

Research Article

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Ergodicity, Maximum Entropy Production, and Steepest Entropy Ascent in the Proofs of Onsager's Reciprocal Relations

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Abstract: We show that to prove the Onsager relations using the microscopic time reversibility one necessarily has to make an ergodic hypothesis, or a hypothesis closely linked to that. This is true in all the proofs of the Onsager relations in the literature: from the original proof by Onsager, to more advanced proofs in the context of linear response theory and the theory of Markov processes, to the proof in the context of the kinetic theory of gases. The only three proofs that do not require any kind of ergodic hypothesis are based on additional hypotheses on the macroscopic evolution: Ziegler's maximum entropy production principle (MEPP), the principle of time reversal invariance of the entropy production, or the steepest entropy ascent principle (SEAP).

Keywords: Onsager relations, ergodicity, maximum entropy production, MEPP, steepest entropy ascent

1 Introduction

The Onsager reciprocal relations were first described and derived by Lars Onsager himself in 1931 [1, 2], and they are now universally considered a milestone of non-equilibrium thermodynamics. This paper does not discuss the importance or the historical development of the Onsager relations, but instead it focuses on their proofs. In fact, the validity of the Onsager relations is the thesis of theorems, and the relations are not simply phenomenological, despite historically they were inspired by phenomenological works such as the thermoelectric effects studied earlier by Thompson and Kelvin. Since 1931, many have written papers proving the Onsager relations in their favorite framework, and some review papers have been written comparing some of the proofs [3, 4] and addressing the very interesting topic of time reversal invariance of the underlying microscopic equations [5]. In this paper we highlight the fact that in every possible proof of the Onsager relations based on the principle of time reversal invariance of the microscopic equations there is actually another strong and important hypothesis, namely an ergodic hypothesis, or a hypothesis closely linked to that. The reader who strongly believes in the validity and the effectiveness of the ergodic hypothesis can be content with the fact that it is central to a very vast and important field like non-equilibrium thermodynamics, while the reader who is skeptical of its validity can take solace in the fact that there are actually three proofs of the Onsager relations that do not require any sort of ergodic hypothesis, because they are based on a macroscopic principle. These three proofs, however, require separate, additional, and unproven hypotheses, or “principles,” on the time evolution of the entropy. The first macroscopic proof was written by Meixner [6] and later by Liu [7] and is based on Thomson's idea that the entropy production rate is unchanged under time reversal. The second macroscopic proof was written by Ziegler [8, 9, 10] and is a consequence of his proposed maximum

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entropy production principle (MEPP). This proof is very simple and elegant, being based on a principle with a clear physical interpretation. However, the principle itself is not universally considered valid, and in fact some express doubts about its validity far from equilibrium [11]. Furthermore, this proof does not explain the Casimir extension of the Onsager relations. The third proof is based on the Steepest Entropy Ascent concept developed by one of us.

The paper is structured as follows. In Section 2 the prescriptions and the statement of the Onsager theorem are given. This is important since there is still confusion about the need to correctly identify the forces and the fluxes used in the reciprocal relations, and this often leads to mistakes. In Section 3 the microscopic proofs of Onsager relations are analyzed, and the ergodic hypothesis is highlighted in each of them. We do not rewrite these proofs, but the interested reader can read them in the references. The microscopic proofs are classified into four groups. The proofs are based on: 1) fluctuation theory (this is the classical proof by Onsager), 2) linear response theory and the Green–Kubo formulas, 3) stochastic dynamics and the theory of Markov processes, and 4) kinetic theory of gases. In Section 4 the macroscopic proofs of Onsager relations are discussed.

2 Onsager–Casimir relations: Prescriptions and statement

The reciprocal relations are the consequence of a theorem, not just phenomenological relations. Whenever in the literature the Onsager relations do not hold for a particular case, it is because the hypotheses are not taken strictly. First, the theorem requires linearity of the force–flux relations, so it only holds near equilibrium. Furthermore, a common source of confusion is Onsager’s notation of forces and fluxes. Coleman and Truesdell [12] remark that thermodynamic forces and fluxes cannot be chosen indiscriminately on the basis of physical intuition, inferred from the formula for the entropy production and the linear force–flux constitutive relations. Instead, they need to be chosen following strict criteria, the important point being that forces must be the derivatives of the entropy with respect to some thermodynamic variables and fluxes must be the time derivatives of those same thermodynamic variables. Thus, in general it is logical to pick the thermodynamic variables and later define forces and fluxes. We now review the prescriptions of the theorem. For simplicity, we will not consider external magnetic fields, Coriolis forces, or the Casimir extension of the Onsager relations.

