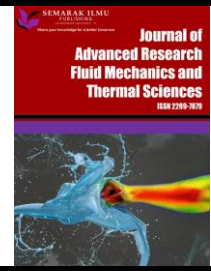




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A Quasi-Statistical Approach to the Boltzmann Entropy Equation Based on a Novel Energy Conservation Principle

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ABSTRACT

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Boltzmann entropy equation is gained according to the statistical mechanics directly and general dependence between entropy and probability is obtained. Based on the second law of thermodynamics with a glance at the Boltzmann entropy equation, it can be deduced that physical processes are done in a direction that the probability of the system and total entropy increase. In fact, the possible process performing states and their entropy variations will be determined at a specific energy level. In this paper, an entropy equation is gained by using a new quasi-statistical approach to the physical processes as well as a novel energy conservation principle. The variation of the "energy structure equation", as an equation to formulate the performed process using activated energy components of the system and their dependence, is studied in different possible paths by using the energy conservation principle directly. Despite the classical mechanics that all particles are studied, in the novel approach, "particular processes" as all processes that have the same active independent energy components are studied at "various conditions"; in other words, all conditions that same energy amount is applied to the system. One of the advantages of this novel approach is that the volume of the needed calculations will be decreased mainly in comparison with the Boltzmann entropy equation. Dependence of the entropy and rate of the energy components is gained from the novel energy conservation principle. The gained relation, expressed by energy components of the system, is considered with no constraints on the structure of the system but has a common basis with the Boltzmann entropy equation. In fact, by using a novel macroscopic-statistical approach, the entropy variation of a physical system is studied.

1. Introduction

The principles of mechanics express the connection between forces and motion of bodies. These principles bring an essential conclusion by considering energy exchange with the system, i.e. sum of kinetic and potential energies of a body is always constant, and if work is also done on the system from the environment around, the sum of the changes in potential and kinetic energies equal to the work had done [1]. The principle of energy conservation is known as a unifying principle in physics

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[2]. Based on this principle, it can be concluded that energy can change the state of the system. When it comes to a rigid body, the work transforms entirely into the kinetic energy of the body. Based on the energy conservation principle, to the extent that the work is done on the system by environmental bodies, kinetic energy increases equally, but if it comes to an elastic body, the sum of elastic strain energy and kinetic energy changes are equal to the work carried out. This issue can also be expressed in the field of thermodynamics as well [1]. Clausius developed two thermodynamic laws in 1865 [3]. The first law is the result of the energy conservation principle for thermal cycles while considering the heat and work as two conventional notions of energy, states that in a closed cycle, the sum of the heat and the work exchanged will be equal. The second law of thermodynamics examines the feasibility of carrying out processes in agreement with the first law. Clausius [3], introduces the concept of entropy and states that the second law of thermodynamics is equivalent to saying that the entropy of the universe is increasing and considers the phrase entropy rising to be a summary of the basic principles of science [3]. The use of the above expression in scientific theories is not easy as we know that Isaac Newton does not pay attention to entropy in compiling the principles of mechanics. In other words, classical mechanics is written reversibly [4]. There are different ideas for applying the second law of thermodynamics on the mechanic and thermodynamic coupling problems at a macroscopic scale [5]. The second law of thermodynamics has attracted many scholars and has not lost its credibility, even with the advent of advanced scientific theories [6,7]. Various mathematical models are proposed for the second law of thermodynamics [8,9]. Second law of thermodynamics has also been proven in various ways [10]. Some of these methods are based on statistical mechanics and some on quantum mechanics [11]. In statistical mechanics, entropy is considered only when depending on the modes available under particular system conditions [12]. Available states are determined at different energy levels by using statistical and probability theory [12]. Boltzmann obtained the entropy relation based on the assumptions of statistical mechanics [13]. This relation is used to calculate the absolute value of entropy, and it is also in the same line with the second law of thermodynamics. Boltzmann entropy relationship also gains entropy dependence on the available energy levels, and also can be used to study the entropy in the particle systems. When processes are reversed, particles can always move in the opposite direction and revert backward. Finally, if the processes are not reversible, based on the second law of thermodynamics, the problem of dissipation of energy arises. In a particle system, the dissipation of energy can be studied by investigating the dynamics of the particles and their paths [14-17].

