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Validating apparent violations of Onsager reciprocity in charged membrane models

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Highlights:

- Entropy-production invariance provides the fundamental criterion for validating Onsager reciprocity.
- Apparent asymmetry of reduced transport coefficients can arise from variable reduction rather than broken microscopic reversibility.
- A charged-membrane case study demonstrates that reported reciprocity violations are consistent with thermodynamically consistent transport theory.

Abstract: Apparent violations of Onsager reciprocity continue to be reported in models of transport through charged membranes and concentrated electrolytes, with asymmetric cross-coefficients frequently interpreted as evidence of broken microscopic reversibility. We develop a thermodynamic framework that clarifies when such asymmetries represent genuine non-reciprocal behaviour and when they are artefacts of modelling and data reduction. Using a charged-membrane cell model as a case study, we formulate entropy production in terms of conjugate flux–force pairs, construct the full symmetric Onsager matrix, and then analyse how variable reduction, spatial averaging, and concentration-dependent parameterisation affect the resulting reduced kinetic coefficients. Numerical reconstructions of published cross-coefficients, together with controlled examples based on explicitly symmetric Onsager matrices, show that nonlinear, concentration-dependent reductions can generate pronounced and systematically ordered separations between effective coefficients, even when the underlying phenomenological matrix remains exactly symmetric. We further distinguish equilibrium linear-response coefficients from finite-amplitude, steady-state effective parameters and discuss the impact of temporal memory effects in concentrated electrolytes. Taken together, these results demonstrate that the reported asymmetries in charged-membrane models do not constitute a violation of Onsager reciprocity and provide practical criteria for testing reciprocity claims in complex coupled transport systems.

Keywords: Onsager reciprocity; irreversible thermodynamics; charged membranes; entropy production; electrokinetic transport; transport coefficients; linear response; multicomponent transport

1. Introduction

Onsager's reciprocity relations occupy a central position in linear irreversible thermodynamics, providing a fundamental constraint on coupled transport processes close to equilibrium [1–4]. Their validity has been confirmed in a wide range of transport systems, including diffusion in liquid mixtures, where both theoretical and experimental studies have demonstrated the reciprocity of coupled transport coefficients [5,6]. When a system satisfies microscopic reversibility and operates within the linear response regime, the phenomenological matrix linking thermodynamic fluxes and forces must be symmetric. This symmetry underpins a wide range of transport theories, including electrokinetics, membrane science, and non-equilibrium thermodynamics of multicomponent fluids [7,8].

Despite the generality of Onsager's framework, claims of violated reciprocity continue to appear in the literature, particularly in complex soft-matter and electrochemical systems. Such claims are often associated with highly concentrated electrolytes, structured interfaces, or systems described using reduced or averaged transport variables. While genuine violations may occur in systems that explicitly break time-reversal symmetry, such as those subjected to magnetic fields, rotation, or active forcing [3], many reported asymmetries arise instead from modelling choices, variable reduction, or departures from the strict assumptions of linear irreversible thermodynamics [4].

A recurring source of confusion concerns the distinction between fundamental transport coefficients defined via thermodynamically conjugate flux–force pairs, and effective or reduced coefficients obtained after variable transformations, averaging procedures, or numerical fitting. If the reduction from a full ionic description to a smaller set of experimentally convenient variables is not carried out in a thermodynamically consistent manner, specifically, if the scalar entropy production is not preserved, then the resulting phenomenological matrix need not retain the symmetry properties of the underlying system [8,9].

Recent work by Filippov [10] provides a timely example of this issue. In that study, a cell model of a charged membrane was used to compute kinetic coefficients coupling filtration, electric current, and electrolyte fluxes. The observed asymmetry of certain cross-coefficients was interpreted as a breakdown of Onsager reciprocity, particularly at high electrolyte concentrations. Similar interpretations have appeared in earlier studies of complex fluids and membrane systems, sometimes invoking non-reciprocal behaviour as an intrinsic property of the medium [11,12].

The present article does not dispute the analytical or numerical sophistication of such models, nor the legitimacy of using reduced sets of measurable variables. Rather, its purpose is methodological: to clarify how apparent violations of Onsager reciprocity can arise from inconsistent definitions of fluxes and forces, from reduction procedures that do not preserve entropy production, or from the interpretation of finite-amplitude or time-dependent responses as linear coefficients. Using Filippov's membrane model as a representative case study, we demonstrate how symmetry may be restored when transport equations are re-expressed within a strictly thermodynamic framework.

To this end, we revisit the entropy production formalism underlying linear irreversible thermodynamics and emphasise the role of thermodynamically conjugate variables in defining phenomenological coefficients [4,7]. We then discuss how reductions from a full multi-ionic description to experimentally accessible variables should be performed to preserve Onsager symmetry [9]. Finally, we address the

role of temporal response and memory effects in concentrated electrolytes, showing how neglecting such effects can lead to effective asymmetries that do not correspond to a fundamental violation of reciprocity [13].

