Beyond Onsager-Casimir Relations: Shared Dependence of Phenomenological Coefficients on State Variables

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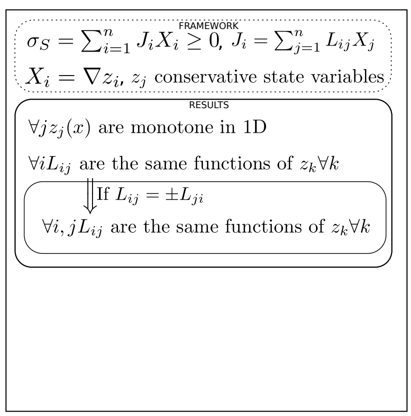
Abstract

Phenomenological coefficients in linear non-equilibrium thermodynamics have been considered to be independent, apart from restrictions due to the Onsager-Casimir reciprocal relations and the requirement to have non-negative entropy production. Recently it has been shown that functional constraints between these coefficients may hold, restricting their dependence on state variables, especially in the case of coupled phenomena. Here we demonstrate that such restrictions require only mild assumptions on the system of interest, and are in fact much more constraining than previously reported. Such constraints vastly reduce the set of plausible models for constitutive relations, and allow for simpler experimental determinations of dependencies in coupled systems. These results may also clarify inconsistencies in the literature regarding constitutive models used which do not obey these thermodynamic constraints.

Graphical TOC Entry



Linear nonequilibrium thermodynamics. Linear non-equilibrium thermodynamics (LNET) has been widely applied as a suitable framework providing thermodynamically consistent constitutive relations even in situations that are not in the vicinity of equilibrium where its usage is justified.[1–3] This is related to the fact that for certain phenomena (in particular those related to transport) the linear flux-force relationship well approximates the system's response, enabling modeling and analysis of coupled processes – the most outstanding aspects of the linear theory. For a taste of the wide range of applications see, for example,.[1–4]

The Nobel laureate Onsager revealed that the matrix of phenomenological coefficients might be symmetric[5,6] entailing significant implications theoretically and experimentally. In a recent study[7] it was shown that there is a significant addition to the symmetric structure of phenomenological coefficients with a great potential in further constraining constitutive relations. Particularly, the dependence of the phenomenological coefficients L_{ij} on state variables may be shared among some or all of these coefficients.

We now provide a definite and general statement about these constraints in linear non-equilibrium models: every linear non-equilibrium model with couplings between conservative state variables that correspond to forces with gradient structure has to satisfy certain functional constraints. Such constraints apply even to situations where Onsager's reciprocal relations are not valid. However, if they are applicable in such situations, then the functional constraints are even more restrictive. In either case this entails a significant implication on plausible model formulations, LNET constitutive theory and likely a need to revisit many existing models carefully. To this end we provide a few illustrations of these implications in commonly used models in the literature.

Congruent dependence of phenomenological coefficients on state variables. A linear non-equilibrium thermodynamic framework provides constitutive relations to close governing equations in the bulk by considering linear flux-force relations, which are valid at least near equilibrium. It is motivated by the bilinear nature of entropy production given by[1]

$$0 \leq \sigma_S = \sum_i J_i X_i, \tag{1}$$

where the fluxes J_i include extent of chemical reactions or fluxes of heat, diffusion, and electric charge, whereas the X_i denote the corresponding thermodynamic forces, e.g. chemical affinity or gradients of inverse temperature, chemical potential over temperature, and electric potential. The choice of linear flux-force relations,

$$J_i = \sum_j L_{ij} X_j, \tag{2}$$

with a positive semi-definite matrix $\mathbf{L}$ of phenomenological coefficients includes many of the empirical laws (e.g. Fourier, Ohm, Fick), and provides a simple means of describing interesting non-trivial coupling phenomena (e.g. Maxwell-Stefan diffusion, thermo-diffusion, thermo-electricity, electro-kinetics) while the second law is always satisfied.