Today, entropy has an important role in the relevant analysis of many new subjects of science that some of which can be seen in the references [18-22]. Therefore, the establishment, as well as development of suitable models, methods, and practical entropy definitions are the most important challenges for this matter [20-22]. Because of the ability of the Boltzmann entropy equation to calculate the absolute value of the entropy in different physical systems, some researchers tried to develop it as a practical method for calculating entropy in configurationally systems, named configurational entropy [23-25]. Therefore, low needed calculating, generality, accuracy, convergence, and etc. must be considered seriously in presented models and formulations [26-27]. Using the kinematic theory of dissipated energy concepts, Shahsavari *et al.*, studied the entropy production in physical processes, and established a practical relation to the irreversibility as well as its components [28].

In this paper, by presenting a new model of energy structure for physical systems, and by studying the variation of the novel energy structure equation for the same energy applying to the system in different conditions, a novel energy conservation principle is obtained. Also, a quasi-statistical relation to the entropy is extracted by considering the rate of the energy components of the system in this innovative energy conservation equation. In fact, one of the advantages of this novel approach

is that a particular process in various conditions is studied instead of studying the particles of the system which is common in statistical physics that can decrease the volume of the needed calculations mainly.

2. The Physical Significance of the Entropy

Classical thermodynamics examines entropy changes in a physical process based on a macroscopic perspective [29-30]. Whereas statistical mechanics calculates the absolute value of entropy by using a microscopic approach as well as the statistical perspective. According to Planck's theorem, the entropy of a physical system in a particular state depends on the probability of its occurring [31]. Also, there are relevant papers in the same line with the entropy significance and dissipated energy in the different physical systems [32-35]. So

$$S = f(W) \tag{1}$$

That S is entropy and W is the probability of the particular state occurring. The second law of thermodynamics indicates that the total entropy of a particular state of the system is the sum of the entropy of its sub-systems, while according to the statistical and probability theory, the probability of a particular state of a physical system is equal to the product of probabilities of its sub-systems. So function f must satisfies the following conditions [31]

$$S = S_1 + S_2 \tag{2}$$

$$f((W_1 \cdot W_2) = f(W_1) + f(W_2) \tag{3}$$

where W_1 and W_2 are probabilities of sub-systems 1 and 2. Therefore, entropy is calculated as follows

$$S = k \ln(W) + constant \tag{4}$$

That k is a universal constant. Based on the Eq. (4), the general dependence between entropy and probability is determined. In fact, Eq. (4) analyses the macroscopic state of the system based on its microscopic states in its energy level. In other words, it can be calculated that the probability of a physical system depends on the all states that are available at a particular energy level. Entropy is qualified by irregularity. For example, in accordance with theory of electro-magnetic radiation, this irregularity is based on monochromatic vibrations of any resonator if although it remains in a stable stationary field of radiation. By non-regularity, the amplitude and phase of vibration change permanently, [31]. Plank [13] determined the entropy equation as a function of its energy distortion at a particular level of energy

$$S = k[(N + P) \ln(N + P) - N \ln(N) - P \ln(P)] \tag{5}$$

where N is resonators, and P is an integer. Also, W is a function of the number of particles of the system, and a weighting factor of energy levels for particle systems [13]. As an example, Fermi-Dirac established Eq. (6) as follows

$$W = \prod_j \frac{g_j!}{(g_j - 1)! N_j!} \tag{6}$$

That N_j is the particles number of the system with the g_j as the weighting factor of energy level. As can be seen, statistical mechanics, directly, uses examining each particle energy state to examine the states of a system. In other words, the Boltzmann entropy equation can be applied to the particle systems to calculate entropy. Applying the Boltzmann entropy equation to the systems where particles do not have much freedom due to various constraints, as may be known as configurational systems [25-27], is more difficult from other systems with interacting particles.

