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Onsager's reciprocity relations: The connection between micro and macrophysics

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ABSTRACT. The Onsager reciprocity relations formulated and derived from the premises of statistical mechanics sixty two years ago lie at the foundations of irreversible thermodynamics. In this paper we mainly review the basic ideas behind their origin emphasizing on their microscopic aspects. Next, we discuss the kinetic theoretical approach justifying their validity and give a brief derivation placing them well beyond the local equilibrium states of dilute gases. We also discuss how using modern techniques of statistical mechanics, efforts have been made to show that they might even hold true in states not necessarily close to equilibrium. An attempt is made to relate this type of work with another approach based on the so called adiabatic elimination of fast variables. The main conclusion simply underlines the fact that up to now this is practically an open question. Other aspects of the problem are also presented.

RESUMEN. Las relaciones de reciprocidad de Onsager fueron formuladas a partir de las bases de la mecánica estadística hace ya más de sesenta años y constituyen los cimientos de la termodinámica irreversible. En este trabajo haremos principalmente una revisión de las ideas básicas que las originaron subrayando los aspectos microscópicos. En seguida discutimos el enfoque de la teoría cinética mediante el cual se puede justificar su validez y daremos una derivación breve que permite extenderlas a estados que están muy alejados del equilibrio local en gases diluidos. También discutimos cómo usando las técnicas modernas de la mecánica estadística se han llevado a cabo intentos para probar su validez en estados que no necesariamente están cercanos al estado de equilibrio. Hacemos un intento en relacionar todo este trabajo con otro enfoque al problema basado en la técnica conocida como la eliminación adiabática de variables rápidas. La conclusión principal simplemente subraya el hecho de que, hasta hoy en día, esta pregunta permanece esencialmente abierta. Se presentan también algunos otros aspectos relevantes del problema.

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1. INTRODUCTION

The theory of phenomena occurring among non equilibrium states of many body systems or the decay of a non equilibrium state to an equilibrium one is still an unfinished subject. From a very general point of view, the dilute gas model described by the Boltzmann equation valid for states as far from equilibrium as we wish has never been solved, for realistic cases beyond the linear regime and response theory, which is valid for arbitrary

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hamiltonians has hardly overcome the linear threshhold; non-linear response is also a rather incipient theory. In the linear regime, where the two best known approaches of non equilibrium statistical physics overlap, the so called Onsager reciprocity relations (ORR) play a very important role. In this paper we want to review the physical ideas behind these relations and their possible extension to non-linear regimes in the light of rather recent works.

To accomplish this goal we have structured this paper as follows: Sect. 2 is devoted to review the main ideas behind the ORR within the context of linear irreversible thermodynamics (LIT). Since this material is fully developed in the literature we shall restrain ourselves in giving mathematical details. In Sect. 3 we will discuss some attempts that have been made to generalize the ORR beyond the domain of LIT using the kinetic theoretical model for a dilute gas. The surprising outcome of this analysis is that one actually proves that the ORR are valid in a linear regime but far beyond local equilibrium states. Other important consequences of these features are also pointed out. In Sect. 4 we discuss the validity of ORR for arbitrary non equilibrium states using the ideas set forth by Hurley and Garrod over ten years ago. More recent results are also related to work along these lines carried out by other workers. Some concluding remarks are left for Sect. 5.

2. THE ORR AND LIT

It is a great coincidence that the writing of this paper happens precisely in the 90th anniversary of Lars Onsager's birth and slightly more than the 60th birthday of the famous reciprocity relations first published in February of 1931. This work is therefore a modest tribute to the thinking of a great man who may be considered without any doubt, the father of modern irreversible thermodynamics.

For a review paper concerned with the enormous incidence that Onsager's work has had in theoretical chemistry nothing is better that to reproduce *ad verbatim* part of the introduction of his master work in this field [1], to get a direct grasp of how he conceived the physical meaning of reciprocity. One reads:

"When two or more irreversible transport processes (heat conduction, electrical conduction and diffusion) take place simultaneously in a thermodynamic system the processes may interfere with each other. Thus an electric current in a circuit that consists of different metallic conductors will in general cause evolution or absorption of heat at the junctions (Peltier effect). Conversely, if the junctions are maintained at different temperatures an electromotive force will usually appear in the circuit, the thermoelectric force: the flow of heat has a tendency to carry the electricity along.

"In such cases one may naturally suspect reciprocal relations by analogy to the reciprocal relations which connect forces and displacements in the equilibrium theory of mechanics and in thermodynamics. Relations of this type have been proposed and discussed by many writers. The earliest of them all is due to W. Thomson,[1] it deals with thermoelectric phenomena. We shall cite Thomson's reciprocal relation in a simple form as

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[1] W. Thomson (Lord Kelvin), *Proc. Roy. Soc. Edinburgh* 1854, p. 123, *Collected Papers I*, pp. 237-41.

