot p(t)), \mathbf{d}_D L(q(t), v(t))) \in D_{\Delta_{T^*Q}}(q(t), p(t))$,

where $\mathbf{d}_D L : TQ \to T^*(T^*Q)$, $\mathbf{d}_D L(q,v) := \left(q, \frac{\partial L}{\partial v}, -\frac{\partial L}{\partial q}, v\right)$

■ Dirac system on P: $((\dot q(t), \dot v(t), \dot p(t)), \mathbf{d}E(q(t), v(t), p(t))) \in D_{\Delta_P}(q(t), v(t), p(t))$,

■ Hamilton-Dirac system: $((\dot q(t), \dot p(t)), \mathbf{d}H(q(t), p(t))) \in D_{\Delta_{T^*Q}}(q(t), p(t))$.

- All these systems are implicit differential-algebraic equations which imply the Lagrange-d'Alembert equations for nonholonomic mechanics;
- We shall show similar Dirac formulations of thermodynamics at two levels: "mechanical" and "thermodynamical" symplectic forms.

NEXT STEPS (FGB & Yoshimura [2017])

(I) A general class of constraints of thermodynamic type
($C_V \subset T\mathcal{Q} \times_{\mathcal{Q}} T\mathcal{Q} \rightsquigarrow C_K \subset T\mathcal{Q}$, converse to Chetaev)

(II) Dirac formulations for this general class

(III) Application to thermodynamics:
$\mathcal{Q} = Q \times \mathbb{R}$;
$C_V =$ "variational constraint of thermodynamics";
$\Omega_{T^*\mathcal{Q}} = dq^i \wedge dp_i + dS \wedge d\Lambda$: "thermodynamical" symplectic form

(IV) Dirac formulations based on the "mechanical" symplectic form
$\Omega_{T^*Q} = dq^i \wedge dp_i$

Geometric structures in thermodynamics:

• Equilibrium thermodynamics: mainly studied via contact geometry, following Gibbs [1873a,b] and Carathéodory [1909], by Hermann [1973], Mrugala [1978, 1980], Mrugala, Nulton, Schon, and Salamon [1991].
Contact manifold = thermodynamic phase space
Contact form = Gibbs form, $\theta = dx_0 - p_i dx^i$, x_0 energy, (x^i, p_i) conjugated ext./int. variables.
Thermodynamic properties are encoded by Legendre submanifolds.

• Step towards a geometric formulation of irreversible processes: Eberard, Maschke, and van der Schaft [2007], Favache, Dochain, Maschke [2010], ... by lifting port Hamiltonian systems to the thermodynamic phase space.
Underlying geometric structure: contact form.

3.4 Nonlinear constraints of thermodynamic type

Definition (Constraints of thermodynamic type)

Constraints $C_V \subset TQ \times_Q TQ$ and $C_K \subset TQ$ such that

$$C_K := \{(q,v) \in TQ \mid (q,v) \in C_V(q,v)\}$$

Associated Lagrange-d'Alembert equations:

$$(q(t),\dot{q}(t)) \in C_V(q(t),\dot{q}(t)) \quad \text{and} \quad \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} \in C_V(q(t),\dot{q}(t))^\circ,$$

3.5 Induced distribution

$$C_V \subset TQ \times_Q TQ \qquad \rightsquigarrow \qquad \Delta_{\mathcal{P}} \quad \text{on} \quad \mathcal{P} = TQ \oplus T^*Q$$

$$\Delta_{\mathcal{P}}(q,v,p) := \left(T_{(q,v,p)}\pi_{(\mathcal{P},Q)}\right)^{-1}(C_V(q,v)) \subset T_{(q,v,p)}\mathcal{P}, \quad \text{for all } (q,v,p) \in \mathcal{P}.$$

Locally:

$$\Delta_{\mathcal{P}}(q,v,p) = \left\{(q,v,p,\delta q,\delta v,\delta p) \in T_{(q,v,p)}\mathcal{P} \mid (q,\delta q) \in C_V(q,v)\right\}.$$

3.6 Induced Dirac structure

- Presymplectic form $\omega_{\mathcal{P}} := \pi^*_{(\mathcal{P},T^*\mathcal{Q})}\Omega_{T^*\mathcal{Q}}$ on $\mathcal{P}$ induced from $\Omega_{T^*\mathcal{Q}}$ on $T^*\mathcal{Q}$ by $\pi_{(\mathcal{P},T^*\mathcal{Q})} : \mathcal{P} \to T^*\mathcal{Q}$.
- Distribution $\Delta_{\mathcal{P}} \subset T\mathcal{P}$

$\rightsquigarrow$ induced Dirac structure

$$D_{\Delta_{\mathcal{P}}}(x) := \Big\{(v_x, \alpha_x) \in T_x\mathcal{P} \times T^*_x\mathcal{P} \;\Big|\; v_x \in \Delta_{\mathcal{P}}(x) \text{ and } \\ \langle \alpha_x, w_x\rangle = \omega_{\mathcal{P}}(x)(v_x, w_x) \;\text{ for all }\; w_x \in \Delta_{\mathcal{P}}(x)\Big\},$$

3.7 Dirac formulation on the Pontryagin bundle

Lagrangian $L : T\mathcal{Q} \to \mathbb{R}$;

Generalized energy $\mathcal{E} : \mathcal{P} \to \mathbb{R}$, $\mathcal{E}(q, v, p) := \langle p, v\rangle - L(q, v)$.