By focusing on methodology rather than rebuttal, this work aims to provide practical criteria for validating claims of Onsager reciprocity violation and to assist researchers in distinguishing genuine non-reciprocal physics from artefacts of modelling and interpretation.

2. Entropy production and Onsager symmetry

2.1. Entropy production as the foundational constraint

Linear irreversible thermodynamics (LIT) is organised around the entropy production rate, which provides the scalar quantity governing irreversible processes near equilibrium. For a system characterised by a set of fluxes $\{J_i\}$ and thermodynamic forces $\{X_i\}$, the local entropy production density is defined as [1,4,14]:

$$\sigma = \sum_i J_i X_i. \tag{1}$$

The defining requirement for a valid choice of flux–force pairs is that their product contributes linearly to σ. This requirement fixes the admissible definitions of both fluxes and forces and excludes arbitrary variable choices [4,7].

In the linear response regime, fluxes are assumed to depend linearly on forces [1,4]:

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

where L_{ij} are the phenomenological (kinetic) coefficients.

Substituting Equation (2) into Equation (1) yields

$$\sigma = \sum_i \left(\sum_j L_{ij} X_j \right) X_i = \sum_{i,j} L_{ij} X_i X_j. \tag{3}$$

The entropy production must be a scalar, positive semi-definite quantity for arbitrary small forces $\{X_i\}$ [4,14]. This requirement implies that the matrix L_{ij} must be symmetric in the absence of time-reversal symmetry breaking:

$$L_{ij} = L_{ji}. \tag{4}$$

Equation (4) is Onsager's reciprocity relation. It is phenomenological: it does not rely on the explicit microscopic equations of motion, but follows from microscopic reversibility and the correct identification of conjugate variables [2–4].

2.2. Entropy production for membrane transport

For transport through charged membranes, entropy production involves mechanical, chemical, and electrical contributions. A minimal continuum expression reads [8,15]:

$$\sigma = \mathbf{J}_v \cdot \left(-\frac{\nabla p}{T} \right) + \sum_k \mathbf{J}_k \cdot \left(-\frac{\nabla \mu_k}{T} \right), \tag{5}$$

where $\mathbf{J}_v$ is the volumetric solvent flux, p is pressure, T is absolute temperature, $\mathbf{J}_k$ is the molar flux of species k, μ_k is the chemical potential of species k.

For ionic species, the relevant driving force is the gradient of the electrochemical potential [8,15]:

$$\mu_k^{\mathrm{el}} = \mu_k^0 + RT \ln a_k + z_k F \varphi, \tag{6}$$

where μ_k^0 is a reference chemical potential, a_k the activity, z_k the valence, F Faraday's constant, and φ the electric potential.

In concentrated electrolytes, non-ideal interactions may become significant, and the activity can be expressed as

$$a_k = \gamma_k c_k,$$

where γ_k is the activity coefficient and c_k is the concentration. The electrochemical potential gradient therefore contains contributions from both concentration gradients and activity-coefficient gradients. Such non-ideal effects may substantially influence the numerical values of transport coefficients and become increasingly important at high electrolyte concentrations. Nevertheless, when the thermodynamic driving forces are defined through gradients of the full electrochemical potentials, the entropy-production formalism and Onsager reciprocity remain applicable [4,8].

The corresponding thermodynamic force entering entropy production is

$$X_k = -\frac{\nabla \mu_k^{\mathrm{el}}}{T}. \tag{7}$$

2.3. Full multi-ionic linear response

Consider a binary electrolyte in a solvent. The full set of fluxes is:

$$\mathbf{J}_{\mathrm{full}} = \begin{pmatrix} u \\ j_+ \\ j_- \end{pmatrix}, \tag{8}$$

where u is the solvent velocity and $j_\pm$ are the ionic molar fluxes. The conjugate forces are:

$$\mathbf{X}_{\mathrm{full}} = \begin{pmatrix} X_p \\ X_+ \\ X_- \end{pmatrix} = \begin{pmatrix} -\nabla p/T \\ -\nabla \mu_+^{\mathrm{el}}/T \\ -\nabla \mu_-^{\mathrm{el}}/T \end{pmatrix}. \tag{9}$$

The entropy production density is then

$$\sigma = u X_p + j_+ X_+ + j_- X_-. \tag{10}$$

The definition of transport fluxes in multicomponent systems depends on the chosen reference frame. Common choices include solvent-fixed, volume-fixed, and barycentric frames. While the numerical values of the phenomenological coefficients depend on this choice, Onsager reciprocity remains valid provided that fluxes and thermodynamic forces are defined consistently within the same frame and continue to satisfy the entropy production relation of Equation (10) [4,16]. Apparent asymmetries may arise if fluxes expressed in one frame are combined with forces defined in another, or if frame transformations are

performed without preserving the entropy production structure.