Consider an isolated system (a system enclosed by rigid immovable walls through which neither matter nor energy can be exchanged) characterized by a number of independent, time-dependent macroscopic variables that describe the non-equilibrium states of the system at the chosen level of description. These variables can have deviations from their equilibrium values $A_i^{eq} = A_i^{eq}(E, V, \mathbf{n})$, *i. e.*, the values that make the non-equilibrium¹ entropy $S=S(\mathbf{A})$ of the system maximum

$$\left. \frac{\partial S}{\partial A_i} \right|_{A_i^{eq}} = 0 \quad (1)$$

for fixed energy E , volume V , and number of particles \mathbf{n} . A maximum of the entropy, and thus an equilibrium state, exists only for a fixed energy, volume, and number of particles. Thus, to have the forces and fluxes relative to these quantities (for example temperature gradients and heat fluxes) we would need to consider a system composed of two or more subsystems. Then E , V , and \mathbf{n} are only conserved for the overall system, but not for the subsystems. In this case, it is necessary to introduce vector currents of quantities (note that these are not fluxes in Onsager’s notation). For the details, see Callen [17]. Then we obtain a very similar formula

¹ For the operative definition of the entropy of a system in a non-equilibrium state and its additivity for separated subsystems, see [13, 14, 15]. Note also that Carati, Maiocchi, and Galgani show that entropy can be defined starting from the microscopic dynamics, without requiring the dynamics to be ergodic [16]. Following instead the familiar approach based on the Gibbs ensembles, ergodicity would be a requirement to define the entropy from the microscopic dynamics. Thus, ergodicity is required only to prove the Onsager relations in the microscopic formulations.

(see the end of this section) for the entropy production as the one we will shortly review, only that in that case we will use gradients of the forces and currents instead of fluxes.²

The deviations of all the \mathbf{A} variables from their equilibrium values are denoted by α ,

$$\alpha_i = A_i - A_i^{eq} \quad (i = 1, 2, \dots, n). \quad (2)$$

Onsager and Machlup [18] formulated rules for a correct choice. First, they need to be additive³ variables. This is because speaking of fluctuations for intensive quantities is conceptually ill-defined (see for example the large literature [19, 20] on the idea of temperature fluctuations). Onsager and Machlup's idea for defining variables for a system out of equilibrium is to consider the system as made of several small subsystems, each near local equilibrium⁴ and each containing a statistically large number of molecules: the α variables must be macroscopic variables which refer to these subsystems.

In addition, Onsager and Machlup assume that the α must be algebraic sums of molecular variables. This eliminates pathological variables like nonadditive functions of extensive variables and implies that, if these molecular variables are weakly coupled, algebraic sums of them behave as Gaussian random variables. This is because the fluctuations of the variables, by virtue of the Central Limit Theorem, have Gaussian distributions about the equilibrium values.

So far we may think that the α are the actual time-varying observables we just defined. However, this would mean that the fluxes are instantaneous time derivatives, which would have very large fluctuations that are not necessarily reproduced on successive repetitions of the same conditions. This would imply that any macroscopic law that includes these fluxes has a very detailed time variation. This should not happen for well-defined variables that describe a macroscopic system. To address this problem, Casimir [21] in 1945 suggested that the macroscopic flux J should be defined as the time-averaged rate of change of this ensemble average over a mesoscopic time τ , which is an (arbitrary) intermediate time between the collision time of the molecules and the relaxation time of the system as a whole. This is the common way to define the fluxes; see for example the recent paper by Patitsas [22]. This definition of the fluxes in terms of time averages is the reason why in linear response theory one has to make the ergodic hypothesis to define the linear transport coefficients (see Section 3.2). What is not very elegant with this proposal is that it requires an explicit time scale to be incorporated into the basic definition of J . To overcome this problem La Cour and Schieve [23] defined α as the large- n expected value of the observable using large deviation theory.

