

Research Article

Variational Principles of Thermodynamics in a Rayleigh Gas Model

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Abstract

Using an analytically solvable model of a Rayleigh gas as an example, variational principles of irreversible thermodynamics are proposed. These principles are formulated for both isolated (without sources) and open (with sources) systems. It is shown that in an isolated system, entropy production is minimal during relaxation to an equilibrium state. Thus, Prigogine's principle of minimum entropy production is satisfied in an isolated system. In an open system with sources, during relaxation from an equilibrium state to a nonequilibrium state, entropy production is maximal, in accordance with Ziegler's principle. The concepts of free and forced relaxation are introduced. Free relaxation is the transition of a system from a state far from equilibrium to a state close to equilibrium. Moreover, at each moment of relaxation, entropy production is minimal, i.e., the principle of minimum entropy production is satisfied. During forced relaxation, a system transitions from a state close to equilibrium to a state far from equilibrium, in which case entropy production is maximized. Thus, the variational principle of irreversible thermodynamics for isolated systems is the principle of minimum entropy production, and for open systems, it is the principle of maximum entropy production.

Keywords

Fokker–Planck Equation, Green's Function Method, Open Systems, Entropy Production, Negentropy Production, MEPP, Prigogine's Principle

1. Introduction

Variational principles allow us to derive fundamental equations from a single integral principle and form the basis for the formulation of most sections of physics. In thermodynamics, these are Prigogine's principles of minimum entropy production (MinEPP) [1, 2] and Ziegler's principles of maximum entropy production (MEPP) [3, 4]. A nonequilibrium isolated system relaxes to equilibrium producing entropy (free relaxation), and in equilibrium the entropy production is zero, and

the entropy is maximum. An open system, depending on the boundary conditions, can relax in either the direction of equilibrium or the direction of nonequilibrium state (forced relaxation); during relaxation to equilibrium, entropy increases and entropy is produced, while during relaxation to nonequilibrium, entropy decreases and negentropy is produced. For more details, see [5], which details the second law of thermodynamics in isolated and open systems. This paper is a development

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of [5]. Here, the extreme properties of entropy production in isolated and open systems are discussed. Ziegler considered MEPP a generalization of the principle of maximum entropy (the second law), i.e. "a more accurate version of the fundamental law of thermodynamics" [4], indeed, it follows from MEPP that not only $\sigma \geq 0$, but also $d\sigma \leq 0$. The latter condition was shown for the Rayleigh gas in [6]. Thus, MEPP is, following Ziegler, a more rigorous formulation of the second law for forced relaxation. In [7] it is stated that "MEPP forces the system to choose not only the most probable of its possible macrostates, but also the most probable trajectory of movement to this macrostate." Indeed, if the second law speaks of an increase in entropy during relaxation, then MEPP requires that at each subsequent point of the relaxation curve the entropy production be greater than the value at the previous point. Thus, MEPP is a more complete (strict) formulation of the second law. MinEPP was formulated by the Belgian school of thermodynamics headed by I. Prigogine. Thus, in Thermodynamics of nonequilibrium processes (TNP), there are two diametrically opposed principles - the principle of minimum and maximum entropy production. It is clear that the same value cannot be both minimum and maximum for one thermodynamic object. This state of affairs requires a detailed explanation. Martyushev in [8] believes that it is impossible to contrast these principles, since they relate to different thermodynamic states, but he did not indicate which states. This work is devoted to the analysis of the original works of the authors of these principles, with the aim of determining the conditions and states in which the principles under study are realized. In order to then create these conditions and states in a model system, with the aim of determining in this system the states under which both principles will be realized in one thermodynamic system under different conditions.