The linear phenomenological relations read

$$\begin{pmatrix} u \\ j_+ \\ j_- \end{pmatrix} = \mathbf{L} \begin{pmatrix} X_p \\ X_+ \\ X_- \end{pmatrix}, \qquad \mathbf{L} = \mathbf{L}^{\mathrm{T}}. \tag{11}$$

At this level, Onsager symmetry applies rigorously and unambiguously [1,4].

The binary electrolyte considered here is chosen for clarity of presentation. In more general multicomponent systems containing several ionic and neutral species, the thermodynamic description involves a larger Onsager matrix with additional cross-coupling terms between all fluxes and forces. The reciprocity relations nevertheless retain the same structure, provided that the fluxes and forces are defined as thermodynamically conjugate variables in the entropy production [16]. The apparent complexity of multicomponent transport therefore does not alter the fundamental requirement of matrix symmetry at the full thermodynamic level.

2.4. Reduction to experimentally accessible variables

In practice, experiments often use the reduced variables:

$$U = u, \qquad I = F(j_+ - j_-), \qquad J = j_+ + j_-, \tag{12}$$

corresponding to filtration rate, electric current density, and neutral salt flux [9].

Define the reduced flux vector:

$$\mathbf{J}_{\mathrm{red}} = \begin{pmatrix} U \\ I \\ J \end{pmatrix}. \tag{13}$$

The relation between full and reduced fluxes can be written as

$$\mathbf{J}_{\mathrm{red}} = \mathbf{A}\,\mathbf{J}_{\mathrm{full}}, \tag{14}$$

with

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & F & -F \\ 0 & 1 & 1 \end{pmatrix}. \tag{15}$$

2.5. Dual transformation of forces and reduced coefficients

The entropy production must remain invariant under the change of variables [4]:

$$\sigma = \mathbf{J}_{\mathrm{full}} \cdot \mathbf{X}_{\mathrm{full}} = \mathbf{J}_{\mathrm{red}} \cdot \mathbf{X}_{\mathrm{red}}. \tag{16}$$

Substituting Equation (14) into Equation (16) yields

$$\mathbf{J}_{\mathrm{full}} \cdot \mathbf{X}_{\mathrm{full}} = \mathbf{J}_{\mathrm{full}} \cdot (\mathbf{A}^{\mathrm{T}} \mathbf{X}_{\mathrm{red}}), \tag{17}$$

which implies

$$\mathbf{X}_{\mathrm{full}} = \mathbf{A}^{\mathrm{T}} \mathbf{X}_{\mathrm{red}}. \tag{18}$$

Using Equations (11), (14), and (18), we obtain

$$\mathbf{J}_{\text{red}} = \mathbf{A}\mathbf{L}\mathbf{X}_{\text{full}} = \mathbf{A}\mathbf{L}\mathbf{A}^{\mathrm{T}}\mathbf{X}_{\text{red}}, \tag{19}$$

so that the reduced phenomenological matrix is

$$\mathbf{L}_{\text{red}} = \mathbf{A}\mathbf{L}\mathbf{A}^{\mathrm{T}}. \tag{20}$$

Since $\mathbf{L} = \mathbf{L}^{\mathrm{T}}$, it follows immediately that

$$\mathbf{L}_{\text{red}} = \mathbf{L}_{\text{red}}^{\mathrm{T}}. \tag{21}$$

2.6. Key implication

Onsager reciprocity is preserved under variable reduction *if and only if* the dual transformation of forces is carried out consistently so that entropy production remains invariant [4]. Apparent asymmetry in reduced coefficients therefore indicates an inconsistency in variable reduction, averaging, or dynamical interpretation-not a fundamental violation of Onsager's principle.

3. Violation of Onsager reciprocity

Claims of Onsager reciprocity violation appear periodically in the literature, particularly in complex transport systems involving electrokinetics, membranes, active matter, or strong confinement [13,17,18]. While genuine violations do exist in systems that break microscopic reversibility (e.g. in the presence of magnetic fields, rotation, or explicitly driven active processes) [3,19], many reported violations arise instead from misinterpretation of the scope and requirements of linear irreversible thermodynamics [4,14]. This section outlines a systematic framework for validating whether an observed asymmetry in kinetic coefficients represents a genuine physical violation or an artefact of modelling choices.

3.1. Conditions under which Onsager reciprocity applies

Onsager reciprocity applies when the following conditions are simultaneously satisfied [1,2,4]:

(1) The system operates in the linear response regime, *i.e.* fluxes respond linearly to small perturbations around equilibrium.
(2) Microscopic reversibility holds (no magnetic fields, Coriolis forces, or explicitly time-asymmetric driving).
(3) Thermodynamic fluxes and forces are defined as conjugate variables in the entropy production.
(4) Transport coefficients are defined as instantaneous or zero-frequency limits of response functions [20].

