THE SECOND LAW OF THERMODYNAMICS FOR OPEN SYSTEMS

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Abstract: By solving the Fokker - Planck equations, the distribution functions of heavy particles in a thermostat of light particles (Rayleigh gas) with and without external sources of heavy particles were previously obtained. From the obtained non-stationary distribution functions, having determined the entropy according to L. Boltzmann, analytical expressions for the production of entropy in open and isolated systems are found. The first introduced the concept of production of negentropy. The algebraic sum of the entropy and negentropy productions is defined as the generalized entropy production. It is shown that the sign of the generalized production of entropy determines the direction of relaxation of the open system, and the equality of the generalized production of entropy to zero ensures the balance of entropy and the stationarity of the state of the system. The second law of thermodynamics in open systems is formulated as, *when an open system relaxes into a nonequilibrium stationary state, the generalized production of entropy decreases in absolute value and is equal to zero in a stationary nonequilibrium state.*

Key words: Fokker - Planck equation, Second Law of Thermodynamics, open systems, entropy production, negentropy, negentropy production.

Introduction

The second law of thermodynamics, discovered by R. Clausius in 1865, is still being discussed for its violation or possible deviation from it. These hypothetical violations are refuted over and over again, as well as their inconsistency is proved [1]. This is because the main parameter of the second law, entropy, is not directly measured like other thermodynamic parameters and does not have such an understandable statistical (microscopic) interpretation as temperature or pressure. On the other hand, thermodynamics is a phenomenological science, and

a microscopic examination is necessary for a deeper understanding of its provisions. This task is to some extent solved by statistical thermodynamics.

Since the second law considers *the transition* (relaxation) from a nonequilibrium state to an equilibrium one, it is better to implement the microscopic description by the kinetic theory, the results of which have an explicit time dependence. L. Boltzmann in his famous H - theorem, carried out the first such consideration, which is a microscopic substantiation of the second law for isolated systems [2].

In this article, it is proposed, using the previously obtained analytical solutions of the Fokker - Planck kinetic equations, to analyze the second law in isolated and open systems. A review of entropy production in exactly solvable systems is given in [3]. This article considers the production of entropy for both discrete and continuous spectrum and obtains rigorous mathematical results. In the present work, without pretending to mathematical rigor, physical results are obtained, which in the future can serve as the basis for the thermodynamics of open systems.

1. **The second law in an isolated system.**

In an isolated system, the second law is determined by the expression for the production of entropy $\sigma \geq 0$, i.e. in an isolated system, in the process of relaxation to equilibrium, entropy is produced. The equal sign refers to the equilibrium state. Further analysis of the production of entropy within the framework of phenomenological thermodynamics is impossible since, there is no time in it, therefore, we obtain an expression for σ from the solution of the kinetic equation.

Consider a Rayleigh gas (a small admixture of heavy particles in a thermostat of light particles). Due to the low concentration of the heavy component and the large difference in the masses of the particles of the mixture, the establishment of equilibrium in the heavy component is a slow process and occurs against the background of the Maxwellian distribution of thermostat particles. In [4], the integral of elastic collisions of rigid spheres into the Boltzmann equation by expanding in powers of $(m_L/m)^{1/2}$, where m_L and m are the masses of thermostat and impurity particles, respectively, reduced to the form of the Fokker - Planck differential operator in the form of

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

with initial and boundary conditions

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

where F (x, τ) is the distribution function of heavy particles, x = ε / kT_L, τ =t/τ_R are dimensionless energies and time, ε is the energy of heavy particles, T_L is the thermostat temperature, τ_R is the relaxation time of the Rayleigh gas [4]. The solution (1) with the initial and boundary conditions (2) has the form of [4]

$$\mathrm{F(x,\tau)} = \frac{2n_0}{\sqrt{\pi}}\mathrm{x^{1/2}e^{-x}} + x^{1/2}e^{-x}\int_0^\infty \varphi(\xi)\sum_{m=1}^{\infty}\frac{\Gamma(m+1)}{\Gamma(m+3/2)}L_m^{1/2}(x)L_m^{1/2}(\xi)e^{-m\tau}d\xi\ , \qquad (3)$$

where $L_m^{1/2}$ (x) are Laguerre polynomials, Γ (m) is the gamma function, n_0 is the initial number of particles. Solution (3) is applicable for almost all x, except for $(m/m_L)^{1/2} < x < (m_L / m)^{1/2}$, where the Fokker - Planck equation (1) is not applicable [4].