Onsager suggested that a symmetric property among the phenomenological coefficients (corresponding to independent forces) may be valid[5,6] so that

$$L_{ij} = L_{ji}, \tag{3}$$

which is known as Onsager's principle or Onsager's reciprocal relations. Their derivation is based on some controversial assumptions within statistical mechanics, hence their implications on macroscopic theory has not been unequivocally accepted.[8–10] Nevertheless one may consider this symmetry property as an assumption of the macroscopic linear non-equilibrium thermodynamic framework and subject it to experimental testing. Despite its perhaps questionable derivation it has been repeatedly shown to be valid in a range of macroscopic phenomena.[11–15] Casimir soon afterwards extended Onsager's result to distinguish a symmetry property in the system based on time-reversal symmetry of state variables

$$L_{ij} = P(z_i)P(z_j)L_{ji}, \tag{4}$$

which is referred to as Onsager-Casimir's reciprocal relations and where $P(z_j) = \pm 1$ denotes the parity of state variable z_j with respect to the time-reversal transformation.[16]

Onsager-Casimir's reciprocal relations can be viewed either as restrictions (constraints) or as powerful relations with significant theoretical and experimental benefits, for example in reducing the number of necessary experiments and providing relations among seemingly unrelated coefficients. However, it has to be borne in mind that the linearity of this flux-force relation specifies the relation of fluxes to forces, not to state variables z_j in general. Hence, although forces are typically gradients of state variables[1,3] as in the mentioned examples, the phenomenological coefficients L_{ij} are generally functions of state variables. It has been recently shown that further restrictions concerning the matrix of phenomenological coefficients $\mathbf{L}$ may be required[7] in the case of Onsager's reciprocal relation, Eq. (3), and which we briefly recapitulate here. In particular, let $X_j = \nabla z_j$ correspond to constant fluxes J_j in a one dimensional stationary medium, and assume that it is possible to set up the system in such a way that $X_2 = \nabla z_2(x) = z_2'(x) = 0$ (by controlling the boundary conditions, i.e. $z_2(x) = z_2^{BC}$) while being outside of equilibrium, i.e. $X_1(x) \neq 0$. We then have

$$\begin{aligned} &L_{11}(z_1, z_2^{BC}) = \tilde{L}_0(z_1)\tilde{L}_{11}(z_2^{BC}), \\ &L_{21}(z_1, z_2^{BC}) = L_{12}(z_1, z_2^{BC}) = \tilde{L}_0(z_1)\tilde{L}_{12}(z_2^{BC}), \end{aligned}$$

i.e. $L_{11},\ L_{12} = L_{21}$ have to share the same functional dependency on the state variable z_1, as a consequence of coupling and Onsager's principle, i.e. $L_{ij} = L_{ji} \neq 0$. If in addition $L_{22}(z_1)$

is invertible [1], all phenomenological coefficients have to depend in the same way on z_1, i.e.

$$L_{ij}(z_1, z_2^{BC}) = f(z_1, z_2^{BC})\bar{L}_{ij}(z_2^{BC}). \tag{5}$$

We shall refer to this observation as "functional constraints." The assumption of constant fluxes is not a trivial one but it applies to a wide variety of applications particularly in transport processes. It is directly related to conservation laws and determines the choice of state variables z_j via conjugate forces X_j following from entropy production; see[7] for more details, as well as the top row in Fig. 1 and the discussion below.

We now improve these results of functional constraints by extending the result to Onsager-Casimir's reciprocal relation while relaxing essentially all subsidiary assumptions starting with the single vanishing force outside of equilibrium [2].

Theorem 1 *In a system governed by linear non-equilibrium relations it is* always *possible to choose boundary conditions such that all forces but one vanish while keeping the system outside of equilibrium.*

Proof can be found in Supplementary Information.

An immediate corollary of Theorem 1 is that there are functional constraints on the phenomenological coefficients' dependence on state variables. Consider (2) with $X_i = 0$, $\forall i \neq j$. Then one obtains a system of n equations which must all be constant (as the fluxes are constant), and hence L_{ij} must share the same functional dependence on $\mathbf{z}$, $\forall j$. Repeating this argument for each force we have that $L_{ij}(\mathbf{z}) = f_j(\mathbf{z})g_{ij}(z_1, \ldots, z_{j-1}, z_{j+1}, \ldots, z_n)$, $\forall i, j$.

Note that the assertion of functional constraints can be inverted in the following sense. When do the linear flux-force relations allow a solution for $X_{i_0} \neq 0$ while $X_k = 0$, $\forall k \neq i_0$?