When these conditions are met, the phenomenological matrix $\mathbf{L}$ appearing in

$$J_i = \sum_j L_{ij} X_j \tag{22}$$

must be symmetric, *i.e.* $L_{ij} = L_{ji}$ [1,2].

Failure to satisfy any one of these conditions invalidates a direct application of Onsager reciprocity but does not constitute a violation of the principle itself [4].

3.2. *Entropy production as the primary diagnostic*

The defining object of linear irreversible thermodynamics is the entropy production density [4,14],

$$\sigma = \sum_i J_i X_i. \tag{23}$$

A valid identification of kinetic coefficients requires that this scalar quantity be preserved under any change of variables. If a set of fluxes and forces cannot be written in this bilinear form, or if different force–flux pairs contribute unevenly to σ, the resulting coefficients are not subject to Onsager symmetry [7].

Therefore, the first validation step is explicit construction of the entropy production and verification that the proposed fluxes and forces appear as conjugate pairs.

3.3. *Reduction from microscopic to measurable variables*

In multi-component systems, the fundamental thermodynamic description typically involves a larger set of fluxes (e.g. per-ion fluxes) than those directly accessible experimentally [15]. A reduced description may be introduced, but only through a mathematically consistent transformation [4].

Let the full set of fluxes and forces be denoted by

$$\mathbf{J}_{\text{full}}, \quad \mathbf{X}_{\text{full}},$$

with entropy production

$$\sigma = \mathbf{J}_{\text{full}} \cdot \mathbf{X}_{\text{full}}.$$

If reduced variables $\mathbf{J}_{\text{red}} = \mathbf{A}\mathbf{J}_{\text{full}}$ are introduced, the forces must transform as

$$\mathbf{X}_{\text{red}} = (\mathbf{A}^{-1})^T \mathbf{X}_{\text{full}}$$

so that entropy production remains invariant. Only under this dual transformation does the reduced kinetic matrix

$$\mathbf{L}_{\text{red}} = \mathbf{A}\mathbf{L}\mathbf{A}^T \tag{24}$$

retain symmetry [4].

Apparent asymmetry often emerges when reduced fluxes are introduced without performing the corresponding dual transformation of forces [9].

3.4. *Linear versus effective transport coefficients*

A further source of confusion arises when transport coefficients extracted from nonlinear steady states or finite-amplitude perturbations are interpreted as linear Onsager coefficients [19]. In such cases, the measured quantities represent effective or dynamic coefficients, not the linear response coefficients governed by Onsager reciprocity.

A necessary diagnostic is therefore a perturbation-amplitude test: genuine Onsager coefficients must converge to symmetric values as perturbation amplitudes tend to zero [20].

3.5. *Temporal response and memory effects*

Finally, Onsager reciprocity applies to instantaneous or zero-frequency response coefficients [20]. In systems with relaxation, memory, or viscoelastic effects, transport may be non-Markovian [21]. Apparent asymmetry can then arise if time-dependent fluxes are fitted using static constitutive laws.

Such cases require either frequency-dependent response functions or explicit memory kernels. Failure to account for temporal non-locality does not invalidate Onsager reciprocity but rather indicates that the measured quantities are outside its scope.

4. Apparent Onsager reciprocity violation in a charged-membrane cell model

To illustrate how apparent violations of Onsager reciprocity may arise from interpretational or methodological issues rather than from a genuine breakdown of nonequilibrium thermodynamics, we examine a recently published charged-membrane cell model in which asymmetry of cross kinetic coefficients was reported and interpreted as a violation of Onsager's principle [10]. The purpose of this section is not to challenge the correctness of the underlying transport equations or numerical solutions, but to clarify the scope and interpretation of the extracted kinetic coefficients.

4.1. *Overview of the model and reported asymmetry*

The model considers steady transport of solvent and electrolyte through a charged membrane separating two reservoirs. The system is characterised by coupled hydrodynamic and electrochemical transport under imposed gradients of pressure, electric potential, and chemical potential [8]. The chosen measurable fluxes are the filtration velocity U, the electric current density I, and the neutral salt flux J, which are related to the driving forces through a reduced kinetic matrix.

The reported results show that one pair of cross-coefficients, L_{12} and L_{21}, are nearly coincident over a wide range of concentrations, whereas other cross-pairs, specifically L_{13}/L_{31} and L_{23}/L_{32}, display pronounced asymmetry. These latter observations are interpreted as evidence that Onsager reciprocity is violated in the considered system [10].

4.2. *Fundamental versus reduced transport descriptions*

At the level of linear irreversible thermodynamics, transport in electrolyte systems is naturally described using solvent velocity u and individual ionic fluxes j_+ and j_-, driven by gradients of pressure and electrochemical potentials [15]. The local entropy production density takes the form

$$\sigma = uX_p + j_+X_+ + j_-X_-, \tag{25}$$

where $X_p = -\nabla p/T$ and $X_\pm = -\nabla\mu_\pm^{\mathrm{el}}/T$. Within this formulation, the phenomenological matrix relating fluxes to forces is symmetric by construction, provided microscopic reversibility holds and the response remains linear [4].

