

## Article

# On the Validity of a Linearity Axiom in Diffusion and Heat Transfer

Raj Kumar Arya <sup>1</sup>, Devyani Thapliyal <sup>1</sup>, George D. Verros <sup>2,\*</sup>, Neetu Singh <sup>3</sup>, Dhananjay Singh <sup>4</sup>, Rahul Kumar <sup>5</sup>, Rajesh Kumar Srivastava <sup>6</sup> and Anurag Kumar Tiwari <sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar 144011, Punjab, India

<sup>2</sup> Department of Chemistry, Aristotle University of Thessaloniki, P.O. Box 454 Plagiari Thes., 57500 Epanomi, Greece

<sup>3</sup> Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala 147004, Punjab, India

<sup>4</sup> Department of Chemical Engineering, I.E.T. Lucknow (Sitapur Road), Lucknow 226021, Uttar Pradesh, India

<sup>5</sup> Department of Chemical Engineering, University of Petroleum and Energy Studies, Dehradun 248007, Uttarakhand, India

<sup>6</sup> Department of Biotechnology, GITAM School of Technology, GITAM (Deemed to be University), Gandhi nagar, Rushikonda, Visakhapatnam 530045, Andhra Pradesh, India

\* Correspondence: gdverros@gmail.com; Tel.: +30-69-7-272-2651

**Abstract:** In this work, the linearity axiom of irreversible thermodynamics for diffusion and heat transfer has been re-examined. It is shown that this axiom is compatible with the entropy production invariance principle with respect to a reference quantity for diffusion and heat transfer in the Euclidean space. Moreover, the underlying relations of the other principles of irreversible thermodynamics for multi-component diffusion and heat transfer, such as the quasi-equilibrium and the Onsager reciprocal relations (ORR) with the entropy production invariance, are re-examined. It was shown that the linearity principle postulates for diffusion and heat transfer and could be directly derived from the entropy production invariance axiom. It is believed that this work could not only be used for the drying of polymer coatings but also for pedagogical purposes. It may also be generalized; thus, leading to a generalized framework for irreversible thermodynamics.

**Keywords:** axioms; linearity axiom; irreversible thermodynamics; Onsager reciprocal relations; pedagogical; equilibrium; coatings; drying; diffusion; heat transfer



**Citation:** Arya, R.K.; Thapliyal, D.; Verros, G.D.; Singh, N.; Singh, D.; Kumar, R.; Srivastava, R.K.; Tiwari, A.K. On the Validity of a Linearity Axiom in Diffusion and Heat Transfer. *Coatings* **2022**, *12*, 1582.

<https://doi.org/10.3390/coatings12101582>

Academic Editors: Yasong Sun, Bohayra Mortazavi and Eduardo Guzmán

Received: 8 August 2022

Accepted: 17 October 2022

Published: 19 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The field of irreversible thermodynamics is a powerful tool for the macroscopic description of processes with an application not only to the Euclidean space but also to the relativistic framework [1–3]. Irreversible thermodynamics is based on axioms far and beyond those of equilibrium thermodynamics. The axiomatic foundation is the subject of intensive research from the early days of irreversible thermodynamics [4–17]. These principles were discussed in detail in several textbooks and reviews [4–17]. In particular, the field of irreversible thermodynamics is crucial for many transport processes, including nanofluids, fluid mechanics in complex geometries, and heat transfer, etc. [18–23].

Classical irreversible thermodynamics (CIT), often known as linear or the Onsagerian thermodynamics, was the earliest and the most successful approach to irreversible thermodynamics. In 1931, the Onsagerian theory was proposed for the first time with the definition of a general reciprocity relationship in the mutual interference of two simultaneous irreversible processes. The totality of the known theory of irreversible thermodynamics was based on the application of this one basic theorem. The statistical approach has been used to derive the Onsager reciprocity theorem, which was originally derived using a thermodynamic approach. The matrix of resistance coefficients in flux-force interactions

is symmetrical in the absence of the magnetic fields and assuming linearly independent fluxes or thermodynamic forces. This is referred to as the Onsager reciprocal relations postulate. (ORR:  $L_{ij} = L_{ji}$ ) [24–29].

In particular, Onsager derived, for the first time, these relations by using the concept of microscopic reversibility [24,25]. Casimir [26] developed further this theory. Experimental evidence for the ORR was provided by D.G. Miller [27,28]; thus, eliminating any doubt [29] about the validity of the Onsager reciprocal relations (ORR).