a symmetric condition for the relations which connect the forces with the velocities. The electric current we shall call J_1, the heat flow J_2. The current is driven by the electromotive force, which we shall call X_1. In corresponding units the "force" which drives the flow of heat will be

$$X_2 = -\frac{1}{T}\,\mathrm{grad}\,T,$$

where T denotes the absolute temperature (Carnot). If the heat flow and the current were completely independent we should have relations of the type

$$X_1 = R_1 J_1,$$
$$X_2 = R_2 J_2,$$

where R_1 is the electrical resistance and R_2 a "heat resistance". However, since the two processes interfere with each other we must use the more complicated phenomenological relations

$$X_1 = R_{11} J_1 + R_{12} J_2,$$
$$X_2 = R_{21} J_1 + R_{22}, J_2, \tag{1}$$

Here Thomson's contention is

$$R_{12} = R_{21}. \tag{2}$$

"Thomson arrived at this relation from thermodynamic reasoning, but he had to make one additional assumption, namely: *"The electromotive forces produced by inequalities of temperature in circuit of different metals, and the thermal effects of electric current circulating in it, are subject to the laws which would follow from the general principles of the thermodynamic theory of heat if there were no conduction of heat from one part of the circuit to another"*. Thomson thought this assumption very plausible. Even so, he cautiously considered his reciprocal relation (2) a conjecture, to be confirmed or refuted by experiment, since it could not be derived entirely from fundamental principles known at that time. At present Thomson's relation is generally accepted, because it has been confirmed within the limits of error of the best measurements. As regards the theory, the same relation has frequently been found as a by-product of investigations in the electron theory of metals. However, Thomson's relation has not been derived entirely from recognized fundamental principles, nor is it known exactly which general laws of molecular mechanics might be responsible for the success of Thomson's peculiar hypothesis."

Following this rationale, Onsager's approach to the question of reciprocity was very original. He first gave a full discussion of mutual interaction of irreversible processes namely, heat conduction in anisotropic bodies and its analogy with chemical reactions. These examples have been widely discussed in the literature [3–6] so that we shall avoid going into the details here. Nevertheless it is important to point out that after this work was understood an avalanche of similar applications was undertaken for a wide variety of systems. The main outcome of these efforts was that Onsager's reciprocity relations were confirmed experimentally and their range of applicability was in many cases assessed. A review of this works was performed several years ago by Miller [7]; more recently other people [8] have contributed to broaden the class of systems that obey the reciprocity relations.

But the most remarkable contribution of Onsager to this problem was the fact that he actually derived the reciprocity relations from the basic laws of microphysics. And it is this aspect of his work as well as its repercussions what we want to stress in this paper. In his first contribution, [1] Onsager announced that he wanted to derive a whole class of reciprocity relations using the *microscopic reversibility* assumption. This assumption is far from being a trivial one as Casimir stressed many years later [4]. Indeed every student of physics knows that the fundamental equations governing the motion of individual particles in the absence of time and/or velocity dependent hamiltonians, are symmetric under time reversal ($t \rightarrow -t$). This restriction was later removed by Onsager himself so to include systems in which magnetic fields, Coriolis forces and similar effects are present [2]. Ignoring these cases for the time being, Onsager extended this fundamental property of the equations of motion of microphysics to the set of macroscopic variables describing the spontaneous fluctuations around the equilibrium state of a thermodynamic system. This is not all. The equations of motion for the fluctuating variables, taken to be linear in such variables are also taken to be the ones which describe the average behavior of the fluctuations themselves. This leads to an apparent contradiction, noticed by Onsager himself and also brought up by Casimir [4]. Yet, once the fundamental idea of Onsager is taken as an assumption the rest of the proof follows at once [4,6]. To fully appreciate this point we quote the master work once more:

"We shall comment on another question regarding the premises of the derivation, although the substance of a satisfactory answer is known from a famous discussion between Loschmidt and Boltzmann. We have assumed microscopic reversibility, and at the same time we have assumed that the average decay of fluctuations will obey the ordinary laws of heat conduction. Already an apparent contradiction occurs when we consider the simpler case of heat conduction in one dimension. Let α be a displacement of heat $\bar{\alpha}$ its average value, then:

$$\dot{\alpha} = \frac{d\bar{\alpha}}{dt} = -K\alpha. \tag{3}$$

Microscopic reversibility requires

$$\bar{\alpha}(\tau, \alpha') = \bar{\alpha}(-\tau, \alpha'). \tag{4}$$

Clearly

$$\dot{\alpha}(\tau, \alpha') = -\dot{\alpha}(-\tau, \alpha')$$

and

$$\dot{\alpha}(0, \alpha') = -\dot{\alpha}(-0, \alpha') = 0.$$

According to the ordinary laws for conduction of heat $\bar{\alpha}$ decreases for positive τ (if $\alpha' > 0$). According to (4), then, $\bar{\alpha}$ increases for negative τ (average growth of fluctuations), and $\bar{\alpha} = 0$ for $\tau = 0$. It may appear somewhat startling that we apply (4), to fluctuations, only for $\tau > 0$, and not for $\tau \leq 0$. Yet in this there is no logical contradiction —but such a statement disappoints our expectation of continuity in nature. However, the objection is removed when we recognize that (4) is only an approximate description of the process of conduction, neglecting the time needed for acceleration of the heat flow. This time τ_0 is probably rather small, *e.g.* in gases it ought to be of the same order of magnitude as the average time spent by a molecule between two collisions. For practical purposes the time-lag can be neglected in all cases of heat conduction that are likely to be studied, and this approximation is always involved in the formulation of laws like (4). Even the differential form of these equations is justified, because we can usually choose a time Δt such that

$$1 \gg K\Delta t \gg K\tau_0.$$

Then following $t = \tau_0$, which is practically the same as $t = 0$, we have a time interval $\Delta t \gg \tau_0$ in which (by (4)) α and therefore $d\alpha/dt$ are sensible constant. We may also recall that the time needed for equalization of temperature in a body is proportional to the square of its linear dimensions l, *i.e.*

$$K \sim \frac{1}{l^2}.$$

In gases $K\tau_0$ should be of the order l^2/Λ^2, where Λ is the mean free path. The ordinary laws for conduction on heat are therefore asymptotic laws for $l \gg \Lambda$."