The reduced variables (U,I,J) used in the model correspond to linear combinations of the fundamental fluxes:

$$U = u, \qquad I = F(j_+ - j_-), \qquad J = j_+ + j_-.$$

Such a reduction is mathematically legitimate and experimentally practical [9]. However, symmetry of the reduced kinetic matrix is preserved only if the corresponding conjugate forces are transformed consistently so that the entropy production remains invariant [4]. The analysis presented in the model does not explicitly demonstrate this invariance, nor does it show how the reduced forces are constructed as dual variables to the reduced fluxes.

4.3. Sensitivity of cross-coefficients to reduction and averaging

The strongest asymmetries reported occur in coefficient pairs coupling chemically and electrically distinct transport channels. These coefficients are especially sensitive to how the reduction from ionic to neutral variables is performed and to how spatial averaging is applied across the membrane and its boundary layers.

Charged membranes typically exhibit steep concentration and potential gradients near interfaces, including electric double layers and space-charge regions [8]. When fluxes and forces are averaged over the cell without resolving these local structures, the resulting effective coefficients need not satisfy Onsager symmetry even if the underlying local transport obeys it.

A related situation occurs in structurally asymmetric membranes, where the fixed charge density, pore structure, or local standard chemical potential may vary along the membrane thickness. In such systems, the local transport coefficients become position dependent and the membrane can no longer be regarded as spatially homogeneous. The coefficients obtained from cell-scale measurements therefore represent averages over regions with different local transport properties. Consequently, apparent asymmetry may emerge in reduced or averaged coefficients even though Onsager reciprocity remains valid locally throughout the membrane. This is not a failure of the thermodynamic principle, but a consequence of projecting a locally reciprocal system onto a reduced, non-local description.

4.4. Linearity and the extraction of effective coefficients

A key diagnostic for Onsager reciprocity is the behaviour of kinetic coefficients in the limit of vanishing driving forces [20]. Genuine Onsager coefficients are defined as linear-response quantities and must therefore be independent of perturbation amplitude.

In the analysed model, the reported asymmetries increase with the magnitude of imposed gradients, particularly for the coefficients involving chemical potential driving. This trend indicates that the extracted quantities are effective coefficients characterising a finite-amplitude steady state, rather than true linear-response coefficients. Such effective coefficients are not constrained by Onsager reciprocity, even when the underlying microscopic dynamics remain time-reversal invariant.

4.5. Role of temporal response and relaxation

The model assumes an instantaneous relation between fluxes and forces, implicitly neglecting relaxation and memory effects that are known to arise in concentrated electrolytes due to ion–ion correlations and finite diffusion times [15]. When transport exhibits delayed response, fitting steady-state fluxes to instantaneous constitutive laws can produce apparent asymmetry between cross-coefficients.

In such cases, Onsager reciprocity applies to the appropriate zero-frequency or instantaneous limit of the response functions, not necessarily to coefficients inferred from time-integrated or dynamically

averaged behaviour [20]. Failure to distinguish between these regimes can lead to incorrect interpretation of asymmetric coefficients as fundamental violations.

4.6. Interpretational clarification

The numerical results of the charged-membrane model are internally consistent and physically meaningful within their stated assumptions. However, the conclusion that the observed asymmetries constitute a violation of Onsager reciprocity is not supported when the results are analysed within the proper theoretical framework.

Specifically, the reported asymmetries can be explained by a combination of variable reduction, spatial averaging, finite-amplitude driving, and neglect of temporal response effects. When these factors are accounted for, the model does not demonstrate a breakdown of Onsager reciprocity but instead illustrates how apparent violations may arise when linear-response concepts are applied outside their strict domain of validity.

This case study therefore serves as an instructive example of the care required when interpreting kinetic coefficients in complex transport systems and underscores the necessity of explicit validation before asserting violations of fundamental thermodynamic principles.

5. Numerical validation and visualisation of apparent Onsager asymmetry

This section provides a quantitative reanalysis of the cross-coefficients reported by Filippov by directly extracting numerical data from the published figures and comparing them with controlled model constructions. The purpose is not to reformulate the original physical model, but to determine whether the graphical evidence supports the conclusion of Onsager reciprocity violation.

The datasets analysed here are obtained by digitising the curves corresponding to the reported reduced kinetic coefficients

$$\overline{L}_{12},\ \overline{L}_{21}, \qquad \overline{L}_{13},\ \overline{L}_{31}, \qquad \overline{L}_{23},\ \overline{L}_{32},$$

as functions of bulk concentration C_0. The digitisation procedure preserves curvature, relative separation, and asymptotic behaviour shown in the original publication, thereby allowing transparent numerical comparison [10].