Other than the Onsager reciprocal relations, non-equilibrium thermodynamics close to the equilibrium is based on the linearity axiom and quasi-equilibrium axiom as well. Therefore, one of the most important principles for irreversible thermodynamics is the linearity axiom. This principle states that the fluxes ( $\mathbf{J}$ ) are linear functions of thermodynamic forces ( $\mathbf{X}$ ) (linearity axiom:  $\mathbf{J} = \mathbf{L}\mathbf{X}$ ). The quasi-equilibrium axiom states that equilibrium thermodynamics relations are still valid in a differential (local) form. Equilibrium thermodynamic laws apply to those systems which are not in equilibrium, as long as the gradients are not too significant, according to quasi-equilibrium. The correlation between entropy production, fluxes, and forces is described by the axioms of quasi-linear thermodynamics of irreversible processes.

The aim of this work is to investigate the underlying relation between the axioms of irreversible thermodynamics for heat transfer and diffusion. Diffusion and heat transfer are important in many industrial processes, such as coating formation by drying, separations, etc. Therefore, the clarification of non-equilibrium principles is crucial for deriving the fundamental laws of these processes [30,31].

Moreover, a vital question arises regarding coating formation by drying: should we resort to higher order approximations, such as the quadratic approximation, due to steep polymer concentration gradients observed in the drying of many polymer thin film systems, such as the acetone/cellulose acetate system and also in the case of glassy polymer coatings formation [30,31]? A major task of this work is to examine the relation of the linearity axiom with other principles, such as the entropy production invariance axiom. The motivation of this research is to re-examine the validity of the linearity axiom, which is crucial for many processes, such as the drying of polymeric coatings.

The application of the entropy production invariance, however, is not a new idea; Niven [32], for example, examined the invariance properties of the thermodynamic entropy production of shear-flow systems in its global (integral), local (differential), bilinear, and macroscopic formulations, including dimensional scaling, invariance to fixed displacements, rotations or reflections of the coordinates, time antisymmetry, Galilean invariance, and Lie point symmetry. Subsequently, the underlying relations between the entropy production invariance and the axioms of irreversible thermodynamics for heat transfer and diffusion have been re-examined.

## 2. Theoretical Section and Results

The starting point of this analysis was to define the dissipation function ( $\Psi$ ) representing the uncompensated Gibbs free energy transferred to the environment as the product of the entropy production rate per unit volume ( $\sigma$ ) multiplied by the Temperature  $T$ :  $\Psi = \sigma T$ . The entropy production rate per unit volume ( $\sigma$ ) was further analyzed as the product of fluxes and the thermodynamic forces.

For example, the thermodynamic forces for heat transfer in an isotropic body in the absence of elastic contribution, external forces, mass transfer, and chemical reactions are written as [10]:

- Close to equilibrium:  $\mathbf{X}_q = -\frac{\nabla T}{T^2}$
- Extended thermodynamics region:  $\mathbf{X}_q = -\frac{\nabla T}{T^2} - A \frac{\partial J_q}{\partial t}$

where,  $a$  is a thermodynamic parameter. The Fourier law as well the hyperbolic Cattaneo equation is directly derived from the above equations by applying the linearity axiom [10].

A crucial question arises from the above analysis: what are the theoretical grounds of the linearity postulate? Or in other words, ‘Why has the linearity postulate been so successful in deriving the fundamental laws even from far to equilibrium in such cases as heat transfer or diffusion in the Extended Thermodynamics Framework [10]’?

To answer this question, we had to resort to the other axioms, such as the invariance of entropy production to a reference quantity. To examine this principle, firstly we had defined the reference systems. Let us define the body where an irreversible process, such as heat transfer, is taking place as system I. The system of an observer outside the system I is defined as the system II. An observer in system II is measuring dissipation energy of system I as well as the heat flux and the temperature of this system by using proper instruments. These instruments have to be calibrated relative to a reference temperature  $T_0$ . It is reasonable to take as reference temperature the calibration temperature  $T_0$ . From the theoretical point of view, one can simply establish the necessity of reference quantity by using the Taylor expansion of a continuous flux around a reference quantity located at system II.

