

**Functional constraints on phenomenological coefficients**

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Thermodynamic fluxes (diffusion fluxes, heat flux, etc.) are often proportional to thermodynamic forces (gradients of chemical potentials, temperature, etc.) via the matrix of phenomenological coefficients. Onsager's relations imply that the matrix is symmetric, which reduces the number of unknown coefficients. In this article we demonstrate that for a class of nonequilibrium thermodynamic models in addition to Onsager's relations the phenomenological coefficients must share the same functional dependence on the local thermodynamic state variables. Thermodynamic models and experimental data should be validated through consistency with the functional constraint. We present examples of coupled heat and mass transport (thermodiffusion) and coupled charge and mass transport (electro-osmotic drag). Additionally, these newly identified constraints further reduce the number of experiments needed to describe the phenomenological coefficient.

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Classical irreversible thermodynamics (CIT) (described by Meixner [1] and thoroughly summarized by de Groot and Mazur [2]) has been very successful in modeling transport, reaction kinetics or viscous effects. It has been applied to many engineering problems, including coupled heat, mass, and charge transport [3]. A fundamental assumption of the theory is the linear force-flux relations,

$$\mathbf{J}_i = \sum_j L_{ij} \mathbf{X}_j, \quad (1)$$

where  $\mathbf{J}_i$  and  $\mathbf{X}_i$  are the thermodynamic fluxes and forces, respectively.  $L_{ij}$  form a matrix of phenomenological coefficients  $\mathbf{L}$ . These coefficients are functions of the local thermodynamic state of the system, expressed in terms of the state variables.

The success of CIT with respect to other nonequilibrium thermodynamic (NET) frameworks is closely related to the accessibility of experimental assessment of the closure (constitutive) relations. The challenge of identifying the transport coefficients can be onerous; for  $n$  coupled processes  $n^2$  phenomenological parameters need to be identified together along with their dependence on state variables (and boundary conditions). Hence, *a priori* relations between coefficients can significantly reduce the necessary experimental effort to assess all the model parameters. The second law of thermodynamics, which is expressed as non-negativity of local entropy production  $\sigma_s = \sum_i \mathbf{J}_i \mathbf{X}_i \geq 0$ , imposes constraints on  $\mathbf{L}$ .  $\mathbf{L}$  must be positive semidefinite. The Onsager reciprocal relations (ORR) require equivalence of  $L_{ij}$  and  $L_{ji}$  [4,5].

ORR follow from microscopic time reversibility of the evolution equations while assuming that the decay of spontaneous

(microscopic) perturbations follow the same constitutive laws as the (macroscopic) perturbations produced by external stimuli when these phenomenological laws may be approximated as linear. Onsager's and Casimir's observations result in<sup>1</sup>

$$L_{ij} = P(x_i)P(x_j)L_{ji},$$

where parity of a scalar state variable  $x_j$  is denoted by  $P$  [7]. Parity is defined as even for state variables that do not change under time-reversal transformation and odd for variables that do change a sign under this transformation. Time-reversal transformation is clearly defined on the microscopic level and from there it is extended to different levels via projections. If  $\mathbf{x}$  denotes the microscopic state variables and  $\mathbf{y}$  the macroscopic ones, the requirement for commutation of the projection  $\pi(\mathbf{x}) = \mathbf{y}$  with time-reversal transformations on both levels defines the parity of macroscopic state variables. Even though the validity of the ORR is based on several assumptions about properties of a given system, it has been successfully applied in situations where fulfillment of these assumptions is unclear.

The main objective of this work is to show that there are further constraints on phenomenological coefficients in addition to ORR within CIT. This claim is motivated by our recent observation of correlation transport coefficients for water and proton transport across Nafion membranes [8]. Our experimental data suggest that for a certain class of models not only must the cross-coefficients (also referred to as off-diagonal) be equal (due to ORR) but even the diagonal coefficients have to share the same functional dependence on the

<sup>1</sup>More precisely, this relation holds in the absence of magnetic field or rotation of the system and for scalar state variables. Note that reciprocal relations with a transpose on one side are valid for vectorial and tensorial quantities; see, e.g., [2,6].

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thermodynamic state of the system as the cross-coefficients, i.e., the matrix of the phenomenological coefficient can be written as a scalar function of state variables multiplied by a constant positive semidefinite matrix.

Further, we hypothesize that these functional restrictions are generally valid in CIT framework when entropy production in the one-dimensional (1D) stationary case can be expressed solely in terms of constant fluxes and corresponding forces. This assumption applies to a wide range of problems. Particularly this hypothesis is relevant in CIT framework within mechanical equilibrium, where velocity has already relaxed. Indeed, the crucial requirement that leads to the functional constraints is that thermodynamic fluxes are constant in the one-dimensional stationary case, and fluxes of mass and total energy, which are the state variables of CIT within mechanical equilibrium, fulfill that requirement. Hence these functional constraints should apply to all models covered by Kjelstrup and Bedeaux [3] to list an example.

