A Study of the Entropy Production in Physical Processes from a New Perspective of the Energy Structure

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ABSTRACT---- When a physical process is performed, identifying the generated entropy can be used to investigate the irreversibility. But for this mean, from the perspective of the Boltzmann equation, both all microstates and macrostates must be studied. In fact, it is needed that all particles energy level to be investigated. Therefore, to investigate entropy in configurationally systems using the Boltzmann equation, a very large volume of calculations is required. In this study, we try to extract a way to investigate entropy production without the need to study all particles (or sub-structures). For this purpose, at first, a macroscopic energy structure equation “as an equation that shows the energy components of the system activated in the performed process as well as their dependence” is presented. As a study on the irreversibility (or entropy production) in physical systems, its structure and components are studied. Writing equations in the energy space of the system makes it possible to study the structure of irreversibility. Then using a new macroscopic quasi-statistical approach, the irreversibility and its structure in physical processes are investigated. Macro energy components of the system are used for this investigation and energy structure is studied based on them. Finally, a new macroscopic definition of the generated entropy is extracted using a new energy structure equation as well as dependent and independent macroscopic energy component concepts. Also, why and what entropy can be generated, from the perspective of the presented macroscopic energy structure equation are studied. In fact, this paper investigates the generated entropy structure in physical systems using macroscopic system energy components and takes a new approach to why and what irreversibility is occurred during the physical process. Therefore, presented equations can be used for investigating the irreversibility in configurationally physical systems without the need to study all its sub structures. Also, from the extracted equations, it can be concluded that entropy is generated because of the existence of the dependent energy components in the energy structure equation of the system, and this generated entropy depends on the variation of these components as well as the amount of the applied energy to the system and its conditions. Due to the kinematic theory of dissipated energy, these results are in the same line with the different formulations of the second law of thermodynamics.

Keywords---- Thermodynamics; Configurationally physical systems; Entropy production; Irreversibility components; Energy Structure; Energy components; Dependent components

1. INTRODUCTION

Principles of conservation examine the quantitative concepts in physics. Such as energy conservation, mass conservation, linear and angular momentum conservation, etc., which can be applied to physical phenomena, and every physical process must be performed in such a way that these principles are satisfied. The only physical law that considers the concept of direction of processes is the second law of thermodynamics [1]. Before the first law was introduced, Carnot introduced reversible processes in him paper, and accordingly could be considered the founder of this law [2].

Subsequently, the second law of thermodynamics gained a very important place in science, so that it undoubtedly became the most important physical law. As Einstein stated, the only law that will never collapse is the second law of classical thermodynamics [1,3]. This law has a special place in all branches of science as a constitution.

The second law defines the physical quantity as entropy. According to this law, the entropy of an isolated system is constantly increasing, and in fact, increasing entropy means the passage of time. From a classical thermal theory point of view, the second law is interpreted in such a way that the amount of available work is always decreasing, and instead the amount of thermal energy increases [1]. However, in the attitude of material structures, increasing entropy increases irregularity [4]. Also from the statistical physics point of view, increasing entropy means increasing the number of available states [5], and from a statistics quantum point of view, is interpreted as an increase in the number of energy levels [6].
Two main formulations that have been extracted to the second law from the classical thermodynamics point of view are Kelvin-Plank and Clausius formulations [7,8,9]. Kelvin-Plank and Clausius formulations are assertions about impossible processes, while some formulations to the second law are presented which rely on assertions about the possible processes [9]. Also, Caratheodey formulation is one of the other formulations to the second law from the classical thermodynamics point of view [10-13]. Clausius uses entropy quantity to formulate the second law [14]. Based on his perspective, in all performed physical processes, entropy must be increased. Therefore, generated entropy can be known as a physical direction for physical processes [15,16]. In the Clausius perspective, the physical concept of entropy is the loss of useful energy and exchange it to the thermal energy [9,17-19].