The entropy production invariance principle in the local form (differential) for heat transfer in Euclidean space simply requires that the entropy production in system I is invariant of the calibration temperature  $T_0$ :

$$\frac{\partial \sigma}{\partial T_0} = \frac{\partial J_q X_q}{\partial T_0} = 0 \tag{1}$$

The linearity axiom for heat transfer in an isotropic body is directly derived from the above equation by separating variables:  $\frac{\partial \ln J_q}{\partial T_0} = -\frac{\partial \ln X_q}{\partial T_0} = \lambda_0$ , or  $J_q = L_q X_q; L_q = e^{2\lambda_0 T_0}$ .

The  $\lambda$  parameter does not depend either on  $J_q$  or on  $X_q$ .

The entropy production invariance for n-component isothermal and isobaric diffusion in an isotropic body by taking into account that the flux for this case is defined as  $J_i = c_i(v_i - v^*)$  and requires the entropy production to be invariant by adding to the flux a constant and uniform velocity  $v_0$  ( $v \rightarrow v + v_0$ ). In other words, the entropy production ( $\sigma$ ) and the dissipation function ( $\Psi$ ) are invariant in the Euclidean space for an observer located at the ground (system I) if the diffusing system is placed on a vehicle (system II) moving with a constant and uniform velocity  $v_0$  [5–10]. The entropy invariance for diffusion is not a new idea; the origin of this idea could be found in the pioneering work of Onsager [33] for diffusion.

This principle in the local (differential) form is written as:

$$\frac{\partial \sigma}{\partial v_0} = \frac{\partial \sum_{i=1}^n J_i X_i}{\partial v_0} = 0 \tag{2}$$

- Close to equilibrium:  $X_i = -\frac{(\nabla \mu_i)_{T,P}}{T}$
- Extended thermodynamics region:  $X_i = -\frac{(\nabla \mu_i)_{T,P}}{T} - b_i \frac{\partial J_i^*}{\partial t}$

where,  $\mu_i$  is the chemical potential of the i-th component,  $v^*$  stands for the velocity of the center of mass,  $b_i$  is a thermodynamic parameter.

Please note, the quasi-equilibrium principle for isothermal and isobaric multi-component diffusion ( $\sum_{i=1}^n c_i X_i = 0$ ) is also directly derived from the entropy production invariance principle (Equation (2)).

At this point, new fluxes, defined relative to an arbitrary reference velocity  $v^\neq$ , are introduced [34]:

$$J_i^\neq = c_i(v_i - v^\neq); v^\neq = \sum_{i=1}^n w_i v_i; \sum_{i=1}^n w_i = 1 \tag{3}$$

If these new fluxes are introduced in the dissipation function, then the dissipation function is invariant under the transformation of the new set of fluxes due to the quasi-equilibrium principle [34]:

$$\Psi = \sum_{i=1}^n T J_i^{\neq} \cdot X_i \quad (4)$$

Please note, the fluxes  $J_i^{\neq}$  are also linearly dependent, since from Equation (3):

$$\sum_{i=1}^n J_i^{\neq} w_i / c_i = 0 \quad (5)$$

For binary diffusion the above equation and the entropy production invariance principle are written as:

$$J_1^{\neq} w_1 / c_1 + J_2^{\neq} w_2 / c_2 = 0 \quad \frac{\partial \sigma}{\partial v_0} = \frac{\partial (J_1^{\neq} X_1 + J_2^{\neq} X_2)}{\partial v_0} = 0$$

The linearity axiom for binary diffusion in the Euclidean space could be directly derived by following similar arguments as for the heat transfer case. In particular, by taking into account the above equations and eliminating  $J_2$  or  $J_1$  from the above entropy invariance equation, the following equations have been derived:

$$\begin{aligned} \frac{\partial \sigma}{\partial v_0} = \frac{\partial (J_1^{\neq} X_1')}{\partial v_0} = 0; X_1' &= X_1 - w_1 c_2 X_2 / w_2 c_1 \\ \frac{\partial \sigma}{\partial v_0} = \frac{\partial (J_2^{\neq} X_2')}{\partial v_0} = 0; X_2' &= X_2 - w_2 c_1 X_1 / w_1 c_2 \end{aligned} \quad (6)$$

or

$$\begin{aligned} \frac{\partial \ln J_1^{\neq}}{\partial v_0} &= - \frac{\partial \ln X_1'}{\partial v_0} = \lambda_1 \\ \frac{\partial \ln J_2^{\neq}}{\partial v_0} &= - \frac{\partial \ln X_2'}{\partial v_0} = \lambda_2 \end{aligned} \quad (7)$$

The  $\lambda_i$  parameter depends neither on  $J_i^{\neq}$  nor on  $X_i$ .