The obvious consequence of Onsager's analysis is that since he is restricting himself to the study of fluctuations around the equilibrium state and the equations of motion that describe the decay of the fluctuations are linear in the fluctuating variables, the theory is expected to be valid only close to equilibrium. This is indeed the case and it is therefore not surprising that the ORR are in fact the cornerstone of what is now known as linear irreversible thermodynamics (LIT). This theory, as first conceived by Onsager, is quite different in its basic ideas, although similar in the use of a common language, as the theory afterwards proposed by L. Meixner in Germany and further developed by Prigogine and de Donder in Belgium and de Groot, Mazur and Casimir in Holland.

Very few thermodynamicists have set back to think about the relationship between these two approaches, which is neither obvious nor trivial [12,13] yet both use the ORR which are the basic subject of this review. Moreover, in both theories although with rather different mathematical statements, the so called local equilibrium assumption is postulated. We shall not deal here with the subtleties of this concept, it has been done in a recent paper [14], but it is important to stress that in LIT the validity of the ORR is automatically linked to the postulate of local equilibrium. Since LIT has been justified using the kinetic theoretical model of a dilute gas through the Chapman-Enskog solution to the Boltzmann equation [15,16] and the time correlation function of linear response theory, [17–19] where in each case the ORR relations are derived, a general feeling, if not a strong idea has prevailed, that the natural domain of validity of the ORR is determined by the content of the local equilibrium assumption. Nevertheless in the past twenty years a large amount of apparently unrelated work about non-equilibrium phenomena has thrown results which clearly show that this is not the case. We shall turn our attention to these facts in the following sections.

3. THE ORR BEYOND LOCAL EQUILIBRIUM

The kinetic derivation of the ORR relies on two basic assumptions. The first one is related to the linearization of Boltzmann's equation by assuming that the single particle distribution function for the dilute gas may be expanded in a power series of an adequate parameter, Knudsen's parameter, which is in a general way of speaking, a measure of the spatial inhomgeneities in the system. The first term in this series leads to the hydrodynamic regime for an ideal gas, the Euler fluid, the second term to the Navier-Stokes regime and higher order terms to higher order in the gradients hydrodynamics [20]. When the expansion is kept up to first order in the parameter and applied to a multicomponent mixture the cross effects among several transport processes appear. The second assumption, the one which really allows the presence of the hydrodynamic regime, states that the single particle distribution is a time independent functional of the locally conserved variables. For a multicomponent mixture these are the local concentrations, the local mass density, the local (hydrodynamic) momentum and the local energy density through which the temperature is introduced. This statement is the kinetic version of the local equilibrium assumption [12,16]. A systematic computation of the different fluxes in the system aided with the symmetry properties of the linearized collision kernel of the Boltzman equation is enough to show the validity of Onsager's relations [10]. In this sense they are intimately connected with the local equilibrium assumption.

On the other hand the above scheme is not the only one suitable for solving Boltzmann's equation. In 1949 H. Grad in his work about the properties and solution to Boltzmann's equation [21] posed the following question: suppose that the gas has observable states which require for their description more than the ordinary locally conserved densities, mass, momentum and energy. Is there any way in which such solutions may be extracted from the Boltzmann equation and the additional variables properly identified? The answer came through the now well known Grad's moments method. One expands the distribution function in terms of a complete set of functions, namely, tensorial Hermite polynomials in the velocity $\vec{v}$ of a particle around a local Maxwellian distribution function. Recall that the Boltzmann equation for $f(\vec{r},\vec{v},t)$ the single particle distribution function, is given by

$$\frac{\partial f}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} = J(ff), \tag{5}$$

where $J(ff)$ is the collision term whose explicit form is not needed here. One then writes that [21]

$$f(\vec{r},\vec{v},t) = f^{(0)}(\vec{r},\vec{v}/n,\vec{u},T)\sum_{n=0}^{\infty}\frac{1}{n!}a_i^{(n)}(\vec{r},t)\mathcal{H}_i^{(n)}, \tag{6}$$

that [21]

$$f(\vec{r},\vec{v},t) = f^{(0)}(\vec{r},\vec{v}/n,\vec{u},T)\sum_{n=0}^{\infty}\frac{1}{n!}a_i^{(n)}(\vec{r},t)\mathcal{H}_i^{(n)}, \tag{6}$$

where $\mathcal{H}_i^{(n)}$ is a tensor with n subscripts as well as a polynomial of the n^{th} degree. The coefficients $a_i^{(n)}$ are also tensors of order n and a summation over i is implied. $f^{(0)}$ is a local Maxwellian namely,

$$f^{(0)}(\vec{r},\vec{v}/n,\vec{u},T) = n\left(\frac{m}{2\pi k_{\mathrm{B}}T(\vec{r},t)}\right)^{\frac{3}{2}}\exp\left\{-\frac{1}{2}\frac{m(\vec{v}-\vec{u}(\vec{r},t))^2}{k_{\mathrm{B}}T(\vec{r},t)}\right\}, \tag{7}$$

where $n(\vec{r},t)$ is the local density, $\vec{u}(\vec{r},t)$ the hydrodynamic velocity, $T(\vec{r},t)$ the local temperature, k_{B} is Boltzmann's constant and m the mass of the particles.

