



The Onsager Reciprocity Relations Revisited

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Abstract The Onsager relations are discussed and it is suggested that they should be interpreted as there is a frame of reference where all the transport processes are independent. The concepts are illustrated with isobarothermal diffusion in simple metallic phases as well as complex ionic systems. A transformation from lattice-fixed frame of reference to number-fixed frame gives the Kirkendall effect as a cross effect.

Keywords Irreversible transport processes · Thermodynamics · Entropy production · Frame of reference · Onsager relations · Diffusion · Kolrausch's law

1 Introduction

In a legendary article from 1931 Onsager¹ discussed cases where two or more irreversible transport processes occur simultaneously, e.g. heat and electric conduction. When occurring alone each process is described by a linear

relation between the flux J and the gradient in a thermodynamic potential, e.g. Fourier's law and the Ohm's law. They can both be written in the form

$$J = -LX \quad (\text{Eq 1})$$

The flux is the transported amount expressed per unit area and unit time in the direction of the driving force X which is the gradient of the appropriate thermodynamic potential. L is a phenomenological coefficient that represents a conductivity in the medium under consideration. When several processes occur simultaneously it is observed experimentally that one process may also depend on the driving force for another process, i.e. there are cross effects. For n simultaneous processes one would write

$$J_i = - \sum_j^n L_{ij} X_j \quad (\text{Eq 2})$$

Figure 1 summarizes the processes of heat, electric and diffusive transport and their cross effects.

Inspired by Thomson (Kelvin) Onsager then showed that under some conditions

$$L_{ij} = L_{ji} \quad (\text{Eq 3})$$

This is referred to as the Onsager reciprocity relations and was a major reason for awarding him with the Nobel prize in chemistry 1968. His mathematical proof is somewhat complex and is based on a number of assumptions and particularly the principle of microscopic reversibility. Onsager introduced the latter concept to represent that at equilibrium a process goes in the forward direction as often as in the backward direction. It is thus usually claimed that the relations hold close to equilibrium. However, the physical nature of this principle and how it relates to the underlying molecular laws is less clear. Over the years the

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	Flux	Heat	Electric	Diffusion
Force				
Temperature gradient		Fourier	Seebeck	Soret Thermal migration
Voltage		Peltier	Ohm	Electro migration
Chemical potential gradient		Dufour	Volta (galvanic cell)	Fick

Fig. 1 Classical cross effects

reciprocity relations have been discussed and criticized frequently. The criticism by Truesdell² is particularly concise and clear. It is also remarkable that Onsager did not consider transport processes at all in his proof but rather a generalized chemical reaction. The purpose of the present article is to demonstrate that the proof can be performed for transport processes and in a much simpler way with a straight forward physical meaning. We shall demonstrate that the relations hold even when the system is far from equilibrium as long as fluxes and forces are represented by the linear relation Eq 2.

In the following we shall use vector–matrix notation and write the flux as a columnar vector J with each element representing the flux of a certain quantity and X as a columnar vector with the conjugated driving forces as elements. L is thus a square matrix with elements L_{ij} and the same number of rows and columns as n , the number of transport processes considered. Equation 2 thus is written in the same form as Eq 1

$$J = -LX \tag{Eq 4}$$

and Eq 3 then is

$$L = L^T \tag{Eq 5}$$

where L^T is the transpose of L , i.e. the matrix obtained by exchanging rows and columns. Equation 5 thus means that L is a symmetric matrix. The L matrix is referred to as the phenomenological matrix.

2 Entropy Production and Driving Forces

From a thermodynamic point of view the negative gradient of a potential ϕ_i yields a force to give a flux J_i of its corresponding conjugated extensive quantity. Using ∇ to

Table 1 Examples of thermodynamic potentials

Transported quantity	Potential
Heat	$-1/T$
Atoms or species i	μ_i/T
Electric charge	ψ
Volume	$-P$

denote the gradient operator the driving force thus is $-\nabla\phi_i$. The flux and the driving force are conjugated thermodynamic quantities. Examples of transported quantities and conjugated thermodynamic potentials are given in Table 1.

where T is the temperature, μ_i the chemical potential of i , ψ the electric potential and P the pressure.