From the above Equation (7) one could directly show that the linearity axiom is compatible with the entropy invariance principle for binary isothermal diffusion in the Euclidean space:

$$\begin{aligned} J_1^{\neq} &= L_{11} X_1 + L_{12} X_2; L_{11} = e^{2\lambda_1 v_0}; L_{12} = -(w_1 c_2 / w_2 c_1) e^{2\lambda_1 v_0} \\ J_2^{\neq} &= L_{21} X_1 + L_{22} X_2; L_{21} = -(w_2 c_1 / w_1 c_2) e^{2\lambda_2 v_0}; L_{22} = e^{2\lambda_2 v_0} \end{aligned} \quad (8)$$

The generalization to multi-component diffusion by the mathematical induction method does not create any fundamental difficulty.

The findings of this work for binary diffusion are in accordance with the literature [7–9]. In particular, one could directly derive from the above equations the geometric rule ( $L_{12}^2 = L_{21}^2 = L_{11} \times L_{22}$ ), which is valid for binary solutions [7–9]. The Fick's law or the Maxwell–Stefan equation for diffusion could be directly derived from Equation (4) by further using the linearity axiom and the quasi-equilibrium axiom.

Regarding the implementation of the theory for multi-component diffusion to a real system, the example of a ternary isothermal diffusing system placed on a vehicle moving with a constant and uniform velocity  $v_0$  as reported by L. Onsager [33] has been chosen. The entropy production for this ternary isothermal diffusing system is written as:  $\sigma = \sum_{i=1}^3 J_i^{\neq} X_i$ .

By using the volume average velocities ( $w_i = C_i \bar{V}_i$ ) and the quasi-equilibrium principle, the following equations could be directly derived [28]:

$$\begin{aligned} \sigma &= J_1^\neq X_{1T} + J_2^\neq X_{2T} \\ X_{1T} &= \left(1 + \frac{C_1 \bar{V}_1}{C_3 \bar{V}_3}\right) X_1 + \left(\frac{C_2 \bar{V}_1}{C_3 \bar{V}_3}\right) X_2 \\ X_{2T} &= \left(\frac{C_1 \bar{V}_2}{C_3 \bar{V}_3}\right) X_1 + \left(1 + \frac{C_2 \bar{V}_2}{C_3 \bar{V}_3}\right) X_2 \end{aligned} \quad (9)$$

where,  $\bar{V}_i$  is the partial molar volume of the  $i$ -th substance.

The linearity axiom applied to Equation (9) states:

$$J_1^\neq = L_{11} X_{1T} + L_{12} X_{2T}; J_2^\neq = L_{21} X_{1T} + L_{22} X_{2T} \quad (10)$$

The entropy invariance principle for the above systems requires:

$$\frac{\partial (J_1^\neq X_{1T} + J_2^\neq X_{2T})}{\partial v_0} = 0 \text{ or } \frac{\partial (J_1^\neq X_{1T})}{\partial v_0} = -\frac{\partial (J_2^\neq X_{2T})}{\partial v_0} = \lambda_3 \quad (11)$$

or

$$J_1^\neq X_{1T} = \lambda_3 v_0; J_2^\neq X_{2T} = -\lambda_3 v_0 \quad (12)$$

In the derivation of the above equations the integration constants were set equal to zero. The Equation (11) could be further transformed as:

$$J_1^\neq \frac{\partial X_{1T}}{\partial v_0} + X_{1T} \frac{\partial J_1^\neq}{\partial v_0} = \lambda_3 J_2^\neq \frac{\partial X_{2T}}{\partial v_0} + X_{2T} \frac{\partial J_2^\neq}{\partial v_0} = -\lambda_3 \quad (13)$$

By further using Equation (12), the above equations are written as:

$$\frac{\partial \ln(X_{1T})}{\partial v_0} + \frac{\partial \ln(J_1^\neq)}{\partial v_0} = \frac{1}{v_0} \frac{\partial \ln(X_{2T})}{\partial v_0} + \frac{\partial \ln(J_2^\neq)}{\partial v_0} = \frac{1}{v_0} \quad (14)$$