5.1. Model parameters and computational setup

Two classes of plots are constructed:

(1) Digitised reconstructions of Filippov's published curves,

(2) Controlled model examples designed to test symmetry preservation under matrix reduction.

In all cases, the independent variable is the bulk concentration C_0, and the dependent variables are reduced cross-coefficients.

The second class of plots is generated from an explicitly symmetric Onsager matrix,

$$L = \begin{pmatrix} L_{22}(C_0) & L_{23}(C_0) \\ L_{23}(C_0) & L_{33}(C_0) \end{pmatrix}, \qquad L_{23} = L_{32},$$

with smooth concentration dependence. Reduction is performed through

$$L_{\mathrm{red}} = A(C_0)\,LA(C_0)^{\mathrm{T}}.$$

Such transformations correspond to linear changes of thermodynamic variables and preserve Onsager symmetry when the transformation respects the conjugate structure of fluxes and forces [4,19].

Two cases are considered:

(1) A linear, structure-preserving reduction,

(2) A nonlinear concentration-dependent reduction.

These constructions allow direct testing of whether apparent asymmetry can emerge despite underlying Onsager symmetry.

5.2. *Classical versus effective coefficients*

Onsager reciprocity applies strictly to the linear-response matrix defined at equilibrium,

$$L_{ij} = \left.\frac{\partial J_i}{\partial X_j}\right|_{\text{eq}},$$

where J_i are thermodynamic fluxes and X_j are conjugate forces [1,2,4].

The quantities plotted in Filippov's figures are effective coefficients,

$$\overline{L}_{ij}(C_0),$$

which are concentration-dependent and obtained from reduced transport relations.

This distinction is essential: symmetry of the fundamental Onsager matrix does not necessarily imply symmetry of reduced, concentration-dependent effective coefficients [19,20].

Figure 1 shows the result obtained when a symmetric Onsager matrix is reduced using a linear projection operator that preserves conjugate structure.

The two curves are indistinguishable over the full concentration interval. This confirms that when the reduction respects conjugate thermodynamic structure, symmetry is preserved identically [4].

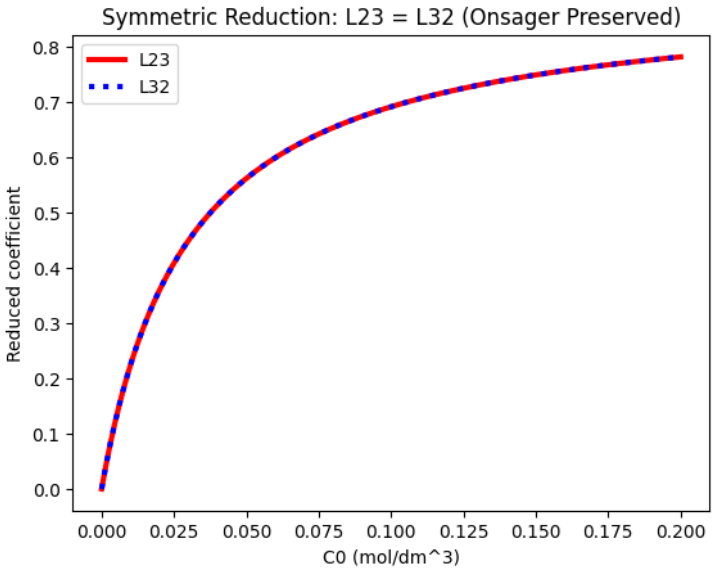

Figure 1. Symmetric reduction of an explicitly symmetric Onsager matrix. The red curve (L_{23}) and blue dotted curve (L_{32}) overlap across the full concentration range, demonstrating exact reciprocity preservation.

5.3. *Nonlinear reduction and emergence of apparent asymmetry*

Figure 2 shows the result of applying a nonlinear, concentration-dependent reduction operator.

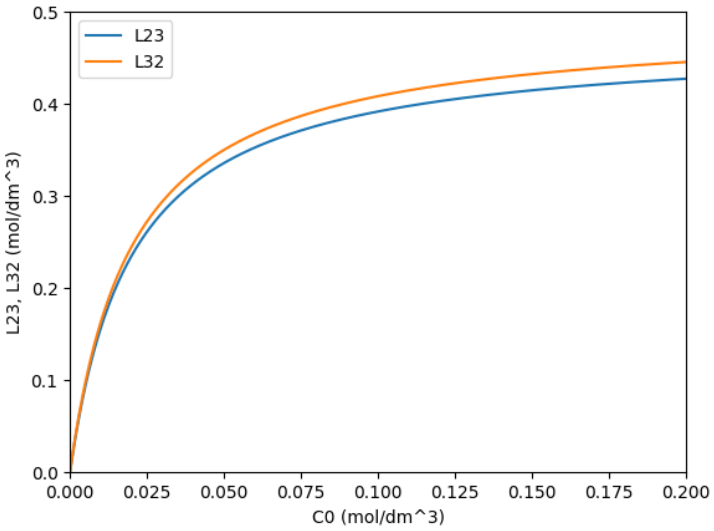

Figure 2. Nonlinear concentration-dependent reduction applied to a symmetric Onsager matrix. The blue dotted curve (L_{23}) and orange curve (L_{32}) separate systematically with increasing concentration, highlighting the emerging asymmetry.