2.1 The Local Entropy Production

All irreversible processes produce entropy. Each process contributes to the total entropy production σ in the volume element under consideration by the amount $-J_i\nabla\phi_i > 0$. This relation is fundamental and stems from the combined first and second law of thermodynamics and an entropy balance, i.e. it does not depend on any model. As can be seen σ is expressed per volume and time. In vector–matrix notation we thus have the local entropy production.

$$\sigma = -J^T\nabla\Phi \tag{Eq 6}$$

where J^T is the transpose of J and the columnar vector $\nabla\Phi$ has the elements $\nabla\phi_i$.

The local entropy production is a measure of the irreversibility and is independent of the choice of frame of reference for the fluxes. If fluxes and forces are expressed in an arbitrary frame of reference we would thus write

$$\sigma = -J'^T X \tag{Eq 7}$$

Consequently if σ is known in one frame of reference and the fluxes are transformed by a matrix A

$$J' = AJ \tag{Eq 8}$$

it is necessary to transform also the driving forces to keep σ the same in order to make Eq 7 generally valid.

2.2 Transformation of Fluxes and Forces

Transform the fluxes with the matrix A according to Eq 8. As shown by several authors, e.g. Truesdell² and Lorimer,³ the driving forces then must be transformed with a matrix B , i.e. $\nabla\Phi' = B\nabla\Phi$, in such a way that the entropy production is invariant

$$J^T \nabla \Phi = (J')^T \nabla \Phi' = (AJ)^T B \nabla \Phi = J^T A^T B \nabla \Phi \quad (\text{Eq 9})$$

thus $A^T B = I$, where I is the unity matrix and it follows that $B = (A^T)^{-1}$ and

$$\nabla \Phi' = (A^T)^{-1} \nabla \Phi \quad (\text{Eq 10})$$

or

$$\nabla \Phi = (A^T) \nabla \Phi' \quad (\text{Eq 11})$$

The L matrix must be transformed accordingly

$$AJ = J' = AL \nabla \Phi = ALA^T \nabla \Phi' \quad (\text{Eq 12})$$

Thus

$$L' = ALA^T \quad (\text{Eq 13})$$

It should be noted that if the L matrix is symmetric Eq 13 will guarantee that also L' must be symmetric.

2.3 The Onsager Reciprocity Relations

In accordance with the reciprocity relations¹ the matrix L is always symmetric, i.e. $L = L^T$, provided that certain measures are taken. The most important ones are that the fluxes are independent and that fluxes and forces are chosen so that Eq 7 holds because the entropy production does not depend on frame of reference. As mentioned Onsager’s proof is not so easy to follow but from Eq 13 one may conclude that if there is a frame of reference where the processes are independent, i.e. the L matrix is diagonal and symmetric in a trivial sense, it is evident from Eq 13 that also L' will be symmetric although the off-diagonal elements are non-zero. It should be emphasized that it is well known that all real symmetric matrices can be diagonalized by the appropriate transformation.⁴

It is now suggested that the physical meaning of the reciprocity relations is that there is a frame of reference in which the true character of the processes as being independent is revealed by the L matrix being diagonal. The reason why we often do not see this is because we are looking at the processes in an inappropriate frame of reference and the only thing we see is that although the matrix has non-zero off-diagonal elements it is symmetric. An alternative proof of the reciprocity relations was presented by Verros and Testempasi in 2006.⁵ The proof is rather lengthy but seems to be based on the same ideas as discussed here.

3 Application to Isobarothermal Diffusion - Frame of Reference

We shall now demonstrate the preceding discussion with the case of isobarothermal diffusion. The reason for choosing this case is that it is practically important and there exist a large amount of experimental data. We consider a system with C components, i.e. its composition may be varied by adding the components in C different ways. Of course the fractions of the different components can only be varied in $C - 1$ different ways because they have to sum up to unity. In the following we will express the composition in terms of mole fractions x_i calculated from the molar content N_i of the different components i .

$$x_j = \frac{N_j}{\sum_{i=1}^C N_i} \quad (\text{Eq 14})$$

It this follows directly that $\sum_{j=1}^C x_j = 1$.

3.1 Lattice-Fixed Frame

In a crystalline material it may seem natural to represent diffusion with the crystalline lattice as reference. One may then imagine “inert” markers that are fixed to the lattice as reference points. We call this frame of reference the lattice-fixed frame of reference. The C fluxes are independent in the lattice-fixed frame of reference. This means that there is no way to calculate one of the fluxes if one knows the $C - 1$ other fluxes. However, often it is more convenient to consider diffusion in other frames, e.g. during mixing and interdiffusion where the interest is the exchange of atoms. In a binary system one may be interested in how the two components mix with each other. A transfer of one component is then always balanced by an opposite transfer of the other component. This mean that the two fluxes are no longer independent when this frame of reference is used.