Dirac system: $\big((q, v, p, \dot{q}, \dot{v}, \dot{p}), \mathbf{d}\mathcal{E}(q, v, p)\big) \in D_{\Delta_{\mathcal{P}}}(q, v, p)$ is equivalent to

$$(q, \dot{q}) \in C_V(q, v), \quad p - \frac{\partial L}{\partial v} = 0, \quad v = \dot{q}, \quad \dot{p} - \frac{\partial L}{\partial q} \in C_V(q, v)^\circ.$$

3.8 Case of thermodynamics of simple systems

– Given are

$$L = L(q, v, S) : TQ \times \mathbb{R} \to \mathbb{R} \quad \text{and} \quad F^{\rm fr} : TQ \times \mathbb{R} \to T^*Q.$$

– Choose:

$$\mathcal{Q} := Q \times \mathbb{R} \ni (q, S)$$

$$C_V := \left\{ (q, S, v, W, \delta q, \delta S) \in T\mathcal{Q} \times_{\mathcal{Q}} T\mathcal{Q} \;\middle|\; \frac{\partial L}{\partial S}(q, v, S)\delta S = \left\langle F^{\rm fr}(q, v, S), \delta q \right\rangle \right\},$$

(codimension one submanifold)

– Determine: C_K from C_V as above:

$$C_K = \left\{ (q, S, v, W) \in T\mathcal{Q} \;\middle|\; \frac{\partial L}{\partial S}(q, v, S)W = \left\langle F^{\rm fr}(q, v, S), v \right\rangle \right\},$$

$\rightsquigarrow$ gives the phenomenological constraint for simple systems: OK!!

Theorem (Dirac formulation of the thermodynamics of simple systems)

Consider a simple system with $L = L(q, v, S) : TQ \times \mathbb{R} \to \mathbb{R}$ *and* $F^{\rm fr} : TQ \times \mathbb{R} \to T^*Q$. *Then the following statements are equivalent:*

- $x(t) := (q(t), S(t), v(t), W(t), p(t), \Lambda(t)) \in \mathcal{P}$ *satisfies the Dirac dynamical system*

$$\big((x, \dot{x}), \mathbf{d}\mathcal{E}(x)\big) \in D_{\Delta_{\mathcal{P}}}(x).$$

- $x(t) := \big(q(t), S(t), v(t), W(t), p(t), \Lambda(t)\big) \in \mathcal{P}$ *satisfies*

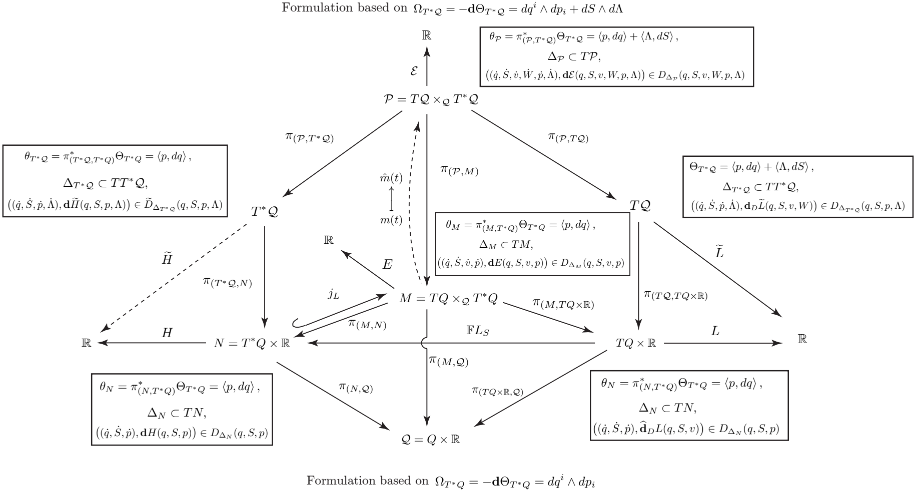
$$\left\{ \begin{array}{l} \left(\dot{p}(t) - \dfrac{\partial L}{\partial q}(q(t), v(t), S(t))\right) \dfrac{\partial L}{\partial S}(q(t), v(t), S(t)) \\ \qquad = -\left(\dot{\Lambda}(t) - \dfrac{\partial L}{\partial S}(q(t), v(t), S(t))\right) F^{\rm fr}(q(t), v(t), S(t)), \\ \dfrac{\partial L}{\partial S}(q(t), v(t), S(t))\dot{S}(t) = \left\langle F^{\rm fr}(q(t), v(t), S(t)), \dot{q}(t) \right\rangle, \\ p(t) = \dfrac{\partial L}{\partial v}(q(t), v(t), S(t)), \quad \Lambda(t) = 0, \quad v(t) = \dot{q}(t), \quad W(t) = \dot{S}(t). \end{array} \right. \tag{1}$$