These functional constraints must be satisfied for a model to be physically consistent, as discussed below. This study proves the validity of functional constraints to a certain class of CIT models. Many measurements have been done for coupled heat, mass, and charge transport but we have not seen any mention of consistency of the diagonal and of-diagonal transport coefficients. We include experimental measurements of coupled water and ion transport phenomena which are in agreement with the theoretical findings. Additionally, the existence of the functional constraints reduces the number of experiments necessary to identify the linear constitutive relations.

## II. MAIN RESULT

In this section we formulate our main conjecture with precisely defined assumptions. In the Discussion and Conclusion section we provide reasoning for this conjecture and formulate a more general hypothesis about functional constraints for CIT models.

Assumptions are as follows.

- (1) The system is described by one-dimensional stationary CIT.
- (2) The spatial variation of the state variables are consistent with their fluxes being constant in space.
- (3) For simplicity consider only two independent forces and assume that one of them can vanish everywhere while the other stays nonzero.

The main conjecture is as follows: If the above assumptions are satisfied for a given CIT model, then all the phenomenological coefficients must share the same functional dependency of the thermodynamic state variable which does not correspond to the thermodynamic force that can vanish everywhere without imposing global thermodynamic equilibrium (as in assumption 3). The proof of the main result follows.

Consider a 1D system  $[0, L]$  with two coupled processes at steady state. The linear force-flux relations read

$$\mathbf{J}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2, \quad (2a)$$

$$\mathbf{J}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2. \quad (2b)$$

Thermodynamic forces are typically proportional to gradients of conjugates of state variables [9] (also referred to as

intensive state variables)  $y_j$ . The number of state variables is in general unrelated to the number of coupled processes. State variables are chosen (via transformation) such that the forces are proportional to their gradients  $\mathbf{X}_j = \mathbf{X}_j(y_j)$ . As we consider only two coupled processes (two closures) the remaining state variables are enslaved to these two  $y_1, y_2$  (see the last section with particular illustrations of this theory).

If we know that  $\mathbf{X}_2$  vanishes everywhere in the system for some boundary condition  $y_2(0) = y_2(L) = y_2^{\text{BC}}$  we have

$$\frac{\mathbf{J}_1(y_2^{\text{BC}})}{\mathbf{J}_2(y_2^{\text{BC}})} = \frac{L_{11}(y_1(x), y_2^{\text{BC}})}{L_{21}(y_1(x), y_2^{\text{BC}})}.$$

As fluxes  $\mathbf{J}_1, \mathbf{J}_2$  are constant (spatially independent) and phenomenological coefficients depend on space only via state variable  $y_1(x)$  we observe that  $L_{11}$  and  $L_{21} = L_{12}$  have to share the same functional dependency on  $y_1$ . These functional constraints follow, however, if and only if one can set  $\mathbf{X}_2 = 0$  everywhere in the system while still being outside of equilibrium ( $\mathbf{X}_1 \neq 0$ ).

The fourth phenomenological coefficient  $L_{22}$  cannot be arbitrary as is subjected to constraints due to the second law of thermodynamics. We shall show that if  $L_{22}$  is monotonically dependent on  $y_1$  then it has to share the same functional dependency as the remaining phenomenological coefficients. Particularly, as  $\mathbf{L}$  is symmetric and has to be a positive semidefinite matrix due to the second law of thermodynamics, we require that  $L_{11} \geq 0, L_{22} \geq 0$  and  $L_{22}L_{11} - L_{12}L_{21} \geq 0$ . Let us denote the shared dependency of  $L_{11}$  and the cross-coefficients as  $\tilde{F}(y_1)$ . Further, let the fourth coefficient  $L_{22}$  be a monotonous function of  $y_1$ , i.e.,  $L_{22} = f(y_1)$  with  $f$  invertible. Hence

$$(L_{11}(y_1), L_{12}(y_1), L_{21}(y_1)) = (L_{11}^0, L_{12}^0, L_{21}^0)F(L_{22}),$$

where  $F(L_{22}) = \tilde{F} \circ f^{-1}(L_{22})$  and 0 in the superscript denotes a constant.