By introducing the  $m$  parameters, Equation (14) could be written as:

$$\begin{aligned} \frac{\partial \ln(X_{1T})}{\partial v_0} &= \frac{m_1}{v_0} \quad \frac{\partial \ln(J_1^\neq)}{\partial v_0} = \frac{1-m_1}{v_0} \\ \frac{\partial \ln(X_{2T})}{\partial v_0} &= \frac{m_2}{v_0} \quad \frac{\partial \ln(J_2^\neq)}{\partial v_0} = \frac{1-m_2}{v_0} \end{aligned} \quad (15)$$

The  $m$  parameters do not depend on  $v_0$ . By integrating the above equations and by introducing the integration constants  $k$ , the above equations are written as:

$$X_{1T} = k_1 v_0^{m_1} \quad X_{2T} = k_2 v_0^{m_2} \quad J_1^\neq = k_3 v_0^{1-m_1} \quad J_2^\neq = k_4 v_0^{1-m_2} \quad (16)$$

By comparing Equation (16) with the linearity axiom (Equation (10)), the conductivity coefficients  $L_{ij}$  are written as:

$$\begin{aligned} L_{11} &= (1 - Y_1) \frac{k_3}{k_1} v_0^{1-2m_1} \quad L_{12} = Y_1 \frac{k_3}{k_2} v_0^{1-m_1-m_2} \\ L_{21} &= (1 - Y_2) \frac{k_4}{k_1} v_0^{1-m_1-m_2} \quad L_{22} = Y_2 \frac{k_4}{k_2} v_0^{1-2m_2} \end{aligned} \quad (17)$$

where,  $Y$  is an adjustable parameter introduced to describe the contribution of each term to the linearity principle.

Let us now consider the actual diffusing system LiCl/KCl/H<sub>2</sub>O placed on a vehicle moving with a constant and uniform velocity. The conductivity coefficients  $L_{ij}$  by using the transformed thermodynamic forces (please see Equations (9) and (10)) were reported by D.G. Miller [28] in his landmark work for the validity of the Onsager reciprocal relations as:  $L_{11} = -0.200$ ,  $L_{12} = 0.0605$ ,  $L_{21} = 0.0586$ ,  $L_{22} = -0.283$ .

These conductivity coefficients were scaled out by  $10^{-8}/RT$  and have the units  $\text{molescm}^{-1} \text{s}^{-1}$ .  $R$  is the universal gas rate constant. Strongly related to the entropy production invariance principle is the uniqueness axiom of phenomenological resistance, or conductivity coefficients with respect to frames of reference in the Euclidean space [35–38]. In other words, the conductivity coefficients of the diffusing system placed on a vehicle moving with a constant and uniform velocity are identical to the conductivity coefficients measured at the ground.

Clearly, Equation (17) is very rich in adjustable parameters. For example, by assuming that the conductivity coefficients are uniquely defined, and by assuming values for the  $m_1$  and  $m_2$  parameters, one could directly estimate the pro-exponential parameters (see Equation (17)) by using standard methods of non-linear regression analysis. In particular, by assuming a constant uniform velocity  $v_0$  equal to 3 m/s and by setting the  $m_1$  and  $m_2$  parameters equal to 0.3, the conductivity coefficient data for the system LiCl/KCl/H<sub>2</sub>O [28] was exactly reproduced for the following adjustable parameters values:

$$(1 - Y_1) \frac{k_3}{k_1} = -0.1289 \quad Y_1 \frac{k_3}{k_2} = 3.9 \times 10^{-2} \quad (1 - Y_2) \frac{k_4}{k_1} = 3.78 \times 10^{-2} \quad Y_2 \frac{k_4}{k_2} = -0.1824$$

The above parameters were scaled out by  $10^{-8}/RT$ .

The strongest evidence for the entropy invariance principle is the fact that this principle coincides with the Galilean invariance for diffusion. The origin of applying Galilean invariance to diffusion could be found in the pioneering work of Prigogine [5] for diffusion. Regarding real processes, such as multi-component diffusion and electrokinetic phenomena, additional experimental evidence about both the linearity postulate and the Onsager reciprocal relations could be found in the work of D.G. Miller [27,28].