3.2 Frames of Reference with Dependent Fluxes

In practical assessment of diffusion data other frames of reference are used. These type of frames are defined by introducing a dependence between the fluxes, i.e.

Table 2 Examples of frames of reference

Frame of reference	a_i
Number fixed	1
Volume fixed	V_i
Mass fixed	m_i
Solvent A fixed	δ_{Ai}
Substitutional fixed	δ_{is}

$$\sum_{i=1}^C J_i a_i = 0 \tag{Eq 15}$$

where the amount of diffusing species is expressed in mol. Examples of such frames are given in Table 2, where m_i is the molar mass, δ_{ik} , the Kronecker delta that is 1 when $i = k$ and 0 otherwise and s stands for a substitutional element. The number-fixed frame is identical to the volume-fixed frame when all elements have the same partial molar volume V_i . The substitutional-fixed frame is identical to the volume fixed frame when all substitutional elements have the same volume V_S , and the interstitial elements do not contribute to the molar volume. The molar volume is denoted V_m .

In all the frames of reference where a dependency is introduced between the C fluxes one flux is superfluous because it can be calculated from the other fluxes. In order to keep the number of independent “fluxes” the same we may replace one arbitrarily chosen flux with another quantity which is of interest. We shall return to this aspect in the next section.

3.3 Transformation Between Frames of Reference

Transformation from one frame of reference to any other frame of reference is achieved by multiplying the fluxes with a transformation matrix. Suppose that the fluxes J are known in one frame of reference and one would like to transform to another frame denoted by a “prime” as J' . The fluxes are then transformed by multiplication with a transformation matrix A .

$$J' = AJ \tag{Eq 16}$$

For example, if the fluxes J are known in the lattice-fixed frame of reference transformation with the matrix A gives the fluxes in any other frame defined by Eq 16.

$$A = \begin{bmatrix} 1 - x_1 a_1/a_m & -x_1 a_2/a_m & \dots & -x_1 a_C/a_m \\ -x_2 a_1/a_m & 1 - x_2 a_2/a_m & \dots & -x_2 a_C/a_m \\ \vdots & \vdots & \ddots & \vdots \\ -x_C a_1/a_m & -x_C a_2/a_m & \dots & 1 - x_C a_C/a_m \end{bmatrix} \tag{Eq 17}$$

where $a_m = \sum_{k=1}^C a_k x_k$.

The transformation matrix thus has the elements $a_{ik} = \delta_{ik} - x_i a_k/a_m$. As mentioned in the previous section one flux is now superfluous which means that information is lost in the transformation and the A matrix defined by Eq 17 is singular and cannot be inverted. Consequently it is not possible to perform the reverse transformation.

The sum of fluxes expressed in the lattice-fixed frame gives the net flow of atoms and is related to the migration

velocity v_K of Kirkendall markers expressed in the number-fixed frame⁶.

$$v_K/V_m = - \sum_{i=1}^C J_i \tag{Eq 18}$$

By the same token $\sum_{i=1}^C J_i V_i$ represents the net-flow of volume relative the lattice. We will thus replace an arbitrarily chosen row in A with $a_{ik} = b_i$ and the final A matrix is, if we chose to replace the C :th row

$$A = \begin{bmatrix} 1 - x_1 a_1/a_m & -x_1 a_2/a_m & \dots & -x_1 a_C/a_m \\ -x_2 a_1/a_m & 1 - x_2 a_2/a_m & \dots & -x_2 a_C/a_m \\ \vdots & \vdots & \ddots & \vdots \\ b_1 & b_2 & \dots & b_C \end{bmatrix} \tag{Eq 19}$$

Transforming to the number-fixed frame and taking all $b_i = -1$ the C :th flux thus is $J'_C = - \sum_{i=1}^C J_i = v_K/V_m$, i.e. the Kirkendall velocity expressed in the number-fixed frame. Consequently no information has been lost by using the A matrix defined in this way and the reverse transformation may be performed, e.g. it is possible to transform from number-fixed to lattice-fixed frame of reference. This of some practical importance because experimental evaluation of diffusion coefficients are often based on measured concentration profiles, e.g. using the so-called Boltzmann-Matano method and if one has also measured marker movement in the number-fixed frame one may calculate the diffusivities in the lattice-fixed frame.

