Formulation Lagrangienne de l’irréversibilité et articulation avec les symétries de Lie pour la mise en évidence de relations d’invariance en rhéologie

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A thermodynamic approach of relaxation

Basic assumption :

“The Gibbs relation is valid for situations outside equilibrium”

→ Internal energy potential $E = E(\boldsymbol{y}, \boldsymbol{z})$

$\boldsymbol{y}$: extensive controlled variables $\rightsquigarrow (s, \gamma)$

$\boldsymbol{z}$: extensive internal variables (microstructure)

→ Extensity property $\boxed{E(\lambda \boldsymbol{y}, \lambda \boldsymbol{z}) = \lambda E(\boldsymbol{y}, \boldsymbol{z})}$ (Callen)

Euler relation

$$\boxed{E = \frac{\partial E}{\partial \boldsymbol{y}} \cdot \boldsymbol{y} + \frac{\partial E}{\partial \boldsymbol{z}} \cdot \boldsymbol{z}}$$

→

$$\left\{ \begin{array}{ll} \text{Intensive observable variables} & \boldsymbol{Y} = \dfrac{\partial E}{\partial \boldsymbol{y}} \\ \text{Generalized non equilibrium forces} & \boldsymbol{A} = -\dfrac{\partial E}{\partial \boldsymbol{z}} \end{array} \right.$$

Thermodynamic framework of relaxation

$$\begin{pmatrix} \dot{\boldsymbol{Y}} \\ -\dot{\boldsymbol{A}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{a}^{\boldsymbol{u}} & \boldsymbol{b} \\ \boldsymbol{b}^{\boldsymbol{T}} & \boldsymbol{g} \end{pmatrix} \begin{pmatrix} \dot{\boldsymbol{y}} \\ \dot{\boldsymbol{z}} \end{pmatrix}$$

Thermodynamic information

$$\boldsymbol{a}^{\boldsymbol{u}} = \frac{\partial^2 E}{\partial \boldsymbol{y}^2}$$

Tisza matrix

$$\boldsymbol{g} = \frac{\partial^2 E}{\partial \boldsymbol{z}^2}$$

Dissipation matrix

$$\boldsymbol{b} = \frac{\partial^2 E}{\partial \boldsymbol{y} \partial \boldsymbol{z}}$$

Coupling matrix

$\Leftrightarrow$

Maxwell relations for E

$$\boxed{\frac{\partial^2 E}{\partial x_i \partial x_j} = \frac{\partial^2 E}{\partial x_j \partial x_i} \quad (\text{where } \boldsymbol{x} = \boldsymbol{y} \text{ or } \boldsymbol{z})}$$

$\longrightarrow$

E remains a thermodynamic potential during the evolution

Kinetic equations for the internal variables

$\boldsymbol{z}$: non controlled variables outside equilibrium
(internal reorganizations)

→ Kinetics law $\boxed{\dot{\boldsymbol{z}} = \boldsymbol{L} \cdot \boldsymbol{A}}$

$L_{ij} = L_{ji}$
(Onsager's properties)

→ Relaxed state $\boxed{-\dot{\boldsymbol{A}}^{\boldsymbol{r}} = 0}$

$$-\dot{\boldsymbol{A}} = \boldsymbol{b}^{\boldsymbol{T}} \cdot \dot{\boldsymbol{y}} + \boldsymbol{g} \cdot \dot{\boldsymbol{z}} \quad \Longrightarrow \quad \begin{cases} \dot{\boldsymbol{z}}^{r} = -\boldsymbol{g}^{-1} \cdot \boldsymbol{b}^{\boldsymbol{T}} \cdot \dot{\boldsymbol{y}} \\ \dot{\boldsymbol{z}} = -(\boldsymbol{L} \cdot \boldsymbol{g})(\boldsymbol{z} - \boldsymbol{z}^{\boldsymbol{r}}) \end{cases}$$