It was also shown that the Onsager reciprocal relations (ORR) for diffusion close to the equilibrium were necessarily fulfilled by using the uniqueness resistance coefficient axiom with respect to the frames of reference and the linearity postulate as well as the entropy invariance principle [37,38].

Thapliyal et al. [39] applied the entropy production invariance for isothermal and isobaric diffusion in the linear extended thermodynamics region to further investigate the validity of Onsager reciprocal relations (ORR) in this area. Verros and Arya [40] showed that the ORR axiom is also necessarily fulfilled for heat transfer close to the equilibrium in an anisotropic solid by using the transformation of frames of reference combined with the uniqueness axiom and the linearity axiom.

Ågren [41] suggested that the Onsager relations should be interpreted as there is a frame of reference where all the transport processes in diffusion are independent. Moreover, Zi-Kui Liu [42] showed in a recent work that the ORR could be directly derived by using only the linearity postulate, and proposed a generalized theory for cross phenomena.

The above work for both ORR and quasi-equilibrium axioms is a clear indication that these axioms are not only strongly related to each other for the heat transfer and diffusion case, but they are also both related to the linearity principle. Moreover, this work shows that the linearity axiom is compatible with more general principles, such as the entropy production invariance axiom; thus, further validating the linearity axiom for heat transfer or multi-component diffusion in the Euclidean space. The authors hope that this work will attract the interest of other colleagues to further investigate the fundamental irreversible thermodynamics relations in the Euclidean space.

### 3. Conclusions

In this work, the validity of the linearity postulate for heat transfer and multi-component diffusion was re-examined. It has been shown that:

- The linearity postulate is a reasonable approximation for both diffusion and heat transfer in the Euclidean space.
- The linearity postulate for heat transfer and diffusion is compatible with the entropy production invariance in the Euclidean space.

This is in accordance to the previous work in the field. This work could be further used due to its simplicity for further understanding the coating formation by drying and pedagogical purposes, or even to develop a new framework for irreversible thermodynamics axioms.

**Author Contributions:** Conceptualization, R.K.A.; Data curation, R.K.S.; Formal analysis, D.S.; Investigation, N.S., R.K. and A.K.T.; Methodology, R.K.A. and D.T.; Project administration, G.D.V.; Supervision, R.K.A. and G.D.V. All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors are grateful to Sarada Paul Roy for language corrections, proof-reading, and editing. The reviewers of this work are also acknowledged for their helpful and constructive comments.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Nomenclature

$A, b$	thermodynamic parameter
$C_i$	molar concentration of the $i$ -th substance
$k$	integration constant
$J$	flux
$L$	phenomenological coefficients relating fluxes with thermodynamic driving forces
$R$	universal gas constant
$T$	absolute temperature
$T_0$	reference absolute temperature
$t$	time
$\mathbf{v}^*$	velocity of the center of mass
$\mathbf{v}_0$	constant and uniform velocity
$\mathbf{v}_i$	velocity of the $i$ -th substance
$\mathbf{v}^\neq$	arbitrary reference velocity
$\bar{V}_i$	partial molar volume of the $i$ -th substance
$w_i$	weighting factors whose sum is equal to unity
$X$	thermodynamic driving force
$X_{1T}$	transformed thermodynamic driving force
<b>Greek Letters</b>	
$\lambda$	parameter of the system
$\mu_i$	chemical potential of the $i$ -th substance
$\sigma$	entropy production rate per unit volume
$\Psi$	dissipation function

## References

- Li, S.-N.; Cao, B.-Y. Generalized variational principles for heat conduction models based on Laplace transform. *Int. J. Heat Mass Transf.* **2016**, *103*, 1176–1180.
- Li, S.-N.; Cao, B.-Y. On Entropic Framework Based on Standard and Fractional Phonon Boltzmann Transport Equations. *Entropy* **2019**, *21*, 204. [[CrossRef](#)] [[PubMed](#)]
- Parker, M.C.; Jaynes, C. A Relativistic Entropic Hamiltonian–Lagrangian Approach to the Entropy Production of Spiral Galaxies in Hyperbolic Spacetime. *Universe* **2021**, *7*, 325. [[CrossRef](#)]
- Curie, P. *Oeuvres. Publiées Par Les Soins de la Société Française de Physique*; Guthier-Villars: Paris, France, 1908.
- Prigogine, I. *Etude Thermodynamique des Phénomènes Irréversibles*; Dunod: Paris, France, 1947.
- Truesdell, C.A. *Rational Thermodynamics*; Springer: New York, NY, USA, 1984.
- Tyrrell, H.J.V.; Harris, K.R. *Diffusion in Liquids: A Theoretical and Experimental Study*; Butterworths: London, UK, 1984.
- De Groot, S.R.; Mazur, P. *Non-Equilibrium Thermodynamics*, 2nd ed.; Dover Publications: New York, NY, USA, 1984; pp. 11–82.