The values of phenomenological coefficients cannot be known prior to the theoretical model formulation. One can identify, interpret, and measure a coefficient only after a theoretical framework suitable for the experiment at hand is identified. We claim that thermodynamic consistency should require plausibility of the model for all thermodynamically admissible values of coefficients. In other words, the model has to be formulated first and then the assessment of parameter values follows. Further we expect that a given thermodynamic model applies to a wide variety of materials with independent coefficient values. Both these conjectures suggest that we can assume  $L_{22}$  taking arbitrary large values irrespective to values of the other coefficients. Given  $F$  is an analytic function of  $L_{22}$ , we can show that indeed  $F(L_{22}) \propto L_{22}$ . This follows from the assumption of  $F$  being analytic,  $F(L_{22}) = \sum_{n=1}^{\infty} a_n(L_{22})^n$ , and from the second law of thermodynamics,

$$F(L_{22})(L_{11}^0 L_{22} - (L_{12}^0)^2 F(L_{22})) \geq 0,$$

which has to hold for all values of  $L_{22}$ . For  $L_{22} \ll 1$  we have

$$F(L_{22})(L_{11}^0 L_{22} - (L_{12}^0)^2 F(L_{22})) \sim -(L_{12}^0 a_0)^2 \geq 0,$$

and hence  $a_0 = 0$ . Similarly for large values of  $L_{22}$  it follows that  $a_n = 0, n \in \{2, 3, \dots\}$  which completes the proof.

A few remarks about the assumptions are in place. The second assumption of constantness (both in space and time where time independence is an immediate consequence of the stationary state) of fluxes in the steady-state condition of the system can be satisfied by a careful choice of fluxes  $\mathbf{J}_i$ . The identification of such fluxes is linked to conserved quantities and hence to balance equations. For example, if no chemical reactions are taking place, mass fluxes are constant due to the continuity condition and mass conservation. If reactions are taking place, total mass is conserved. Similarly total linear momentum is conserved (as partial velocities and barycentric velocity are constant). Further, charge, total angular momentum or conservation of total energy can be used for fluxes related to thermal effects as in thermodiffusion; see below.

The third assumption can be rewritten as a requirement that enforcing one of the forces to be zero everywhere does not imply (global) thermodynamic equilibrium. For example, the gradient of chemical potential of one species can be zero everywhere while the gradient of chemical potential for another species is nonzero, or the gradient of chemical potential can be nonzero even if the system is isothermal. Although this assumption is quite natural, the range of its validity remains unclear to the authors.

### III. CLASS OF MODELS WHERE ASSUMPTIONS ARE MET

In this section we explore the domain of applicability and relevance of the main result. Particularly in a class of models where a force is equal to the gradient of a spatially monotonous conjugate variable (e.g., gradient of temperature) assumption 3 is fulfilled since setting the same Dirichlet boundary conditions for the conjugate variable makes the variable constant in the whole spatial domain. In other words, models implying a maximum principle (in the mathematical sense [10]) for a conjugate variable are compatible with the crucial third assumption and consequently the functional constraints do apply.

A remark about the role of boundary conditions (BCs) is in order. The purpose of monotonicity is to show that one of the thermodynamic forces  $\mathbf{X}_j$  has to vanish for identical BCs on the left and right side of the domain. Either  $\mathbf{X}_j$  needs to be shown to vanish everywhere in the system for such BCs or the model has to imply monotonous dependence not only for a particular choice of BCs but rather for a whole range of BCs including those leading to zero force  $\mathbf{X}_j$  everywhere.

First consider a simple CIT model that is without coupling, but which illustrates both that a force can be zero (Assumption 3) due to monotonicity and also that this property of monotonicity can be an intrinsic and hidden property of a model. Afterwards we give an example where the same ideas can be used to show that the hypothesis can hold even in models with coupling.

#### A. Simple heat transfer

Consider a heat transfer model within CIT, i.e.,  $\mathbf{J}_q = -L(T)\nabla T$ , yielding the heat equation,

$$\partial_t T - \nabla \cdot (L(T)\nabla T) = f(t, x).$$

Hence the steady-state temperature distribution field without any sources  $f(t, x)$  in one dimension satisfies

$$L(T)T'' + \frac{dL(T)}{dx}T' = 0 \text{ in } \Omega = [0, l].$$

We shall use the following 1D maximum principle for nonlinear operators that is a simple corollary of [11], Theorem 21, p. 48. If  $w = 0$  is a solution of the differential equation,

$$u'' + H(x, u, u') = 0 \text{ in } \Omega, \quad (3)$$

where  $H, \partial_y H, \partial_z H$  are continuous and where  $\partial_y H \leq 0$  everywhere in  $\Omega$ . Then, if one of the following conditions is satisfied, any solution  $u$  of (3) is monotonous in space.