[1] There are two further "technical" assumptions, that (i) the phenomenological coefficients are analytic in state variables and (ii) a constitutive relation should hold for all parameter values, where the idea is that it is reasonable to require the validity of governing (or constitutive) relations over a wide range of values of phenomenological coefficients as constitutive model is chosen prior to its parameter estimation or measurement.

[2] Note that this assumption is intuitively understood to hold. For example the mere existence of an isothermal system is implicitly stating that one can assume to have $T(x) = T_0$ everywhere in the system regardless of coupling phenomena, hence exactly $X_2 = 0$ while $X_1 \neq 0$ in the present notation.

It is exactly when L_{k,i_0} share the same functional dependency on z_{i_0} for all k as immediately follows from Eq (2) from the multiple terms involving X_{i_0} (to prevent an overdetermined system) and therefore we have that functional constraints are equivalent to the plausibility of enforcing all but one of the forces to vanish everywhere while remaining out of equilibrium. With the assertion of Theorem 1 we have that any linear non-equilibrium model with forces as gradients has to comply with functional constraints in the phenomenological coefficients describing non-zero coupling among conservative state variables.

The mentioned equivalence between functional constraints and forces can be supplemented by a further observation. One can show that in addition to functional constraints we practically always (once state variables are analytic in space, see Supplementary Information) have monotonicity of all conservative state variables in one dimension which allows for experimental verification of this observation and in fact assessment whether linear flux-force relations do apply in a given system. Finally, as the monotonicity of state variables for all boundary conditions follows from functional constraints, it also guarantees the possibility to set $X_{i_0} \neq 0$ while $X_j = 0,\ j \neq i_0$. We have

Theorem 2 *The following three statements in a linear non-equilibrium system, with small conservative fluxes, nonzero coupling and $z_j(x)$ analytic, are equivalent:*

1. *the possibility to set all forces but one outside of equilibrium to zero;*
2. *functional constraints: $\forall i,\ L_{ij}$ share the same dependence on z_j;*
3. *monotonicity of state variables in one dimensional space provided state variables are analytic functions of the spatial coordinate.*

These results are summarised in Fig. 1.

Finally, we shall now show that this congruent dependence of all the phenomenological coefficients on the state variables is a direct consequence of Onsager's reciprocal relations and the functional constraints following from the possibility to set forces to zero independently outside of equilibrium.

First, we show that a stronger variant of functional constraints holds as a consequence of monotonicity of state variables. Denoting the boundary values of the state variables by $\mathbf{z}^{BC}$, we see from

$$L_{ij}(\mathbf{z}) = L_{kj}(\mathbf{z}) \frac{J_i(\mathbf{z}^{BC})}{J_k(\mathbf{z}^{BC})}, \tag{6}$$

that one can now use monotonicity of *all* state variables $\mathbf{z}$ to show [3] that the phenomenological coefficients in the same column share the same functional dependence on all state variables.

Finally, if Onsager-Casimir's reciprocal relations, Eq. (4), apply to a given system, they transfer this dependence to all columns of the phenomenological matrix enforcing a congruent dependence on the state variables. Hence we have shown

Theorem 3 *A stronger variant of functional constraints – $\forall i$, L_{ij} share the same functional dependence on z_k, $\forall k$ – is valid as a consequence of monotonicity of state variables. If, in addition, Onsager-Casimir's reciprocal relations hold in the considered system, the phenomenological matrix has to satisfy $L_{ij}(\mathbf{z}) = f(\mathbf{z})\bar{L}_{ij}$ with $\bar{\mathbf{L}}$ a constant semi-definite matrix.*

Before providing some illustrations of these findings we summarise the functional constraints in a diagram with all the relations and assumptions in place in Fig 1.

Diffusion in ternary mixture As a simple illustration of the above constraints consider an isothermal (constant temperature T), isobaric, non-viscous, non-reacting (each constituent's mass is then conserved) ternary mixture with no external forces.[3] With partial densities ρ_α, mass fractions $c_\alpha = \rho_\alpha / \sum_\beta \rho_\beta$, partial velocities $\mathbf{v}_\alpha$, diffusive fluxes $\mathbf{J}_\alpha = \rho_\alpha(\mathbf{v}_\alpha - \sum_\beta c_\beta \mathbf{v}_\beta)$, and chemical potentials μ_α, one can write the entropy production in the

[3] By setting all state variables but one, z_{k_0}, to a constant obtaining $L_{ij}(z_{k_0}(x))/L_{kj}(z_{k_0}(x)) = a\ const$ from where the functional constraint follows. Note that the fluxes can be dependent only on the boundary values due to the conservative nature of state variables and the stationarity of the considered state.