2. Minimum Entropy Production Principle (MinEPP)

In the linear thermodynamics of irreversible processes, I. Prigogine formulated the principle of minimum entropy production (MinEPP) [9]. This principle states that in a system in which thermodynamic flows are related to forces by a linear relationship, and kinetic coefficients are symmetrical, when some of the forces are kept constant, a necessary sufficient condition for stationarity is the minimum production of entropy [2]. Prigogine connected the increase in entropy (second law) with the direction of time [9]. This is due to the requirement of system stability, i.e. entropy serves as a Lyapunov function. Entropy is a Lyapunov function for isolated systems. Thus, the second law of thermodynamics is a consequence of the stability of the system, i.e. the system tends to move to its stable state. In an open system, there is an external influence that takes the system from an equilibrium, stable state to a

non-equilibrium state. The balance between the external influence and the process tending to return the system to an equilibrium state ensures the stationarity of the state.

The next important theorem is MinEPP [1, 2], mentioned above. This theorem states that the production of entropy by a system in a stationary state sufficiently close to equilibrium is minimal. For systems whose state changes over time (and subject to the same boundary conditions), the entropy production is greater, i.e. in a system in a dynamic relaxing state, the production of entropy is greater than in a stationary nonequilibrium state [2]. MinEPP imposes even stricter boundary conditions on the system than linear equations.

$$J_k = \sum_i L_{ki} X_i \quad (1)$$

where J_k and X_i are, respectively, thermodynamic fluxes and forces, L_{ki} are kinetic coefficients. This theorem is valid only within the framework of a theory expressed by strictly linear equations, i.e., it is fulfilled only for systems whose deviations from equilibrium are small, and the phenomenological coefficients of the corresponding equations L_{ki} can be considered constant values. When given boundary conditions do not allow the system to reach thermodynamic equilibrium, (i.e., a state in which it no longer produces entropy and $dS = 0$), the system stops in a state of "minimum dissipation" and produces a minimum of entropy.

3. MinEPP in an Exactly Solvable Rayleigh Gas Model

Thus, Prigogine's theorem is applicable in the linear approximation during relaxation from nonequilibrium to equilibrium states. To verify this, consider the entropy production in a Rayleigh gas (a small admixture of heavy particles in a thermostat of light particles) during the relaxation of the initial nonequilibrium distribution function (DF) to the final equilibrium one. In a Rayleigh gas, due to the large difference in the masses of the mixture particles and the low concentration of the heavy component, the establishment of equilibrium in the heavy component occurs against the background of a Maxwellian distribution of the thermostat particles and is a slow process. In [10], the elastic collision integral of hard spheres in the L. Boltzmann equation, expanded in powers of $(m_l/m)^{1/2}$, where m_l and m are the masses of the thermostat and impurity particles, respectively, is reduced to the form of a Fokker-Planck differential operator of the form.

$$\frac{\partial F}{\partial \tau} = \frac{\partial}{\partial x} \left[\left(x - \frac{1}{2} \right) F(x, \tau) + x \frac{\partial F}{\partial x} \right] \quad (2)$$

with initial and boundary conditions

$$F(x, 0) = \varphi(x) \quad \text{and} \quad j = \frac{\partial F}{\partial x} + \left(x - \frac{1}{2} \right) F(x, \tau) = 0, \quad \text{for } x = 0, x \rightarrow \infty \quad (3)$$

where $F(x, \tau)$ is DF of heavy particles,, $x = \varepsilon/kT_L$, $\tau = t/\tau_R$ are the dimensionless energies and time, respectively, ε is the energy of heavy particles, T_L is the thermostat temperature, $\varphi(x)$ is the initial DF, τ_R is the relaxation time of the Rayleigh gas [1]. Solution (2) with boundary conditions (3) was obtained in [1] as

$$F(x, \tau) = \frac{2n_0}{\sqrt{\pi}} x^{\frac{1}{2}} e^{-x} + x^{\frac{1}{2}} e^{-x} \int_0^\infty \varphi(\xi) \sum_1^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x) L_m^{\frac{1}{2}}(x_0) e^{-m\tau} d\xi, \tag{4}$$

where $L_m^{1/2}(x)$ are the Laguerre polynomials, $\Gamma(m)$ is the gamma function, n_0 is the initial number of particles. Solution (4) is applicable for almost all x with the exception of $(m_L/m)^{1/2} > x > (m/m_L)^{1/2}$, where the Fokker–Planck equation (2) is not applicable. Having defined the entropy according to Boltzmann in the form [5].