- (1)  $H(x, y, z) = H(x, z)$ .
- (2)  $H(x, y, z) = H(x, y + \alpha, z) \forall \alpha \in \mathbb{R}$ .
- (3)  $w = w_0$  is a constant solution of (3).
- (4)  $u$  is a solution  $\Rightarrow u + u_0$  is a solution  $\forall u_0 \in \mathbb{R}$ .
- (5)  $H(x, w_0, 0) \leq 0$  for a constant  $w_0 < 0$  and also  $H(x, w_0, 0) \geq 0$  for  $w_0 \geq 0$ .

Consider the stationary state heat equation in one dimension as stated above:

$$T'' + \underbrace{\frac{L'(T)}{L(T)}}_{H(x, T, T')} (T')^2 = 0 \text{ in } \Omega = [0, l], \quad (4)$$

with  $L' = dL/dT$  and where the second law of thermodynamics requires  $L(T) > 0$ . Equation (4) has a solution  $T = T_0 \forall T_0 \in \mathbb{R}$  and  $H, \partial_y H, \partial_z H$  are continuous once  $L \in C^2(\mathbb{R}_+)$ . Finally,  $\partial_y H \leq 0$  iff  $L''L - (L')^2 \leq 0$  which is satisfied once  $L$  is convex in  $T$  or if  $L(T) = aT^m$ ,  $a > 0$ ,  $m > 0$  or  $L(T) = L_0 \exp^{kT}$ . As all these properties are valid everywhere in  $\Omega$ , i.e., also for all its subsets, maximum principle yields monotonicity of a solution  $T(x)$  of the stationary problem (4) as a consequence of finding minimum and maximum on boundaries of  $A$ ,  $\forall A \subset \Omega$ . Therefore we may conclude that in typical situations when  $L(T) = L_0 T^m$  or  $L(T) = L_0 \exp(kT)$  for  $L_0 > 0$ ,  $m > 0$ ,  $k > 0$  the temperature field has to be monotonous in space no matter what the boundary or initial conditions are.

#### B. Thermodiffusion model

Let us extend these thoughts to a CIT model with coupling and check whether a similar situation can occur. For this purpose we shall use the standard formulation of the thermodiffusion CIT model from [3], i.e., including Soret's and Dufour's effects. Entropy production reads

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \frac{1}{T} (\nabla \mu_1)_T, \quad (5)$$

where we consider transport of heat and of one component (the second component is assumed to be at rest but can be straightforwardly generalized via the Gibbs-Duhem relation [3]). A possible choice of forces are the gradient of chemical potential at constant temperature  $-\frac{1}{T}(\nabla \mu_1)_T = -\frac{1}{T}(\nabla \mu_1 + s_1 \nabla T)$  and the gradient of inverse temperature  $\nabla \frac{1}{T}$  causing diffusion flux  $\mathbf{J}_1$  and the reduced heat flux  $\mathbf{J}_q = \mathbf{J}_q^{\text{tot}} - \sum_{\alpha} h_{\alpha} \mathbf{J}_{\alpha} = \mathbf{J}_{en} - \sum_{\alpha} h_{\alpha} \mathbf{J}_{\alpha}$  (being the difference between total heat flux and transfer of heat due to diffusion), respectively, where  $s_{\alpha}$

and  $h_\alpha$  denotes partial specific entropy and enthalpy [12,13]. The inverted linear flux-force relations in one dimension read [3]

$$\frac{\partial}{\partial x} \frac{1}{T} = r_{11} \mathbf{J}_q + r_{12} \mathbf{J}_1 \quad (6a)$$

$$-\frac{1}{T} \left( \frac{\partial \mu_1}{\partial x} \right)_T = r_{21} \mathbf{J}_q + r_{22} \mathbf{J}_1, \quad (6b)$$

where the matrix  $\mathbf{r}$  with entries  $r_{ij}$  is typically referred to as the resistivity matrix. For our purposes of discussion of thermodynamic compatibility a different choice of fluxes (and hence forces) is preferred. Particularly, one must rewrite the entropy production in such a way that fluxes in the linear flux-force relations are constant in the steady-state operation. As heat flux is not suitable, we choose diffusion flux  $\mathbf{J}_1$  (constant due to mass balance) and total energy flux  $\mathbf{J}_{en}$  (conservation of energy). All the fluxes appearing in the entropy production (5) can be rewritten in terms of these constant fluxes while requiring appropriate modifications of forces,

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \frac{1}{T} (\nabla \mu_1)_T = \mathbf{J}_{en} \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \nabla \left( \frac{\mu_1}{T} \right).$$