Moreover, system (1) *implies the evolution equations for the thermodynamics of simple systems*

$$\left\{ \begin{array}{l} \dfrac{d}{dt}\dfrac{\partial L}{\partial \dot{q}}(q(t), \dot{q}(t), S(t)) - \dfrac{\partial L}{\partial q}(q(t), \dot{q}(t), S(t)) = F^{\rm fr}(q(t), \dot{q}(t), S(t)), \\ \dfrac{\partial L}{\partial S}(q(t), \dot{q}(t), S(t))\dot{S}(t) = \left\langle F^{\rm fr}(q(t), \dot{q}(t), S(t)), \dot{q}(t) \right\rangle \end{array} \right.$$

3.9 Other Dirac formulations of nonequilibrium thermodynamic

(FGB & Yoshimura [2017])



INTERMEDIATE SUMMARY

- Finite dimensional thermodynamical systems: simple and non-simple systems;
- Fundamental examples: piston problem, membrane transport, chemical reactions;
- Variational formulation for simple systems:
  inclusion of matter transport & chemical reactions
  $\rightsquigarrow$ thermodynamic displacements W^A and ν^a.
- Variational formulation for (non-simple) simple systems:
  inclusion of heat conduction $\rightsquigarrow$ thermal displacement Γ^A.
- Constraints set in thermodynamics: $C_V \rightsquigarrow C_K$ (converse to Chetaev)
- Underlying geometric objects: Dirac structures:

$$C_V \subset TQ \oplus_Q T^*Q \quad \rightsquigarrow \quad \Delta_{\mathcal{P}} \subset T\mathcal{P} \quad \rightsquigarrow \quad D_{\Delta_{\mathcal{P}}} \subset T\mathcal{P} \oplus T^*\mathcal{P}$$

$$\big((x, \dot{x}), \mathbf{d}\mathcal{E}(x)\big) \in D_{\Delta_{\mathcal{P}}}(x), \quad x = (q, S, v, W, p, \Lambda) \in \mathcal{P}$$

4.1 Geometry of continuum mechanics (e.g. Marsden & Hughes [1983])

- 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: $\varphi(t) \in \text{Emb}(\mathcal{B}, \mathcal{S})$

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

- Reference fields: $\rho_{\rm ref}(X)$, $S_{\rm ref}(X)$, $G_{\rm ref}(X)$, and others

- Spatial fields: $g(x)$, ...

- Lagrangian: $L : T\,\text{Emb}(\mathcal{B}, \mathcal{S}) \to \mathbb{R}$, general form

$$\begin{aligned} L(\varphi, \dot\varphi) &= \int_{\mathcal{B}} \mathfrak{L}(\varphi, \dot\varphi, D\varphi)\mu_{G_{\rm ref}} \\ &= \int_{\mathcal{B}} \left[\frac{1}{2}\rho_{\rm ref}|\dot\varphi|^2_g \mu_{G_{\rm ref}} - \text{E}(D\varphi, \rho_{\rm ref}, S_{\rm ref}, G_{\rm ref})\mu_{G_{\rm ref}} - \rho_{\rm ref}\mathcal{V}(\varphi) \right] \mu_{G_{\rm ref}} \end{aligned}$$

- Boundary conditions:

I) free boundary

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

4.2 Hamilton's principle in reversible continuum mechanics

- Equations of motion: Hamilton's principle

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

$$\rightsquigarrow \rho_{\mathrm{ref}} \frac{D\dot{\varphi}}{Dt} = \mathrm{DIV}\, \mathbf{P}^{\mathrm{cons}} + \rho_{\mathrm{ref}} \mathbf{B}^{\mathrm{cons}},$$

$$\mathbf{P}^{\mathrm{cons}} := \left(\frac{\partial \mathrm{E}}{\partial D\varphi} \right)^{\sharp_g} : \text{Piola-Kirchhoff stress tensor}$$

$$\mathbf{B}^{\mathrm{cons}} := -(\mathbf{d}\mathcal{V} \circ \varphi)^{\sharp_g} : \text{material body forces}$$

- $\mathbf{P}(X) : T^*_X\mathcal{B} \times T^*_x\mathcal{S} \to \mathbb{R}$ a two-point tensor field;
- $\mathrm{DIV}\, P^a = P^{aA}{}_{|A} = P^A{}_{a,A} + P^L{}_a \Gamma^A_{LA} - P^A{}_l \gamma^l_{an} \varphi^n{}_{,A}$, relative to G_{ref} and g
- D/Dt relative to g.

- Boundary conditions:

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

- Spatial representation:

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

$$\rho := \varphi_* \rho_{\rm ref} \ \text{ mass density}$$

$$b := \varphi_* (G^\sharp_{\rm ref}) \ \text{ Finger deformation tensor}$$

$$s := \varphi_* S_{\rm ref} \ \text{ spatial entropy}$$

$\rightsquigarrow$ spatial Lagrangian

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

- Equations of motion

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

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

Variational principles: Holm, Marsden & Ratiu [1998]

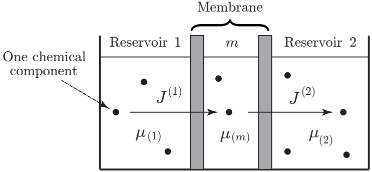
Free boundary & nonlinear elasticity: FGB, Marsden & Ratiu [2013]

5. Viscous and heat conducting multicomponent reacting fluid

A fluid of K chemical components subject to the irreversible processes of:

- Viscosity
- Heat conduction
- Diffusion
- Chemical reactions

$\leadsto$ Extend the approach developed for matter transport and chemical reactions:



and $\sum_A \nu'^a_A A \underset{a_{(2)}}{\overset{a_{(1)}}{\rightleftarrows}} \sum_A \nu''^a_A A$

$\leadsto$ Define the thermodynamic displacements:

$$W^A(t,X) \text{ with } \dot{W}^A = \mu^A \quad \text{and} \quad \nu^a(t,X) \text{ with } \dot{\nu}^a = \mathcal{A}^a$$

- Lagrangian: $L : T\,\mathrm{Emb}(\mathcal{B},\mathcal{S}) \times \mathcal{F}(\mathcal{B})^N \times \mathcal{F}(\mathcal{B}) \to \mathbb{R}$, general form

$$L(\varphi,\dot\varphi,\varrho_A,S) = \int_{\mathcal{B}} \left[\frac{1}{2}\varrho|\dot\varphi|^2\mu_{G_{\rm ref}} - \mathrm{E}(D\varphi,\varrho_A,S)\mu_{G_{\rm ref}}\right], \quad \varrho_A\text{: mass density of } A$$

- Variational principle:

$$\delta\int_{t_1}^{t_2}\left(L(\varphi,\dot\varphi,\varrho_A,S) + \int_{\mathcal{B}}\varrho_A\dot W^A\mu_{G_{\rm ref}} + \int_{\mathcal{B}}(S-\Sigma)\dot\Gamma\mu_{G_{\rm ref}}\right)dt = 0$$

Phenomenological constraint: analogy with the discrete case:

$\dfrac{\partial L}{\partial S_A}\dot\Sigma_A = \left\langle F^{\mathrm{fr}(A)},\dot q\right\rangle$	friction/viscosity	$\dfrac{\partial \mathfrak{L}}{\partial S}\dot\Sigma = -\,\mathbf{P}^{\rm fr} : \nabla\dot\varphi$
$+\displaystyle\sum_{B=1}^{N}(J_S^{\rm fr})_B\dot\Gamma^B$	heat conduction	$+\,\mathbf{J}_S\cdot\nabla\dot\Gamma$
$+\displaystyle\sum_{B=1}^{N}(J_A^{\rm fr})_B\dot W^B$	diffusion	$+\,\mathbf{J}_A\cdot\nabla\dot W^A$
$+\,J_a\dot\nu^a$	chemical reactions	$+\,J_a\dot\nu^a$
$-\,\varrho R$		$-\,\rho r$

Variational constraint: $\dot\square \quad \rightsquigarrow \quad \delta\square$

Theorem (Variational formulation for multicomponent reacting fluids)

The variational formulation

$$\delta \int_{t_1}^{t_2} \left[L(\varphi, \dot{\varphi}, \varrho_A, S) + \int_{\mathcal{B}} \varrho_A \dot{W}^A \mu_{G_{\rm ref}} + \int_{\mathcal{B}} (S - \Sigma)\dot{\Gamma} \mu_{G_{\rm ref}} \right] dt = 0,$$

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

$$\frac{\partial \mathfrak{L}}{\partial S}\dot{\Sigma} = -(\mathbf{P}^{\rm fr})^{\flat_g} : \nabla^g \dot{\varphi} + \mathbf{J}_S \cdot \nabla\dot{\Gamma} + \mathbf{J}_A \cdot \nabla \dot{W}^A + J_a \dot{\nu}^a - \rho_{\rm ref} R,$$

$$\frac{\partial \mathfrak{L}}{\partial S}\delta\Sigma = -(\mathbf{P}^{\rm fr})^{\flat_g} : \nabla^g \delta\varphi + \mathbf{J}_S \cdot \nabla\delta\Gamma + \mathbf{J}_A \cdot \nabla \delta W^A + J_a \delta\nu^a,$$

and $\delta\Gamma|_{\partial\mathcal{B}} = 0$, $\delta W^A|_{\partial\mathcal{B}} = 0$ *yields the multicomponent reacting fluid equations*

$$\begin{cases} \rho_{\rm ref}\dfrac{D\mathbf{V}}{Dt} = \mathrm{DIV}(\mathbf{P}^{\rm cons} + \mathbf{P}^{\rm fr}) + \rho_{\rm ref}\mathbf{B}^{\rm cons}, \quad \mathbf{V} = \dot{\varphi}, \quad \dot{\Sigma} = \dot{S} + \mathrm{DIV}\,\mathbf{J}_S \\ \dot{\varrho}_A + \mathrm{DIV}\,\varrho_A = J_a \nu_A^a \\ \mathfrak{T}(\dot{S} + \mathrm{DIV}\,\mathbf{J}_S) = (\mathbf{P}^{\rm fr})^{\flat_g} : \nabla^g \mathbf{V} - \mathbf{J}_S \cdot \nabla\mathfrak{T} - \mathbf{J}_A \cdot \nabla \Upsilon^A + J_a \Lambda^a + \rho_{\rm ref} R, \end{cases}$$

Moreover: $\delta\Gamma|_{\partial\mathcal{B}}$, $\delta W^A|_{\partial\mathcal{B}}$ *free* $\Rightarrow \mathbf{J}_S \cdot \mathbf{N}^{\flat_G}|_{\partial\mathcal{B}} = 0, \mathbf{J}_A \cdot \mathbf{N}^{\flat_G}|_{\partial\mathcal{B}=0}$.
If in addition $\rho_{\rm ref} R = 0$, *then the fluid is adiabatically closed.*

- spatial (Eulerian) representation:
reduction by symmetry of the variational formulation.