$$S(\tau) = k \int_0^\infty \left(\ln \frac{F(x, \tau)}{\sqrt{x}} - 1 \right) F(x, \tau) dx \tag{5}$$

where k is Boltzmann’s constant, for the change in entropy we obtain

$$\frac{dS}{d\tau} = -k \int_0^\infty \left(\ln \frac{F(x, \tau)}{\sqrt{x}} \right) \frac{\partial F}{\partial \tau} dx \tag{6}$$

By inserting into (6) the DF (4), an expression for the change in entropy is obtained in the form¹.

$$\frac{dS}{d\tau} = kn_0 L_1^{\frac{1}{2}} e^{-\tau} + k \frac{\sqrt{\pi}}{2} \sum_{m=1}^\infty \frac{m\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} \left[\int_0^\infty \varphi(\xi) L_m^{\frac{1}{2}}(\xi) d\xi \right]^2 e^{-2m\tau} \tag{7}$$

From (7) it follow that

$$\sigma(\tau) = k \frac{\sqrt{\pi}}{2} \sum_{m=1}^\infty \frac{m\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} \left[\int_0^\infty \varphi(\xi) L_m^{\frac{1}{2}}(\xi) d\xi \right]^2 e^{-2m\tau} \geq 0. \tag{8}$$

Expression (7), obtained in [5], describes the entropy production during the relaxation of the initial nonequilibrium DF to equilibrium. As can be seen from (7), entropy production, in accordance with the second law, during relaxation from a nonequilibrium state to an equilibrium one is positive [5]. Here, we consider property (7) in more detail. From expression (6), it is clear that $\sigma(\tau)$ decreases, and $d\sigma/d\tau < 0$. Consequently, each point is a local minimum, and $\sigma(\infty)$ is an absolute minimum equal to zero. Thus, during relaxation from an arbitrary (nonequilibrium) state to an equilibrium state, entropy increases with minimal entropy production. At each moment in time, entropy is produced (second law). The entropy produced at the next moment is less than the entropy produced at the previous moment (MinEPP). Since the system under consideration is isolated, its final state is equilibrium, and will be realized when considering an open system in point 6.

4. The Principle of Maximum Entropy Production (MEPP)

Currently, MEPP is widely used to interpret experimental results. "The MEPP model has been used for the first time to

accurately predict fracture conditions for a number of binary alloys for which no previous theoretical model had been able to provide predictability. The model considers steady-state solidification under conditions close to and far from equilibrium" [3] (p. 1). Therefore, determining the scope and conditions of applicability of MEPP is becoming especially relevant.

To determine the scope of MEPP, it is necessary to consider the conditions under which MEPP was proven in 1961 [4].

Ziegler's principle is valid for non-stationary systems relaxing to their stationary state, i.e. when a nonstationary system relaxes to its stationary state, it obeys MEPP [6].

“Numerous experimental investigations spanning over sixty years have failed to comprehensively validate any of the existing solid-liquid interface growth instability models. With the MEPP model, for the first time, breakdown conditions are predicted with a fair degree of accuracy for a number of binary alloys where no previous theoretical model had predictability” [11] (p. 1).