It is indeed a delicate task to choose the variables properly. The idea is that there are many levels of description of a system, obtained by coarse graining the previous one, starting from the microscopic description [24, 25, 26, 27]. In a coarse-grained model, we should look for the slow-varying variables, the ones that dictate the evolution of the system. These are the important ones to choose to study the system, whereas the fast variables will immediately follow the evolution of the slow ones and thus their detailed evolution is irrelevant.

Near equilibrium, we can expand the entropy of the system to the second order as

$$S(\boldsymbol{\alpha}) \approx S|_{eq} - \frac{1}{2} \sum_i \sum_j H_{ij}(\mathbf{0}) \alpha_i \alpha_j, \quad (3)$$

where H is the positive definite,⁵ symmetric Hess matrix, defined as

$$H_{ij}(\boldsymbol{\alpha}) \equiv \frac{\partial^2 S(\boldsymbol{\alpha})}{\partial \alpha_i \partial \alpha_j}, \quad (4)$$

and $S|_{eq}$ is the entropy of the system at equilibrium, which is a function of the equilibrium values A_i^{eq} . If the entropy S of the system (as a function of the α) and all the α (as functions of time) are differentiable, then, for

² Note that to obtain this formula one needs to add important hypotheses on the local dependence of the entropy on the thermodynamic variables and on the relation between the entropy flux and the fluxes of the conserved properties.

³ An additive property is one whose magnitude is the sum of that of the subsystems. This is what is often called an extensive property, as in the current IUPAC definition. However, on this issue see again [13, 14].

⁴ Hence we can define variables that are only defined in equilibrium.

⁵ H is positive definite because the entropy at equilibrium is maximum (see (1)). Outside of equilibrium, *i. e.*, for $\alpha \neq 0$, the entropy must be lower, so H must be strictly positive definite.

an isolated system displaced from equilibrium, from the chain rule we have the well-known formula for the (non-negative) rate of entropy generation by irreversibility inside the system

$$\dot{S}(\boldsymbol{\alpha}) \equiv \frac{dS(\boldsymbol{\alpha})}{dt} = \sum_j X_j J_j, \quad (5)$$

where taking into account eq. (3) the derivatives

$$X_i \equiv \frac{\partial S(\boldsymbol{\alpha})}{\partial \alpha_i} \simeq - \sum_j H_{ij}(\mathbf{0}) \alpha_j \quad (6)$$

are the thermodynamic forces which drive the system back towards equilibrium and

$$J_i \equiv \dot{\alpha}_i \equiv \frac{d\alpha}{dt} \quad (7)$$

are the time rates of change or fluxes of the variables. Note that these so-called fluxes are not currents, and both the forces and the fluxes are zero at equilibrium (where the system is in a stationary state $d\alpha/dt|_{eq} = 0$ and, by equations (1) and (2), $\partial S/\partial \alpha_i|_{eq} = 0$ and $\alpha_i|_{eq} = 0$). The fluxes are independent and so are the forces, because the thermodynamic variables are chosen independent. It would be an unnecessary complication to choose them otherwise (see [28] Chap. 6 Par. 5).

Off equilibrium, the material tries to restore equilibrium. It resists to imposed fluxes by building up forces, or it resists imposed forces by building up fluxes. Thus, forces and fluxes are not independent from each other and can be seen as functions of each other: $X_i = X_i(\mathbf{J})$ or, equivalently, $J_i = J_i(\mathbf{X})$.

Onsager's reciprocal relations are only valid near equilibrium,⁶ and this hypothesis will be used in all of the proofs. If we linearize $J_i = J_i(\mathbf{X})$ around equilibrium, remembering that $J_i|_{eq} = 0$, we get

$$J_i(\mathbf{X}) \simeq \sum_j L_{ij} X_j, \quad (8)$$

where $L_{ij} = \partial J_i/\partial X_j|_{eq}$ and, therefore, is independent of the X_j .⁷ Onsager's reciprocity states that

$$L_{ij} = L_{ji}. \quad (9)$$

Of course, we could linearize $X_i = X_i(\mathbf{J})$ instead, to get $X_i \simeq \sum_j R_{ij} J_j$, where $R_{ij} = \partial X_i/\partial J_j|_{eq} = (L^{-1})_{ij}$, and Onsager's relations would be $R_{ij} = R_{ji}$. Combining (8) with (6) we see that linearizing the force-flux relation is equivalent to linearizing the regression of fluctuations to equilibrium

$$\dot{\alpha}_i = - \sum_j M_{ij} \alpha_j, \quad (10)$$

where the M matrix is related to L and H by $M = LH$.