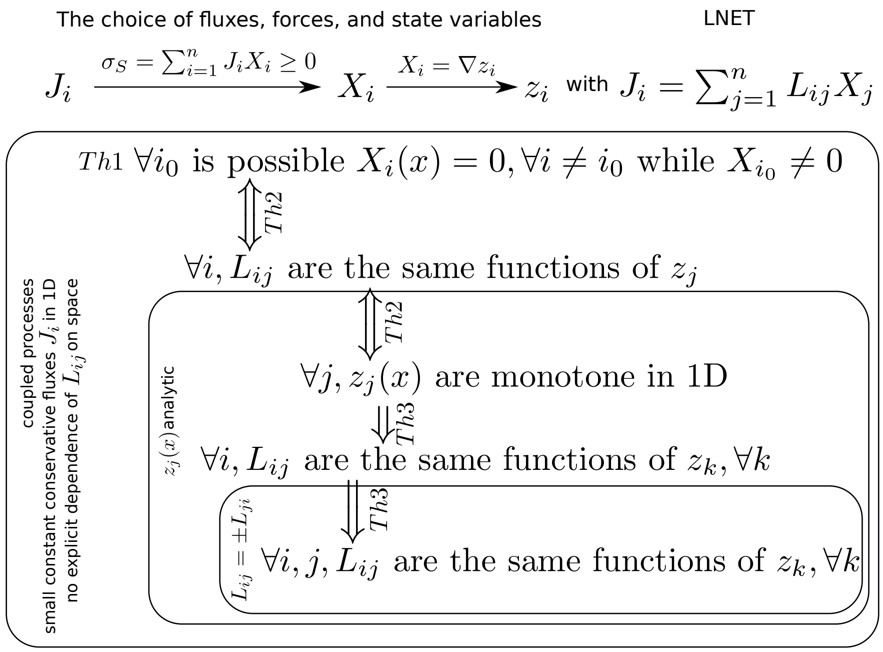


Figure 1: A summary of functional constraints. Each box represents a situation where assumptions specified in vertical texts apply.

system as

$$T\sigma_s = -\sum_{\alpha=1}^{2} J_\alpha \cdot \nabla(\mu_\alpha - \mu_3) = -\sum_{\alpha=1}^{2} J_\alpha \left(1 + \frac{c_\alpha}{c_n}\right) \cdot \nabla\mu_\alpha,$$

where we use only two independent mass fluxes (hence $\det \mathbf{L} \neq 0$ and note that the sum of all diffusive fluxes vanishes from their definition) and similarly one thermodynamic force (the gradient of chemical potential) is not independent as the Gibbs-Duhem relation reveals.

A diffusion coefficient is typically a coefficient relating the gradient of concentrations or mass fractions to their diffusive fluxes. Functional constraints (assuming non-zero coupling and Onsager's reciprocal relations to hold as both being a standard assumption in transport phenomena) entail

$$D_{ij} = \frac{\partial \mu_j}{\partial c_j} f(c_1, c_2) = \frac{1}{c_j} f(c_1, c_2). \tag{7}$$

Note that then some of the well-studied problems of cross-diffusion are not consistent with these requirements as is, for example, the case with,[17] where the form of the diffusion matrix in the case of cross-diffusion does not obey (7).

Thermo-diffusion Let us now consider a typical example where Onsager's reciprocal relations are recognised as powerful tools. The measurable coefficients are typically defined[2] via the heat flux caused by the inverse temperature gradient $J_q = \partial_x T^{-1}$ and molar mass flux driven by the gradient of chemical potential at constant temperature $J_m = -\frac{1}{T}(\mu_m)_T$. If we denote the resistance matrix with this choice of fluxes and forces as $\mathbf{r}$ and molar concentration of the moving component as n_m we have

