axioms

Article

On the Validity of Onsager Reciprocal Relations (ORR) for Heat Transfer in Anisotropic Solids

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Abstract: In this work, we investigate the validity of axioms such as Onsager Reciprocal Relations (ORR) for heat transfer in irreversible thermodynamics close to equilibrium. We show that the ORR for this case could be directly derived by introducing the widely accepted concept of heat transfer coefficients into the entropy production rate and by assuming that the thermal conductivity coefficients are uniquely defined. It is believed that this work can not only be used for pedagogical purposes but may also be generalized to other processes beyond heat transfer, thus leading to a generalized framework for transport phenomena and irreversible thermodynamics.

Keywords: axioms; heat transfer; irreversible thermodynamics; anisotropic solid; onsager reciprocal relations; pedagogical; equilibrium

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1. Introduction

The field of irreversible thermodynamics close to equilibrium is a powerful tool for the macroscopic description of processes. One of the most important principles for irreversible thermodynamics close to equilibrium is Onsager Reciprocal Relations (ORR). This principle states that in the absence of magnetic fields and assuming linearly independent fluxes (**J**) or thermodynamic forces (X) (Linearity Axiom: $\mathbf{J} = \mathbf{L}.\mathbf{X}$), the matrix of phenomenological coefficients (**L**) in the flux–force relations is symmetric (ORR: $L_{ij} = L_{ji}$) [1–8].

Onsager derived these relations for the first time in 1931 [9,10]. The starting point for developing the theory was the heat transfer experiments of Voigt and Curie [5,6] in an anisotropic solid. Onsager used the principle of microscopic reversibility by applying the invariance of the equations of motion for the atoms and molecules with respect to time reversal (the transformation $t \rightarrow -t$). This means that the mechanical equations of motion (classical as well as quantum mechanical) of the particles are symmetrical with respect to time. In other words, the particles retrace their former paths if all the velocities are reversed. Onsager also made a principal decision: the transition from molecular reversibility to microscopic reversibility can be made. It is important to remember that Onsager did not use a particular molecular model. Therefore, the results and limitations of the theory are valid for all materials and the theory can be related to continuum theory [3]. Casimir further developed this theory [11].

Although there is experimental evidence for the validity of ORR [12,13], doubts about the proof of this principle have been raised in the literature [14,15].

For example, in Rational Thermodynamics [13], Truesdell remarks that "Onsager's and Casimir's claim that their assertions follow from the principle of microscopic reversibility which has been accepted with little question … the reversibility theorem and Poincare's recurrence theorem make irreversible behavior impossible for dynamical systems in a classical sense. Something must be added to the dynamics of conservative systems, something which is not consistent with it, in order to get irreversibility at all" [16].

Apart from Euclidean space and engineering problems, ORR also plays an important role in cosmology problems such as the relativistic framework [17]. To be more specific, a recent paper by Parker and Jeynes [17] also identified this apparent paradox by using a relativistic entropic Hamiltonian–Lagrangian approach to study the entropy production of spiral galaxies in hyperbolic space time.

Today, ORR are considered by most authors in the field to be an axiom [1,3–7,18]. In our previous work, we examined the theoretical grounds of ORR for multi-component diffusion close to equilibrium [19], for coupled heat and mass transfer in an isotropic fluid [20], as well as for multi-component diffusion far from equilibrium in the extended thermodynamics framework [21]. The aim of this work is to examine the validity of ORR for heat transfer in an anisotropic solid in the absence of elasticity, mass transfer, or chemical reactions.

2. Theoretical Section and Results

The starting point of this analysis is to write the entropy production rate per unit volume (σ) for heat transfer in an anisotropic solid in the absence of elasticity, mass transfer, or chemical reactions. We note that in an anisotropic solid, the flow of heat $\mathrm{J_q}$ may not be in the direction of the temperature gradient; a temperature gradient in one direction can cause the heat to flow in another direction. The entropy production is as follows [5,6]:

$$\boldsymbol{\sigma} = \sum_{\iota=1}^{3}\sum_{j=1}^{3}\mathrm{J_{qi}}\frac{\partial}{\partial \mathrm{x_j}}\left(\frac{1}{\mathrm{T}}\right)\boldsymbol{\delta}_{\mathrm{i}} = -\sum_{\iota=1}^{3}\sum_{j=1}^{3}\mathrm{J_{qi}}\frac{1}{\mathrm{T}^2}\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}}\boldsymbol{\delta}_{\mathrm{i}} \tag{1}$$

in which x_i are the Cartesian coordinates, T is temperature, and $\boldsymbol{\delta}_\mathbf{i}$ is the unit vector in the i-th direction. By further applying the linearity axiom, the phenomenological laws for this system are as follows:

$$\mathbf{J}_{\mathrm{qi}} = \sum_{j=1}^{3}\mathrm{L_{ij}}\frac{\partial}{\partial \mathrm{x_j}}\left(\frac{1}{\mathrm{T}}\right)\boldsymbol{\delta}_{\mathrm{i}} = \sum_{j=1}^{3}\left(-\frac{\mathrm{L_{ij}}}{\mathrm{T}^2}\right)\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}}\boldsymbol{\delta}_{\mathrm{i}} \tag{2}$$

For anisotropic solids, the heat conductivity K is a tensor of the second rank. The Fourier law of heat conduction is then written as follows:

$$\mathbf{J}_{\mathrm{qi}} = -\sum_{j=1}^{3}\mathrm{K_{ij}}\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}}\boldsymbol{\delta}_{\mathrm{i}} \tag{3}$$

Comparison of (2) and (3) and application of ORR leads to symmetrical relations $L_{ij} = L_{ii}$ or $K_{ij} = \mathrm{K}_{ji}$.

In order to investigate the theoretical grounds of ORR, the local heat transfer coefficients ($\mathbf{h_{loc}}$) close to equilibrium are introduced:

$$-\mathrm{K_{ij}}\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}} = \mathrm{h_{loc,ij}}(\mathrm{T}-\mathrm{T_0}) \text{ or } -\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}} = \frac{\mathrm{h_{loc,ij}}}{\mathrm{K_{ij}}}(\mathrm{T}-\mathrm{T_0}); i,j = 1,\ 2,\ 3 \tag{4}$$

In this way, the temperature gradient is replaced by the temperature difference [22]. This idea can be found in many textbooks [1,23,24] as the definition of the local heat transfer coefficients close to equilibrium ($\mathrm{h_{loc,ij}}$). $\mathrm{T_0}$ is a constant absolute temperature measured at a given point. The value of the local heat transfer coefficient $\mathrm{h_{loc,ij}}$ depends not only on the value of the reference temperature $\mathrm{T_0}$, but also on its position.

The following equation is directly derived from Equation (4):

$$\frac{\mathrm{h_{loc,ij}}}{\mathrm{K_{ij}}}\frac{\partial \mathrm{T}}{\partial \mathrm{x_j}} = \frac{\mathrm{h_{loc,11}}}{\mathrm{K_{11}}}\frac{\partial \mathrm{T}}{\partial \mathrm{x_1}} \text{ or } \frac{\partial \mathrm{T}}{\partial \mathrm{x_j}} = \frac{a_{11}}{a_{\mathrm{ij}}}\frac{\partial \mathrm{T}}{\partial \mathrm{x_1}},\ a_{ij} = \frac{\mathrm{h_{loc,ij}}}{\mathrm{K_{ij}}} i = 2,3;\ j = 1,\ 2,\ 3 \tag{5}$$

By combining the Fourier law of heat conduction (Equation (3)) with the definition of local heat transfer coefficients (Equation (4)), the following equation could be directly obtained:

$$\mathrm{J_{qi}} = \sum_{\mathrm{j=1}}^{3} \mathrm{h_{loc,ij}}(\mathrm{T} - \mathrm{T_0})\delta_{\mathrm{i}} \mathrm{or} \frac{\mathrm{J_{qi}}\delta_{\mathrm{i}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,ij}}} = (\mathrm{T} - \mathrm{T_0}) \tag{6}$$