The first few Hermite polynomials are

$$\begin{aligned} &\mathcal{H}^{(0)} = 1, && \mathcal{H}_i^{(1)} = V_i, \\ &\mathcal{H}_{ij}^{(2)} = V_iV_j - \delta_{ij}, && \mathcal{H}_{ijk}^{(3)} = V_iV_jV_k - (V_i\delta_{jk} + V_j\delta_{ik} + V_k\delta_{ij}), \end{aligned} \tag{8}$$

and so on.

The coefficients $a_i^{(n)}(\vec{r},t)$ in Eq. (6), which now play the role of the additional variables required to specify the system's states are given by

$$a_i^{(n)}(\vec{r},t) = \frac{1}{\rho}\int f(\vec{r},\vec{v},t)\mathcal{H}_i^{(n)}(\vec{v})\,d\vec{v}, \tag{9}$$

where $\rho = mn(\vec{r},t)$. When one now insterts the expansion given in Eq. (6) into the Boltzmann equation (5) and equates coefficients of $\mathcal{H}_i^{(n)}$, he arrives to a set (infinite) of coupled differential equations which we shall not bother to write down. The important feature of these equations is that their structure has the general form

$$\frac{\partial a_i^{(n)}(\vec{r},t)}{\partial t} + \text{linear terms } a_i^{(n)}, a_i^{(n+1)}, \cdots + \text{bilinear terms } a_i^{(n)}a_i^{(n+1)}, +$$

$$\text{linear terms } a_i^{(n)} \times \left\{\begin{matrix}\operatorname{grad}\rho\\ \operatorname{grad}\vec{u}\\ \operatorname{grad}T\end{matrix}\right\} = \text{coefficient} \times \sum_{s=1}^{\infty}\frac{1}{s}\left\{\mathcal{H}^{(s)}\mathcal{H}^{(i)}\right\} + \text{bilinear collision terms,}$$

where $\{\mathcal{H}^{(s)}\mathcal{H}^{(i)}\}$ is the well known collision bracket of the two functions inside the brackets [21,22]. From the infinite sequence of equations, too complicated to be examined in detail, one now introduces two assumptions. The first one consists in dropping all the bilinear terms including the products of $a_i^{(n)}$ times the gradients of the conserved variables. The resulting equations are now linear in the variables $a_i^{(n)}$ and referred to as the linearized Grad equations. Their explicit form is not needed here so that the reader interested in these details may refer to the literature [21,23]. The second assumption is that one requires a truncation procedure to obtain a closed set of equations by setting all coefficients from a given n on equal to zero. Here this procedure will *not* be required.

In order to relate this problem with irreversible thermodynamics one now restores to the usual procedure. If one takes the Boltzmann equation (5) multiplies both sides by $\ln f$ and integrates over velocity space, after a slight rearrangement of the terms winds up with an entropy balance type equation [10],

$$\frac{\partial(\rho s)}{\partial t} + \operatorname{div} \vec{J}_s = \sigma, \tag{10}$$

where

$$\rho s = -k_{\mathrm{B}} \int (\ln f - 1) f \, d\vec{c}, \tag{11a}$$

$$\vec{J}_s = -k_{\mathrm{B}} \int (\ln f - 1) f \vec{c} \, d\vec{c}, \tag{11b}$$

$$\sigma = -k_{\mathrm{B}} \int (\ln f J(ff) \, d\vec{c} > 0, \tag{11c}$$

and $\vec{c} \equiv \vec{v} - \vec{u}(\vec{r}, t)$ is the chaotic velocity.

We must emphasize here that these steps are merely formal. The last inequality, Eq. (11c) is a consequence of the H theorem. As long as f is *not* expressed in terms of the thermodynamic variables describing the states of the system Eqs. (11a–c) are absolutely meaningless. Indeed in LIT their physical meaning becomes evident only after f is expressed in terms of the locally conserved densities through the local equilibrium assumption. Thus the question arises about what form of f should we use. In earlier work [24,25] we examined in detail how these results are related to irreversible thermodynamics when 13 and 26 moments are taken as the additional states variables. In fact for 26 moments we showed [24] the structure of the entropy density, which is a quadratic form of the moments and further it is a positive definite function. Using a linearized form of this expression and following Onsager's procedure one may define forces and fluxes, find a relationship between them and then show that the proportionality coefficients satisfy the reciprocity condition. Here we shall do it in general [26], that is we shall keep the infinite set of moments $a_i^{(n)}(\vec{r}, t)$ as additional state variables. Therefore restating the above we are thinking of a dilute monoatomic gas whose states are characterized by a set $\mathcal{G}$ defined as $\mathcal{G} \equiv \{\rho(\vec{r}, t), \vec{u}(\vec{r}, t), T(\vec{r}, t), a_i(\vec{r}, t), \ldots, a_i^{(\infty)}(\vec{r}, t)\}$. Clearly we are far beyond local equilibrium although in a linear regime: the $a_i^{(n)}$'s satisfy the linearized Grad equations and further in the evaluation of *all* quantities appearing in Eq. (11a–c) $\ln f$ will be developed in a power series expansion as follows. Since,

$$f = f^{(0)}\left\{1 + \sum_{r=1}^{\infty}\frac{1}{r!}a_i^{(r)}(\vec{r},t)\mathcal{H}_i^{(r)}(\vec{v})\right\}, \tag{12}$$