3.4 Transforming from Lattice-Fixed Frame of Reference to Some Other Frames

In this section the transformation from lattice-fixed to other frames of reference is discussed. In Sect. 3.5 transformation between arbitrary frames of reference will be discussed.

3.4.1 Volume-Fixed Frame of Reference

The volume-fixed frame is defined by $a_i = V_i$ for all species i , see Eq 15 and Table 2. Consequently $a_m = V_m$ and the transformation matrix is

$$A = \begin{bmatrix} 1 - x_1 V_1/V_m & -x_1 V_2/V_m & \dots & -x_1 V_C/V_m \\ -x_2 V_1/V_m & 1 - x_2 V_2/V_m & \dots & -x_2 V_C/V_m \\ \vdots & \vdots & \ddots & \vdots \\ -V_1 & -V_2 & \dots & -V_C \end{bmatrix} \tag{Eq 20}$$

The last row gives $v_K = -\sum_{i=1}^C J_i V_i$, i.e. the Kirkendall velocity in the volume-fixed frame of reference.

3.4.2 Number-Fixed Frame of Reference

The number-fixed frame is defined by $a_i = 1$ for all species i , see Eq 16 and Table 2. Consequently $a_m = 1$ and the transformation matrix is

$$A = \begin{bmatrix} 1 - x_1 & -x_1 & \dots & -x_1 \\ -x_2 & 1 - x_2 & \dots & -x_2 \\ \vdots & \vdots & \ddots & \vdots \\ -1 & -1 & \dots & -1 \end{bmatrix} \tag{Eq 21}$$

3.5 Transforming Between Arbitrary Frames of Reference

If we denote J^0 as the flux in the lattice-fixed frame of reference we may transform to any other frame J^1 by $J^1 = A^{0 \rightarrow 1} J^0$, where J^1 denotes the fluxes in the new frame of reference. Or we may transform to J^2 by $J^2 = A^{0 \rightarrow 2} J^0$. In fact we can transform from 1 to 2 by $J^2 = A^{1 \rightarrow 2} J^1$ and we find that $A^{1 \rightarrow 2} = A^{0 \rightarrow 2} (A^{0 \rightarrow 1})^{-1}$ where $(A^{0 \rightarrow 1})^{-1}$ denotes the inverse of $A^{0 \rightarrow 1}$.

4 The Concept of Mobility

As mentioned a negative gradient of a thermodynamic potential $-\nabla\phi_i$ is a force to move something. The mobility M_i of a “particle” i is introduced from the assumption that its velocity v_i is proportional to the force $-\nabla\phi_i$ acting on it, i.e

$$v_i = -M_i \nabla\phi_i \tag{Eq 22}$$

Suppose we have generalized “particles”, i.e. atoms, molecules, electrons, energy quanta etc. Except for a very short acceleration time the behaviour represented by Eq 22 is expected when a particle moves in a media with friction. The flux of i particles is obtained by multiplication with their concentration c_i .

$$J_i = c_i v_i = -c_i M_i \nabla\phi_i \tag{Eq 23}$$

Introducing the $C * C$ matrix L with the diagonal elements $c_i M_i$ and all other elements zero we have in vector–matrix notation

$$J = -L \nabla\Phi \tag{Eq 24}$$

4.1 Mobility in Isobarothermal Processes Without Electric Gradients

If all temperature, pressure and electric gradients can be neglected the local entropy production expressed in the lattice-fixed frame of reference is

$$\sigma = -\frac{1}{T} J^T \nabla\mu \tag{Eq 25}$$

where J is the columnar vector containing the C diffusive fluxes in the lattice-fixed frame of reference. $\nabla\mu$ is the columnar vector containing the C chemical potential gradients $\nabla\mu_i$. It should be emphasized that temperature may still vary in time but slow enough to level out any temperature differences in the considered volume. This is often a very good approximation on the micro-structural level. This may be understood from the fact that the thermal diffusivity in solid metals is in the order of $10^{-5} \text{ m}^2\text{s}^{-1}$ and from Einstein’s formula the time needed to achieve a homogeneous temperature over a distance of 1 mm is around 10^{-1} s . One can then consider the local Gibbs energy dissipation, i.e. $-T\sigma$, and use $-\nabla\mu_i$ as the driving force, i.e. Eq 23 is usually written.