$\boxed{\boldsymbol{\tau} = (\boldsymbol{L} \cdot \boldsymbol{g})^{-1}}$

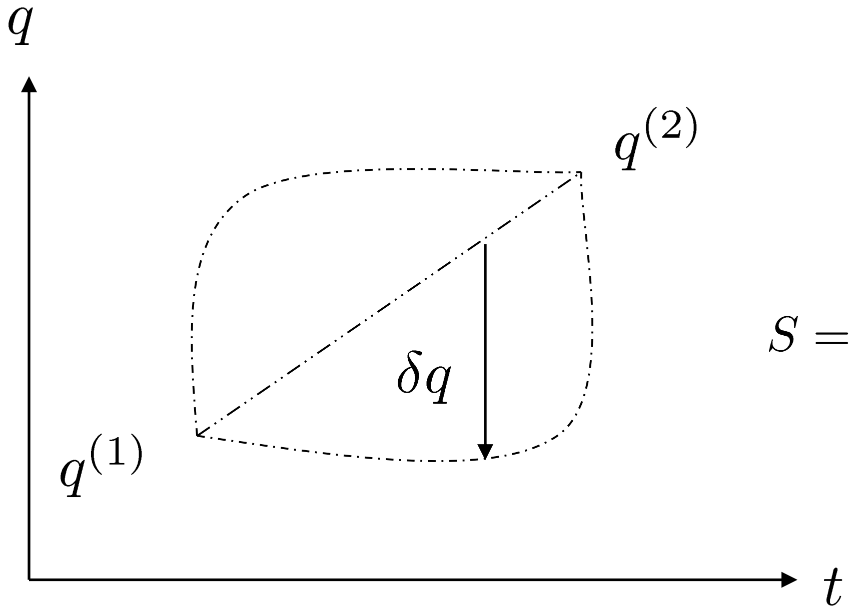
Relaxation time

→ Internal variables evolution
(kinetic information)

$$\boxed{\dot{z}_k = -\frac{z_k - z_k^r}{\tau_k}}$$

Constitutive law and least action principle

Challenge : conciliate Hamiltonian dynamics with irreversible thermodynamics



$$S = \int_{t_1}^{t^2} dt \int_{\Omega_1} L d\Omega$$

PLA : $\delta S = 0$ with respect to the variations of the d.o.f. δq_i

$L = L((q_i, \dot{q}_i, \nabla q_i, \dots), i = 1 \dots N$ Lagrange density

→ Euler-Lagrange equations (necessary conditions) :

$$-\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \nabla . \left(\frac{\partial L}{\partial \nabla q_i}\right) + \frac{\partial L}{\partial q_i} = 0$$

Least action principle: historical perspective

- Helmholz : first attempts to reduce the principle of TIP to general principles of mechanics
- Onsager (1931) : principle of least dissipation or energy, cornerstone of modern TIP
- Gyarmati : integral principle of thermodynamics → force variation at constant fluxes combined with energy balance

Lagrange densities having arguments not being of the type $\{q, \dot{q}\}$

→ Euler-Lagrange equations $-\nabla.\left(\frac{\partial L}{\partial \nabla q_i}\right) + \frac{\partial L}{\partial q_i} = 0$ truncated from their temporal dimensions

→ Non-Hamiltonian action $S = \int_{\Omega_t} L d\Omega$

Lagrangian formulation of the constitutive laws

$$\text{Constitutive law in rate form : } \mathbf{P} = \begin{cases} \boldsymbol{P}_{Y}\left(\boldsymbol{y},\boldsymbol{z}\right) = \dot{\boldsymbol{Y}} - \boldsymbol{e}_{,\mathrm{yy}}.\dot{\boldsymbol{y}} - \mathbf{e}_{,\mathrm{yz}}.\dot{\mathbf{z}} = 0 \\ \mathbf{P}_{\mathbf{A}}\left(\boldsymbol{y},\boldsymbol{z}\right) = \dot{\mathbf{A}} - \mathbf{e}_{,\mathrm{zy}}.\dot{\mathbf{y}} - \mathbf{e}_{,\mathrm{zz}}.\dot{\mathbf{z}} = 0 \end{cases}$$

Self-adjunction condition of the Frechet derivative of $\mathbf{P}$:

$$Dp = Dp^{\star} \rightarrow e_{,x_j x_i} = e_{,x_i x_j}, x \in \{\boldsymbol{y},\boldsymbol{z}\}$$

→ Maxwell conditions for internal energy satisfied due to its status of potential

→ Existence theorem of a Lagrangian [Santilli] :

$\mathbf{P}(\mathbf{u}) = \left\{\mathrm{P_i}\left(\mathbf{x},\mathbf{u}^{(\mathrm{n})}\right), \mathrm{i} = 1\ldots\mathrm{q}\right\}$ system of PDE's for the dependent variables $\mathbf{u}$.

System $\mathbf{P}(\mathbf{u}) = 0$ extremum of a functional integral $S = \displaystyle\int_{\Omega} L d\Omega$,

viz $P_i = E_i(L)$, iff $(Dp)_{ij} = (Dp^{\star})_{ij}$.