Hence let us further consider

$$\mathbf{X}_1 = \frac{\partial}{\partial x} \frac{1}{T} = R_{11} \mathbf{J}_{en} + R_{12} \mathbf{J}_1, \quad (7a)$$

$$\mathbf{X}_2 = -\nabla \left( \frac{\mu_1}{T} \right) = R_{21} \mathbf{J}_{en} + R_{22} \mathbf{J}_1, \quad (7b)$$

where the matrix  $\mathbf{R}$  with entries  $R_{ij}$  is an inverse to the matrix  $\mathbf{L}$  of phenomenological coefficients. Onsager relations imply  $R_{12} = R_{21}$  and  $r_{12} = r_{21}$ . The ORR are in accordance with the following relations among the resistivity matrices:

$$r_{11} = R_{11}, \quad r_{12} = R_{12} + R_{11} h_1 = r_{21}, \quad (8)$$

$$r_{22} = R_{22} + 2R_{12} h_1 + h_1^2 R_{11}. \quad (9)$$

The first formulation with the nonconstant flux of reduced heat is used for identification of measurable quantities with simple relations to the resistivity matrix  $\mathbf{r}$ . With  $\lambda = \frac{1}{T^2 r_{11}}$  being the thermal conductivity at zero mass flux and  $q_1^* = -\frac{r_{12}}{r_{11}}$  the measurable heat of transfer at constant temperature [3] we have from (6a)

$$T' = -\frac{1}{\lambda} (\mathbf{J}_q - q_1^* \mathbf{J}_1) = -\frac{1}{\lambda} (\mathbf{J}_{en} - (q_1^* + h_1) \mathbf{J}_1).$$

Under the assumption of  $\lambda$  and  $q_1^*$  being constant we get

$$T'' = \frac{1}{\lambda} h_1' \mathbf{J}_1 \quad (10)$$

as the total flux of energy  $\mathbf{J}_q^{\text{tot}} = \mathbf{J}_{en}$  and the mass flux  $\mathbf{J}_1$  are constant, not the reduced heat flux  $\mathbf{J}_q$ . In general it holds  $c_p = \left( \frac{\partial h}{\partial T} \right)_p > 0$  and hence temperature is monotonous in space for all boundary and initial conditions as follows from the maximum principle stated above. Then we have that  $L_{22}, L_{12} = L_{21}$  and  $R_{11}, R_{12} = R_{21}$  share the same functional dependence on concentration  $c_1$  as  $L_{22} = (\det \mathbf{R})^{-1} R_{11}$ ,  $L_{12} = -(\det \mathbf{R})^{-1} R_{12}$ .

The model considered that the stationary equation for temperature distribution was uncoupled from the other equation for state variable  $c_1$ . If this is not the case, the analysis of monotonicity becomes complex. We were not able to analyze the model for thermodiffusion as presented in [6] because the elliptic equations describing the model in the stationary case are strongly coupled (and the identified coefficients, e.g., heat conductivity, have to further depend on state variables due to the second law). The maximum principles for strongly coupled systems are difficult to analyze due to complex assumptions [10,14]. Perhaps this is an underdeveloped field [15] but which would find an application here.

#### IV. IMPLICATIONS FOR CIT MODELS

The value of the main result is twofold: (1) the existence of functional constraints reducing the number of necessary experiments for assessment of phenomenological coefficients; (2) verification of thermodynamic consistency of models.

We shall now focus on the latter and illustrate this idea on the thermodiffusion example. Particularly, is it plausible to assume  $\lambda$  and  $q_1^*$  as constants?

As we have  $R_{11} = r_{11} = \frac{1}{T^2 \lambda}$  and  $R_{12} = -\frac{1}{T^2 \lambda} (q_1^* + h_1)$  we require the partial specific enthalpy to be independent of  $c_1$  (as is the case with ideal gas) as otherwise the model with the assumption of constant  $\lambda$  and  $q_1^*$  would be ill-defined due to different functional dependence on  $c_1$  which would be contradictory with what was found above. Finally, if we introduce the so-called interdiffusion coefficient, following [3],  $D_1 = -\left( \frac{\mathbf{J}_1}{\partial c_1 / \partial x} \right)_{\mathbf{X}_1=0}$  and again assume it being constant, we see that the fourth coefficient,

$$R_{22} = \frac{R}{D_1} c_1^{-1} + \frac{R_{12}^2}{R_{11}},$$

does not share the same dependency on  $c_1$  (note that  $R$  denotes the gas constant). This would imply that  $L_{11} = (\det \mathbf{R})^{-1} R_{22}$  is not monotonous in  $c_1$  which is a contradiction. Hence we obtained a nontrivial conclusion that the presented thermodiffusion model is *not* a thermodynamically plausible model if we assume constant coefficients  $q_1^*, \lambda, D_1$ .