By introducing the above Equations (5) and (6) into Equation (1), one can write the entropy production rate per unit volume in terms of the local heat transfer coefficients as follows:

$$\begin{aligned}
\sigma = -\sum_{\mathrm{j=1}}^{3}\sum_{\iota=1}^{3} \mathrm{J_{qi}} \frac{1}{\mathrm{T^2}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_j}} \delta_{\mathrm{i}} = &-\left(\frac{\partial \mathrm{T}}{\partial \mathrm{x_1}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_2}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_3}} \right) \frac{1}{\mathrm{T^2}} \left| \mathrm{J_{q1}} \right| \\
&- \left(\frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_1}} + \frac{\partial \mathrm{T}}{\partial \mathrm{x_2}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_3}} \right) \frac{1}{\mathrm{T^2}} \left| \mathrm{J_{q2}} \right| \\
&- \left(\frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_1}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}} \frac{\partial \mathrm{T}}{\partial \mathrm{x_2}} + \frac{\partial \mathrm{T}}{\partial \mathrm{x_3}} \right) \frac{1}{\mathrm{T^2}} \left| \mathrm{J_{q3}} \right|
\end{aligned} \tag{7}$$

The transformation of entropy production rate by introducing linearly dependent thermodynamic forces or fluxes is not a new idea; the origin of this idea can be found in the pioneering work of Lorimer [25,26] for multi-component diffusion close to equilibrium. However, the linearly dependent thermodynamic forces or fluxes for heat transfer in anisotropic media in this work are defined with the aid of heat transfer coefficients.

The next step is to apply to the above transformed entropy production equation the Linearity Axiom, by also taking into account that $K'_{ij} = L'_{ij}/T^2$:

$$\begin{aligned}
\mathrm{J_{q1}} &= -\mathrm{K}'_{11} \left(1 + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}} \frac{a_{11}}{a_{12}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}} \frac{a_{11}}{a_{13}} \right) \frac{\partial \mathrm{T}}{\partial \mathrm{x_1}} \delta_1 \\
\mathrm{J_{q2}} &= -\mathrm{K}'_{22} \left(1 + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}} \frac{a_{22}}{a_{21}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}} \frac{a_{22}}{a_{23}} \right) \frac{\partial \mathrm{T}}{\partial \mathrm{x_2}} \delta_2 \\
\mathrm{J_{q3}} &= -\mathrm{K}'_{33} \left(1 + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,1j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}} \frac{a_{33}}{a_{31}} + \frac{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,2j}}}{\sum\limits_{\mathrm{j=1}}^{3} \mathrm{h_{loc,3j}}} \frac{a_{33}}{a_{32}} \right) \frac{\partial \mathrm{T}}{\partial \mathrm{x_3}} \delta_3
\end{aligned} \tag{8}$$

If Equation (5) is introduced into Equation (3), then the Fourier law is written as follows:

$$\begin{aligned} \mathrm{J}_{\mathrm{q}1} &= -\mathrm{K}_{11}\left(1+\frac{\mathrm{K}_{12}}{\mathrm{K}_{11}}\frac{a_{11}}{a_{12}}+\frac{\mathrm{K}_{13}}{\mathrm{K}_{11}}\frac{a_{11}}{a_{13}}\right)\frac{\partial \mathrm{T}}{\partial \mathrm{x}_1}\delta_1 \\ \mathrm{J}_{\mathrm{q}2} &= -\mathrm{K}_{22}\left(1+\frac{\mathrm{K}_{21}}{\mathrm{K}_{22}}\frac{a_{22}}{a_{21}}+\frac{\mathrm{K}_{23}}{\mathrm{K}_{22}}\frac{a_{22}}{a_{23}}\right)\frac{\partial \mathrm{T}}{\partial \mathrm{x}_2}\delta_2 \\ \mathrm{J}_{\mathrm{q}3} &= -\mathrm{K}_{33}\left(1+\frac{\mathrm{K}_{31}}{\mathrm{K}_{33}}\frac{a_{33}}{a_{31}}+\frac{\mathrm{K}_{32}}{\mathrm{K}_{33}}\frac{a_{33}}{a_{32}}\right)\frac{\partial \mathrm{T}}{\partial \mathrm{x}_3}\delta_3 \end{aligned} \tag{9}$$