“The Maximum Entropy Production Principle (MEPP) stands out as the over-arching principle governing life phenomena in nature. However, its explanatory power beyond heuristics remains controversial. On the one hand, MEPP has been successfully applied mainly to non-living systems that

¹Since we are interested in large τ , then $\ln \frac{F(x, \tau)}{\sqrt{x}}$ can be written as $\ln \frac{F(x, \tau)}{\sqrt{x}} = \ln \left[\frac{2}{\sqrt{\pi}} n_0 e^{-x} + e^{-x} \int_0^\infty \varphi(\zeta) \sum_1^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} L_m^{1/2}(x) L_m^{1/2}(\zeta) e^{-m\tau} d\zeta \right] = \ln \frac{2}{\sqrt{\pi}} n_0 e^{-x} + \frac{\sqrt{\pi}}{2n_0} \int_0^\infty \varphi(\zeta) \sum_1^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} \times L_m^{1/2}(x) L_m^{1/2}(\zeta) e^{-m\tau} d\zeta$ since the second term is much less than one.

are far from thermodynamic equilibrium. On the other hand, the basic assumptions underlying MEPP's theoretical underpinnings and range of applicability increase the potential for conflicting interpretations." [12] (p. 120). To determine the scope of applicability of MEPP, we need to consider under what conditions MEPP was proven.

TNP is based on transport equations similar to those in kinetics, i.e., flows are linear functions of thermodynamic forces (1). The proportionality coefficients are kinetic coefficients that are independent of flows and forces. The dependence of flows on forces (1) is a central relationship in TNP, which is why K. Eckart called it the thermodynamic equation of motion. The proportionality coefficients between flows and forces, the called kinetic coefficients of phenomenological equations (1), played an important role in the development of linear TNP. The property of time-reversal invariance expresses the fact that the mechanical equations of particle motion are symmetric with respect to time. This means that when the sign of all velocities changes, the particles will move in the direction opposite to the trajectories they previously traversed. Based on this microscopic property of the equations, L. Onsager formulated a macroscopic theorem, the reciprocity relation:

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, n) \quad (9)$$

Reciprocity relations (9) were derived by L. Onsager in 1931². Subsequently, they were generalized by Casimir [13] to the case of vector and tensor forces, as well as to thermodynamic forces that do not change their sign when the sign of time is reversed [14]. Of course, the discovery of the reciprocity relation was an important milestone in the history of thermodynamics. Despite its apparent simplicity, it has a deep physical meaning that has not yet been fully understood. Onsager also believed that variational principles in TNP should follow from the reciprocity condition [15]. The variational principle following from the reciprocity relations is also discussed in [16]. Ziegler in [23] showed that the reciprocity relations can be interpreted as the principle of greatest dissipation, which in the modern sense corresponds to the MEPP [3]. In continuum mechanics, where the MEPP was first formulated, systems are considered whose state is determined by mechanical position coordinates x_k and temperature $\theta > 0$. A change in x_k is a purely irreversible process, while a change in θ is reversible. As noted above, Ziegler's principle (MEPP) states that when a non-stationary nonequilibrium system passes into a stationary state, it obeys the MEPP [3]. Note that the Maximum Entropy Production Principle, or MEPP, is applicable in both linear and nonlinear domains. In [4] (p. 415) it is suggested that "if, according to the second law, every closed system tends to a state of maximum entropy, then this assumption does not seem unreasonable for the system, under the influence of given forces X_k^i , to change its state in such a way that the maximum entropy is produced within it at each moment of time." This intuitive statement is given in one form or another in many papers [17, 18]. This statement implies that MEPP does not contradict the second