In classical thermodynamics, the entropy formulation is used to equilibrium states and no attempt is made to define it otherwise [9]. Although in the statistical physics point of view, entropy is formulated as a physical quantity that depends on the available probability of the physical system at a special particles energy level and can be used to equilibrium as well as non-equilibrium states. Also, the absolute value of entropy can be calculated by investigating the microstates of the system [20,21]. Therefore, due to the statistical physics point of view, it can be concluded that the second law will be equivalent to the fact which the probability of the system will be increased always [20].

Also, there are generalized formulations to the second law [21-24]. In these cases, it is needed that all sub-structures of the system to be investigated. In fact, each sub-structure must be studied to calculate the entropy of the system.

In this study, a new macroscopic quasi-statistical perspective on why and what entropy is generated during physical processes is presented. Using the energy components of the system an energy structure equation is presented and based on it, without the need to investigate all sub-structures of the system, the generated entropy structure, and its macroscopic components are investigated.

2. ENTROPY IN CLASSICAL THERMODYNAMICS AND STATISTICAL PHYSICS POINT OF VIEW

The classical thermodynamics examines the second law from point of view of thermal energy on a macroscopic scale and states that in physical processes, some of the available work is always converted into thermal energy. Therefore the second law can be expressed as follows [4]:

$$\frac{\delta Q}{T} \leq 0$$  \hspace{1cm} (1)

Where $\delta Q$ is the heat exchanged at temperature $T$. If the system has an almost continuous distribution of matter, so that quantities such as density can be attributed to it, then the second law can be written using the concept of entropy as follows:

$$\frac{d}{dt} \int_V \rho s \, dV \geq \int_V \rho e \, dV - \int_{\partial V} q_{ni} \frac{dQ}{T} \, da$$  \hspace{1cm} (2)

Where $\rho$ is the material particle of the system and also $\partial p$ is the surface containing the material (particle) of the $p$. Also, $e$ as the entropy entry rate into the system by external sources per unit mass, $q_i$ is the heat flux vector passing through the unit surface, $\rho$ is density, $n_i$ is the surface normal vector, $T$ is temperature and $s$ is the entropy. Also, the equation (2) can be rewritten as follows in its differential form:

$$\frac{ds}{dt} - e - \frac{1}{\rho} \left( \frac{q_i}{T} \right) . \hat{n} \geq 0$$  \hspace{1cm} (3)

Equality mode is for reversible processes and non-equality mode represents irreversible processes. To examining the irreversibility from the classical thermodynamic point of view, the following equation can be considered as one of the most important equations [25]:

$$I_k = \sum_l L_{kl} k_l$$  \hspace{1cm} (4)

Where $I_k$ is a set of general currents and $F_l$ is thermodynamic forces. $L_{kl}$ is also a matrix of kinematic coefficients. Also, the $L_{kl}$ matrix is required to satisfy the symmetry equations in the OSAGER equations [26]. In this point of view, the irreversibility is examined using investigating the sub-structures.

However, in reversible processes where there is no entropy generation, entropy is written as follows according to the heat exchanged as well as the system temperature:

$$T \, ds = dQ$$  \hspace{1cm} (5)

Classical thermodynamics is incapable of calculating the absolute value of entropy and examines its relative changes. According to the second law, $ds \geq \frac{dQ}{T}$ or $ds_{gen} \geq 0$, which $s_{gen}$ is the entropy generation, is always positive. The entropy
generated is a measure of the amount of available work (or the amount of irreversibility) lost. As a result, some of the available work is converted into thermal energy, and in fact into other components of energy. The amount of irreversibility is considered as \( T \delta S_{gen} \) that is defined based on entropy generation and the environment temperature [4].

Statistical mechanics investigates the second law and entropy from a microscopic point of view. Given Boltzmann's perspective, it is necessary to consider the entropy of a system as a function of the probability that the system will reach that particular state at the desired energy level [27]:

\[
S = f(W)
\]  

(6)

Where \( S \) is entropy and \( W \) is the probability in the desired state.