Having defined the Boltzmann entropy in the form of

$$S(\tau)=-k\int_0^\infty\left(\ln\frac{F(x,\tau)}{\sqrt{x}}-1\right)F(x,\tau)dx, \qquad (4)$$

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

$$\frac{dS}{d\tau}=-k\int_0^\infty\left(\ln\frac{F(x,\tau)}{\sqrt{x}}\right)\frac{\partial F}{\partial\tau}dx \qquad (5)$$

Substituting (3) into (5), we have

$$\frac{dS}{d\tau}=kn_0L_1^{1/2}(x)e^{-\tau}+k\frac{\sqrt{\pi}}{2}\sum_{m=1}^{\infty}\frac{m\Gamma(m+1)}{\Gamma(m+3/2)}\left[\int_0^\infty\varphi(\xi)L_m^{1/2}(\xi)d\xi\right]^2e^{-2m\tau}, \qquad (6)$$

The first term in (6) is the entropy change due to the flow to or from the thermostat, the second is an irreversible change, i.e. entropy production due to an irreversible process of relaxation to equilibrium

$$\sigma(\tau)=k\frac{\sqrt{\pi}}{2}\sum_{m=1}^{\infty}\frac{m\Gamma(m+1)}{\Gamma(m+3/2)}\left[\int_0^\infty\varphi(\xi)L_m^{1/2}(\xi)d\xi\right]^2e^{-2m\tau}\geq 0. \qquad (7)$$

As can be seen from (7), the production of entropy (in accordance with the second law) in the process of relaxation from a nonequilibrium state to an equilibrium state is positive and decreases, reaching minimum zero value in equilibrium at τ→∞.

2. **The second law in an open system.**

In open systems, the change in entropy is given by the following expression

$$dS = d_i S + d_e S,$$

where dS is the total change in the entropy of the system, d_eS and d_iS are reversible and irreversible entropy changes, respectively. d_eS is the reversible

change in entropy, containing all flows of entropy both into the system and out of the system. An irreversible change in entropy $d_i S > 0$, since the final state of relaxation of an open system is a stationary nonequilibrium state in which entropy is constantly produced. The entropy balance must be ensured by the outflow of the produced entropy. This outflow of entropy is sometimes called the flow of negentropy into the system. The term negentropy introduced by L. Brillouin.

To analyze the second law in an open system, let us consider the relaxation of the initial equilibrium distribution function of Rayleigh particles into a final nonequilib-rium stationary distribution under the action of external sources of particles. Let us choose a δ-shaped source of heavy particles as an external source. This source introduces monoenergetic heavy particles with energy x_0 into the system, which, then colliding with the particles of the thermostat, form the current distribution function. To prevent the accumulation of particles in the system, we introduce a "chemical" reaction to remove thermalized particles with the current distribution function from the system. In this case, the Fokker - Planck equation has the form of

$$\frac{\partial F}{\partial \tau} = \frac{\partial}{\partial x}\left[\left(x-\frac{1}{2}\right)F + x\frac{\partial F}{\partial x}\right] - K\tau_R F(x,\tau) + \eta\tau_R \delta(x-x_0), \qquad (8)$$

with initial and boundary conditions (2), where $x_0 = \varepsilon_0 / kT_L$ is the dimensionless energy of particles δ - source, $\varphi(x)=\frac{2n_0}{\sqrt{\pi}} x^{1/2} e^{-x}$ - initial equilibrium distribution function, ε_0 - energy of particles δ - source, k - Boltzmann constant, n_0 - the initial number of particles, K is the constant of the chemical reaction, and η is the power of the δ - source. For this model an analytical solution in the form of an expansion in Laguerre polynomials, was obtained by us earlier [5].