$$\begin{aligned}
\lambda &= -\frac{J_q}{\nabla T}\Big|_{J_m=0} = \frac{1}{T^2 r_{qq}},\\
q_m^* &= \frac{J_q}{J_m}\Big|_{dT=0} = -\frac{r_{qm}}{r_{qq}},\\
D_m &= -\frac{J_m}{\nabla n_m}\Big|_{dT=0} = \frac{1}{T}\frac{\partial(\mu_m)_T}{\partial n_m}\left(r_{mm} - r_{qq}(q_m^*)^2\right)^{-1},\\
D_T &= -\frac{J_m}{n_m \nabla T}\Big|_{dn_m=0} = \frac{q_m^*}{n_m T^2}\frac{\partial(\mu_m)_T}{\partial n_m}\left(r_{mm} - r_{qq}(q_m^*)^2\right)^{-1}.
\end{aligned}$$

As follows from the above definitions, the thermal conductivity λ is defined at zero mass flux, q_m^* represents the reduced heat (or measurable heat) of transfer at a constant temperature, D_m is the interdiffusion coefficient and finally D_T is the thermal diffusion coefficient. The usual Soret and Dufour coefficients are then $s_T = D_T/D_m$ and $D_D = q_m^* D_m$.

Closer inspection reveals[7] that a slightly different choice of forces has to be carried out to exploit mass and energy conservation. If we denote the resistance matrix with this choice of fluxes and forces as $\mathbf{R}$ then functional constraints yield the following structure of the experimentally accessible phenomenological coefficients

$$
\begin{aligned}
\lambda &= \frac{1}{T^2 R_{qq}} = \frac{1}{T^2 \bar{R}_{qq} f(n_m, T)}, \\
q_m^* &= -\frac{R_{qm} + R_{qq} h_m}{R_{qq}} = -\frac{\bar{R}_{qm} + \bar{R}_{qq} h_m}{\bar{R}_{qq}}, \\
D_m &= \frac{1}{T f(n_m, T)} \frac{\partial (\mu_m)_T}{\partial n_m} \left(\bar{R}_{22} - \frac{\bar{R}_{12}^2}{\bar{R}_{11}} \right), \\
D_T &= \frac{q_m^*}{n_m T^2} \underbrace{\left(\bar{R}_{22} - \frac{\bar{R}_{12}^2}{\bar{R}_{11}} \right)}_{\geq 0},
\end{aligned}
\tag{8}
$$

where $\bar{\mathbf{R}}$ denotes a constant symmetric positive-definite matrix, h_m denotes partial specific enthalpy and $f(n_m, T)$ represents the shared functional dependency on the state variables.

The significance of functional constraints is that if a dependence on state variables (temperature and concentration) is proposed based on experimental data, functional constraints entail a significant restriction on such possible dependency. In particular, if a relation for any of the phenomenological coefficients is proposed, as e.g. in[18,19] for the Soret coefficient, one has to check if the implied forms of all the remaining phenomenological coefficients (8) are plausible and correspond to experimental data. If not, the proposed relation cannot be used.

Generality of functional constraints Despite the fact that the conclusions about functional constraints were shown only for one-dimensional and stationary systems, we expect the results to extend to any model which involves (arbitrary small but non-zero) coupling of conserved variables. Namely, the physics underlying observed phenomena is seldom dependent on the dimensionality of the problem and that applies even when specific phenomena appear only in certain dimensions. Similarly, mathematical formulations of a given phenomena should not change in principle and hence a one-dimensional model should be seen as a mere application of the model to a particular situation as a special case. We note that the monotonicity result may not hold in higher dimensions, but in general functional constraints will still apply. Analogously, the stationary state is a limiting case of a more general framework. However obvious these observations might be, they provide a crucial step from the results derived above in the one-dimensional and stationary setting to a general requirement for a model stemming from a linear non-equilibrium thermodynamic framework.