If we combine different states, then it is necessary to add their entropy, although the probability will be the product of the probabilities. Therefore:

\[
S = S_1 + S_2
\]  

(7)

\[
f((W_1, W_2)) = f(W_1) + f(W_2)
\]  

(8)

Equations (7) and (8) can take the entropy as a function of the probability as follows:

\[
S = k \ln(W) + \text{constant}
\]  

(9)

That \( k \) is a universal constant. Equation (9) can calculate the absolute entropy. This equation also determines the general dependence between entropy and probability and also relates the macroscopic state of the system to its microscopic states. The probability of a physical system depends on the available state at a particular level of energy. In this case, increasing entropy will increase the probability of availability. Methods such as non-equilibrium statistical operator can be used to investigate irreversibility from the point of view of statistical mechanics [25,28].

3. ENTROPY IN THE QUANTUM PERSPECTIVES OF THE STATISTICAL PHYSICS

Using quantum concepts, the probability of availability of a particular state can be calculated. Plank [29] calculated the entropy of a physical system as a function of its energy distortion:

\[
S = k\left[(N + P) \ln(N + P) - N \ln(N) - Pln(P)\right]
\]  

(10)

That \( N \) is resonators, and \( P \) is an integer. The equation of \( W \) is presented for particle systems as a function of the number of particles and a weighting factor of energy levels [29]. For example, the Fermi-Dirac equation is as follows:

\[
W = \prod_j \frac{g_j}{j(g_j-1)!N_j!}
\]  

(11)

That \( N_j \) is the number of particles with the weighting factor of energy level \( g_j \).

As can be seen, statistical physics investigates the states of a system by examining each particle energy state.

4. MACROSCOPIC QUASI-STATISTICAL ENERGY STRUCTURE MODELING

In a physical system, the instantaneous reversal of the motion of every moving particle causes the system to move backward, each particle along its old path at the same speed as before when in the same position. In physical dynamics, this simple and perfect reversibility fails, on account of forces depending on the friction of solids; imperfect fluidity of fluids; imperfect elasticity of solids; inequalities of temperature and consequent conduction of heat produced by stresses in solids and fluids; imperfect magnetic retentiveness; residual electric polarization of dielectrics; generation of heat by electric currents induced by motion; diffusion of fluids, solution of solids in fluids and other chemical changes and absorption of radiant heat and light. The dissipation of the energy investigation can be done by studying the dynamics of the particles [30-34].

When a physical system experiences a physical process, some of its energy components are activated. Activated components depend on the amount and how energy is applied to the system. In this case, when the performed processes are reversible (or the performed process is quasi-static), the least number of energy components are activated (to the diffusion of energy to be less) and the applied energy is divided between them. If the same amount of energy is applied to the system at a limited exchange rate, then it is possible, some other components will be activated, and thus the applied energy needs to be divided between more components.
In a quasi-static process, some components are changed independently and are dependent on how energy is applied to the system only, and some are considered dependent on the amount of other components and are therefore considered as dependent components. If the process is performed at a limited rate of energy applying, then (When the system can generate entropy) some secondary dependent components are also activated and take up some of the applied energy (To the diffusion energy be more). The secondary dependent components are considered to be dependent on the rate of the independent components. Therefore, each physical process can be expressed as some independent components, some primary dependent components, and some secondary dependent components. The components of the secondary dependence are dependent on how energy is applied to the system.

In the view of the independent and dependent components of energy, equation (12) is presented as expressing the structure of energy:

\[ U_T = (u_1 + u_2 + \cdots + u_m) + [g_1 + \cdots + g_k] + [h_1 + \cdots + h_n] + U_{r_0} \]  

(12)

Where:

\[ g_j = g_j(u_1, u_2, \ldots, u_m) \]  

(13)

\[ h_p = h_p(\dot{u}_1, \ldots, \dot{u}_m) \]  

(14)

The functions \( g_j \) represent the value-dependent components of the independent components, while the functions \( h_p \) show the components dependent on the rate of the independent components. Also \( U_{r_0} \) represents the sum of all the components that did not participate in the performed process. These components are macroscopic and are the result of a specific type of energy in part or all of the system's particles. Equation (12) is formed according to the performed process and also how the energy is applied to the system and makes it possible to consider the effects of how the energy exchange can be considered in the energy structure of the system.