For a system composed of infinitesimal cells of volume dV , we can define densities like $s = dS/dV$ and the entropy production density is found (see Callen [17]) to be given by

$$\dot{s} = \sum_j \nabla X_j \cdot \mathbf{I}_j, \quad (11)$$

where \mathbf{I}_j are the current densities of the thermodynamic scalar quantities α_j between adjacent cells. We then introduce the transport coefficients \hat{L}_{ij} by linearizing

$$\mathbf{I}_i = \sum_j \hat{L}_{ij} \nabla X_j. \quad (12)$$

For each force-current pair (i, j) , the transport coefficient \hat{L}_{ij} is a rank-2 tensor and Onsager symmetry requires that the Cartesian components of these tensors are related by $\hat{L}_{ij}^{kl} = \hat{L}_{ji}^{lk}$, where $k, l = x, y, z$.

Note that this formulation uses currents instead of fluxes and gradients of forces (using the definition of forces and fluxes given by Onsager). De Groot and Mazur in Chap. 6 [28] show how to convert these quantities,

⁶ Equation (8) is a Taylor expansion so it is valid only near equilibrium. As long as the neglected higher-order terms in the expansion are small, the equations still hold. As an example of the Onsager relations breaking down far from equilibrium, see [29].
⁷ L is independent of the forces, but it is still a function of the thermodynamic variables.

and therefore they prove the validity of the Onsager relations for some particular cases. Note that in general the proofs of the Onsager relations involve the fluxes and forces as defined by Onsager, but some proofs (for example the proof that uses the Green–Kubo formula in Section 3.2) use currents and gradients of forces instead.

3 Microscopic proofs

3.1 Fluctuation theory

There are various versions of this proof, the first one being Onsager’s original in 1931 [2]. All of them are based on studying the regression of fluctuations of the α variables to equilibrium, and to do so they study the regression of the covariance of the α , *i. e.* the averages of products of two α at different times. While some papers [22] explicitly use the ergodic theorem to go from time averages to ensemble averages of the covariances, this is not strictly necessary as can be seen in a number of other proofs from Jaynes’ [30] to de Groot and Mazur’s [28]. In fact, Landau [31] writes in the preface of his book on Statistical Physics (in which the Onsager relations are discussed) that he consciously avoids the problem of the ergodic hypothesis, but then says that his definition of a statistical averaging is exactly equivalent to a time averaging, which would be a consequence of the system’s ergodicity. Nevertheless, there is an additional hypothesis needed in all of these proofs, *i. e.*, the Boltzmann principle

$$S = k_B \ln W, \quad \text{or, equivalently,} \quad W^{-1} = \exp[-k_B^{-1}S]. \quad (13)$$

This is the link between the microscopic world and the macroscopic, between the microscopic dynamics and the thermodynamic entropy: entropy is a measure of the number of possible microstates of a system in thermodynamic equilibrium. This concept is easily extended to a quasi-equilibrium (or partial-equilibrium) model of non-equilibrium states whereby the system is assumed to be in thermodynamic equilibrium with respect to the fast variables but not with respect to the slow (macroscopic) variables A_i whose deviations from the full equilibrium with the same E , V , and \mathbf{n} we denote by $\alpha_i = A_i - A_i^{eq}$. Thus, the non-equilibrium probability distribution can be written as

$$f(\alpha_1, \dots, \alpha_n) \propto \exp[-k_B^{-1}S(\alpha_i)]. \quad (14)$$

Boltzmann’s principle, despite its success, remains quite obscure in its justification. Reference [32] shows that it is actually possible to prove this principle, *i. e.*, to link Clausius’ entropy and Boltzmann’s entropy, with an argument that can be traced back to Helmholtz and Boltzmann and that is based on a weak ergodic hypothesis, which states that the time averages are equal to the microcanonical averages. To prove Onsager’s relations one needs the Boltzmann principle, and to prove this principle one needs an ergodic hypothesis. It is not the full ergodic hypothesis, but we need the time averages to be equal to the ensemble averages; this would be a consequence (in fact the most famous theorem) of the full ergodic hypothesis.