In this paper, by presenting a novel model for the structure of energy in physical systems, the principle of energy conservation is directly applied to extract a quasi-statistical equation related to entropy. In this novel approach, the independent energy components of the system are examined without any constraint on the structure of the system. In other words, in place of investigating all particles of the system, a particular process in various conditions is studied. Therefore, a practical approach is established to the systems with a high number of particles such as configurational systems.

3. Energy Structure in Physical Systems

The second law of thermodynamics establishes a time direction to the physical processes. In fact, the second law of thermodynamics classifies physical processes into reversible and irreversible processes. When energy is applied to the system in a zero rate, performed process can be done in its reversible state, but in a non-zero rate of energy applying, performed process will be done in its irreversible state. And in fact, more value of the applied energy will be converted to the heat in comparison with the reversible state [5,8,12].

In a system, a momentary reversal of the motion of any moving particle causes the system to move backward, each particle remaining along its old path at the same speed and in the same position as before. In physical dynamics, this simple and complete reversibility is lost due to the forces related to the friction of solids. For example, Incomplete fluidity of liquids; incomplete stretching of solids; Inequality of temperature and as a result conduction of heat produced by stress in solids and fluids; Imperfect magnetic retention; Residual electrical polarization of dielectrics; Heat generation by electric currents caused by motion; Diffusion of liquids, solution of solids in liquids and other chemical changes and absorption of heat and radiant light are some of them. In fact, energy dissipation can be studied by studying particle dynamics [14-17]. In fact, to a general study of the irreversibility in physical processes, we need to consider its effects on the final state of the system when some energy is applied to the system. This needs that we focus on the energy components of the system and their dependence in different conditions of energy applying [28]. In this paper, the paths of various energy changes of the particle system are the base of this study. Instead of investigating a special particle, a physical system at a particular process in various conditions is studied. Figure 1 shows a physical system with its energy distribution components, and in the exchange of energy with the environment.

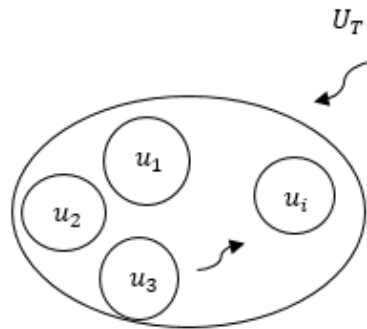


Fig. 1. Scheme of a physical system with energy distribution

It is assumed that the whole energy of a physical system consists of some independent components as well as dependent components and remaining unchanged ones. The dependent components are function of the amounts and rate of independent components as follows

$$U_T = (u_1 + u_2 + \dots + u_m) + [g_1 + \dots + g_k] + [h_1 + \dots + h_n] + U_{T_0} \quad (7)$$

where

$$g_j = g_j(u_1, u_2, \dots, u_m) \quad (8)$$

$$h_p = h_p(\dot{u}_1, \dots, \dot{u}_m) \quad (9)$$

That U_T is the whole energy, g_j and h_p are the independent components of energy, and also U_{T_0} is sum of the all components that don't change during performed process.

When a "particular process", as all processes that have the same active independent components, is performed, some of the components (m components of u_i) change independently and form the performed process. Changes in other components involved in the process, will depend on the amounts and rate of independent components. Since components h_p depend on the rate of independent components, they will be effective in only non-statically paths, and can be used for showing dissipation energy and irreversibility. Therefore, these components are directly depended on process conditions and how the energy is applied to the system. Eq. (7) shows the general form of process energy structure which describe all processes that can be done with m active components as independent energy components. By using of this equation, it isn't need to know the state of all particles, and only a particular process in various conditions will be investigated.