Possible Lagrangian $L = \displaystyle\int_0^1 \mathbf{u} P(\lambda\mathbf{u})\mathrm{d}\lambda = \int_0^1 \mathbf{u_i}\mathrm{P_i}(\lambda\mathbf{u})\mathrm{d}\lambda$

$$\rightarrow L = \int_0^1 \left[\mathbf{y}.\mathbf{P}_{\mathrm{Y}}\left(\lambda\mathbf{y},\lambda\mathbf{z}\right) + \mathbf{z}.\mathbf{P}_{\mathrm{A}}\left(\lambda\mathbf{y},\lambda\mathbf{z}\right)\right]$$

Lagrangian formulation of the constitutive laws (2)

Account for extensity of order -1 of second derivatives of e :

$$e_{,yy}\left(\lambda y, \lambda z\right) = \frac{e_{,yy}(y,z)}{\lambda} \qquad e_{,yz}\left(\lambda y, \lambda z\right) = \frac{e_{,yz}(y,z)}{\lambda}$$

$$e_{,zy}\left(\lambda y, \lambda z\right) = \frac{e_{,zy}(y,z)}{\lambda} \qquad e_{,zz}\left(\lambda y, \lambda z\right) = \frac{e_{,zz}(z,z)}{\lambda}$$

and extensity order 0 of the intensive variables :

$$\mathbf{Y}(\lambda\mathbf{y}, \lambda\mathbf{z}) = \mathbf{Y}(\mathbf{y}, \mathbf{z})\,;\ \mathbf{A}(\lambda\mathbf{y}, \lambda\mathbf{z}) = \mathbf{A}(\mathbf{y}, \mathbf{z})$$

$$\rightarrow L = \mathbf{y}.\dot{\mathbf{Y}} - \mathbf{z}.\dot{\mathbf{A}} + \mathbf{e}_{,\mathrm{y}}.\dot{\mathbf{y}} + \mathbf{e}_{,\mathrm{z}}.\dot{\mathbf{z}} + \frac{\mathbf{d}}{\mathbf{dt}}\left(\mathbf{e}_{,\mathrm{y}}.\mathbf{y} + \mathbf{e}_{,\mathrm{z}}.\mathbf{z}\right)$$

Equivalent Lagrangian : the Euler-Lagrange equations are nil, viz
$E_i(U) = 0, \forall i = 1 \ldots q$, iff U is the generalized divergence of a quadrivector $\mathbf{P}$:

$$Div\boldsymbol{P} = \sum_{i=1}^{4} \frac{dP_i}{dx_i} \equiv \frac{dP_t}{dt} + \frac{dP_x}{dx} + \frac{dP_y}{dy} + \frac{dP_z}{dz}$$

Lagrangian formulation of the constitutive laws (3)

→ use Gibbs-Duhem relation : $\mathbf{y}.\dot{\mathbf{Y}} - \mathbf{z}.\dot{\mathbf{A}} = 0 \Rightarrow \mathrm{L} = \mathbf{e}_{,\mathrm{y}}\dot{\mathbf{y}} + \mathbf{e}_{,\mathrm{z}}\dot{\mathbf{z}} = \dfrac{\mathrm{de}(\mathbf{y},\mathbf{z})}{\mathrm{dt}}$

→ Stationarity condition of the action integral $\delta S = \delta e = \delta \displaystyle\int_0^t \frac{de}{dt} dt = \delta \int_0^t de = 0$

Physical sense

internal energy keeps its status of a potential function during dynamic evolution.

Generalization of Poincaré lemma to functional forms [Olver, 1993] :

$$\delta\omega = \int_\Omega [d\mathbf{u} \wedge (\mathbf{D}^*_{\mathbf{P}} - \mathbf{D}_{\mathbf{P}})]\mathbf{dx}) \qquad P = \{P_i(\mathbf{x}, \mathbf{u}^{(\mathbf{n})}), \mathbf{i} = \mathbf{1}..\mathbf{q}\}$$

let one-form $\omega = \displaystyle\int_\Omega (\mathbf{P}.\mathbf{du})\mathbf{dx}$ $\qquad D_P$ Frechet derivative of $\mathbf{P}$

if ω is written in the form $\omega = \delta\psi$ with $\psi = \int_\Omega L(\mathbf{x}, \mathbf{u}^{(\mathbf{n})})\mathbf{dx}$

⟶ Get following equivalence : $\omega = \delta\psi = \delta \int_\Omega L(\mathbf{x}, \mathbf{u}^{(\mathbf{n})})\mathrm{dx} \Leftrightarrow \delta\omega = \delta\delta\psi = 0$