we take the full second term within brackets as a perturbation around $f^{(0)}$, call it ϕ and so

$$\ln f = \ln f^{(0)} + \ln(1+\phi) \simeq \ln f^{(0)} + \phi^2 + \cdots, \tag{13}$$

keeping terms up to second order in ϕ. Therefore inserting Eq. (13) into Eqs. (11a–c) we get that

$$\rho s = \rho s_0 - \frac{nk_{\mathrm{B}}}{2}\sum_{r=1}^{\infty}\frac{1}{r!}a_i^{(r)}(\vec{r},t)a^{(r)}(\vec{r},t), \tag{14}$$

where ρs_0 is the local entropy density for the gas. Also,

$$(\vec{J}_s)_j = \frac{q_j}{T} - \frac{nk_{\mathrm{B}}}{T}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{\frac{1}{2}}\sum_{r=1}^{\infty}a_i^{(r)}\left\{a_i^{(r+1)} + \delta_j a^{(r-1)}\right\}, \tag{15}$$

q_j being the j^{th} component of the heat flux and δ_j Grad's short notation for tensorial homogeneity [27]. Finally

$$\sigma = n^2 k_{\mathrm{B}}\sum_{r,s=1}^{\infty}\frac{1}{r!s!}a_i^{(r)}a_i^{(s)}\left\{\mathcal{H}^{(r)},\mathcal{H}^{(s)}\right\} > 0, \tag{16}$$

the entropy production being always positive definite since for $r = s$ the collision brackets are non negative and for $r \neq s$ one can show that the resulting combinations form a semipositive quadratic form [26]. These results call for one's attention. In Eqs. (14) and (15) one gets as the first terms those appearing in LIT as a consequence of the local equilibrium assumption. The second terms are (negative!) corrections due to the presence of the non-conserved variables $a_i^{(n)}(\vec{r},t)$. Indeed one can prove that these variables obey relaxation type equations with positive relaxation times whose values depend only on collision brackets so they may be evaluated for different intermolecular potentials. All these details are fully discussed in Ref. [26]. We now show that in this linearized version of extended non-equilibrium thermodynamics Onsager's relations still hold true. Using Onsager's definition, the generalized forces are given by

$$X^{(r)} = \left[\frac{\partial(\rho s)}{\partial a_i^{(r)}}\right]_{a^{(s)}\neq a^{(r)}} = \frac{nk_{\mathrm{B}}}{r!}a_i^{(r)}(\vec{r},t), \tag{17}$$

whence

$$\sigma_s = \sum_{s=1}^{\infty} J^{(s)} X^{(s)}. \tag{20}$$

Moreover, using Eq. (17) the fluxes can be also rewritten as

$$J^{(s)} = -\frac{1}{k_{\mathrm{B}}} \sum_{r=1}^{\infty} \{\mathcal{H}_i^{(r)}, \mathcal{H}_i^{(s)}\} X^{(r)}, \tag{21}$$

or finally,

$$J^{(s)} = \sum_{r=1}^{\infty} L^{(r)(s)} X^{(r)}, \tag{22}$$

where the "generalized transport coefficients" are given by $k_{\mathrm{B}}^{-1}\{\mathcal{H}_i^{(r)}, \mathcal{H}^{(s)}\}$. Since collision brackets are symmetric under the exchange of indices [24] $\{\mathcal{H}^{(r)}, \mathcal{H}^{(s)}\} = \{\mathcal{H}^{(s)}, \mathcal{H}^{(r)}\}$ it follows that the coefficients $L^{(r)(s)}$ obey the reciprocity property. This is a rather rewarding result since we find that there is a linearized version of non-equilibrium thermodynamics valid as far as we please from the local equilibrium state for which the ORR relations are still valid. This last phrase requires clarification since by taking an infinite set of moments we have extended the thermodynamic state space to include an infinite number of non-conserved local variables $(N, \vec{u}, T; a^{(i)}(\vec{r}, t), \ldots, a^{(\infty)}(\vec{r}, t))$. Indeed if we keep the whole set $\{a^{(i)}(\vec{r}, t)\}$ we may loosely say that we are as far from local equilibrium as the model allows and any truncation in this set of variables will clearly restrict the deviations from local equilibrium. In any case, the time evolution equations of these variables has been taken as linear. This is a strong restriction, but within it the above results are valid. The full consequences of this result from a phenomenological point of view remain to be explored in the future [26].

It is important to remark that Eqs. (15)-(22) are a consequence of two approximations, the linearization of the macroscopic equations for the moments as explained in the last paragraph of p. 676 and the expansion of $ln f$ in power series of ϕ as indicated in Eq. (13). In this sense they can be easily understood as a straightforward generalization of the kinetic basis of extended irreversible thermodynamics that has been previously discussed in other reviews about the subject [14]. However, the procedure itself throws no light whatsoever on the old problem raised about ten years ago concerning the compatibility between higher order hydrodynamics and the local equilibrium assumption [20]. This question remains unsolved and clearly pertains to a non-equilibrium theory. To finish with this section it is pertinent to remark that neither the forces as given in Eq. (17) nor the fluxes given in Eq. (19) have the conventional form. In some cases they do reduce to combinations of the heat flux and the stress tensor [26]. Such cases are related to the well known Navier-Stokes and Burnett regimes of hydrodynamics [21].