4. A Novel Energy Conservation Principle

In the classical thermodynamics, the first and final states assumed to be fixed and the heat and work transformed between these states are studied. Therefore, in different paths, according to the energy conservation principle, the internal energy change is constant but the work and heat changes in different paths are not equal [29-30]

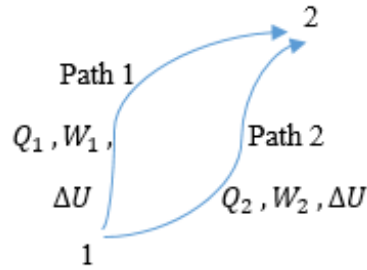


Fig. 2. System behavior in different paths with fixed first and final states

In the novel approach, as shown in Figure 2, the energy applying to the system in different paths are constant, and the variation of the independent components are studied:

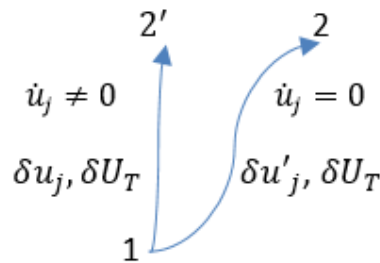


Fig. 3. System behavior by applying the equal energy in different paths

That δu_j is the variation of the u_j when $\dot{u}_j \neq 0$ as the value of energy δU_T is given to the system, and $\delta u'_j$ is the variation of the u_j when $\dot{u}_j \cong 0$ as the value of energy δU_T is given to the system. In path 1-2, performed process is quasi-static, although in other paths the process performs in general. Each path has a specific constant \dot{u}_j as the rate of the component u_j . Path 1-2 has the least energy diffusion when the equal energy is applied to the system at different paths. This path is used as a reference path to show energy diffusion differences between this path and other paths. The more energy diffusion shows the more irreversibility in the process performed. It should be noted that the variation of \dot{u}_j is calculated from reference path to general paths.

Therefore, according to the Eq. (7), the following equation must be satisfied between these paths

$$\sum_{i=1}^m (\delta u_i) + \sum_{q=1}^k \sum_{i=1}^m \left(\frac{\partial g_q}{\partial u_i} \delta u_i \right) + \sum_{p=1}^n \sum_{i=1}^m \left(\frac{\partial h_p}{\partial \dot{u}_i} \delta \dot{u}_i \right) = \sum_{i=1}^m \delta u'_i + \sum_{q=1}^k \sum_{i=1}^m \left(\frac{\partial g_q}{\partial u_i} \delta u'_i \right) \quad (10)$$

Eq. (10) should be satisfied in general. Therefore, the Eq. (11) must be governed on each independent component. For example, for component u_j

$$\delta u_j + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j} \delta u_j \right) + \sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j} \delta \dot{u}_j \right) = \delta u'_j + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j} \delta u'_j \right) \quad (11)$$

Or

$$\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right) (\delta u_j - \delta u'_j) = - \left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right) \delta \dot{u}_j \quad (12)$$

Eq. (12) relates general paths to the path 1-2 as a reference path. Therefore

$$- \left[\frac{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right)} \right] = \frac{(\delta u_j - \delta u'_j)}{\delta \dot{u}_j} \quad (13)$$

$$- \left[\frac{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right)} \right] \left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) = \frac{(\delta u_j - \delta u'_j)}{\delta \dot{u}_j} \left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) \quad (14)$$

$$\left[\frac{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right)} \right] \left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) = - \frac{(\delta u_j - \delta u'_j)^2}{\dot{u}_j \delta \dot{u}_j} = -2 \frac{(\delta u_j - \delta u'_j)^2}{\delta (\dot{u}_j^2)} \quad (15)$$

Because the quasi-static path is used as the reference path, therefore

$$\left[\frac{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right)} \right] \left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) \leq 0 \quad (16)$$