By assuming that the thermal conductivity coefficients are uniquely defined ($K'_{ij} = K_{ij}$) and by comparing Equation (8) with Equation (9), one can directly obtain the following:

$$\begin{aligned} &\mathrm{K}_{12}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},1\mathrm{j}} = \mathrm{K}_{11}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},2\mathrm{j}};\ \mathrm{K}_{13}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},1\mathrm{j}} = \mathrm{K}_{11}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},3\mathrm{j}} \\ &\mathrm{K}_{21}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},2\mathrm{j}} = \mathrm{K}_{22}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},1\mathrm{j}};\ \mathrm{K}_{23}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},2\mathrm{j}} = \mathrm{K}_{22}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},3\mathrm{j}} \\ &\mathrm{K}_{31}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},3\mathrm{j}} = \mathrm{K}_{33}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},1\mathrm{j}};\ \mathrm{K}_{32}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},3\mathrm{j}} = \mathrm{K}_{33}\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},2\mathrm{j}} \end{aligned} \tag{10}$$

Let us now derive $\mathbf{J}_{q1}$ in terms of $\mathbf{J}_{q2}$ by further using Equations (3) and (10):

$$\begin{aligned} \mathrm{J}_{\mathrm{q}1} &= -\frac{\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},1\mathrm{j}}}{\sum_{\mathrm{j}=1}^{3}\mathrm{h}_{\mathrm{loc},2\mathrm{j}}}\left(\mathrm{K}_{21}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_1}+\mathrm{K}_{22}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_2}+\mathrm{K}_{23}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_3}\right)\delta_1 = \\ &= -\frac{\mathrm{K}_{11}}{\mathrm{K}_{12}}\left(\mathrm{K}_{21}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_1}+\mathrm{K}_{22}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_2}+\mathrm{K}_{23}\frac{\partial \mathrm{T}}{\partial \mathrm{x}_3}\right)\delta_1 \end{aligned}$$

By further comparing the above equation with the Fourier law (Equation (3)), one can directly obtain $K_{21} = K_{12}$. Following similar arguments, one can directly obtain the remaining ORR for anisotropic heat transfer: $K_{31} = K_{13}$, $K_{23} = K_{32}$. Please note that using uniquely defined phenomenological coefficients is not a new idea [19–21]; the origin of this idea can also be found in the pioneering works of Lorimer [25,26] for the phenomenological coefficients and frames of reference for transport processes. There are also similarities of this work to our previous work on the validity of ORR in multi-component diffusion. In both the cases, symmetry occurs due to the existence of a reference quantity such as a constant and uniform velocity (Galilean Invariance) for multi-component diffusion [19–21], or a reference temperature as in this work. However, the Galilean Invariance applied to the multi-component diffusion case is related to the quasi equilibrium postulate.

The main advantage of this approach is its simplicity without resorting to the tools of Statistical Mechanics. The major task of this work is to develop pedagogical methods for ORR, for which the authors have tried to use the simplest analytical way using mathematical formalism. Future work in this area could also include the generalization of this work to far from equilibrium thermodynamics, such as Extended Thermodynamics [18] or the inclusion of chemical reactions in thermodynamics close to equilibrium. The further examination of the Linearity Axiom is also a challenge.

3. Conclusions

In this work, the validity of ORR for heat transfer in an anisotropic solid close to equilibrium was re-examined. The ORR for this case was re-derived with the aid of heat transfer coefficients and by assuming uniquely defined thermal conductivity coefficients. This work eliminates any doubt about ORR for heat transfer close to equilibrium. This work could be further used for pedagogical purposes due to its simplicity, or even to develop a new framework for the axioms of irreversible thermodynamics.

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Nomenclature

A	thermodynamic parameter
h_{loc}	close to equilibrium local heat transfer coefficients
$\mathbf{J}$	flux
$\mathbf{K}$	thermal conductivity coefficient
$\mathbf{L}$	phenomenological coefficients relating fluxes with thermodynamic driving forces
T	absolute temperature
T_0	reference absolute temperature
T	time
x_j	space coordinate
$\mathbf{X}$	thermodynamic driving force
Greek Letters	
Σ	entropy production rate per unit volume

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