Eulerian variables:

$$\mathbf{v} = \dot{\varphi} \circ \varphi^{-1}, \quad \rho_A = \varrho_A \circ \varphi^{-1} J_\varphi^{-1}, \quad s = S \circ \varphi^{-1} J_\varphi^{-1}$$

Eulerian thermodynamic displacements:

$$\sigma = \Sigma \circ \varphi^{-1} J_\varphi^{-1}, \quad \gamma = \Gamma \circ \varphi^{-1}, \quad w^A = W^A \circ \varphi^{-1}, \quad \upsilon^a = \nu^a \circ \varphi^{-1}.$$

Eulerian thermodynamic fluxes:

$$\boldsymbol{\sigma}^{\rm fr} := \text{"}(\varphi_* \mathbf{P}^{\rm fr})\text{"} J_\varphi^{-1}, \quad \mathbf{j}_S := (\varphi_* \mathbf{J}_S) J_\varphi^{-1}, \quad \mathbf{j}_A := (\varphi_* \mathbf{J}_A) J_\varphi^{-1}, \quad j_a := J_a \circ \varphi^{-1} J_\varphi^{-1}$$

Eulerian phenomenological constraint:

$\frac{\partial \mathfrak{L}}{\partial S} \dot{\Sigma} = - \mathbf{P}^{\rm fr} : \nabla \dot{\varphi}$	viscosity	$\frac{\partial \ell}{\partial s} \bar{D}_t \sigma = - \boldsymbol{\sigma}^{\rm fr} : \nabla \mathbf{u}$
$+ \mathbf{J}_S \cdot \nabla \dot{\Gamma}$	heat conduction	$+ \mathbf{j}_s \cdot \nabla D_t \gamma$
$+ \mathbf{J}_A \cdot \nabla \dot{W}^A$	diffusion	$+ \mathbf{j}_A \cdot \nabla D_t w^A$
$+ J_a \dot{\nu}^a$	chemical reactions	$+ j_a D_t v^a$
$- \varrho R$		$- \rho r, \quad r := R \circ \varphi^{-1}$

Variational constraint: $\quad D_t \square \quad \rightsquigarrow \quad D_\delta \square$

Theorem (Eulerian version)

The variational formulation

$$\delta \int_{t_1}^{t_2} \left[\ell(\mathbf{v}, \rho_A, s) + \int_{\mathcal{S}} \rho_A D_t w^A \, \mu_g + \int_{\mathcal{S}} (s - \sigma) D_t \gamma \, \mu_g \right] dt = 0,$$

with no-slip boundary conditions $\mathbf{v}|_{\partial \mathcal{S}} = 0$*, and with phenomenological and variational constraints*

$$\begin{aligned} \delta \mathbf{v} &= \partial_t \boldsymbol{\zeta} + [\boldsymbol{\zeta}, \mathbf{v}], \\ \frac{\partial \ell}{\partial s} \bar{D}_t \sigma &= -(\boldsymbol{\sigma}^{\mathrm{fr}})^{\flat_g} : \nabla^g \mathbf{v} + \mathbf{j}_S \cdot \nabla D_t \gamma + \mathbf{j}_A \cdot \nabla D_t w^A + j_a D_t \nu^a - \rho r, \\ \frac{\partial \ell}{\partial s} \bar{D}_\delta \sigma &= -(\boldsymbol{\sigma}^{\mathrm{fr}})^{\flat_g} : \nabla^g \boldsymbol{\zeta} + \mathbf{j}_S \cdot \nabla D_\delta \gamma + \mathbf{j}_A \cdot \nabla D_\delta w^A + j_a D_\delta \nu^a, \end{aligned}$$

and $\delta \gamma|_{\partial \mathcal{S}} = 0$, $\delta w^A|_{\partial \mathcal{S}} = 0$ *yields the multicomponent reacting fluid equations*

$$\begin{cases} \rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\operatorname{grad} p + \operatorname{div} \boldsymbol{\sigma}^{\mathrm{fr}}, \quad p = \frac{\partial \varepsilon}{\partial \rho_A} \rho_A + \frac{\partial \varepsilon}{\partial s} s - \varepsilon, \\ \partial_t \rho_A + \operatorname{div}(\rho_A \mathbf{v}) + \operatorname{div} \mathbf{j}_A = j_a \nu_A^a, \\ T(\partial_t s + \operatorname{div}(s \mathbf{v}) + \operatorname{div} \mathbf{j}_S) = (\boldsymbol{\sigma}^{\mathrm{fr}})^{\flat_g} : \operatorname{Def} \mathbf{v} - \mathbf{j}_S \cdot \nabla T - \mathbf{j}_A \cdot \nabla \mu^A + j_a \mathcal{A}^a + \rho r, \end{cases}$$

- Thermodynamic phenomenology: Linear case:

thermodynamic affinities $\simeq$ thermodynamic fluxes

Positive quadratic forms & Onsager's reciprocal relations & Curie's principle.