9. Kuiken, G.D.C. *Thermodynamics of Irreversible Processes—Applications to Diffusion and Rheology*, 1st ed.; Wiley: New York, NY, USA, 1994; pp. 1–135.
10. Jou, D.; Lebon, G.; Casas-Vazquez, J. *Extended Irreversible Thermodynamics*, 3rd ed.; Springer: Berlin/Heidelberg, Germany, 2001; pp. 39–70.
11. Bird, R.B.; Stewart, W.E.; Lightfoot, E.N. *Transport Phenomena*, 2nd ed.; Wiley: New York, NY, USA, 2002; pp. 764–798.
12. Demirel, Y.A.; Sandler, S.I. Nonequilibrium Thermodynamics in Engineering and Science. *J. Phys. Chem. B* **2004**, *108*, 31–43. [[CrossRef](#)]
13. Öttinger, H.C. *Beyond Equilibrium Thermodynamics*, 1st ed.; Wiley: New York, NY, USA, 2005.
14. Demirel, Y. *Nonequilibrium Thermodynamics, Transport and Rate Processes in Physical, Chemical and Biological Systems*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2007; pp. 1–144.
15. Rastogi, R.P. *Introduction to Non-Equilibrium Physical Chemistry*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2007.
16. Michaelides, E.E. Transport Properties of Nanofluids. A Critical Review. *J. Non Equil. Thermodyn.* **2013**, *38*, 1–79. [[CrossRef](#)]
17. Kondepudi, D.; Prigogine, I. *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, 2nd ed.; Wiley: New York, NY, USA, 2015; pp. 333–455.
18. IHussain, Z.; Khan, S.; Ullah, A.; Ikramullah; Ayaz, M.; Ahmad, I.; Mashwani, W.; Chu, Y. Extension of optimal homotopy asymptotic method with use of Daftardar–Jeffery polynomials to Hirota–Satsuma coupled system of Korteweg–de Vries equations. *Open Phys.* **2020**, *18*, 916–924. [[CrossRef](#)]
19. Khan, S.; Selim, M.M.; Khan, A.; Ullah, A.; Abdeljawad, T.; Ikramullah; Ayaz, M.; Mashwani, W.K. On the Analysis of the Non-Newtonian Fluid Flow Past a Stretching/Shrinking Permeable Surface with Heat and Mass Transfer. *Coatings* **2021**, *11*, 566. [[CrossRef](#)]
20. Khan, S.; Selim, M.; Gepreel, K.; Ullah, A.; Ikramullah; Ayaz, M.; Mashwani, W.; Khan, E. An analytical investigation of the mixed convective Casson fluid flow past a yawed cylinder with heat transfer analysis. *Open Phys.* **2021**, *19*, 341–351. [[CrossRef](#)]
21. Ullah, A.; Ikramullah; Selim, M.M.; Abdeljawad, T.; Ayaz, M.; Mlaiki, N.; Ghafoor, A. A Magnetite–Water–Based Nanofluid Three-Dimensional Thin Film Flow on an Inclined Rotating Surface with Non-Linear Thermal Radiations and Couple Stress Effects. *Energies* **2021**, *14*, 5531. [[CrossRef](#)]
22. Shah, Z.; Kumam, P.; Ullah, A.; Khan, S.N.; Selim, M.M. Mesoscopic Simulation for Magnetized Nanofluid Flow within a Permeable 3D Tank. *IEEE Access* **2021**, *9*, 135234–135244. [[CrossRef](#)]
23. Rizk, D.; Ullah, A.; Ikramullah; Elattar, S.; Alharbi, K.A.M.; Sohail, M.; Khan, R.; Khan, A.; Mlaiki, N. Impact of the KKL Correlation Model on the Activation of Thermal Energy for the Hybrid Nanofluid (GO + ZnO + Water) Flow through Permeable Vertically Rotating Surface. *Energies* **2022**, *15*, 2872. [[CrossRef](#)]
24. Onsager, L. Reciprocal Relations in Irreversible Processes I. *Phys. Rev.* **1931**, *37*, 405–426. [[CrossRef](#)]