Provided balance of the number of particles n = η / K, with the initial equilibrium distribution function, this solution has the form of

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

Having determined the entropy according to Boltzmann in the form (4) for the change in entropy, we obtain (5). Substituting (8) into (5), we have

$$\frac{dS}{d\tau} = \left(\frac{dS}{d\tau}\right)^{F.P.} + \left(\frac{dS}{d\tau}\right)^{Ch} + \left(\frac{dS}{d\tau}\right)^{\delta}, \qquad (9)$$

where the contribution to the change in entropy from the Fokker - Planck operator has the form of [5]

$$\left(\frac{dS}{d\tau}\right)^{F.P.} = -k\int_0^\infty \left(\ln\frac{F(x,\tau)}{\sqrt{x}}\right)\frac{\partial}{\partial x}\left[\left(x-\frac{1}{2}\right)F + x\frac{\partial F}{\partial x}\right]dx = \quad (10)$$

$$= k\frac{\eta\tau_R}{1+K\tau_R}L_1^{1/2}(x_0)\left[1-e^{-(1+K\tau_R)\tau}\right] + k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R\sum_{m=1}^{\infty}\frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2\left(1-e^{-(m+K\tau_R)\tau}\right)^2 +$$

$$+ 0\left[(K\tau_R)^2\right]$$

As can be seen from (10), 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, and the second is the irreversible production of entropy.

$$\sigma(\tau) = k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R\sum_{m=1}^{\infty}\frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2\left(1-e^{-(m+K\tau_R)\tau}\right)^2 \geq 0 \quad (11)$$

In a stationary 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 from (11), the steady state entropy production is maximum and is equal to

$$\sigma(\tau) = k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R\sum_{m=1}^{\infty}\frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2 \quad (12)$$

For an open system, there is an expression $dS/d\tau = d_iS/d\tau + d_eS/d\tau$, where $d_iS/d\tau = = \sigma$, $d_eS/d\tau$ is a reversible change in entropy. In an open system $\sigma > 0$, and $d_eS/d\tau$ can be either positive or negative. Apparently, in nonlinear thermodynamics, irreversible processes not only produce entropy, but can also absorb it, i.e. produce negentropy. The term "production of negentropy" was introduced to emphasize the absorption of entropy by irreversible processes.

An isolated system relaxes from a nonequilibrium state to an equilibrium state, while the entropy increases and the production of entropy is positive and equal to zero in equilibrium. An open system relaxes into a stationary nonequilibrium (dynamically equilibrium) state. In this case, the entropy of the final state can be either greater or less than the entropy of the initial state. Therefore, during relaxation from the initial to the final state, entropy will either be produced or absorbed. The steady state entropy balance for the system under study described by Eq. (8) with boundary conditions (2) was shown in [6]. Here it is necessary to analyze the balance of reversible (flux) and irreversible (produced / absorbed) entropy in nonstationary conditions. The contribution to the change in entropy from the Fokker - Planck term was obtained above in (10). Next, we calculate the nonstationary contributions to the changes in entropy from the chemical reaction and from the δ-source.

The change in entropy due to a chemical reaction can be obtained in the form of

$$\left(\frac{dS}{d\tau}\right)^{Ch} = kK\tau_R \int_0^\infty \left(\ln \frac{F(x,\tau)}{\sqrt{x}}\right) F(x,\tau)dx = -\frac{3}{2}k\eta\tau_R + k\frac{\eta\tau_R K\tau_R}{1+K\tau_R} L_1^{1/2}(x_0)\left[1-e^{-(1+K\tau_R)\tau}\right] + 0\left[(K\tau_R)^2\right] \quad (13)$$

A chemical reaction that removes particles with a current distribution function from the system, as can be seen from (13), makes only reversible contributions to the change in entropy, due to decrease in particles and change in energy.

The greatest interest lies in the change in entropy due to the δ - source, since this source introduces particles ordered in the energy space into the system

$$\left(\frac{dS}{d\tau}\right)^{\delta} = -k\eta\tau_R \int_0^\infty \left(\ln \frac{F(x,\tau)}{\sqrt{x}}\right) \delta(x-x_0)dx =$$

$$= \frac{3}{2}k\eta\tau_R - k\eta\tau_R L_1^{1/2}(x_0) - k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R \sum_{m=1}^{\infty} \frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2\left[1-e^{-(m+K\tau_R)\tau}\right] + 0\left[(K\tau_R)^2\right] \quad (14)$$