- Vectorial processes of heat conduction (Fourier law), diffusion (Fick law) and their cross effects (Soret ($\mathcal{L}_{AS}$) and Dufour ($\mathcal{L}_{SA}$) effects):

$$-\begin{bmatrix} \mathbf{j}_S \\ \mathbf{j}_A \end{bmatrix} = \begin{bmatrix} \mathcal{L}_{SS} & \mathcal{L}_{SB} \\ \mathcal{L}_{AS} & \mathcal{L}_{AB} \end{bmatrix} \begin{bmatrix} \nabla T \\ \nabla \mu^B \end{bmatrix}$$

Mass conservation $M^A \mathbf{j}_A = 0$ imposes $M^A \mathcal{L}_{AS} = M^A \mathcal{L}_{AB} = 0$.

- Scalar processes of bulk viscosity and chemistry and their possible cross-phenomena.

$$\begin{bmatrix} \operatorname{Tr} \boldsymbol{\sigma}^{\rm fr} \\ j_a \end{bmatrix} = \begin{bmatrix} \mathcal{L}_{00} & \mathcal{L}_{0b} \\ \mathcal{L}_{a0} & \mathcal{L}_{ab} \end{bmatrix} \begin{bmatrix} \frac{1}{3} \operatorname{div} \mathbf{v} \\ \mathcal{A}^b \end{bmatrix}$$

- Tensorial process:

$$(\boldsymbol{\sigma}^{\rm fr})^{(0)} = 2\mu (\operatorname{Def} \mathbf{v}^{\sharp_g})^{(0)}$$

The associated friction stress reads

$$\boldsymbol{\sigma}^{\rm fr} = 2\mu \operatorname{Def} \mathbf{v} + \left(\frac{1}{9} \mathcal{L}_{00} - \frac{2}{3}\mu \right) (\operatorname{div} \mathbf{v}) g^\sharp + \frac{1}{3} \mathcal{L}_{0b} \mathcal{A}^b g^\sharp,$$

$\mu \geq 0$ first coefficient of viscosity (shear viscosity);

$\zeta := \frac{1}{9}\mathcal{L}_{00} \geq 0$ second coeff. of viscosity (bulk viscosity, notoriously difficult to measure!)

Conclusion I

- We established a variational derivation of the nonequilibrium thermodynamics of discrete and continuum systems.
  (Macroscopic description!!!)
- Extension of Hamilton's principle to incorporate irreversible processes (viscosity, heat conduction, diffusion, chemical reaction, phase changes, ...)
- For continuum systems: analogy with discrete systems $\rightsquigarrow$ work in Lagrangian description
  Eulerian formulation is obtained by reduction by symmetry
- How does it work?
  given thermodynamic fluxes J_α and thermodynamic affinities X^α
  1) Define the thermodynamic displacements: Λ^α, with $\dot{\Lambda}^\alpha = X^\alpha$
  2) Compute the critical points w.r.t. constraints (C_K and C_V)

$$\frac{\partial L}{\partial S}\dot{\Sigma} = \sum_\alpha J_\alpha \dot{\Lambda}^\alpha + P^{\mathrm{ext}}, \qquad \frac{\partial L}{\partial S}\delta\Sigma = \sum_\alpha J_\alpha \delta\Lambda^\alpha$$

  3) Get the complete set of evolution equations (mechanical equations, reaction-diffusion, thermal equations, ...)

Conclusion II

- Can we use temperature as the independent variable in the variational formulation?
  $\rightsquigarrow$ Yes: Free energy Lagrangian formulation (FGB & Yoshimura [2017])
- Is there a geometric object underlying this variational formulation?
  $\rightsquigarrow$ Yes: Dirac structures (based on the "mechanical" or "thermodynamical" symplectic form)
- Does it allow for the development of a reduction theory in thermodynamics?
  $\rightsquigarrow$ Yes: such reduction extends the various Lagrangian reduction processes used in classical mechanics
- Does it allow for the development of a variational numerical integrators in thermodynamics?
  $\rightsquigarrow$ Yes: in development (FGB & Yoshimura [2017]).
- Useful for modelling?
  $\rightsquigarrow$ Yes: e.g., meteorological applications: consistent inclusion of irreversible processes in the various approximations of atmospheric dynamics (FGB [2017]).

Thank you

6.1 Atmospheric circulation dynamics

Atmosphere of Earth = 1) dry air (ideal gas)

2) water in three phases:

– vapor

– liquid: in suspension (clouds) & precipitating

– solid: in suspension (clouds) & precipitating

3) aerosols: solid and liquid particles in suspension (other than water)

Earth atmosphere = multicomponent and multiphase fluid with the irreversible processes of:

- Precipitation
- Phase changes
- Chemical reactions
- Viscosity
- Heat conduction
- Diffusion

In absence of precipitation, ice phase, and aerosols
ρ_d (dry air), ρ_v (vapor), and ρ_c (couds)

Continuity equations:

$$\partial_t \rho_d + \operatorname{div}(\rho_d \mathbf{v} + \mathbf{j}_d) = 0, \quad \partial_t \rho_v + \operatorname{div}(\rho_v \mathbf{v} + \mathbf{j}_v) = j_v, \quad \partial_t \rho_c + \operatorname{div}(\rho_c \mathbf{v}) = j_c,$$

with $\mathbf{j}_d + \mathbf{j}_v = 0$ and $j_v + j_c = 0$
($j_v + j_c \neq 0$ if the precipitating component is considered).
($j_v < 0$: $v \to c$, $\quad j_v > 0$: $c \to v$)