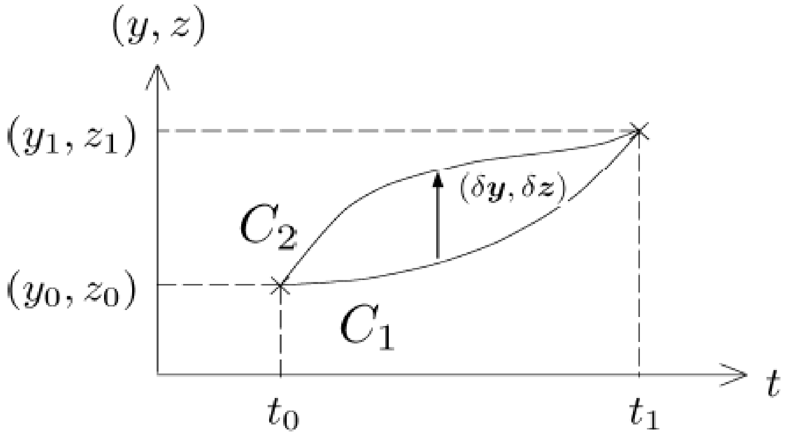
$$dd\psi = \sum_{1<i<j<q} \left(\frac{\partial^2\psi}{\partial u_i \partial u_j} - \frac{\partial^2\psi}{\partial u_j \partial u_i}\right) du_i \wedge du_j = 0 \Leftrightarrow \frac{\partial^2\psi}{\partial u_i \partial u_j} = \frac{\partial^2\psi}{\partial u_j \partial u_i}$$

⟶ Maxwell's conditions for the functional ψ

Lagrange formalism associated to the internal energy

$$\frac{\partial^2 E}{\partial x_i \partial x_j} = \frac{\partial^2 E}{\partial x_j \partial x_i}$$

(where $\boldsymbol{x} = \boldsymbol{y}$ or $\boldsymbol{z}$)



$$\int_{C_1} dE(\boldsymbol{y}, \boldsymbol{z}) = \int_{C_2} dE(\boldsymbol{y}, \boldsymbol{z})$$

$$\left\{ \begin{array}{l} \delta \displaystyle\int_{t_0}^{t_1} \dot{E} dt = 0 \\ \boxed{\text{Lagrangian} \quad L = \dot{E}} \end{array} \right.$$

$$\left. \begin{array}{l} \dfrac{\partial \dot{E}}{\partial \boldsymbol{y}} - \dfrac{d}{dt}\left(\dfrac{\partial \dot{E}}{\partial \dot{\boldsymbol{y}}}\right) = 0 \\ \dfrac{\partial \dot{E}}{\partial \boldsymbol{z}} - \dfrac{d}{dt}\left(\dfrac{\partial \dot{E}}{\partial \dot{\boldsymbol{z}}}\right) = 0 \end{array} \right\} \Leftrightarrow \begin{pmatrix} \dot{\boldsymbol{Y}} \\ -\dot{\boldsymbol{A}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{a}^u & \boldsymbol{b} \\ \boldsymbol{b}^T & \boldsymbol{g} \end{pmatrix} \begin{pmatrix} \dot{\boldsymbol{y}} \\ \dot{\boldsymbol{z}} \end{pmatrix}$$

(Euler-Lagrange equations)

Incorporation of the kinetics of internal variables

relations $\dot{z}_k = -\dfrac{z_k - z_k^r}{\tau_k}$ not contained in the lagrangian $L = \dot{\psi}$

$\longrightarrow$ considered as N constraints (N dissipative modes) $\displaystyle\int_{t_0}^{t_1} \left(\dot{z}_k + \frac{z_k - z_k^r}{\tau_k}\right) dt = 0$

$\longrightarrow$ Constrained lagrangian (lagrangian multipliers λ_k) :