The first term in (14) is an increase in entropy due to an increase in the number of particles; it is compensated by the removal of particles through chemical reaction. The second term is the entropy flux caused by the energy content of the introduced particles; it is compensated in the stationary state by the sum of flux terms in the chemical reaction and in the Fokker - Planck operator. The third term is the production of negentropy or irreversible absorption of entropy, stimulated in the system by a δ-source and has the form of

$$\tilde{\sigma}(\tau) = -k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R \sum_{m=1}^{\infty} \frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2\left[1-e^{-(m+K\tau_R)\tau}\right] \le 0 \quad (15)$$

The production of negentropy should be understood as negative production (absorption) of positive entropy, and not vice versa. It compensates for the production of entropy in a stationary nonequilibrium state. Thus, the generally accepted opinion, that the entropy produced in a stationary nonequilibrium (dynamically equilibrium) state is compensated by the outflow of entropy (negentropy) [7], is not fulfilled in the considered model. In a steady state, the entropy produced is compensated by the negentropy produced.

As noted above, in an isolated system, the second law of thermodynamics is determined by the inequality σ≥0. “Despite the extremely important information contained in this inequality, it is insufficient for two reasons. First, it is not enough just to know that entropy is increasing. It is necessary to establish the origins of entropy and their power, that is, to find the rate of increase in entropy (the value of σ). Secondly, the general formulation of the second principle does not say what

happens in non-isolated (open) systems capable of exchanging matter and energy with the environment ”[8]. In the previous sections, the contributions of all sources to the change in entropy in a Rayleigh gas with sources (open system) were calculated, i.e. the first part, formulated in the quotation from [8] of the problem has been completed. To complete the second part of the problem, it is necessary to calculate the result of the joint action of all sources of entropy and to obtain a version of the second law in an open system from this expression.

Thus, in order to formulate the second law in the studied (open) system, we use the explicit nonstationary contributions to the changes in the entropy of each term on the right-hand side of Eq. (9), obtained above. Substitute expressions (10), (13), and (14) into (9). Then the total change in entropy during relaxation from an equilibrium state to a nonequilibrium stationary state can be written as

$$\frac{dS}{d\tau} = -k\eta\tau_R L_1^{1/2}(x_0)e^{-(1+K\tau_R)\tau} -$$

$$-k\frac{\sqrt{\pi}}{2}\eta\tau_R K\tau_R\sum_{m=1}^{\infty}\frac{\Gamma(m)}{\Gamma(m+3/2)}\left[L_m^{1/2}(x_0)\right]^2\left[1-e^{-(m+K\tau_R)\tau}\right]e^{-(m+K\tau_R)\tau} \qquad (16)$$

The first term in (16) describes a reversible change in entropy, the second - an irreversible change in entropy. This term in (16) is negative; this is due to the fact that the chosen model relaxes from an equilibrium (with maximum entropy) to a stationary nonequilibrium (with a lower entropy) state. This term could be called the generalized production of entropy, meaning that it is the algebraic sum of the productions of entropy and negentropy, i.e.

$$\Xi(\tau) = \sigma(\tau) + \tilde{\sigma}(\tau).$$

Then, based on the analysis of the balance of production of entropy and negentropy, one of the possible variants of the second law for open systems can be formulated as follows, *when an open system relaxes into a nonequilibrium stationary state, the generalized production of entropy decreases in absolute value and is equal to zero in a stationary nonequilibrium state*

$$|\Xi| \geq 0.$$

3. **Conclusion.**

The production of entropy, in accordance with the second law, in the process of relaxation of an isolated system from a nonequilibrium state to an equilibrium state, is positive and decreases, reaching minimum zero value in equilibrium as $\tau\to\infty$.

In an open system, relaxation, depending on the initial and boundary conditions, can transfer the system from an equilibrium state to a non-equilibrium

state or from one non-equilibrium state to another non-equilibrium state. Therefore, relaxation to a more ordered state produces more negentropy than entropy, while relaxation to a more disordered state produces more entropy. In both cases, in a steady state, a balance of production of entropy and negentropy is achieved. If in an isolated system, during relaxation to equilibrium, the production of entropy decreases and is equal to zero in equilibrium, then in an open system, during relaxation to a stationary state, the modulus of the generalized production of entropy decreases and is equal to zero in a stationary state. The sign of the generalized production of entropy determines the direction of relaxation. If it is positive-the system relaxes in the direction of the equilibrium state, if it is negative - the system moves away from the equilibrium state.

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