And by assuming following variable change

$$\delta U_j = \delta u_j - \delta u'_j \quad (17)$$

Therefore, relation (16) can be rewritten as follows

$$\left[\frac{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{U}_j}\right)\right)}{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial U_j}\right)\right)} \right] \left(\frac{\delta U_j}{\dot{U}_j}\right) \leq 0 \quad (18)$$

Or

$$\left[\frac{\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial U_j}\right)\right)}{\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{U}_j}\right)\right)} \right] \left(\frac{\delta U_j}{\dot{U}_j}\right) \leq 0 \quad (19)$$

Although relation (19) is an inequality, gained directly from the energy conservation principle, and should be satisfied in all processes performed by the system. This relation is also a confirmation of Eq. (7) because it actually indicates the orientation of this equation that it considers physical processes to be time-dependent as well as in the same line with the second law of thermodynamics.

This relation is combined of four terms

The term of $\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial u_j}\right)\right)$: By using of $\sum_{i=1}^k g_i = G$, this term can be rewritten in form $(1 + G_{,j})$. This term directly depends on the inner structure of the system, and not performed process. It also shows the effect of the variation of independent component on the change of G as independent component. This term also shows that to increase independent component, how more energy must be applied to the system.

The term of $\left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial u_j}\right)\right)$: By using of $\sum_{i=1}^k h_i = H$, this term can be rewritten in form $(1 + H_{,j})$ that depend on the internal structure of the system. Also $H_{,j}$ is a quantity that shows the stiffness of the system against the rate of the independent components changes.

The term of δU_j : This term also is the variation of the difference of u_j and u'_j , and shows the amount of energy variation needed to transfer from quasi-static state to a general one.

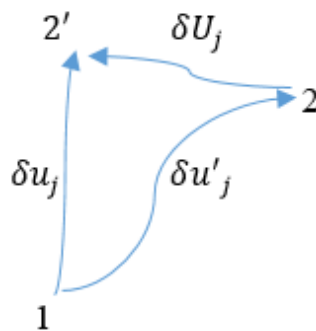


Fig. 4. Difference between two different paths

The term of \dot{U}_j : This term means the rate of difference between u_j and u'_j which relates the transfer rates between quasi-static and general state.

Relation (19) consists of terms relating to the inner structure of the system, gained by applying the principle of energy conservation to the Eq. (7). By considering the energy conservation principle, Eq. (7) and Eq. (19) are equivalent. Therefore, a novel energy conservation principle is presented as follows

According to the energy conservation principle, the states are feasible for a system that relation (19) be satisfied and vice versa.

The above statement can also be taken as an expression of the principle of energy conservation, which, of course is general. By using this novel energy conservation principle, a novel approach is possible to investigate the physical process directional as well as entropy variation as a function of energy components in Macro-State similar to Boltzmann entropy equation.

5. A Novel Approach to the Boltzmann Entropy Equation

By using variable change (17), and rewriting Eq. (12)

$$\left(1 + \sum_{i=1}^k \left(\frac{\partial g_i}{\partial U_j}\right)\right) (\delta U_j) = - \left(\sum_{p=1}^n \left(\frac{\partial h_p}{\partial \dot{U}_j}\right)\right) (\delta \dot{U}_j) \quad (20)$$

By replacing Eq. (20) in the relation (19)

$$\left(-\frac{\delta \dot{U}_j}{\dot{U}_j}\right) \leq 0 \quad (21)$$

Or

$$\delta[\ln(\dot{U}_j)] \geq 0 \quad (22)$$

Relationship (22) is expressed in terms of changes in the energy component of the system, and in fact, represents the direction of the changes. This relation can be used as a criterion for examining the feasibility of a physical process, although directly derived from the energy conservation principle. On this basis, both the history of the system as well as feasible paths to reach from current situation can be studied.