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4. ORR FROM THE BASIC LAWS OF MICROPHYSICS

In this section we wish to review a number of efforts that have been made to better understand the linear regression of fluctuations, which as mentioned in Sect. 2, is the basic assumption from which Onsager derived his results. Moreover, in this quest the natural question arises as to whether or not the reciprocal relations are strictly valid in linear theories of non-equilibrium processes. At this stage it is also important to point out that from the point of view of stochastic processes this extension has also been considered after Onsager and Machlup [28] in the middle fifties took the initial step of linking the spontaneous decay of fluctuations with the theory of stationary gaussian Markoff processes. We shall come back to this point in Sect. 5.

Here the main question to be considered is the condition under which the ORR may be derived either from the classical or quantum Liouville equations. Since these equations are invariant under time reversal for conservative systems it is therefore clear that further assumptions have to be introduced to first obtain irreversible equations governing the time evolution of the system and use them as a starting point of the whole analysis. It is precisely this transition from reversibility to irreversibility the feature that has hampered substantial progress in the field of irreversible statistical mechanics. Further, since as yet no unique answer exists to cope with this question we have to examine many of its different approaches. Consider a system whose states are described by the numerical values of a set of phase space functions $\{\vec{A}(x) = \vec{a}\}$, where x denotes the position of the system in phase space. The statistical description of the system is then contained in a certain probability distribution function $g(\vec{a}, t)\, d\vec{a}$. Using the basic principles of statistical mechanics and with the aid of the projection operator technique [29,30], Zwanzig derived in 1961 [31] and exact kinetic equation for $g(\vec{a}, t)$. The nature, structure and implications of this result have been exhaustively discussed by many people in the two decades that followed the year of its derivation [32–36]. Here we only want to stress the fact that such an equation is non local in $\vec{a}$ space and non local in time. Indeed if the vector $\vec{a}$ is thought of as one whose components are stochastic variables, as Green pioneered in 1952 [37], the equation describes a non linear non markoffian process. In the linear markoffian approximation [31,36] the first moments of $g(\vec{a}, t)$, which we shall call $\vec{\alpha}$ play the role of the hydrodynamic variables in the sense that they obey transport equations typical of LIT, namely,

$$\frac{d\alpha_j(t)}{dt} = \sum_k \int_0^\infty ds\, K_{jk}(s) F_k(\alpha(t)), \tag{23}$$

where F_k is the k^{th} thermodynamical force, $K_{jk}(s)$ a memory function, here instantaneous which depends only on those a's which are constants of the motion such that $K_{jk} = K_{kj}$ meaning that they satisfy the ORR. These results were later extended by Nettleton [38] to the case of anti-reciprocity by incorporating the velocities $\dot{A}_j(x)$ of the phase space functions into the set of observables. Indeed the observables of the system are now provided by the set $\vec{\alpha} \equiv \langle A \rangle$ and $\vec{v} \equiv \langle \dot{A} \rangle$ where $\langle\ \rangle$ denotes an appropriate ensemble average. The reader is referred to the original source for further details [39,40].

After the work of Zwanzig and Nettleton which gives an improvement over the original derivation of the ORR, a great deal of effort was made in understanding the physical aspects of the general kinetic equation for $g(\vec{a}, t)$ rather than searching for extensions of the ORR themselves beyond the linear markoffian regime. The next important step came in 1982 when Hurley and Garrod [41,42] showed how the ORR could be extended to those non-equilibrium states in which the relationship between forces and fluxes ceases to be linear. Previous attempts along these lines had been analyzed earlier, mainly by van Kampen, [43] from a phenomenological point of view, but none from a microscopic basis. The analysis set forth by Hurley and Garrod was mainly a mathematical one, a matrix **P** which may in general be a function of time and of the variables describing the state of the system is shown to satisfy a mathematical identity which leads to an equation that may be considered a generalization of the ORR. In a later paper [4] the physical interpretation of the matrix **P** was given by proving that it is uniquely determined by the correlation function of the dynamical variables $\{A_j(x)\}$. This was rather easily verified for the case of linear markoffian and non-markoffian processes. A characteristic feature of all this work is that the correlation matrix $\mathbf{C}(t)$ involved in the analysis is taken to be an average of the pertinent phase space functions $A_i(x)$ with an equilibrium distribution function so that

$$\mathbf{C}(t) = \int dx_0\, \rho_{\text{eq}}(x_0) \vec{A}(x_t) \vec{A}(x_0), \tag{24}$$

where x_0 is the phase space point at $t = 0$ and x_t at time t and $\rho_{\text{eq}}(x_0)$ the equilibrium probability density at the initial time. This restriction in a way implies that all the results obtained are not valid too far away from equilibrium, a fact that seems to be reinforced by the results of Ref. [44] and other work. Nevertheless it was later proved that the Hurley-Garrod ansatz remains valid even for non-linear markoffian processes and moreover that they equally hold whenever the initial reference state of the system under study is an arbitrary non-equilibrium state, whether steady or not [45]. The general features of such an arbitrariness are qualitatively understood but much more work is required to clarify the full domain of validity of such results as well as their relationship to others valid in the nonlinear regimen [39,40]. The point we want to stress here is that the validity of ORR is no longer restricted to LIT, some of its basic assumptions such as the local equilibrium assumption or the linear relationship between forces and fluxes may be removed and the ORR will still hold true albeit with a much more sophisticated form. How are these results embedded in a corresponding more general macroscopic theory than LIT, is still an open question [26,39].