We have removed all subsidiary assumptions for functional constraints [4] from the previous study[7] while significantly extending their validity and revealing connections to i) monotonicity of state variables in one-dimensional space, ii) stronger variants of functional constraints and iii) Onsager-Casimir's reciprocal relations. In particular, thermodynamic consistency for non-zero coupling of conservative state variables requires congruent dependence of phenomenological coefficients (not explicitly dependent on space) on state variables as a consequence of Onsager-Casimir's reciprocal relations once forces are expressible as gradients. It should be noted that some form of functional constraints remain even when Onsager-Casimir's relations are not considered, which directly follows from Theorems 1 and 2 and as is summarised in Fig. 1. In this sense, functional constraints more fundamentally provide restrictions on plausible model formulations and illustrate their power in revealing perhaps unexpected relations among phenomenological coefficients, in addition to reducing the number of required experiments to identify the constitutive laws. Finally note that the validity of functional constraints has already been demonstrated experimentally in a particular system.[7]

The generality of the obtained result can be used for identification of boundaries of applicability of the linear non-equilibrium theory in a given system. The identified monotonicity of state variables is experimentally accessible in one dimension, and allows for assessment of non-linear flux-force responses by measuring a non-monotonic profile of a conservative state variable in a steady state system. Similarly if the same functional dependency on all the conservative state variables is not shared in all the phenomenological coefficients within the

[4] Analyticity of the state variables in space is still required for showing monotonicity. As an arbitrary function can be approximated by a polynomial to arbitrary precision outside of a set of arbitrarily small measure, we consider this assumption to be rather technical and of limited value in practical applications when the theory is completed by experimental measurements. However, in certain situations like phase transitions the actual discontinuity may be crucial and invalidate the assumption.

linear theory, then Onsager-Casimir's reciprocal relations do not hold in the system of interest, perhaps with the exception of phase transitions or similar abrupt phenomena occurring within the system (not meeting the analyticity assumption of state variables). Note, however, that the functional dependency is conveniently expressed only with a particular choice of fluxes and forces and hence may not be immediately recognised but rather disguised in standard expressions of measurable parameters (as in the above problem of thermo-diffusion).

It should be also mentioned that functional constraints do not follow from the second law of thermodynamics (although are implicitly related to it due to the linear non-equilibrium thermodynamic framework) but they follow from a requirement of inner consistency, i.e. a LNET model to be consistent with the LNET framework. Linear non-equilibrium thermodynamics is not a general theory by far but its validity near equilibrium has been established.[1–3,8] On the contrary, a compliance of more advanced and general theories like GENERIC,[20,21] EIT,[22] or rational thermodynamics[23,24] with LNET is required. This compliance of more general theories together with the statement that LNET is perhaps the most widely and successfully used non-equilibrium theory, suggests that the significance of these functional constraints in constitutive theories can be appreciated.

Phenomenological coefficients have been considered to be independent apart from Onsager-Casimir's reciprocal relations and the stability requirement (the non-negativity of entropy production). However, as this article shows, there are further (functional) constraints on the constitutive theory with or without Onsager-Casimir's reciprocal relations and these have to be systematically considered in model formulation. This inconsistency might be the reason why values of phenomenological coefficients are sometimes reported to vary significantly or, on the other hand, certain functional forms like Arrhenius dependence on temperature appear frequently although being rather well understood in terms of activation energies in reactions but perhaps less clear in diffusion. Additionally, an open and interesting question remains, whether there is an implication of the revealed functional constraints to recently studied thermodynamic uncertainty relations.[25]

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Supporting Information Available: Proof of Theorem 1 is provided together with a proof of monotonicity of state variables in one spatial dimension.

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Supplementary Information of

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1 Proof of Theorem 1

Theorem 1 *In a system governed by linear non-equilibrium relations it is* always *possible to choose boundary conditions such that all forces but one vanish while keeping the system outside of equilibrium.*

Inverting the flux-force relation

$$\mathbf{X} = \mathbf{R}.\mathbf{J}$$

with the resistance matrix $\mathbf{R}$ allows us to solve the flux-force relations for asymptotically small fluxes J_i (close but not at equilibrium), where we scale the length of our domain so that $x \in (0,1)$. Expanding formally the state variables in J_i,

$$z_i = z_i^{(0)} + J_1 z_i^{(10...0)} + J_2 z_i^{(010...0)} + \ldots + J_n z_i^{(0...01)},$$

we get by power matching the leading order problem

$$\partial_x z_j^{(0)} = 0,$$

i.e. constant state variables at leading order. As small but non-zero fluxes J_i require unequal boundary conditions, they have to be satisfied through subleading terms (and require a consistency check of their size a-posteriori). With $\mathbf{z} = (z_1, \ldots, z_n)$ the first order problem reads