6.2 Variational formulation - Lagrangian description

Variational condition:

$$\delta \int_0^T \int_{\mathcal{D}} \Big(\mathfrak{L} + \sum_{k=d,v,c} \varrho_k \dot{W}_k + (S - \Sigma)\dot{\Gamma} \Big) \mu_{G_{\rm ref}} \, dt = 0,$$

subject to the *phenomenological constraint*

$$\frac{\partial \mathfrak{L}}{\partial S} \dot{\Sigma} = -\mathbf{P}^{\rm fr} : \nabla \dot{\varphi} + \mathbf{J}_S \cdot \nabla \dot{\Gamma} + \sum_{k=d,v,c} (\mathbf{J}_k \cdot \nabla \dot{W}_k + J_k \dot{W}_k)$$

and with respect to variations $\delta\varphi$, δS, $\delta\Sigma$, $\delta\Gamma$ subject to the *variational constraint*

$$\frac{\partial \mathfrak{L}}{\partial S} \delta\Sigma = -\mathbf{P}^{\rm fr} : \nabla \delta\varphi + \mathbf{J}_S \cdot \nabla \delta\Gamma + \sum_{k=d,v,c} (\mathbf{J}_k \cdot \nabla \delta W_k + J_k \delta W_k)$$

and with $\delta\varphi(t_i) = \delta\Gamma(t_i) = \delta W_k(t_i) = 0$, $i = 1, 2$.

6.3 Variational formulation - Eulerian description

Variational condition:

$$\delta \int_0^T \int_{\mathcal{D}} \big(\ell + \rho_d D_t w_d + \rho_v D_t w_v + \rho_c D_t w_c + (s-\sigma) D_t \gamma\big)\mu_g \, dt = 0,$$

subject to the *phenomenological constraint*

$$\frac{\partial \mathcal{L}}{\partial s} \bar{D}_t \sigma = -\boldsymbol{\sigma}^{\mathrm{fr}} : \nabla \mathbf{v} + \mathbf{j}_s \cdot \nabla D_t \gamma + \sum_{k=d,v,c} (\mathbf{j}_k \cdot \nabla D_t w_k + j_k D_t w_k)$$

and *variational constraint*

$$\frac{\partial \mathcal{L}}{\partial s} \bar{D}_\delta \sigma = -\boldsymbol{\sigma}^{\mathrm{fr}} : \nabla \boldsymbol{\zeta} + \mathbf{j}_s \cdot \nabla D_\delta \gamma + \sum_{k=d,v,c} (\mathbf{j}_k \cdot \nabla D_\delta w_k + j_k D_\delta w_k)$$

Note: • specific internal energy of moist air:

$$\begin{aligned} u &= q_d C_{vd} T + q_v (L(T) - R_v T) + (q_v + q_c) C_l T \\ &= q_d C_{vd} T + q_v (C_{vv} T + L_{00}) + q_c C_l T, \qquad q_k = \frac{\rho_k}{\rho} \end{aligned}$$

• specific latent heat of vaporization:

$$L(T) = L_v(T_0) + (C_{pv} - C_l)(T - T_0) = L_{00} + (C_{pv} - C_l) T$$

• specific heat capacities: C_{vk}, C_{pk}.

6.4 Thermodynamic phenomenology

Internal entropy production:

$$I = \frac{1}{T}\Big(\boldsymbol{\sigma}^{\rm fr} : \nabla \mathbf{v} - \mathbf{j}_s \cdot \nabla T - \sum_{k=d,v,c} (\mathbf{j}_k \cdot \nabla \frac{\mu_k}{m_k} + j_k \frac{\mu_k}{m_k})\Big).$$

- vectorial and scalar processes:

$$-\begin{bmatrix} \mathbf{j}_s \\ \mathbf{j}_d \\ \mathbf{j}_v \\ \mathbf{j}_c \end{bmatrix} = \begin{bmatrix} L_{ss} & L_{sd} & \cdots \\ L_{ds} & L_{dd} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \nabla T \\ \nabla \frac{\mu_d}{m_d} \\ \nabla \frac{\mu_v}{m_v} \\ \nabla \frac{\mu_c}{m_c} \end{bmatrix}, \qquad \begin{bmatrix} \operatorname{Tr} \boldsymbol{\sigma}^{\rm fr} \\ -j_d \\ -j_v \\ -j_c \end{bmatrix} = \begin{bmatrix} \mathcal{L}_{00} & \mathcal{L}_{0d} & \cdots \\ \mathcal{L}_{d0} & \mathcal{L}_{dd} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \frac{1}{3}\operatorname{div} \mathbf{v} \\ \frac{\mu_d}{m_d} \\ \frac{\mu_v}{m_v} \\ \frac{\mu_c}{m_c} \end{bmatrix}$$

- tensorial process: $(\boldsymbol{\sigma}^{\rm fr})^{(0)} = 2\mu(\operatorname{Def} \mathbf{v})^{(0)}$.