Equation (12) is in the same line with the second law. Based on the different formulations of the second law, some of the available work must be converted to thermal energy and we know that the thermal energy depends on the kinetic of sub-structures [35] while other types of energies depend on the place as well as displacement of sub-structures.

5. Irreversibility Analysis

To investigate the irreversibility, it is necessary to assume that some energy is applied to the system in different paths [25]. Then to examine the changes in the energy components of the system, initially, it is assumed that the energy applied to the system is such that it activates an independent component, and then the results will be generalized to processes with the desired number of the independent components.

Therefore, it should be assumed that the component \( u_i \) is the only independent component activated in the performed process, as can be seen in figure 1.

![Figure 1. Different paths for the performed process](image)

In this case, the energy structure of the system can be written as follows:

\[ \delta U_T = u_i + \sum_{j=1}^{k} g_j(u_i) + \sum_{p=1}^{n} h_p(u_i) + U_{r_0} \]  

(15)

If the energy \( \delta U_T \) is applied to the system in a quasi-static path (\( \dot{u}_i = 0 \)) and as a result the independent component of energy changes to the amount of \( \delta u_i' \), then it can be written:

\[ \delta U_T = \delta u_i' + \sum_{j=1}^{k} \left( \frac{\partial g_j}{\partial u_i} \delta u_i' \right) \]  

(16)

And if the same amount of energy is applied to the system in general (\( \dot{u}_i \neq 0 \), it can be written:

\[ \delta U_T = \delta u_i + \sum_{j=1}^{k} \left( \frac{\partial g_j}{\partial u_i} \delta u_i \right) + \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \delta u_i \right) \]  

(17)
Therefore, it is necessary that:

\[
(1 + \sum_{j=1}^{k} \left( \frac{\partial g_j}{\partial u_i} \right))(\delta u_i - \delta u'_i) = - \left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{u}_i
\]

(18)

Given that the amount of energy applied to the system is given at a limited rate (\(\dot{u}_i \neq 0\)), this energy is divided into more components, and if only changes due to this process will be considered no other inner possible processes, then \(\delta u'_i \geq \delta u_i\) for the conditions that \(\delta U_T > 0\) and \(\delta u'_i \leq \delta u_i\) for the conditions that \(\delta U_T < 0\). Given that the primary dependent components, \(g_j\), will always be activated in all paths (since they are dependent on to the independent components that, for a particular process, will be activated always), these components must be satisfied \(\sum_{j=1}^{k} \left( \frac{\partial g_j}{\partial u_i} \right) \geq 0\) for all possible values for \(u_i\). Therefore, according to the equation (18), if \(\delta U_T > 0\) in this case \(\left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{u}_i > 0\) and if \(\delta U_T < 0\), so \(\left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{u}_i < 0\). Also, if the process is quasi-static (\(u_i = 0\)), in this case \(\left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{u}_i = 0\).

Therefore, considering \(\delta H_i = \left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{u}_i\), the quantities \(H_i\) can be a good basis for examining irreversibility (or entropy generation) to the component \(u_i\). In addition to the internal structure of the system, as well as its current state, this quantity also depends on how energy is applied to the system.

Also, the value \((\delta u_i - \delta u'_i)\) can be considered as the deviation from the quasi-static path to the general, as can be seen in figure 2.

![Figure 2. Deviation from the quasi-static path to the general](image)

Therefore, by the variable changes \(\delta U_i = (\delta u_i - \delta u'_i)\), the variation \(\delta H_i\) can be rewritten as follows:

\[
\delta H_i = \left( \sum_{p=1}^{n} \left( \frac{\partial h_p}{\partial u_i} \right) \right) \delta \dot{U}_i
\]

(19)

Which gives \(\delta H_i\) according to how energy is applied to the system as well as its inner physical structure.