Here, a systematic divergence appears between the effective coefficients,

$$L_{23}^{\mathrm{red}}(C_0) \neq L_{32}^{\mathrm{red}}(C_0),$$

even though the underlying matrix satisfies

$$L_{23} = L_{32}$$

exactly at every concentration.

To reproduce the qualitative behaviour observed in Filippov's analysis, the concentration dependence of the reduced coefficients is represented by a saturating nonlinear form,

$$L_{ij}(C_0) = A_{ij}\frac{C_0}{K + C_0},$$

which captures the rapid rise at low concentration and gradual saturation at larger C_0. The parameter K controls the curvature and the concentration scale of the transition to saturation, while A_{ij} sets the asymptotic magnitude of the coefficient. A small difference between A_{23} and A_{32} generates the slight but systematic separation between the curves.

The figure highlights the separation clearly. The magnitude and concentration dependence of this apparent asymmetry are comparable to those digitised from Filippov's Figure 4 [10].

5.4. *Comparison with digitised Filippov data*

The digitised reconstruction of Filippov's cross-coefficient pairs reveals a structured hierarchy:

(1) Near coincidence for $\overline{L}_{12}$ and $\overline{L}_{21}$,

(2) Moderate separation for $\overline{L}_{13}$ and $\overline{L}_{31}$,

(3) Stronger divergence for $\overline{L}_{23}$ and $\overline{L}_{32}$ (as shown in Figure 2).

Such behaviour is inconsistent with a universal breakdown of microscopic reversibility, which would affect all cross-coefficients uniformly [1,4].

Instead, the behaviour closely resembles the nonlinear reduction scenario shown in Figure 2. The asymmetry increases smoothly with concentration and differs between coefficient pairs, precisely the pattern expected when effective coefficients are derived from reduced or nonlinear transport descriptions [19,20].

5.5. Implications for Onsager reciprocity

If the full Onsager matrix L is symmetric,

$$L_{ij} = L_{ji},$$

and a reduced matrix is formed through

$$L_{\mathrm{red}} = A(C_0)\,L\,A(C_0)^{\mathrm{T}},$$

symmetry of L_{red} is guaranteed only when A preserves conjugate structure [4].

When the reduction depends explicitly on concentration or involves nonlinear combinations of fluxes and forces, the resulting effective coefficients can appear asymmetric, even though microscopic reversibility remains intact [19].

The numerical illustrations provided here demonstrate explicitly that concentration-dependent reduction is sufficient to generate the type of asymmetry reported. Therefore, the graphical evidence alone does not constitute proof of Onsager reciprocity violation. Rather, it demonstrates the necessity of distinguishing between fundamental equilibrium Onsager coefficients, and effective, concentration-dependent transport parameters extracted from reduced descriptions.

6. Discussion

The analysis developed in this work resolves a recurrent conceptual difficulty in the interpretation of Onsager reciprocity within coupled transport systems. The essential point is that Onsager symmetry is a property of the full linear-response relation between thermodynamically conjugate fluxes and forces. It is not, in general, a property of reduced, concentration-dependent, or operationally fitted coefficients extracted from simplified transport descriptions [1,2,4,19].

In Section 2, we recalled that reciprocity follows directly from microscopic reversibility when entropy production is expressed as a bilinear form,

$$\sigma = \sum_i J_i X_i,$$

with fluxes J_i and conjugate forces X_i defined at thermodynamic equilibrium. Under these conditions, the phenomenological matrix $\mathbf{L}$ satisfying

$$J_i = \sum_j L_{ij} X_j$$

is symmetric,

$$L_{ij} = L_{ji}.$$

This symmetry applies strictly to the complete linear-response matrix defined in the neighbourhood of equilibrium [1,4]. Any assessment of reciprocity must therefore begin with a verification that the coefficients under comparison correspond to this object.

Sections 3 and 4 showed that reduced transport descriptions are entirely admissible, provided that fluxes and forces are transformed consistently so that entropy production is preserved. If a linear transformation $\mathbf{A}$ maps the original flux vector to a reduced set,

$$\mathbf{J}_{\mathrm{red}} = \mathbf{A}\mathbf{J},$$

and the conjugate forces are transformed accordingly,

$$\mathbf{X}_{\mathrm{red}} = \mathbf{A}^{-T}\mathbf{X},$$

then the reduced phenomenological matrix

$$\mathbf{L}_{\mathrm{red}} = \mathbf{A}\mathbf{L}\mathbf{A}^{\mathrm{T}}$$

remains symmetric by construction [4]. Apparent violations of reciprocity therefore arise only when this thermodynamic consistency is not maintained, for example when coefficients are inferred after partial elimination of variables, nonlinear reparameterisation, or implicit fitting over finite perturbations [19,20].