$$\partial_x \left(J_1 z_j^{(10...0)} + J_2 z_j^{(010...0)} + \ldots + J_n z_i^{(0...01)} \right) = \sum_{k=1}^{n} J_k R_{jk}(\mathbf{z}^{(\mathbf{0})}), \tag{1}$$

and hence can be rewritten into a system of linear differential equations with identity matrix and constant forcing terms. Thence the first order solutions $z_j^{(10...0)}, z_j^{(010...0)}, \ldots, z_j^{(0...01)}$, are linear functions of space x. Therefore the profiles of state variables in the stationary state for small fluxes J_j is

$$\begin{aligned} z_j(x) &= z_j^{(0)} + J_1 z_j^{(10...0)}(x) + J_2 z_j^{(010...0)}(x) + \ldots + J_n z_j^{(0...01)}(x) \\ &= z_j^{(0)} + \left(J_1 z_j^{(10...0)} + J_2 z_j^{(010...0)} + \ldots + J_n z_j^{(0...01)} \right) \Big|_{x=0} + \\ &\qquad + x \sum_{k=1}^{n} J_k R_{jk}(\mathbf{z}^{(0)}) + \mathcal{O}\left(\sum_{k=1}^{n} J_k \right)^2, \end{aligned} \tag{2}$$

accompanied by boundary conditions $z_j(0) = z_j^L$, $z_j(1) = z_j^R = z_j^L + \epsilon_j$ with the difference being small due to the consistency with the small fluxes assumption. One can immediately see that the choice $z_j^{(10...0)}(0) = z_j^{(010...0)}(0) = \ldots = z_j^{(0...01)}(0) = 0$ allows for the solution $z_j(x) = z_j^L + \epsilon_j x$ while the fluxes J_j are proportional to the difference in state variable values at the boundary ϵ_j confirming the consistency of the solution with the asymptotic assumption.

When choosing $\epsilon_k = 0$ for all $k \neq i_0$ (i.e. zero outer force $X_k = z_k'$), we see that one has $X_{i_0} \neq 0$ while $X_k(x) = \mathcal{O}(\epsilon_k^2)$ everywhere. Similarly one can show that the second subleading contributions would be quadratic in space x and hence the choice $\epsilon_k = 0$ results in $z_k(x) = z_k^L + \mathcal{O}(\epsilon_k^3)$. By repetition one can conclude that for small enough difference in the boundary conditions of one state variable while enforcing the others to have the same boundary values one has an observation that $X_{i_0} \neq 0$ while $X_k(x) = 0,\ \forall k \neq i_0$ which completes the proof of the theorem.

2 Proof of monotonicity of state variables in 1D

The mentioned equivalence between functional constraints and forces can be supplemented by a further observation. Consider a point x_0 inside the given system where the force X_{i_0} vanishes as a state variable reaches an extreme value, i.e. $z_{i_0}'(x_0) = 0$. From the flux-force relations we get at $x = x_0$ that

$$0 = L_{i,i_0} z_{i_0}'' + \sum_{j \neq i_0} L_{ij} z_j'' + (z_j')^2 \frac{\partial L_{ij}}{\partial z_j}, \forall i.$$

As we know that functional constraints do apply, we can rewrite these equations to get

$$0 = L_{i,i_0} z_{i_0}'' + \sum_{j \neq i_0} g_{ij} \underbrace{\left(z_j'' f_j + (z_j')^2 \frac{\partial f_j}{\partial z_j} \right)}_{\zeta_j}, \forall i,$$

which can be considered as a system of linear equations for unknowns $\zeta_1, \ldots, \zeta_{i_0-1}, z_{i_0}'', \zeta_{i_0+1}, \ldots, \zeta_n$ with matrix g_{ij} except the i_0-th column which is L_{i,i_0}. As the determinant of this matrix is proportional [1] to $\det \mathbf{L}$, which is nonzero, so one can infer that $z_{i_0}''(x_0) = 0$. By repeatedly differentiating the flux-force relations one can in fact show by the same argument that all the derivatives of the state variable z_{i_0} have to vanish at $x = x_0$. Thence z_{i_0} is at least locally constant but for z_{i_0} analytic in space this translates into constantness everywhere.

[1] The proportionality coefficient is $\prod_{j \neq i_0} f_j^{-1}$.