$$J_i = -c_i M_i \nabla\mu_i \tag{Eq 26}$$

Introducing the $C * C$ matrix L with the diagonal elements $c_i M_i$ and all other elements zero we have in vector–matrix notation

$$J = -L \nabla\mu \tag{Eq 27}$$

5 Isobarothermal Diffusion in a Binary System

Consider a hypothetical binary system with components A and B . From Eq 26 and the fact that $c_i = x_i/V_m$ one obtains in the lattice-fixed frame of reference

$$J_A = -\frac{x_A}{V_m} M_A \nabla\mu_A \tag{Eq 28}$$

$$J_B = -\frac{x_B}{V_m} M_B \nabla\mu_B \tag{Eq 29}$$

The L matrix in the lattice-fixed frame of reference thus is

$$L = \frac{1}{V_m} \begin{bmatrix} x_A M_A & 0 \\ 0 & x_B M_B \end{bmatrix} \tag{Eq 30}$$

In general $J_A + J_B \neq 0$, i.e. the fluxes are independent in this frame of reference and the L matrix is diagonal. Transformation to the number-fixed frame of reference is performed with the matrix A given by Eq 21. Taking J'_A as dependent flux, i.e. $J'_A = -J'_B$ one obtains

$$A = \begin{bmatrix} -x_B & (1 - x_B) \\ -1 & -1 \end{bmatrix} \tag{Eq 31}$$

It should be observed that with this A matrix the second flux is not the dependent $J'_A = -J'_B$ but it is rather taken as $J_A + J_B$. From Eq 11 one then obtains the new set of forces

$$X_1 = \nabla(\mu_B - \mu_A) \tag{Eq 32}$$

$$X_2 = -[x_A \nabla \mu_A + x_B \nabla \mu_B] \tag{Eq 33}$$

Equation 13 yields the new L matrix

$$L' = \frac{1}{V_m} \begin{bmatrix} x_A x_B (x_B M_A + x_A M_B) & x_A x_B (M_A - M_B) \\ x_A x_B (M_A - M_B) & x_A M_A + x_B M_B \end{bmatrix} \tag{Eq 34}$$

As can be seen the L' matrix has off-diagonal elements but is symmetric and the reciprocity relations are clearly obeyed. In the new frame of reference X_2 vanishes due to the Gibbs–Duhem relation. The fluxes in the new frame of reference thus are

$$J'_1 = -\frac{1}{V_m} [x_A x_B (x_B M_A + x_A M_B)] \nabla(\mu_B - \mu_A) = J'_B = -J'_A \tag{Eq 35}$$

$$J'_2 = \frac{1}{V_m} x_A x_B (M_A - M_B) \nabla(\mu_B - \mu_A) = \frac{v_K}{V_m} \tag{Eq 36}$$

The two fluxes J'_1 and J'_2 are independent and the L' matrix has off-diagonal elements. The Kirkendall effect, represented by the Kirkendall velocity v_K is now a cross effect. In a similar way other phenomena, e.g. electro migration, the motion of atoms in a strong electric field, may be regarded as cross effects.

6 Isobarothermal Diffusion in Ionic Systems

Ionic systems present some additional complications because diffusion occurs by migration of charged constituent species rather than electro-neutral components which have been considered so far. For simplicity, we now only consider elemental ions i , each with a charge Z_i , and the electron e^{-1} with charge $Z_{e^{-1}} = -1$. The electron is considered as a species and as a component that only contains the electron species.

It is common to assume that the diffusional flux J'_i of the ionic species i is described by an individual mobility and the gradient of the chemical potential of the ion i i.e. $\nabla \Lambda_i$. Written as columnar vectors we use J' and $\nabla \Lambda$. The L matrix thus is a square matrix and in the lattice-fixed frame of reference it is diagonal and is denoted L' , i.e.