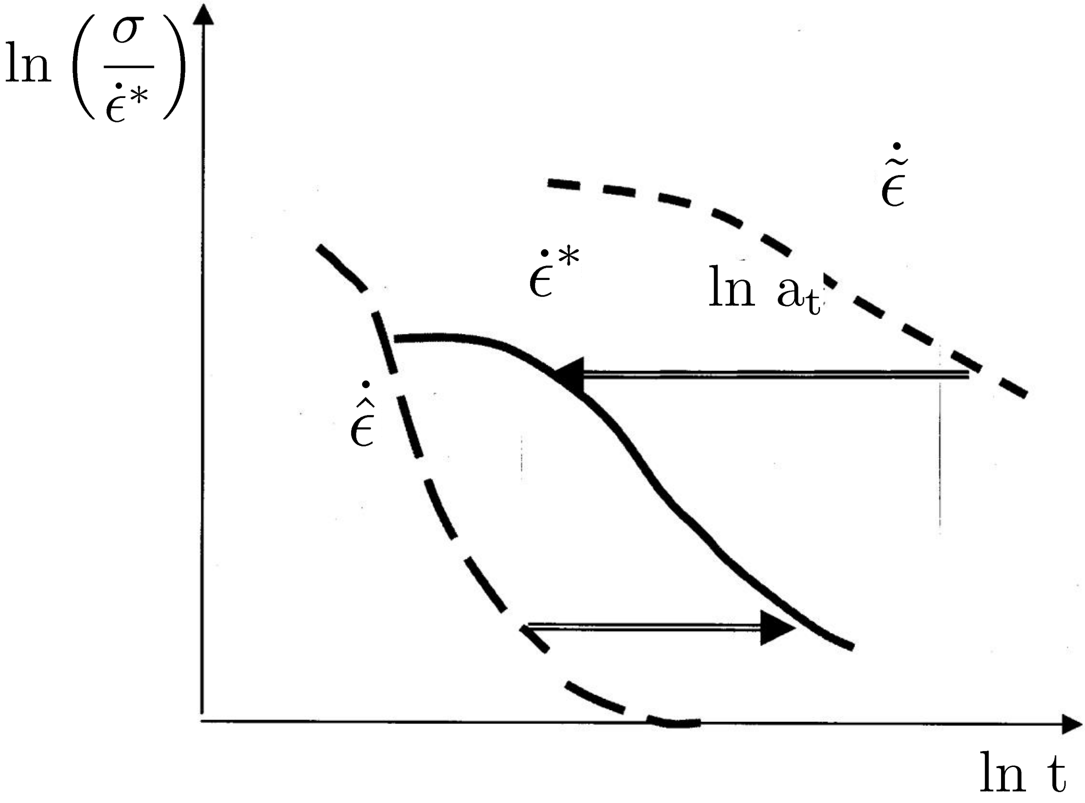
$$\underbrace{\boxed{L = \frac{\partial\psi}{\partial\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}} + \frac{\partial\psi}{\partial\boldsymbol{z}}\cdot\dot{\boldsymbol{z}}} }_{\text{Thermodynamic information}} \underbrace{\boxed{+ \sum_{k=1}^{N}\lambda_k(\dot{z}_k + \frac{z_k - z_k^r}{\tau_k})}}_{\text{Kinetic information}}$$

Stationarity condition of $S \Rightarrow$ state laws and kinetic evolution equations for the internal variables

Symmetries and master response for viscous materials

Time temperature superposition for a viscous behaviour

Isothermal stress relaxation



Shift depends on T

Will be determined later on

Master curve at strain rate $\underline{\underline{\dot{\epsilon}}}^*$ obtained by shifting (shifts a_t)

Variational symmetry condition

Invariance of the functional under a group of symmetry :

$$\int_{t_0}^{t_1} L(t,\boldsymbol{\gamma}^{(1)},\boldsymbol{z}^{(1)},\boldsymbol{\beta}^{(1)},\boldsymbol{A}^{(1)})dt = \int_{\bar{t}_0}^{\bar{t}_1} \bar{L}(\bar{t},\bar{\boldsymbol{\gamma}}^{(1)},\bar{\boldsymbol{z}}^{(1)},\bar{\boldsymbol{\beta}}^{(1)},\bar{\boldsymbol{A}}^{(1)})d\bar{t}$$

$$\boxed{\Leftrightarrow \quad pr^{(1)}\boldsymbol{v}L + LDiv\boldsymbol{\xi} = 0} \; (*)$$

First prolongation : $pr^{(1)}\boldsymbol{v} = \boldsymbol{v} + {\boldsymbol{\phi}_{\boldsymbol{\gamma}}}^t \frac{\partial}{\partial\dot{\boldsymbol{\gamma}}} + {\boldsymbol{\phi}_{\boldsymbol{z}}}^t \frac{\partial}{\partial\dot{\boldsymbol{z}}} + {\boldsymbol{\phi}_{\boldsymbol{\beta}}}^t \frac{\partial}{\partial\dot{\boldsymbol{\beta}}} + {\boldsymbol{\phi}_{\boldsymbol{A}}}^t \frac{\partial}{\partial\dot{\boldsymbol{A}}}$

$${\boldsymbol{\phi}_{\gamma}}^t = \frac{d}{dt}(\boldsymbol{\phi}_{\gamma} - \boldsymbol{\xi}\cdot\gamma) + \boldsymbol{\xi}\cdot\dot{\boldsymbol{\gamma}}$$

Find all $\boldsymbol{v}$ satisfying (*) with $L = \boldsymbol{\beta}\cdot\dot{\boldsymbol{\gamma}} - \boldsymbol{A}\cdot\dot{\boldsymbol{z}} + \sum_{k=1}^{N} \lambda_k(\dot{z}_k + \frac{z_k - z_k^r}{\tau_k})$