A natural question arises: What are the thermodynamically admissible dependencies of phenomenological coefficients? Let us assume that the main result holds, i.e.,  $\mathbf{X}_2$  can be set to zero while not enforcing equilibrium, together with the presumption that  $L_{11}$  is monotonously dependent on concentration  $c_1$  and analytic in  $c_1$ . Then we do not need to meet the assumptions of the maximum principle and we directly have that  $\mathbf{R}(c_1) = f(c_1) \mathbf{R}_0$ . Hence from (8) follows that

$$\lambda \propto \frac{1}{f(c_1)}, \quad D_1 \propto \left( \frac{\partial \mu_1}{\partial c_1} \right)_{T,p} \frac{1}{f(c_1)}.$$

Further as  $D_1$  approaches self-diffusion coefficient  $D_1^{\text{self}} > 0$  with  $c_1 \rightarrow 0$  and  $\lim_{c_1 \rightarrow 0} \left( \frac{\partial \mu_1}{\partial c_1} \right)_{T,p} = \infty$  we conclude that the shared dependency  $f(c_1)$  has to grow to infinity as  $c_1 \rightarrow 0$ . This is a direct generalization of the above result following from maximum principle, particularly that one cannot assume constant measured parameters  $\lambda, q_1^*, D_1$ .

On the other hand, when using a generalized interdiffusion coefficient,

$$\tilde{D}_1 = -\left(\frac{\mathbf{J}_1}{\frac{\partial \mu}{\partial x}}\right)_{\mathbf{x}_1=0} = T\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}^{-1} D_1, \quad (11)$$

constancy of  $\lambda$ ,  $q_1^*$ , and  $\tilde{D}_1$  with respect to  $c_1$  is thermodynamically consistent.

## V. DISCUSSION AND CONCLUSION

How can one obtain the phenomenological force-flux relations? The linear force-flux relations can be seen as a consequence of the quadratic dissipation potential [16],

$$J_i = \frac{\partial \Xi}{\partial X_i}, \quad \Xi = \frac{1}{2} \sum_{ij} L_{ij}(\mathbf{x}) X_i X_j, \quad (12)$$

where the forces are gradients of conjugate variables, and the matrix of phenomenological coefficients depends only on the state variables  $\mathbf{x}$ . The main result of this paper then deals with a particular dependence of the matrix,  $L_{ij} = f(\mathbf{x})\tilde{L}_{ij}$ , where  $\tilde{L}$  is a constant matrix.

From the point of view of statistical physics, such a dissipation potential is a consequence of the existence of a random process complying with the theory of large deviations [17]. The dissipation potential then becomes quadratic in the case of small fluctuations (i.e., near equilibrium), as in the original proof of ORR [4,5]. The appearance of a quadratic dissipation potential, i.e., linear force-flux relations, can be regarded as relatively well justified.

There are two routes to obtain the phenomenological coefficients: (i) to calculate them from a more detailed evolution; (ii) to find them from experimental measurements. The first route is feasible near equilibrium. One can perform, for example, the Chapman-Enskog procedure (see, e.g., [18]), or the fluctuation-dissipation theorem can be employed by means of the Green-Kubo relations [19,20]. However, knowledge of the detailed evolution from a more microscopic standpoint than the CIT theory, is needed to be studied in both cases. The authors of this paper are not aware of any statistical origin of the functional constraints (the main result). The second route is more frequent in practical modeling, and this is the place where constraints like ORR or the proposed functional constraints become extremely useful because of the reduction of the number of experiments needed to find those coefficients.

Where do the particular ideas and illustrations presented above lead us? What is the generality of these observations? We list here a sequence of arguments and elaborate on them below including the connection between Sec. II (assumptions and main result) and Sec. III (particular CIT models invoking monotonicity). Finally we summarize these arguments and the main result into a conjecture about generality of functional constraints in CIT models.

(1) The studied problem has to be such that entropy production in the 1D stationary case can be expressed solely using constant fluxes and corresponding forces. This assumption is not universally valid but applies to a wide range of coupled phenomena and in particular to situations involving transport. Constant fluxes in the 1D stationary case are partial mass fluxes (when no reactions are taking place) or total mass, total linear

momentum, charge, total angular momentum or total energy. CIT in mechanical equilibrium, which has been extremely successful in describing the many transport phenomena [3], fulfils this assumption if there are no chemical reactions and when the state variables are chosen as the conserved ones (mass, total energy, etc.). Such state variables can be chosen within CIT without any loss of generality just by means of a transformation of variables.

(2) Functional constraints have been proved to be correct in 1D stationary state models yielding a spatially monotonous state variable(s); see Sec. III. Note that this key property may not be apparent but is present in a model (we revealed it using Maximum principle). In other words, if a conjugate variable is necessarily monotonous in space, applying the same Dirichlet boundary condition to that variable on both sides of the domain leads to making the corresponding force (gradient of the conjugate variable) vanish in the whole domain. Since the other force can be nonzero at the same time, the hypothesis leading to the main result is valid in that case.