law, but it shouldn't mean that the second law and MEPP are identical. Here it is probably appropriate to repeat Ziegler that MEPP is a more rigorous and complete expression of the second law in TNP. Ultimately, for the second law to be satisfied, it is sufficient that $\sigma(\tau)$ is positive. For example, the second law is satisfied during the relaxation of a nonequilibrium state to an equilibrium state, when entropy production, in accordance with Prigogine's principle, is minimal (see paragraph 1). Also worth noting is Ziegler's interesting idea of a "macroscopic observer." According to Ziegler, changes in entropy flow occur under the control of a macroscopic observer, while changes in entropy within a system are inaccessible to the macroscopic observer. Moreover, "in a thermodynamic process, any flow in phase space not controlled by a macroscopic observer reduces information about the state of the microstate and, therefore, increases entropy" [3]. Ziegler calls this formulation the phase version of the second law of thermodynamics. The value of this formulation lies in the fact that it links entropy production to internal microprocesses, while statements about "information reduction" and "the unobservability of entropy production" require more detailed consideration and physical interpretation. Reversible changes in entropy are always introduced into a system from the outside, so they are controllable and can be quantitatively characterized. Entropy production in a system is almost always characterized qualitatively; it was sufficient that it was produced, but the quantity was not experimentally determined. Although Boltzmann's H-theorem is both a qualitative and quantitative characteristic of the entropy produced by a system, it is now clear that the H-theorem is a microscopic confirmation of the second law of thermodynamics, but at that time the connection between entropy production and the H-theorem was unknown. When Ziegler spoke of the impossibility of defining an irreversible quantity, he apparently had in mind its experimental determination. Endres also argues that "MEPP appears to contradict the principle of minimum entropy production promoted by Onsager, Prigogine, and others" [19] (p. 1). On the other hand, Martyushev [8] argues that MEPP and MinEPP cannot be contrasted, since they refer to different states of the system and are satisfied under different conditions. Each of these principles has its own compelling justification. For example, in [20] a microscopic derivation of MinEPP is given in the regime of a linear response of the system to an external disturbance, and in [21] an experimental confirmation of MEPP is given. From the above, it is clear that both principles are observed in physical systems for various states [8], and for which states this will be shown below.

5. MEPP in an Exactly Solvable Rayleigh Gas Model with Sources

In [6], one of the authors, together with Professor A. I. Osipov (Moscow State University), obtained time-dependent (dynamic) expressions for entropy production in open and isolated systems. Dynamic expressions for entropy production allow us

²It should be noted, that L. Onsager himself considered the reciprocity relation to

be the relation of W. Thomson (Lord Kelvin) [15] p. 406.

to determine the conditions and processes under which MinEPP and MEPP are satisfied. To determine the conditions for the realization of MinEPP and MEPP, analytical solutions are required for an open system in which stationary nonequilibrium states can be realized. In [5], we obtained a solution to the Fokker-Planck equation with sources, i.e., for an open system. We use the results of [5] to analyze the conditions for the realization of MinEPP and MEPP. To analyze Ziegler's principle, we consider the relaxation of the initial equilibrium Rayleigh particle

distribution function to a final nonequilibrium stationary distribution under the influence of external particle sources. We choose a delta-shaped source of heavy particles as the external source. This source introduces monoenergetic heavy particles with energy x_0 into the system, which then, upon collision with the thermostat particles, form the current distribution function. To prevent particle accumulation in the system, we introduce a "chemical" reaction to remove particles from the thermalized system with the current distribution function. The Fokker-Planck equation in this case has the form.

$$\frac{\partial F}{\partial \tau} = \frac{\partial}{\partial x} \left[\left(x - \frac{1}{2} \right) F + x \frac{\partial F}{\partial x} \right] - K\tau_R F(x, \tau) + \eta\tau_R \delta(x - x_0) \tag{10}$$

with initial and boundary conditions (3), where $x_0 = \epsilon_0 / kT_L$ - dimensionless energy of particles δ - source, $\varphi(x) = \frac{2n_0}{\sqrt{\pi}} \chi^{1/2} e^{-x}$ - initial equilibrium distribution function, ϵ_0 - energies of particles of δ - source, k - Boltzmann constant, n_0 - the initial number of particles, K - is the chemical reaction

constant and η - is the power of the δ source. For this model, we obtained an analytical solution in the form of an expansion in Laguerre polynomials and showed the entropy balance in [9]. Provided that the number of particles is balanced $n_0 = \eta/K$, with the initial equilibrium DF, this solution has the form³.