6.5 Explaining entropy production considered in meteorology

Vectorial processes usually expressed in terms of:

- sensible heat flux $\mathbf{j}_s^h = T\big(\mathbf{j}_s - \sum_k \eta_k \mathbf{j}_k\big)$;
- thermodynamic forces $\frac{\nabla T}{T}$ and $(\nabla \frac{\mu_k}{m_k})_T$

$$\rightsquigarrow \quad -\mathbf{j}_s^h \cdot \frac{1}{T}\nabla T - \sum_{k=d,v,c} \mathbf{j}_k \cdot \left(\nabla \frac{\mu_k}{m_k}\right)_T,$$

Define the positive definite matrix

$$\mathsf{A} = \mathsf{M}\mathsf{L}\mathsf{M}^T, \quad \text{for} \quad \mathsf{M} = \begin{bmatrix} T & -T\eta_d & -T\eta_v & -T\eta_c \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$

Then

$$\rightsquigarrow - \begin{bmatrix} \mathbf{j}_s^h \\ \mathbf{j}_d \\ \mathbf{j}_v \\ \mathbf{j}_c \end{bmatrix} = \begin{bmatrix} A_{ss} & A_{sd} & \cdots \\ A_{ds} & A_{dd} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \frac{\nabla T}{T} \\ (\nabla \frac{\mu_d}{m_d})_T \\ (\nabla \frac{\mu_v}{m_v})_T \\ (\nabla \frac{\mu_c}{m_c})_T \end{bmatrix}.$$

Assume $\mathbf{j}_c = 0$, $j_d = 0$, and hence $\mathbf{j}_d + \mathbf{j}_v = 0$ and $j_v + j_c = 0$

$$\rightsquigarrow I = \frac{1}{T}\left(\boldsymbol{\sigma}^{\mathrm{fr}} : \nabla \mathbf{v} - \mathbf{j}_s^h \cdot \frac{1}{T}\nabla T - \mathbf{j}_v \cdot \nabla\left(\frac{\mu_v}{m_v} - \frac{\mu_d}{m_d}\right)_T - j_v\left(\frac{\mu_v}{m_v} - \frac{\mu_c}{m_c}\right)\right)$$

$\rightsquigarrow$ parameterization of the vectorial and scalar processes is of the form

$$-\begin{bmatrix} \mathbf{j}_s^h \\ \mathbf{j}_v \end{bmatrix} = \begin{bmatrix} A_{ss} & A_{sv} \\ A_{vs} & A_{vv} \end{bmatrix} \begin{bmatrix} \nabla T / T \\ \nabla\left(\frac{\mu_v}{m_v} - \frac{\mu_d}{m_d}\right)_T \end{bmatrix}, \quad \begin{bmatrix} \operatorname{Tr} \boldsymbol{\sigma}^{\mathrm{fr}} \\ -j_v \end{bmatrix} = \begin{bmatrix} \mathcal{L}_{00} & \mathcal{L}_{0v} \\ \mathcal{L}_{v0} & \mathcal{L}_{vv} \end{bmatrix} \begin{bmatrix} \frac{1}{3} \operatorname{div} \mathbf{v} \\ \frac{\mu_v}{m_v} - \frac{\mu_c}{m_c} \end{bmatrix},$$

where $A_{sv} = A_{vs}$ and $\mathcal{L}_{0v} = -\mathcal{L}_{v0}$.

- First phenomenological relation: processes of diffusion, heat conduction and thermo-diffusion;
- Second phenomenological relation: coupling of viscous processes and phase changes.

Case of moist air: we compute explicitly in terms of (p, T, q_d, q_v, q_c):

$$\nabla\left(\frac{\mu_v}{m_v} - \frac{\mu_d}{m_d}\right)_T = T\left(R_v \frac{\nabla p_v}{p_v} - R_d \frac{\nabla p_d}{p_d}\right) \quad \text{and} \quad \frac{\mu_v}{m_v} - \frac{\mu_c}{m_c} = R_v T \ln \frac{p_v}{p^*(T)},$$

where $p^*(T)$ is the saturation vapor pressure:

$$p^*(T) = p_0^* \left(\frac{T}{T_0}\right)^{\frac{C_{pv} - C_l}{R_v}} \exp\left[\frac{L_{00}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

(pressure of the vapor at which it is in equilibrium with the liquid phase, at a given temperature).

$\rightsquigarrow$ for moist air, this form of entropy production recovers the one studied in Pauluis & Held [2002]

Advantage of the variational derivation:

$\rightsquigarrow$ systematic way to derive and modelize atmospheric dynamics for arbitrary state equations (non-perfect ideal gas, e.g. Venus)

$\rightsquigarrow$ appropriate formulation for consistent parameterization of irreversible process and their coupling (e.g., phase change + bulk viscosity + chemical reactions)

$\rightsquigarrow$ appropriate formulation for derivation of the effect of irreversible processes on conservation laws, such as circulation theorems

$$\frac{d}{dt}\oint_{c_t}\frac{1}{\rho}\frac{\partial\mathcal{L}}{\partial\mathbf{v}}\cdot d\mathbf{x}=\oint_{c_t}\frac{1}{\rho}\left(\sum_k\rho_k\nabla\frac{\partial\mathcal{L}}{\partial\rho_k}+s\nabla\frac{\partial\mathcal{L}}{\partial s}+\operatorname{div}\boldsymbol{\sigma}^{\mathrm{fr}}\right)\cdot d\mathbf{x}.$$