(3) Monotonicity of the state variable is a sufficient condition for hypothesis but not a necessary one. The coefficients  $L_{12}, L_{21}, L_{11}$  share the same dependence on state variable  $y_1$  if and only if the second force  $X_2$  can be set to zero everywhere in the system while keeping  $X_1$  nonzero, i.e., the system is out of equilibrium. Additionally, the same constraints apply to the fourth coefficient  $L_{22}$  if, e.g., it is a monotonous function of the state variable  $y_1$  and is an analytic function of this variable.

(4) Any reasonable physical model in two or three dimensions and in both stationary and the nonstationary setting should be applicable to the 1D stationary situation as a special case.

(5) Only two coupled processes were considered. However, extension of the presented ideas to a larger number of coupled processes is straightforward.

We shall now discuss the formal and physical meaning of the obtained results in this article in terms of the above five listed arguments and formulate a conjecture about the generality of the results. Let us assume that the system satisfies point 1 above. Then the validity of the functional constraints is equivalent to a possibility of applying a given CIT model to a steady-state 1D system (a natural requirement for a given model irrespective of its dimensionality or stationarity; see point 2) and setting only one force to zero while being outside of equilibrium [point 3]). We remain uncertain about generality of this latter requirement, however, it seems to be natural, e.g., it is used for definitions of physically measurable parameters [3]. Then we propose the following hypothesis as a generalization of the proven main result: *All the phenomenological coefficients in the linear force-flux relations in CIT models, where entropy production in the 1D stationary case can be expressed solely using constant fluxes and corresponding forces, share the same functional dependency on state variables.*

Note that even when this hypothesis is not found to be valid in its full generality, a class of CIT models was identified in Sec. III where monotonicity of state variables on the spatial coordinate is proven and consequently automatically guarantees the validity of the functional constraints as it implies  $\mathbf{X}_1 = 0$  while  $\mathbf{X}_2 \neq 0$ . Additionally, the studied thermodiffusion example showed that this sufficient property of

monotonicity is not intuitive nor apparent and hence there would be no *a priori* indication of the need to enforce such a constraint on the model formulation even if the hypothesis is not valid in general.

### A. Implications for theory

What is the significance of these functional constraints? (1) The number of experiments needed to evaluate the phenomenological coefficients is reduced. (2) The consistency check of theoretical models can be carried out. We choose the thermodiffusion model to illustrate the validity of functional constraints.

Thermodynamic consistency requires that in the case of constant  $\lambda$  and  $q_1^*$ , partial enthalpy has to be independent of  $c_1$  irrespective of the studied material properties which is a nontrivial constraint. Similarly we showed that the presented thermodiffusion model is *not* a thermodynamically plausible model if the coefficients  $q_1^*, \lambda, D_1$  are constants.

The significance of this last observation can be appreciated, for example, as follows. Fick's diffusion law is recovered in the isothermal case from the considered thermodiffusion model with  $D_1$  being the diffusion coefficient. Then we observe that the widely used assumption of the constant diffusion coefficient is thermodynamically inconsistent once the considered system would have a nonzero thermodiffusion coupling in the nonisothermal case. On the other hand, if we let the interdiffusion coefficient scale as  $D_1 \propto c_1^{-1}$ , both matrices  $\mathbf{L}$  and  $\mathbf{R}$  are independent of  $c_1$  and hence thermodynamically consistent.

Finally note that in the case of the isothermal Maxwell-Stefan model the usual assumption of constant Maxwell-Stefan diffusion coefficient  $D_{\alpha\beta}$  is thermodynamically consistent as the resistance matrix  $\tilde{\mathbf{r}}$  shares the same functional dependency if and only if all  $D_{\alpha\beta}$  share the same functional dependency as  $D_{\alpha\beta} = R/\tilde{r}_{\alpha\beta}$  [3], Chap. 12.

### B. Implications for experiments

Our analysis of functional constraints for coupled transport was stimulated by experimental observations of water and proton transport in ionomer membranes. Water diffusion and proton conductivity were both found to increase with membrane water content. But there were no consistency checks between the transport coefficients. We carried out a detailed set of experiments measuring proton current and water flux while systematically controlling the water activity, water activity gradient, temperature, and electric potential gradient.