3.2 Linear response theory

Onsager’s reciprocal relations are a consequence of the Green–Kubo relations [33]. Also a consequence of these relations is Onsager’s regression hypothesis, one of the hypotheses needed in the classical proof of the reciprocal relations, which states that the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible processes.

In linear response theory, the fluctuations of a system around equilibrium are described by a perturbed Hamiltonian like

$$\mathcal{H}(\mathbf{P}, \mathbf{Q}, t) = \mathcal{H}_0(\mathbf{P}, \mathbf{Q}) - \mathcal{F}(t)A(\mathbf{P}, \mathbf{Q}). \quad (15)$$

The evolution of the phase-space probability distribution is described in terms of a Liouville equation.

The reciprocal relations follow by applying the time reversal invariance on the Green–Kubo linear transport coefficients, defined in (12). These are related to the time dependence of the equilibrium fluctuations in the conjugate fluxes

$$\hat{L}_{ij}^{kl} = \beta V \int_0^\infty \langle J_i^k(t) J_j^l(0) \rangle dt, \quad (16)$$

where β is the inverse temperature, V is the system volume, the J are the fluxes, and $k, l = x, y, z$. Equation (16) is an integral of ensemble-averaged time autocorrelation functions. If we take that the fluxes are defined like Casimir suggested in [21], *i. e.*, performing a time-averaged rate of change over a mesoscopic time, then the ergodic assumption allows one to go from this time average to the phase-space average (denoted by $\langle \cdot \rangle$). Note that $\langle A(t) A(0) \rangle \rightarrow 0$ for $t \rightarrow \infty$ is only necessary for ergodicity, while $\int_0^\infty \langle A(t) A(0) \rangle dt < \infty$ is sufficient.

3.3 Stochastic dynamics

Various works including Green [34], Onsager and Machlup [18], as well as de Groot and Mazur [4] developed a proof of the reciprocal relations based on Markov processes, assuming a definite statistical law for the path of the system in the phase space. A Markov process, roughly speaking, is a stochastic process for which the behavior of the process in the future is independent of its behavior in the past. Most, if not all, of these proofs still consider the system as based on time-reversible dynamics, so we include them in the microscopic category. These works, compared to the original proof by Onsager in 1931, are mathematically more complex, but they also answer the question of what is the most probable path that the system will undergo during its evolution. In fact, some of the cited papers are more focused on this question than on the proof of the (already proven) reciprocal relations. For a complete proof in this framework, see Wigner [3].

The macroscopic variables α_i determining the non-equilibrium state on the thermodynamic system are assumed to be Gaussian stochastic, and the entropy is assumed as in eq. (3). The evolution of the α is assumed to satisfy a set of linear Langevin equations

$$\sum_j (L^{-1})_{ij} \frac{d\alpha_j}{dt} = - \sum_j H_{ij} \alpha_j + \eta_i, \quad (17)$$

where η is a white noise vector, *i. e.*, a Gaussian process with $\langle \eta_k(t) \rangle = 0$, and $\langle \eta_k(t) \eta_j(t') \rangle = \delta(t - t') \delta_{kj}$. As already noted by Onsager and Machlup [18], eq. (17) is essentially eq. (10) with an added random force term $\epsilon_i = \sum_j L_{ij} \eta_j$.

It is shown that the covariance matrix $\mathbf{C}(\tau)$ with elements $C_{ij}(\tau) = \langle \alpha_i(t) \alpha_j(t + \tau) \rangle$ has the property

$$\mathbf{C}(\tau_1) \mathbf{C}(\tau_2) = \mathbf{C}(\tau_1 + \tau_2), \quad (18)$$

which is a sufficient condition for the process to be Markovian. It can also be proven that a Gaussian and Markovian process is ergodic, like the Brownian motion for example. An ergodic process allows its statistical properties to be deduced from a single, sufficiently long, random sample of the process, because the process does not change in an inconsistent way.