$$F(x, \tau) = \frac{2n_0}{\sqrt{\pi}} \chi^{1/2} e^{-x} + \eta\tau_R \chi^{1/2} e^{-x} * \sum_{m=1}^{\infty} \frac{\Gamma(m+1)}{(m+K\tau_R)\Gamma(m+\frac{3}{2})} L_m^{1/2}(x) L_m^{1/2}(x_0) (1 - e^{-(m+K\tau_R)\tau}) \tag{11}$$

Having defined the entropy according to Boltzmann in the form (5) for the change in entropy, we obtain (6). Substituting (11) into (6) we have

$$\frac{dS}{d\tau} = \left(\frac{dS}{d\tau} \right)^{FP} + \left(\frac{dS}{d\tau} \right)^{Ch} + \left(\frac{dS}{d\tau} \right)^{\delta} \tag{12}$$

The contributions to the change in entropy from the Fokker-Planck operator, the chemical reaction and the δ source, they were obtained in [5]. Here we are only interested in the contribution to the entropy change from the Fokker-Planck term⁴,

$$\begin{aligned} \left(\frac{dS}{d\tau} \right)^{F.P.} &= - \int_0^{\infty} \left(\ln \frac{F(x, \tau)}{\sqrt{x}} \right) \frac{\partial}{\partial x} \left[\left(x - \frac{1}{2} \right) F + x \frac{\partial F}{\partial x} \right] dx \\ &= \frac{\eta\tau_R}{1+K\tau_R} L_1^{1/2}(x_0) \left[1 - e^{-(1-K\tau_R)\tau} \right] + k \frac{\sqrt{\pi}}{2} \eta\tau_R K\tau_R \sum_{m=1}^{\infty} \frac{\Gamma(m)}{\Gamma(m+\frac{3}{2})} \left[L_m^{1/2}(x) \right]^2 * \left(1 - e^{-(m-K\tau_R)\tau} \right)^2 + 0[(K\tau_R)^2] \end{aligned} \tag{13}$$

As noted earlier, the Fokker-Planck equation was derived from the collision integral of the Boltzmann equation. Therefore, the contribution of the Fokker-Planck equation to the change in entropy contains the production of entropy contains

the production of entropy. As can be seen from (13), this change in entropy consists of two parts: the first is a reversible change in entropy due to the removal (at $x_0 > 3/2$) of energy into the thermostat; the second is the irreversible production of entropy.

$$\sigma(\tau) = k \frac{\sqrt{\pi}}{2} \eta\tau_R K\tau_R \sum_{m=1}^{\infty} \frac{\Gamma(m)}{\Gamma(m+\frac{3}{2})} \left[L_m^{1/2}(x) \right]^2 * \left(1 - e^{-(m-K\tau_R)\tau} \right)^2 + 0[(K\tau_R)^2] \tag{14}$$

In a steady state, the Fokker-Planck operator provides a constant flow of entropy into the thermostat (for $x_0 > 3/2$) and constantly produces entropy. As can be seen (14), the entropy production of a stationary state is a convex function of time and each point $\sigma(\tau)$ is a local maximum, and $\sigma(\infty)$ is an absolute maximum, equal to

$$\sigma(\infty) = k \frac{\sqrt{\pi}}{2} \eta\tau_R K\tau_R \sum_{m=1}^{\infty} \frac{\Gamma(m)}{\Gamma(m+\frac{3}{2})} \left[L_m^{1/2}(x) \right]^2$$

Thus, during relaxation from an equilibrium state to a

³DF (11) was obtained in [5] by the variable substitution method, here (11) is obtained by the Green's function method. See Appendix.

⁴Note that here, when calculating the integral, the logarithm is expanded in powers of the small parameter $K\tau_R$ and the first two terms of the expansion are taken and

it is taken into account that $x^{1/2} e^{-x} L_m^{1/2}(x)$ is an eigenfunction of the Fokker-Planck operator.

nonequilibrium stationary state, the production of entropy, in accordance with the Ziegler principle, is maximum.