Variational symmetry condition

$$\text{Vector generator } \mathbf{v} = \mathbf{v}_{\mathrm{con}} + \mathbf{v}_{\mathrm{obs}} = \left(\xi \frac{\partial}{\partial \mathrm{t}} + \phi^{\epsilon} \frac{\partial}{\partial \epsilon} + \phi^{\mathrm{T}} \frac{\partial}{\partial \mathrm{T}} + \phi^{\mathrm{z_k}} \frac{\partial}{\partial \mathrm{z_k}}\right)$$

$$+ \left(\phi^{\sigma} \frac{\partial}{\partial \sigma} + \phi^{s} \frac{\partial}{\partial s} + \phi^{A_k} \frac{\partial}{\partial A_k}\right)$$

Components of the observable vector field $\mathbf{v}_{\mathrm{obs}}$
calculated from those of the controllable field $\mathbf{v}_{\mathrm{con}}$:

$$\text{Use state laws : } \begin{cases} \sigma = f_{,\epsilon}(\epsilon, T, z) \\ s = -f_{,T}(\epsilon, T, z) \\ A_i = -f_{,z_i}(\epsilon, T, z) \end{cases} \longrightarrow \begin{cases} \delta\sigma = f_{,\epsilon\epsilon}\delta\epsilon + f_{,T\epsilon}\delta T + f_{,z_k\epsilon}\delta z_k \\ \delta s = -f_{,\epsilon T}\delta\epsilon - f_{,TT}\delta T + f_{,z_k T}\delta z_k \\ \delta A_i = -f_{,\epsilon z_i}\delta\epsilon - f_{,T z_i}\delta T + f_{,z_k z_i}\delta z_k \end{cases}$$

$$\begin{cases} \phi^{\sigma} = f_{,\epsilon\epsilon}\phi^{\epsilon} + f_{,T\epsilon}\phi^{T} + f_{,z_k\epsilon}\phi^{z_k} \\ \phi^{s} = -f_{,\epsilon T}\phi^{\epsilon} - f_{,TT}\phi^{T} - f_{,z_k T}\phi^{z_k} \\ \phi^{A_i} = -f_{,\epsilon z_i}\phi^{\epsilon} - f_{,T z_i}\phi^{T} - f_{,z_k z_i}\phi^{zk} \end{cases}$$

→ search for symmetries on a subset of the total jet space

Symmetry condition from the kinetic Lagrangian

Independent variable : time t dependent variables : control variables (ϵ, T, z_k)

Variational invariance of l_{thermo} automatically satisfied :

$$pr^{(1)}v\left(L_{thermo}\right) + L_{therm} Div\xi = 0$$

⟶ search for vector fields $\mathbf{v}$ satisfying invariance condition

$$pr^{(1)}v\left(L_{kine}\right) + L_{kine} Div\xi = 0, \qquad \text{on optimal path } (L_{kine} = 0)$$

Equivalent to local symmetry condition $pr^{(1)}v\left(L_{kine}\right) = 0$

Application: linear viscous behavior

Control variables
(can be controlled during a test)

Observable variables

$$\gamma = \left\{ \begin{array}{l} \text{uniaxial strain tensor } \varepsilon \\[1em] \text{absolute temperature } T \end{array} \right. \begin{array}{c} \longleftrightarrow \\[1em] \longleftrightarrow \end{array} \left. \begin{array}{l} \text{Cauchy stress } \sigma \\[1em] \text{entropy } s \end{array} \right\} = \boldsymbol{\beta}$$

$$\text{Helmholtz free energy} : f(\varepsilon, T, z_k)$$

$$\longrightarrow \boxed{L = \underbrace{\sigma\dot{\varepsilon} - s\dot{T} - \sum_{k=1}^{N} A_k \dot{z}_k}_{\dot{f}} + \sum_{k=1}^{N} \lambda_k \left(\dot{z}_k + \frac{z_k - z_k^r}{\tau_k} \right)}$$