La Cour and Schieve consider stochastic processes in the framework of large deviation theory [23], with similar implications as before. Gallavotti [35, 36, 37] has proven the Onsager relations using his chaotic hypothesis, deriving a fluctuation theorem, then deriving from this the Green–Kubo relations, and then finally the Onsager reciprocal relations. He identifies the rate of entropy production with the rate of contraction of the phase space. His chaotic hypothesis implies ergodicity at equilibrium.

3.4 Kinetic theory of gases

Onsager relations can be proven using the time reversibility of the gas scattering kernel within the framework of the kinetic theory of gases [28, 38, 39]. Of course, this framework is limited to the study of gases, and

it is based on the Boltzmann equation. To derive the Boltzmann equation, one needs the molecular chaos hypothesis (Stosszahlansatz), the assumption that the velocities of colliding particles are uncorrelated and independent of position. Thus, the knowledge of the precise state of a single molecule before a collision will not be a good predictor of the state of the same molecule before the next collision. This decay of correlation is linked to ergodicity: the ergodic hypothesis was considered by Boltzmann and Maxwell a generalization of the molecular chaos hypothesis [40].

4 Macroscopic proofs

4.1 Entropy production invariance under time reversal

Meixner was the first to arrive at this proof in 1973 [6], based on the derivation by Thomson of one of his reciprocal relations for the thermoelectric effect, which is an example of an Onsager relation. To do so, he introduced a principle that states that the entropy production (written as a function of appropriate variables) is unchanged upon time reversal. Liu rediscovered this proof much more recently [7].

Consider an isolated thermodynamic system. We can assume that the time inversion parity of the entropy of the system S is $\text{tip}(S) = +1$. In fact, we are unaware of any non-even entropy. For example, in statistical mechanics the Gibbs entropy formula is $S = -k_B \sum_i p_i \ln p_i$, which is obviously even. In non-equilibrium statistical mechanics, Maes and Netočný [41] obtain the same result. They also show that what they identify as the entropy production rate, identified with a statistical mechanical definition, is also even under time reversal. This is the crucial assumption in this proof of the Onsager relations.

The fact that the entropy production rate is even under time reversal could appear confusing: this is the famous concept of the arrow of time. Entropy, in fact, requires a particular direction in time: as one goes forward in time, the entropy of an isolated system can never decrease. This is possible despite the microscopic dynamics being reversible, because entropy requires a coarse graining. Thus, we assume that for every chosen level of coarse graining both S and \dot{S} are even under time reversal.

For simplicity, consider a system described by two variables α_1 and α_2 . Then $\dot{S} = X_1 J_1 + X_2 J_2$, and using $J_i = \sum_j L_{ij} X_j$ we obtain the entropy production as a function of either X_1 and X_2 or X_1 and J_2 . We have

$$\dot{S} = L_{11} X_1^2 + L_{22} X_2^2 + (L_{12} + L_{21}) X_1 X_2 = (DX_1^2 + J_2^2 + (L_{12} - L_{21}) X_1 J_2) / L_{22}, \quad (19)$$

where $D \equiv L_{11} L_{22} - L_{12} L_{21}$. For \dot{S} to be even under time reversal, every single term of the above two sums has to be even or vanish. Assuming the time inversion parity $\text{tip}(S) = +1$, from $dS = \sum_i X_i d\alpha_i$, it follows that $\text{tip}(X_i) = \text{tip}(\alpha_i)$, and since $J_i = \dot{\alpha}_i$ and $\text{tip}(\dot{\alpha}_i) = -\text{tip}(\alpha_i)$, it follows that $\text{tip}(X_1 J_2) = -\text{tip}(X_1 X_2)$. Since the coefficient preceding the odd one has to be zero, we obtain $L_{12} = -L_{21}$ if $\text{tip}(X_1 X_2) = -1$ and $L_{12} = L_{21}$ if $\text{tip}(X_1 J_2) = -1$. We can summarize the result with $L_{12} = \text{tip}(X_1 X_2) L_{21}$, and since $\text{tip}(X_i) = \text{tip}(\alpha_i)$ we have

$$L_{12} = \text{tip}(\alpha_1 \alpha_2) L_{21}, \quad (20)$$

which is Casimir's extension of the Onsager reciprocal relations. Note that in Casimir's extension in particular no confusion is allowed on which is the force and which is the flux, because the time inversion properties are important.