Before concluding this section a different approach to the validity of the ORR merits full attention. As we mentioned in Sect. 2 one of the first mesoscopic demonstrations of the validity of the whole scheme of LIT, including the symmetric property of the transport coefficients matrix came from the Chapman-Enskog solution of the Boltzmann equation for a multicomponent mixture of dilute gases [10]. This validity, as it is well known, is restricted to the first order in the gradients approximation, the so called Navier Stokes Fourier regime. This consistency can be also obtained by a purely phenomenological and very elegant argument which was published about twelve years ago [46]. However, if one goes to the second or higher order in the gradients approximation, Burnett, super Burnett and so on, the whole scheme breaks down, the entropy becomes gradient dependent and as first noticed by MacLennan in 1974 [47,48] the transport coefficient matrix for the Burnett approximation fails to hold its symmetric character. His analysis also explained the reason for this failure and also provided a method to generalize the ORR. The highlights of his ideas as well as other relevant thoughts about this problem may be found in his recent book on the subject [49]. His work has been recently extended to the case in which a fluid is in non-equilibrium steady state [48] and as pointed out before these results seem to be particular cases of those obtained in Ref. [45]. A comment is now relevant. We said in Sect. 3 that the ORR relations are valid well beyond the local equilibrium state for the case of the dilute gas. Since Grad's thirteen moment solution leads to the Burnett equations and we've found that even for higher orders the ORR are valid under the very specific definitions of forces and fluxes introduced by Onsager, it remains to show if MacLennan's generalized version of the reciprocity relations are equivalent to those arrived at in Sect. 3.

On the other hand a very thorough study of the systematic elimination of fast variables in linear many body systems was undertaken by Titulaer and collaborators during the last decade [50]. The gist of the method lies in the fact that in the transition from a mesoscopic to a macroscopic regime any N body system contains quantities evolving on different time scales. After a certain characteristic time say τ_c those variables whose change occurs for times less that τ_c cease to be independent variables, and become time independent functional of the slow variables [51]. A typical example is provided by the single particle distribution function in a dilute gas; after many collisions have occurred it ceases to be an independent variable for $t > \tau_c$ the mean free collision time and becomes a time independent functional of the locally conserved densities, mass, momentum and energy. This property, as we said before, lies at the core of the Chapman-Enskog method used in solving kinetic equations [10,22,52]. When boundaries are present in the system and near the walls the gradients may be steep, the Chapman-Enskog method does not hold and consequently the ORR may be violated. Indeed, it may then happen that there is a significant difference in the asymptotic values of the slow variables with respect to their initial value, which is usually referred to as the initial slip. this initial slip is responsible for the violation of the ORR in the Burnett equations [48,53] and in other phenomena [49,54]. Since the redefinition of the thermodynamic forces is essential in all this work to restore the validity of the ORR one ought to expect that they are somewhat related to the more sophisticated microscopic methods using projection operator techniques.

5. CONCLUDING REMARKS

Some of the essential points touched in this review call for special attention. The first and most important one is that the reader must appreciate that the domain of applicability of the ORR superseeds in many ways the scope of LIT. At the same time one favors a word of caution. We have seen that there exist many independent ways of extracting the ORR, namely, microscopic methods which so far have relied upon sophisticated mathematical techniques such as projection operator methods, correlation function analysis and others. More mesoscopic methods mainly based either on the moments solution or the Chapman-Enskog algorithm treatment of the Boltzmann equation in the former case and of other systems besides the dilute gas in the latter one, have also shown that the reciprocity property is obeyed beyond the local equilibrium state although in linear phenomena. Among these methods it is pertinent to mention a novel approach to the problem of irreversible processes formulated by J. Keizer which is very well summarized in a recent monograph [55]. There the reader may find all the relevant details of his work as well as the role played by Onsager's reciprocity relations in various aspects of irreversible phenomena. Last, but not least is the extension of Onsager-Machlup's method [28] dealing with fluctuation phenomena as stochastic processes which was later generalized to non linear processes by Green *et al.* [56,57]. Yet up to date all these efforts appear to be unrelated to each other and moreover contrary to what occurred in the linear regime we seem to lack of experiments which teach us how appropriate all these results are. Thus we may conclude this review by saying that beyond the linear regime the validity of the ORR is a promising idea but much more work is required to give a unified theoretical and experimental framework of their final form.

REFERENCES

1. L. Onsager, *Phys. Rev.* **37** (1931) 405 (Hereafter referred to as I).
2. L. Onsager, *Phys. Rev.* **38** (1931) 2264 (Hereafter referred to as II).
3. S.R. de Groot, *Thermodynamics of Irreversible Processes*, North Holland Co., Amsterdam (1952) Sect. 18, Chap. IV.
4. H.G.B. Casimir, *Rev. Mod. Phys.* **17** (1945) 343.
5. C. Garrod and J. Hurley, *Phys. Rev.* **27A** (1983) 1487.
6. L. García-Colín S., *Termodinámica de Procesos Irreversibles*, Colección CBI UAM-Iztapalapa (1989) Cap. 3.
7. D.G. Miller, in *Transport Phenomena in Fluids*, H.J.M. Hanley, ed., Marcel Dekker, New York (1969) Chap. 10.
8. To the authors knowledge, after Miller's paper no other single comprehensive review on the experimental verification of Onsager's relation has been written. For several specific experiments in this subject, too many to list them individually, the interested should refer to the cumulative index of the *J. of Non-equilib. Thermodyn.* (1982-1992).