6. Discussion

When a nonequilibrium isolated system relaxes to an equilibrium state, as shown here, entropy production is minimal. It is known [8] that the equilibrium state of a system in the phase space of states is a point of attraction for all nonequilibrium states. This is an essential aspect of this problem, emphasized by Planck [22]. In this case, the system relaxes freely, without the influence of an external force. If the relaxation of a nonequilibrium isolated system to an equilibrium state is called free relaxation, then the MinEPP condition is satisfied during free relaxation.

In an open system, during relaxation from an equilibrium state to a nonequilibrium state, entropy production is maximal. Since the transition from an equilibrium state to a nonequilibrium state is possible only under the influence of an external force, relaxation from an equilibrium state to a nonequilibrium state can be called forced relaxation. Then, the maximum entropy production principle (MEPP) is satisfied during forced relaxation.

It should be noted that the principle of minimum entropy production (MinEPP) is also satisfied during the relaxation of a system from a state far from equilibrium (with lower entropy) to a state close to equilibrium (with higher entropy), i.e., during relaxation from one nonequilibrium state to another (see point 3). In such processes, entropy production fully satisfies the conditions of minimum entropy production by Prigogine. Relaxation of a nonequilibrium state of an isolated system occurs along a concave trajectory with minimal entropy production, ultimately reaching an equilibrium state. Relaxation in an open system occurs along a convex trajectory with maximum entropy production, ultimately reaching a steady state. In the steady state, entropy is constantly produced, the value of which is determined by the boundary and external conditions.

Appendix

Green's function method for a Rayleigh gas with sources.

To solve (11) with the initial and boundary conditions (3) using the Green function, is necessary to perform the substitution $F(x, \tau) = \exp(-K\tau)P(x, \tau)$ and represent (11) in the form

$$\frac{\partial P}{\partial x} = \frac{\partial}{\partial x} \left[\left(x - \frac{1}{2} \right) P(x, \tau) + x \frac{\partial P}{\partial x} \right] + \Psi(x, \tau) \tag{A-1}$$

with initial and boundary conditions

$$P(x, 0) = \varphi(x), \quad x \frac{\partial P}{\partial x} + \left(x - \frac{1}{2} \right) P(x, \tau) = 0 \quad \text{for } x = 0, x \rightarrow \infty. \tag{A-2}$$

where $P(x, \tau)$ is an auxiliary DF, $\Psi(x)$ is the source function. The remaining notations are the same as in (11).

In accordance with the general provisions of the Green's function method [23], solution (11) can be represented as

7. Conclusions

As we have repeatedly noted, when a nonequilibrium isolated system transitions to an equilibrium state, entropy production is minimal. This means that in an isolated system, Prigogine's theorem is valid in both linear and nonlinear thermodynamics, since we have not introduced thermodynamic flows and forces, and therefore there is no need for a linear relationship between them. Consequently, Prigogine's principle is also applicable in nonlinear thermodynamics. The variational principle of thermodynamics for isolated systems is MinEPP, and for open systems, MEPP. As can be seen from the above, MinEPP and MEPP refer to different states [8] and are satisfied under different conditions. And finally MinEPP and "MEPP are not simply a 'quirk' of theorists who need them for a generalized formulation of thermodynamics or a variational solution of the Boltzmann equation, but a law inherent in nature" [17] (p. 16).

Abbreviations

DF	Distribution Function
TNP	Thermodynamics of Nonequilibrium Processes
MinEPP	Minimum of Entropy Production Principle
MEPP	Maximum of Entropy Production Principle

Author Contributions

Pulat Tadjibaev: Conceptualization, Supervision, Validation, Project administration, Methodology

Diyor Tadjibaev: Data curation, Formal Analysis, Funding acquisition, Writing – original draft

Conflicts of Interest

The authors declare no conflicts of interest.