Pavelka, Klika, and Grmela discuss the time reversal properties of entropy and entropy production in Ref. [5]. Their work proves that the assumption $\text{tip}(S) = \text{tip}(\dot{S}) = +1$ entails the Onsager–Casimir relations in the GENERIC framework and hence also in the SEA framework, in view of their essential equivalence shown in Ref. [42].

4.2 Principle of maximum entropy production

This proof [43] of the Onsager relations is based on the MEPP. Being macroscopic, this proof does not require a mean to go from the (time-reversible) microscopic equations of motion to the macroscopic equations describ-

ing the thermodynamic system. There are many versions of the principle of maximum entropy production in the literature, so to be more precise we are referring to the principle as stated by Ziegler [8, 9, 10] and often referred to as MEPP [43].

Since eq. (5) holds for all systems regardless of their particular force–flux interrelations, it is taken as a general constraint. The MEPP can be stated in either the force or the flux picture. In the force picture, it asserts that for prescribed fluxes J_j the actual forces X_j maximize the entropy production $\dot{S}(\mathbf{X})$ subject to the constraint $\dot{S}(\mathbf{X}) = \sum_i X_i J_i(\mathbf{X})$, *i. e.*,

$$\max_{\mathbf{X}} |_{\mathbf{J}} \quad \dot{S}(\mathbf{X}) - \lambda_X \left[\dot{S}(\mathbf{X}) - \sum_i X_i J_i \right]. \quad (21)$$

This results in Ziegler’s orthogonality condition $\mathbf{J} = -\frac{1-\lambda_X}{\lambda_X} \frac{\partial \dot{S}}{\partial \mathbf{X}}$ where the Lagrange multiplier reduces to $\lambda_X = 2$ near equilibrium, where the force–flux relation $J_i(\mathbf{X})$ can be linearized as in eq. (8) and $\dot{S}(\mathbf{X}) = \sum_i \sum_j X_i L_{ij} X_j$, so that the orthogonality condition becomes $\sum_j (L_{ij} - L_{ji}) X_j = 0$ and, to hold for arbitrary X_j , requires $L_{ij} = L_{ji}$. In the flux picture, the MEPP asserts that for prescribed forces X_j the actual fluxes J_j maximize the entropy production $\dot{S}(\mathbf{J})$ subject to the constraint $\dot{S}(\mathbf{J}) = \sum_i X_i(\mathbf{J}) J_i$, resulting in the orthogonality condition $\mathbf{X} = -\frac{1-\lambda_J}{\lambda_J} \frac{\partial \dot{S}}{\partial \mathbf{J}}$ with $\lambda_J = 2$ and $R_{ij} = R_{ji}$ near equilibrium, where $R_{ij} = (L^{-1})_{ij}$. In either picture, the reciprocity relations emerge as a theorem of the MEPP valid in the near-equilibrium linear regime. However, Ziegler’s idea in postulating and trying to justify the MEPP was that the orthogonality conditions provide a plausible generalization of Onsager’s relations to the non-linear regime.