Experimental conditions (assumptions) :

$$\dot{T} = 0 \qquad \dot{\varepsilon} = constant \qquad \tau_k(T) = \frac{h}{kT}\exp(\frac{\Delta H - T\Delta S_k}{RT})$$

activation enthalpy

activation entropy of kth dissipative mode

Time-temperature superposition principle

Particular solution $\boldsymbol{v}_0$

satisfying $pr^{(1)}\boldsymbol{v}_0 L + L Div \boldsymbol{\xi} = 0$

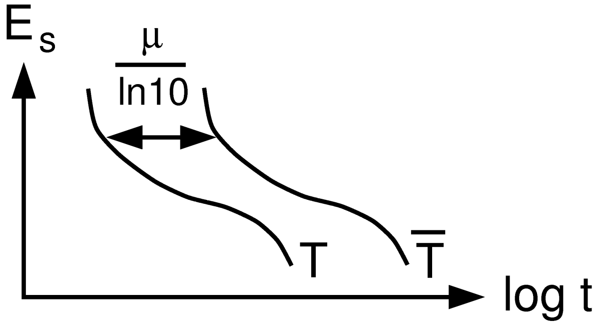
$$\boxed{\boldsymbol{v}_0 = t\frac{\partial}{\partial t} - \frac{RT^2}{RT+\Delta H}\frac{\partial}{\partial T}}$$

$$G_0 \begin{cases} \bar{t} = e^{\mu} t \\ \bar{T} = \exp\left(L_W\left(\frac{\Delta H}{R}\exp\left(\frac{\mu T - T\ln(T^*) + \frac{\Delta H}{R}}{T}\right)\right) - \mu + \ln(T^*) - \frac{\Delta H}{RT}\right) \\ \bar{\sigma} = \sigma \\ \bar{\varepsilon} = \varepsilon \end{cases}$$

⟶ Invariance property for the secant modulus $E_s(t,T) = \dfrac{\sigma(t,T)}{\varepsilon(t,T)}$

$$\boxed{E_s(\log t, T) = E_s(\log t + \tfrac{\mu}{\ln 10}, \bar{T})}$$

$$\boxed{\mu(T,\bar{T}) = \frac{\Delta H(T-\bar{T})}{RT\bar{T}} + \ln\frac{T}{\bar{T}}}$$



Validation with experimental data

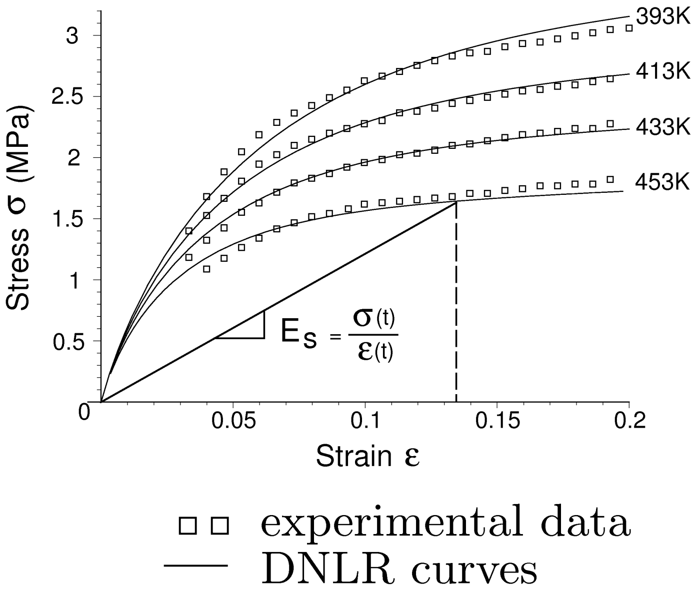
Constitutive equations :

$$\sigma = \sum_{k=1}^{N} \sigma_k$$

$$\left\{\begin{aligned} &\dot{\sigma} - E_u\dot{\varepsilon} + \sum_{k=1}^{N} b_k^1 \frac{z_k - c_k\varepsilon}{\tau_k} = 0 \\ &-\dot{s} + \alpha_u E_u \dot{\varepsilon} + \sum_{k=1}^{N} b_k^2 \frac{z_k - c_k\varepsilon}{\tau_k} = 0 \\ &-\dot{A}_i - b_i^1\dot{\varepsilon} + \sum_{k=1}^{N} g_{ik} \frac{z_k - c_k\varepsilon}{\tau_k} = 0 \end{aligned}\right.$$

$$\dot{\sigma}_k - p_k^0 E_u \dot{\varepsilon} + \frac{\sigma_k - p_k^0 E_r \varepsilon}{\tau_k} = 0$$

$\sigma(t)$ Fit of isothermal tensile curves (PA66)