25. Onsager, L. Reciprocal Relations in Irreversible Processes II. *Phys. Rev.* **1931**, *37*, 2265–2279. [[CrossRef](#)]
26. Casimir, H.B.G. On Onsager Principle of Microscopic Reversibility. *Rev. Mod. Phys.* **1945**, *17*, 343–350. [[CrossRef](#)]
27. Miller, D.G. Thermodynamics of Irreversible Processes: The Experimental Verification of the Onsager Reciprocal Relations. *Chem. Rev.* **1960**, *60*, 16–37.
28. Miller, D.G. Ternary Isothermal Diffusion and the Validity of the Onsager Reciprocity Relations. *J. Phys. Chem.* **1959**, *63*, 570–578. [[CrossRef](#)]
29. Coleman, B.D.; Truesdel, C. On the Reciprocal Relations of Onsager. *J. Chem. Phys.* **1960**, *33*, 28–31. [[CrossRef](#)]
30. Verros, G.D. Application of non-equilibrium thermodynamics and computer aided analysis to the estimation of diffusion coefficients in polymer solutions: The solvent evaporation method. *J. Membr. Sci.* **2009**, *328*, 31–57. [[CrossRef](#)]
31. Arya, R.K.; Thapliyal, D.; Sharma, J.; Verros, G.D. Glassy polymers—Diffusion, sorption, ageing and applications. *Coatings* **2021**, *11*, 1049. [[CrossRef](#)]
32. Niven, R.K. Invariance Properties of the Entropy Production, and the Entropic Pairing of Inertial Frames of Reference by Shear-Flow Systems. *Entropy* **2021**, *23*, 1515. [[CrossRef](#)]
33. Onsager, L. Theories and problems of liquid diffusion. *Ann. N. Y. Acad. Sci.* **1945**, *46*, 241–265. [[CrossRef](#)] [[PubMed](#)]
34. Schmitt, A.; Craig, J.B. Frictional coefficient formalism and mechanical equilibrium in membranes. *J. Phys. Chem.* **1977**, *81*, 1338–1342. [[CrossRef](#)]
35. Lorimer, J.W. Phenomenological Coefficients and Frames of Reference for Transport Processes in Liquids and Membranes Part I—Resistance Coefficients, Friction Coefficients and Generalized Diffusivities in Isothermal Systems. *J. Chem. Soc. Faraday II* **1978**, *74*, 75–83. [[CrossRef](#)]
36. Lorimer, J.W. Phenomenological Coefficients and Frames of Reference for Transport Processes in Liquids and Membranes Part II—Resistance Coefficients in Non-Isothermal Systems. *J. Chem. Soc. Faraday II* **1978**, *74*, 84–92. [[CrossRef](#)]
37. Verros, G.D. On the Validity of the Onsager Reciprocal Relations in Multi-component Diffusion. *Phys. Lett. A* **2007**, *365*, 34–38. [[CrossRef](#)]
38. Verros, G.D. On the Validity of the Onsager Reciprocal Relations in Simultaneous Heat and Multi-component Diffusion. *Phys. A Stat. Mech. Its Appl.* **2007**, *385*, 487–492. [[CrossRef](#)]
39. Thapliyal, D.; Arya, R.K.; Verros, G.D. On the multi-component diffusion in the linear region of the extended thermodynamics framework. *Eur. Phys. J. Plus* **2021**, *136*, 1138. [[CrossRef](#)]

40. Arya, R.K.; Verros, G.D. On the validity of Onsager Reciprocal Relations (ORR) for heat transfer in anisotropic solids. *Axioms* **2022**, *11*, 104. [[CrossRef](#)]
41. Agren, J. The Onsager Reciprocity Relations Revisited. *J. Phase Equilib. Diffus.* **2022**, 1–8. [[CrossRef](#)]
42. Liu, Z.K. Theory of cross phenomena and their coefficients beyond Onsager theorem. *Mater. Res. Lett.* **2022**, *10*, 393–439. [[CrossRef](#)]