4.3 Principle of steepest entropy ascent

An alternative version of MEPP, also providing a generalization of Onsager’s relations to the non-linear regime, is the steepest entropy ascent principle (SEAP), originally advocated by one of us in the framework of quantum thermodynamics [44] and later generalized to several other traditional frameworks of non-equilibrium thermodynamics description [45] and proven to be essentially the same idea that has been adopted for the dissipative part of the GENERIC scheme [42]. According to the SEAP, a non-equilibrium thermodynamic model is well defined if the space of its thermodynamic (macroscopic, slow, rate controlling) variables (here, the α_i) is equipped with a system-dependent metric functional $G(\alpha)$ with respect to which the dissipative component of that system’s dynamics, responsible for its spontaneous relaxation towards equilibrium, is along the direction of steepest ascent of the entropy functional $S(\alpha)$. In this geometrized point of view, for an isolated system the fluxes $J_i \equiv \dot{\alpha}_i$ are viewed as components of a vector \mathbf{J} tangent to the manifold of constant conserved properties where the relaxation path $\alpha(t)$ lies for all times t until the maximum entropy equilibrium state $\alpha(\infty) = \mathbf{0}$ is reached. Equation (5) is valid for all systems and holds independently of the particular metric G characterizing each of them. Therefore, the SEAP asserts that at each point $\alpha(t)$ along the time evolution, the direction of the tangent vector \mathbf{J} is that of steepest entropy ascent compatible with the local values of the forces (interpreted as degrees of disequilibrium) X_i , *i. e.*, among all compatible directions of \mathbf{J} the actual direction maximizes $\sum_i X_i J_i$. Since the maximization is with respect to direction, it requires that we consider equal-length advancements of the trajectory in all possible directions locally tangent to the manifold and then pick the one that increases the entropy the most, with the important proviso that the length of a portion of trajectory is measured with respect to the system’s metric G , *i. e.*,

$$\max_{\mathbf{J}} |_{\mathbf{X}, \alpha} \quad \sum_i X_i J_i - \lambda \left[\sum_i \sum_j J_i G_{ij}(\alpha) J_j - \text{const} \right], \quad (22)$$

which yields eq. (8) with $L = G(\alpha)^{-1}/2\lambda(\alpha)$, namely a non-linear⁸ force–flux relation with conductivities that may be non-linear functions of the non-equilibrium state variables α . This conclusion based on the SEAP, which is a possible extension of Onsager’s results to the far non-equilibrium domain, was first reached in

⁸ The force–flux relation, $J_i = \sum_j L_{ij}(\mathbf{X}) X_j$, is essentially non-linear in the X_j because inverting the $X_i = X_i(\alpha)$ we have $\alpha_i = \alpha_i(\mathbf{X})$ and therefore $L = G(\mathbf{X})^{-1}/2\lambda(\mathbf{X})$, a function of the X_j .

Ref. [46] (last sentence of the paragraph above eq. (24)) where an explicit fluctuation–dispersion expression in terms of Gram determinants and covariances was also given (eq. (34) therein). Near equilibrium, $\mathbf{a} \rightarrow \mathbf{0}$, $L \rightarrow G(\mathbf{0})^{-1}/2\lambda(\mathbf{0})$, and the reciprocity is automatically proven because a metric is by definition symmetric and positive definite and hence it is invertible, and the inverse is symmetric.

5 Conclusions

In the literature there are many microscopic proofs of the Onsager reciprocal relations, which is understandable in view of their importance in the field of non-equilibrium thermodynamics. We have tried to classify all these proofs, based on the time reversal invariance of the microscopic dynamics, into four groups. The need to go from the microscopic equations to the macroscopic ones describing the state of the system means that all these proofs require, sometimes hidden inside some other hypothesis, a loss of correlation in the system, which ultimately allows us to obtain a non-reversible evolution from the microscopic reversible evolution. This loss of correlation allows us to perform ensemble averages on our system near equilibrium by making time averages. This is because an ergodic system covers the entire phase space over a long time, spending more time in regions of the phase space with a proportionally larger volume. In contrast, the macroscopic proofs of the Onsager relations do not require this delicate step going from the microscopic to the macroscopic world. They are based on some additional principles which are not commonly accepted: 1) the time reversal invariance of the entropy production, 2) the MEPP, and 3) the SEAP. While there are still doubts about the validity of the MEPP, this paper shows that its sibling, the SEAP, entails the reciprocal relations near equilibrium and extends the (quasi-)linear force–flux relations to the far non-equilibrium domain, and hopefully will increase the interest in the Steepest Entropy Ascent (SEA) model [45] of non-equilibrium thermodynamics, a model in which this principle is used in a mathematically very detailed way to allow one to make predictions about non-equilibrium systems even far from equilibrium. We also hope that future work will address the obvious connections [47, 48] between the geometric and conceptual foundations of the SEAP and its sibling profound generalization in the field of partial differential equations, now known as “gradient flows,” that has been recently producing a fast-growing stream of important applications in mathematics [49, 50, 51].

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