In a particular setup of water and proton transport experiment in a proton exchange membrane we first carefully assessed the range of applied voltage  $\Phi$  for which linear force-flux relations for  $\mathbf{j}_p$  proton and  $\mathbf{j}_w$  water flux apply:

$$\begin{aligned}\mathbf{j}_p &= L_{pp}\mathbf{X}_p + L_{pw}\mathbf{X}_w, \\ \mathbf{j}_w &= L_{wp}\mathbf{X}_p + L_{ww}\mathbf{X}_w,\end{aligned}$$

where the thermodynamic forces are  $\mathbf{X}_w = -\frac{1}{T}\nabla\mu_w$  and  $\mathbf{X}_p = -\frac{1}{T}F\nabla\Phi$ . This range was found to be narrow,  $\nabla\Phi \in (0, 0.2)$ , and we refer the interested reader to consult [21] where we present the experiment in detail and also reasons for and implications from this observation.

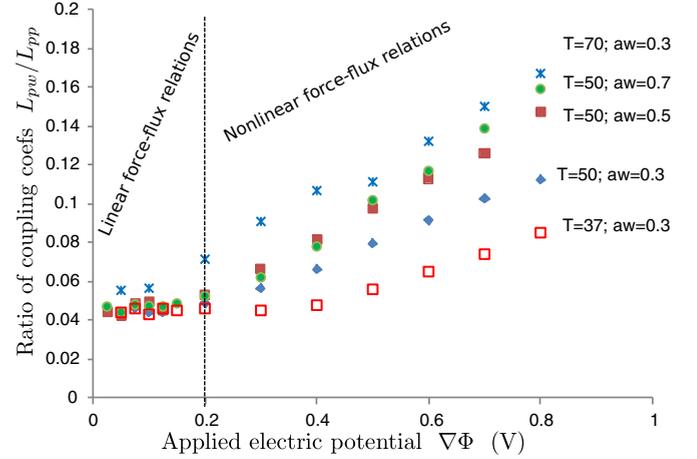


FIG. 1. Experimental verification of the proposed hypothesis for a Nafion membrane electrode assembly. Transport of water and protons are considered and the linear force-flux regime was identified to be for the range  $\nabla\Phi \in (0, 0.2)$  of the applied electric potential  $\nabla\Phi$  across a membrane electrode assembly. Temperature and water activity at open circuit are as noted on the graph. The measured data suggest the same functional dependence of diagonal ( $L_{pp}$ ) and cross- ( $L_{pw} = L_{wp}$ ) coefficients on water concentration.

In Fig. 1 we show that within the range of CIT (linear force-flux relations) the cross-coefficient  $L_{pw} = L_{wp}$  and the diagonal coefficient  $L_{pp}$  indeed do share the same functional dependency on water content (and, in addition, on temperature). Further, in Fig. 2 it is shown that the diagonal coefficients share the same functional dependency on water

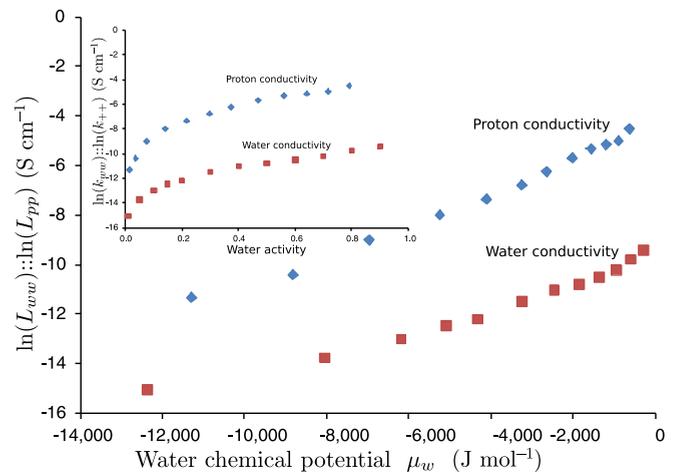


FIG. 2. Experimental verification of the proposed hypothesis for a Nafion membrane electrode assembly. As data indicate, the functional dependency of proton conductivity  $L_{pp}$  and water conductivity  $L_{ww}$  on water concentration can be regarded equal (note that the shift in the logarithmic values corresponds to multiplication by a constant). These observations together with conclusions from Fig. 1 suggest that the proposed hypothesis holds true in the studied situation. Particularly, the whole matrix of phenomenological coefficients shares the same functional dependency on water concentration. The inset graph in the upper right shows the same data plotted as a function of water activity.

activity yielding, with the help of ORR, the result proposed by the hypothesis.

Finally we would like to emphasize the implications of the hypothesis from the experimental perspective. Functional constraints (hypothesis) imply conditions on phenomenological coefficients that have to be met in experimental data in order to be thermodynamically consistent. If this conclusion is not observed, either the measurement, experiment or the used

model (including the CIT framework itself) has to be checked and revised.

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