9. I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Wiley-Interscience, New York, 3rd ed. (1977).
10. S.R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics*, Dover, Mineola, N.Y. (1984).
11. J. Meixner and H. Reik, in *Handbuch der Physik*, S. Flügge, ed., Springer-Verlag, Berlin (1959) Band. III.
12. See Ref. [6], Chap. 6
13. R.M. Velasco and L.S. García-Colín, *J. of Non-equilib. Thermodyn.* **18** (1993) 157.
14. L.S. García-Colín and F.J. Uribe, *J. of Non-equilib. Thermodyn.* **16** (1991) 89.
15. See Ref. [10], Chap. IX.
16. I. Prigogine, *Physica* **15** (1949) 242.
17. W.A. Steele, *Time Correlations Functions in Transport Phenomena in Fluids*, loc. cit, Ref. [7].
18. K. van Vliet, *J. Math. Phys.* **19** (1978) 1345; *ibid.* **20** (1979) 2573.
19. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions*, W.A. Benjamin, Inc. (1975) Chap. 4.
20. L.S. García-Colín, *Physica* **118A** (1983) 341.
21. H. Grad, in *Handbuch der Physik*, S. Flügge, ed., Springer Verlag, Berlin (1958) Band XII.
22. S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, Cambridge 3rd ed. (1970).
23. H. Grad, *Comm. in Pure Applied Math.* **2** (1949) 331.
24. R.M. Velasco and L.S. García-Colín, *J. Stat. Phys.* **69** (1992) 217.
25. L.S. García-Colín and R.M. Velasco, *Rev. Mex. Fís.* **38** (1992) 92.
26. R.M. Velasco and L.S. García-Colín, *J. of Non-equilib. Thermodyn.* **18** (1993) (157).
27. H. Grad, *Comm. in Pure Applied Math.* **2** (1949) 331.
28. L. Onsager and S. Machlup, *Phys. Rev.* **91** (1953) 1505; *ibid.* **91** (1953) 1512.
29. R. Zwanzig, *J. Chem. Phys.* **33** (1960) 1338.
30. H. Grabert, *Projector Operator Techniques in Non-equilibrium Statistical Mechanics*, Springer Verlag, Berlin (1982).
31. R. Zwanzig, *Phys. Rev.* **124** (1961) 983.
32. L.S. García-Colín and J.L. del Río, *J. Stat. Phys.* **16** (1977) 235.
33. J.L. del Río and L.S. García-Colín *J. Stat. Phys.* **19** (1978) 109.
34. L.S. García-Colín and J.L. del Río, *Physica* **96A** (1979) 606.
35. L.S. García-Colín, *KINAM* **1** (1979) 107, and references cited therein.
36. J.L. del Río and L.S. García-Colín, *Rev. Mex. Fís.* **28** (1981) 57 (in English). See also Ref. [30].
37. M.S. Green, *J. Chem. Phys.* **20** (1952) 1281; *ibid.* **22** (1954) 398.
38. R.E. Nettleton, *J. Chem. Phys.* **40** (1964) 112.
39. R.E. Nettleton,*Physica* **144A** (1987) 219; *ibid.* **132A** (1985) 143.
40. R.E. Nettleton and E.S. Fradkin, *Physica* **158A** (1989) 672.
41. J. Hurley and C. Garrod, *Phys. Rev. Lett.* **48** (1982) 1575; R. Harris, J. Hurley and C. Garrod, *Phys. Rev.* **35A** (1987) 1350.
42. J. del Río and A. Hernández Machado, *Phys. Lett.* **122A** (1987) 111.
43. N.G. van Kampen, *Physica* **74** (1973) 1.
44. L.S. García-Colín and J.L. del Río, *Phys. Rev.* **30A** (1984) 3314.
45. L.S. García-Colín and R.F. Rodríguez, *Phys. Rev.* **36A** (1987) 4945.
46. M. Grmela, R. Rosen and L.S. García-Colín, *J. Chem. Phys.* **75** (1981) 5474.
47. J.A. McLennan, *Phys. Rev.* **8A** (1973) 1479; *ibid.* **10A** (1974) 1272.
48. J. Dufty and J.M. Rubí, *Phys. Rev.* **A36** (1987) 222.
49. J.A. McLennan, *Introduction to Non-equilibrium Statistical Mechanics*, Prentice Hall, Englewood Cliffs, N.J. (1989).
50. U.M. Titulaer, in *Non-equilibrium Statistical Mechanics*, E.S. Hernández, editor, World Scientific Inc. (1990) pp. 1–34, and references therein.
51. N.G. van Kampen, *Phys. Reports "C"* **124** (1985) 69.

52. L.S. García-Colín, M.S. Green and F. Chaos, *Physica* **32** (1966) 450.
53. G.F. Hubmer and U.M. Titulaer, *J. Stat. Phys.* **50** (1988) 913.
54. G.F. Hubmer and U.M. Titulaer, *J. Stat. Phys.* **49** (1987) 331.
55. J. Keizer, *Statistical Thermodynamics of Irreversible Processes*, Springer-Verlag, Berlin (1987).
56. H. Grabert and M.S. Green, *Phys. Rev.* **A19** (1979) 1747.
57. H. Grabert, R. Graham and M.S. Green, *Phys. Rev.* **A212** (1980) 2136.