$$P(x, \tau) = \int_0^\infty \varphi(\xi)G(x, \tau; \xi, \theta)d\xi + \int_0^\tau \int_0^\infty \Psi(\xi, \theta)G(x, \tau; \xi, \theta)d\xi d\theta \tag{A-3}$$

where $G(x, \tau)$ is the Green's function of problem (A-1), satisfying the equation.

$$\frac{\partial G}{\partial \tau} = \frac{\partial}{\partial x} \left[\left(x - \frac{1}{2} \right) G + x \frac{\partial G}{\partial x} \right] + \delta(x - \xi)\delta(\tau - \theta) \tag{A-4}$$

The solution (A-4) will be sought in the form of an expansion in Laguerre polynomial.

$$G(x, \tau; \xi, \theta) = x^{\frac{1}{2}}e^{-x} * \sum_{m=0}^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x)L_m^{\frac{1}{2}}(\xi)A_m(\tau, \theta) \tag{A-5}$$

Substituting (A-5) into (A-4) taking into account that

$$\delta(x - \xi) = x^{\frac{1}{2}}e^{-x} * \sum_{m=0}^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x)L_m^{\frac{1}{2}}(\xi)$$

we obtain an equation for $A_m(\tau, \theta)$ in the form.

$$\frac{\partial A_m(\tau, \theta)}{\partial \tau} = -mA_m(\tau, \theta) + \delta(\tau - \theta) \tag{A-6}$$

Solution (A-6), taking into account the causality principle for $G(x, \tau; \xi, \theta)$, will be [23]

$$A_m(\tau, \theta) = \begin{cases} 0, & \text{for } \tau < \theta \\ e^{-m(\tau-\theta)}, & \text{for } \tau \geq \theta \end{cases} \tag{A-7}$$

Substituting (A-7) into (A-5), we obtain the Green's function of problem (A-1) in the form.

$$G(x, \tau; \xi, \theta) = 0 \text{ for } \tau < \theta \tag{A-8}$$

$$G(x, \tau; \xi, \theta) = x^{\frac{1}{2}}e^{-x} * \sum_{m=0}^\infty \frac{\Gamma(m+1)}{\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x)L_m^{\frac{1}{2}}(\xi)e^{m(\theta-\tau)}, \text{ for } \tau \geq \theta$$

As can be seen from (A-8), the obtained Green's function satisfies the reciprocity condition $G(x, \tau; \xi, \theta) = G(\xi, -\theta; x, -\tau)$. The meaning of the reciprocity relation is clear from the definition of the Green's function as the reaction of the Rayleigh gas at the point x at the moment of time τ to a point and instantaneous source acting at the point ξ at the moment of time θ .

Note also that at $\theta = 0$, the Green's function (A-8) will describe the energy distribution of heavy particles in the Rayleigh gas with an initial δ -shaped distribution function. This can be verified by replacing $\varphi(\xi)$ in (4) with $\delta(\xi - x_0)$.

$$P(x, \tau) = \frac{2n_0}{\sqrt{\pi}} x^{1/2} e^{-x} e^{K \tau_R \tau} + \eta \tau_R x^{\frac{1}{2}} e^{-x} * \sum_{m=1}^\infty \frac{\Gamma(m+1)}{(m+K\tau_R)\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x)L_m^{\frac{1}{2}}(x_0) * (e^{K\tau_R \tau} - e^{-m\tau}) \tag{A-9}$$

By reversing the replacement $P(x, \tau) = \exp(K\tau_R \tau) F(x, \tau)$, we have

$$F(x, \tau) = \frac{2n_0}{\sqrt{\pi}} x^{\frac{1}{2}} e^{-x} + \eta \tau_R x^{\frac{1}{2}} e^{-x} * \sum_1^\infty \frac{\Gamma(m+1)}{(m+K\tau_R)\Gamma(m+\frac{3}{2})} L_m^{\frac{1}{2}}(x)L_m^{\frac{1}{2}}(x_0) (1 - e^{-(m+K\tau_R)\tau}) \tag{A-10}$$

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