$$J' = -L' \nabla \Lambda \tag{Eq 37}$$

Equation 37 is sometimes referred to as Kohlrausch’s law. The basic parameters are the diagonal elements L'_i of the L' matrix which also includes the electron transport, $L'_{e^{-1}}$. They are all proportional to the respective ionic mobilities. As the ions are charged there is an extra driving force due to the electric field ψ . We arrange the Z_i values in a columnar vector Z and Eq 37 is modified into

$$J' = -L' [\nabla \Lambda + ZF \nabla \psi] \tag{Eq 38}$$

where F is the Faraday constant. In order to transform to component diffusion the matrix B with elements B_{ki} is introduced. It tells how many moles of component k the ionic species i contains. The ionic species fluxes are thus transformed to component fluxes by

$$J = BJ' \tag{Eq 39}$$

As an example consider diffusion in the hypothetical metal-deficit oxide $M_{1-x}O_1$ with diffusing species M^{+2} , M^{+3} , O^{-2} , e^{-1} and the components M , O and e^{-1} . Clearly $x \geq 0$ with 0 representing the stoichiometric oxide. The B matrix is

$$B = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -2 & -3 & 2 & 1 \end{bmatrix} \tag{Eq 40}$$

The chemical potential gradients of the ionic species are related to the gradients of the component chemical potentials $\nabla \mu$ by

$$\nabla \Lambda = B^T \nabla \mu \tag{Eq 41}$$

where B^T is the transpose of the B matrix.

Using Eq 41 we find that Eq 38 may be written

$$J' = -L' [B^T \nabla \mu + ZF \nabla \psi] \tag{Eq 42}$$

Wagner⁷ suggested in 1933 that in the absence of external electric field ψ would arrange itself in such a way that there would be no charge transfer due to diffusion, i.e. in vector-matrix notation

$$Z^T J' = 0 \tag{Eq 43}$$

Thus the fluxes are not independent and one of them may be eliminated. We will thus eliminate the electron flux. Inserting Eq 42 in Eq 43 yields

$$F \nabla \psi = -\frac{Z^T L' B^T}{Z^T L' Z} \nabla \mu \tag{Eq 44}$$

Inserting Eq 44 in Eq 42 we obtain

$$J' = -L''\nabla\mu \quad (\text{Eq 45})$$

where L'' is

$$L'' = L'B^T - \frac{L'ZZ^T L'B^T}{Z^T L'Z} \quad (\text{Eq 46})$$

Although L' is diagonal L'' is generally a filled matrix. It should also be observed that L'' is not a square matrix but has the same number of rows as the number of species including the electrons and the same number of columns as the number of components including the electrons.

The next step is to transform from species flux to component flux by Eq 39. The result is

$$J = -L\nabla\mu \quad (\text{Eq 47})$$

where L is

$$L = BL'B^T - \frac{BL'ZZ^T L'B^T}{Z^T L'Z} \quad (\text{Eq 48})$$

L is a square matrix with the number of rows and columns equal to the number of components including the electron. It is found that it is symmetric, i.e. Onsager relations are obeyed. It is further found that the row and the column that involve the electron vanish, i.e.

$$L_{ke-1} = L_{e-1k} = 0 \quad (\text{Eq 49})$$

We may thus remove the electron as a component, i.e. $\nabla\mu$ does not contain $\nabla\mu_{e-1}$. In practice we can thus use the convenient Eq 48 and simply skip the row and the column corresponding to the electron because they only contain zeros and we obtain our final L . However, it must be emphasized that the electronic mobility represented by L'_{e-1} will enter in the remaining elements in the matrix because it is included in the scalar quantity $Z^T L'Z$ which is actually the sum $\sum_i Z_i^2 L'_i$ including the electron.

In this section we have thus shown that adopting Kohlrausch's law we can bring the flux equation for ionic systems to the same form as Eq 27 with a symmetric L matrix. As we have previously shown that all legitimate transformations to other frames of reference will keep the matrix symmetric the Onsager relations are valid and stem from the diagonal matrix in Kohlrausch's law.

7 Discussion

It is suggested that the Onsager reciprocity relations are a consequence of the fact that there is a frame of reference where all the considered transport processes are independent and the phenomenological matrix is then diagonal. Transformations of fluxes and forces to other frames under the constraint of an invariant entropy production then

yields symmetric phenomenological matrices. Of course it remains to be proven that there actually exists a frame of reference where the processes are independent. Using his principle of microscopic reversibility Onsager¹ showed that this would always be the case close to equilibrium in a system with chemical reactions. It is easy to show that isobarothermal transport processes based on random jumps will be independent in the lattice-fixed frame and give diagonal L matrices. Accounting for correlation effects will introduce off-diagonal contributions but Manning⁸ showed that in simple systems the L matrix will remain symmetric.

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