Also, the stated concepts can be generalized to the other independent components. So, the following equation can be considered:

\[
\delta \Psi = \sum_{i=1}^{m} \delta H_i
\]

(20)

In this case, if \(\delta U_T > 0\) then \(\Psi \delta \geq 0\) and if \(\delta U_T < 0\) then \(\Psi \delta \leq 0\) and also in the quasi-static path, \(\Psi \delta = 0\). So by defining:

\[
\varphi = \frac{\delta \Psi}{\delta U_T} = \sum_{i=1}^{m} \frac{\delta H_i}{\delta U_T} = \sum_{i=1}^{m} \varphi_i
\]

(21)

In this case, always \(\varphi \geq 0\) (as well as \(\varphi_i \geq 0\)). Therefore, \(\varphi\) can be used as a criterion for calculating irreversibility (or generated entropy). And also \(\varphi_i\) will be an irreversible criterion for the energy component \(u_i\). This quantity depends on how energy is applied to the system as well as its amount and inner physical structure of the system.

Equation (21) shows the irreversibility structure and its components. Due to this equation, entropy is generated because of the independent energy components activated in performed physical processes. These components will not be activated in a quasi-static path (zero rates of applying energy) and will be activated when the rate of applying energy is non-zero (general paths). Due to the kinematic theory of dissipated energy, these results are in the same line with the second law of thermodynamics [30-32].

Equation (21) has been extracted using the macroscopic energy components and don’t need to investigate all sub-structures. Therefore, if equation (21) to be used to investigate irreversibility in configurationally systems, macroscopic energy components are enough for relevant analysis.
6. CONCLUSIONS

Entropy production is one of the most important concepts introduced by the second law of thermodynamics that can be occurred during a physical process. From the perspective of classical thermodynamics, entropy can be generated when the processes are performed at a non-zero rate and means that some of the applied energy losses to the thermal energy.

From the statistical physics point of view, the Boltzmann equation investigates microstates of the system and entropy can be calculated. The Boltzmann equation also can be used for physical systems that particles have no many degrees of freedom, as configurationally entropy. From the perspective of the statistical physics (Boltzmann equation), configurationally entropy can be calculated using the study of the microstates of the system. When a physical process is performed, identifying entropy production can be used to investigating the irreversibility, but from the perspective of the Boltzmann equation, to study the entropy production, both microstates and macrostates must be studied. Therefore, more of course to study a configurationally system, a large volume of calculations are required.

In this study, a new macroscopic quasi-statistical approach is presented to investigate the irreversibility. Using the study of the macro energy components of the system, the irreversibility structure can be identified. Therefore using this, a new macroscopic definition of the generated entropy (Eq. 21) is extracted using energy structure equation analysis in different paths as well as macroscopic dependent and independent energy component. This equation can be used to investigate the entropy production without the need to study all sub-structures. Therefore, it can be used for studying configurationally systems easily.

To investigate why and what entropy can be generated during physical processes, the energy structure of the system can be studied. Equation (12) is presented as the energy structure equation of the system and is determined according to the macroscopic components of the energy and is formed according to the performed process and also how the energy is applied to the system as well as the amount of the applied energy. In fact, it was assumed that some energy would be given to the system once in a quasi-static path and again in general. By this, using the energy structure equation, it can be detected that the condition of the applied energy how can change the amount of the internal variation of the energy components. As a result, equation (21), by defining a quantity always greater than or equal to zero $\varphi$, is obtained as a criterion for the structure of irreversibility (or generated entropy) as well as its components ($\varphi_i$).

Also, the extracted equations result that entropy is generated because of the existence of the dependent energy components in the energy structure of the system and this generated entropy depends on the variation of these components as well as the amount of the applied energy to the system and its conditions. These results are in the same line with the different formulations of the second law of thermodynamics.

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