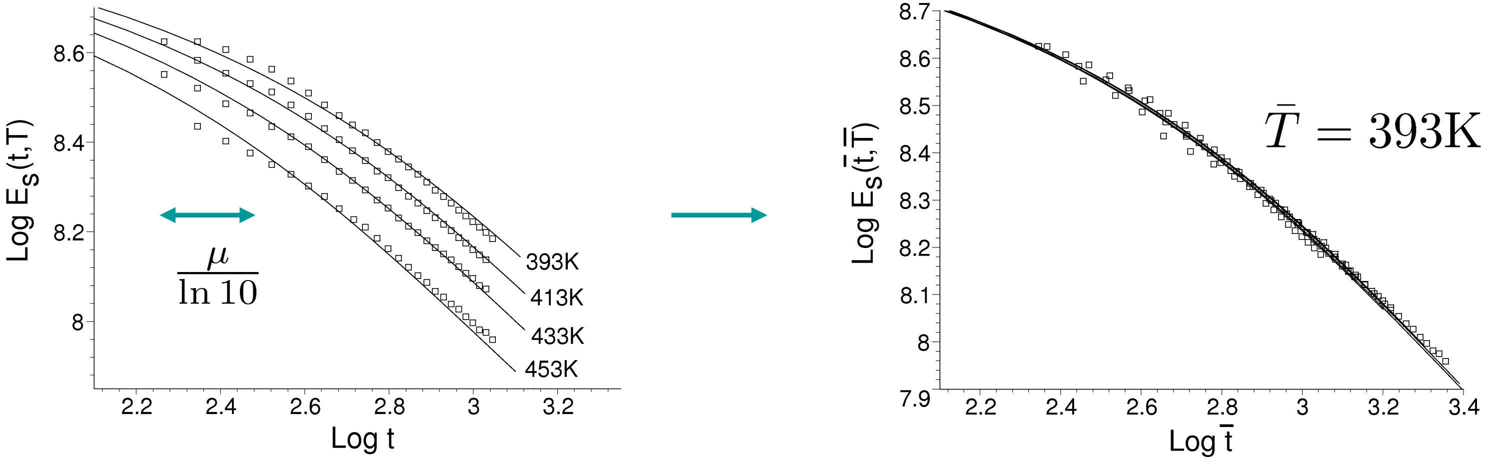
E_u : instantaneous modulus

E_r : relaxed modulus

Relaxation spectrum : $\tau_k = \frac{h}{kT}\exp(\frac{\Delta H - T\Delta S_k}{RT}),\ p_k^0 = \frac{\sqrt{\tau_k}}{\sum_{i=1}^{N}\sqrt{\tau_i}}$

Adjusted parameters: E_u, E_r, τ_{max}

Construction of master curve



$$\mu(T,\bar{T}) = \frac{\Delta H(T-\bar{T})}{RT\bar{T}} + \ln\frac{T}{\bar{T}} \quad \Rightarrow \quad \Delta H = 12.8 \pm 1.4 \text{ kJ.mol}^{-1}$$

$$\frac{\partial \Delta H}{\partial T} \approx 0 \quad \Rightarrow \quad \text{Validity of the Lie group}$$

$$\boldsymbol{v}_0 = t\frac{\partial}{\partial t} - \frac{RT^2}{RT+\Delta H}\frac{\partial}{\partial T}$$

Comparison with the WLF model

Williams, Landel, Ferry empirical formulation for polymers (early seventies)

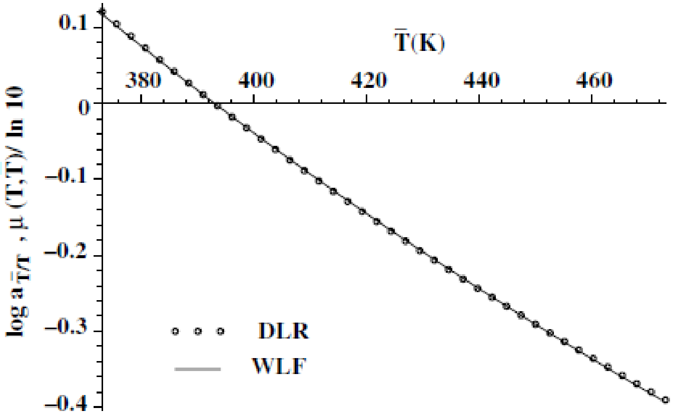
States equivalence property for the secant modulus or relaxation

$$E_s(t,T) = E_s(ta_{T',T},T')\frac{\rho(T)T}{\rho(T')T'}$$

shift factor given by $\log a_{T',T} = \frac{-C_1(T'-T)}{(C_2+T'-T)}$

Reference temperature = glass transition temperature (here 363°K)

C_1, C_2 material coefficients specific to each polymer



Thus, empirical WLF formula and time–temperature equivalence principle consequence of a particular symmetry of the constitutive equations

Summary - Perspectives

- Lie symmetries powerful tool in continuum mechanics of materials: predictive nature, condense mechanical behavior into invariance relations & master responses, thus economy of experiments.

- Lie symmetries can be used to identify a constitutive model from measurements

- Numerical schemes preserving symmetries & conservation laws for dissipative behaviors.