The numerical illustrations in Section 5 make this distinction explicit. Figure 1 demonstrates that when a symmetric matrix is reduced through a transformation preserving conjugate structure, the resulting cross-coefficients overlap within numerical resolution. By contrast, Figure 2 shows that if the reduction depends nonlinearly on concentration, the effective coefficients $\overline{L}_{23}(C_0)$ and $\overline{L}_{32}(C_0)$ can separate in a manner closely resembling the asymmetry reported in Filippov's Figure 4, even though the underlying matrix remains symmetric. This comparison clarifies that concentration-dependent divergence of reduced coefficients does not, in itself, constitute evidence of microscopic symmetry breaking [1,19].

Within this framework, Filippov's model provides a valuable case study. The governing transport equations and numerical implementation are not inherently inconsistent with non-equilibrium thermodynamics. The critical issue concerns interpretation. The observed divergence of certain reduced cross-coefficients was taken as evidence of Onsager reciprocity violation, whereas the present analysis shows that such divergence can emerge naturally from reduction procedures, boundary-layer averaging, and concentration-dependent fitting of effective parameters. Once these modelling aspects are recognised, the graphical asymmetries no longer imply a breakdown of microreversibility [4,8].

The present analysis also applies to asymmetric membrane structures. In practical systems, the fixed-charge density, porosity, or local standard chemical potential may vary across the membrane thickness. Such spatial heterogeneity can produce strongly asymmetric concentration and potential profiles and may lead to effective transport coefficients that differ substantially when evaluated from averaged quantities. Nevertheless, Onsager reciprocity remains valid at the local level provided that the transport equations are formulated using thermodynamically conjugate flux–force pairs and microscopic reversibility is preserved. Apparent asymmetry observed in globally averaged coefficients therefore does not, by itself, imply a breakdown of the underlying reciprocal relations.

It is also important to emphasise that small quantitative discrepancies between nominally symmetric

coefficient pairs cannot be interpreted as proof of reciprocity violation without verifying three conditions: (i) strict linear response, (ii) infinitesimal perturbation amplitude, and (iii) correct identification of conjugate force–flux pairs [19,20]. Numerical discretisation, interpolation, finite concentration increments, and regression procedures can all introduce deviations that vanish in the limit of exact linearisation.

More generally, the present study highlights a methodological principle: Onsager symmetry is a statement about a specific thermodynamic structure, not about arbitrary matrices denoted by L_{ij}. When transport coefficients are defined outside the strict linear-response framework, for instance through coarse graining, elimination of internal variables, or concentration-dependent parameter extraction, symmetry need not survive at the level of the reduced coefficients, even though the fundamental theory remains intact [21].

A practical implication follows. Whenever asymmetry is reported in cross-transport coefficients, the following elements should be stated explicitly: (i) the precise definition of fluxes and forces, (ii) the transformation or reduction procedure applied, (iii) the range of perturbation amplitude, and (iv) whether the coefficients represent equilibrium derivatives or effective parameters fitted over finite concentration intervals. Only under such conditions can one distinguish rigorously between genuine physical symmetry breaking and artefacts arising from modelling, reduction, or interpretation [4,19].

The choice of reference frame should also be specified explicitly in multicomponent transport problems, since reciprocity applies to coefficients defined within a thermodynamically consistent frame and may appear distorted when fluxes are transformed between different frames without the corresponding transformation of forces.

The same considerations apply to concentrated electrolytes with strong activity-coefficient effects, structurally asymmetric membranes, and multicomponent ionic mixtures. Although these systems may generate highly complex effective transport behaviour, such complexity alone does not imply a breakdown of Onsager reciprocity when the underlying thermodynamic description is formulated consistently.

The evidence presented here therefore supports a conservative conclusion: the reported asymmetries in reduced concentration-dependent coefficients do not demonstrate violation of Onsager reciprocity. Rather, they underscore the importance of maintaining thermodynamic consistency when interpreting reduced transport parameters in complex coupled systems.

Declaration of generative AI and AI-assisted technologies

The author used ChatGPT (OpenAI) during the preparation of this manuscript to assist with language editing, improving clarity of expression, formatting, and proofreading. The scientific content, theoretical analysis, mathematical derivations, interpretation of results, and all final decisions regarding the manuscript were developed and verified solely by the author. The author takes full responsibility for the content of the manuscript.

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Conflicts of interest

Elijah Lator is an employee of Latbat Ltd. The author declares that this affiliation does not influence the design, analysis, interpretation, or presentation of the results reported in this manuscript.

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