Given that all of the independent components are applied to relation (22), therefore

$$\delta[\ln(\dot{U}_1)] + \delta[\ln(\dot{U}_2)] + \dots + \delta[\ln(\dot{U}_m)] \geq 0 \quad (23)$$

$$\delta[\ln(\prod_{j=1}^m \dot{U}_j)] \geq 0 \quad (24)$$

By using of $w_{u_j} = \dot{U}_j$, and also $W_u = \prod_{j=1}^m w_{u_j}$, Eq. (24) can be rewriting as follows

$$\delta[\ln(W_u)] = \delta\left[\ln\left(\prod_{j=1}^m w_{u_j}\right)\right] = \sum_{j=1}^m \delta \ln(w_{u_j}) \geq 0 \quad (25)$$

Relation (25) is equivalent to relation (22). These relations are extracted from studying a particular process in various conditions, and not all particles of the system. As shown in Figure 5, in the novel approach for a physical system, particles are classified into energy components. Therefore, in systems such as configurational systems where particles do not have a high degree of freedom [25-27], the new perspective can significantly reduce the needed volume of calculations.

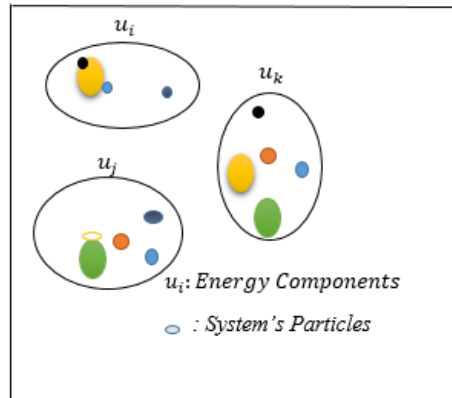


Fig. 5. Energy Component's approach

The expression $(\prod_{j=1}^m \dot{U}_j)$ denotes the multiplication of the rate of all independent energy components. It shows all the ways in which we can apply the equal energy to the system so that m specific independent components are activated in the process. Therefore, Eq. (25) is a quasi-statistical equation, and also gained directly from principle of energy conservation. Although Eq. (25) is a function of the rate of energy components, has common basis with the Boltzmann entropy equation which indicates entropy increasing due to increasing available Micro-States in a physical process.

Similar to the Boltzmann entropy equation, it seems that relation (25) can be used for definition a novel quasi-statistical equation of entropy. This definition can be as follows

$$\delta s = K_{MS} \delta[\ln(W_u)] \quad (26)$$

where K_{MS} is a universal constant that refers to the Macro-States energy components of the system. This coefficient should be calculated by experiments or other methods.

6. Conclusions

The first law deals with the balance of energy in physical processes. The second law of thermodynamics, while formulating the concept of entropy, examines the direction of physical processes. According to the second law of thermodynamics, real processes are always performed in a direction to increase entropy. Classical thermodynamics is able to calculate relative entropy changes with its macroscopic attitude. In classical thermodynamics, by considering zero value for entropy at absolute zero, absolute value of entropy could be calculated. But statistical thermodynamics calculates the absolute amount of entropy by examining the sub-structures of the system's particles. According to Boltzmann's hypothesis, entropy in a physical system depends on the number of available states at the desired energy level. Accordingly, the Boltzmann logarithmic relation is proposed for calculating entropy. The number of available states is also calculated by examining the possible energy levels for the particles, thus entropy can be calculated.

In this paper, innovative Eq. (7) is proposed to consider the total energy for a physical system in a particular process. In fact, a hypothetical process is examined under different conditions, not just individual system particles.

In the novel quasi-statistical perspective, possible processes are investigated under conditions of applying the same amount of energy to the system. In this case, relation (19) is obtained as a condition governing the processes. This relationship is a confirmation of Eq. (7), and on the other

hand, gives a novel expression for the principle of energy conservation. The novel presented approach is quasi-statistical in the sense that both macroscopic energy components are used, and all possible processes are examined.

By using of the expression given for the principle of energy conservation as well as the statistical point of view, the relation (22) is extracted, and from that relation (24) can be deduced which relates the second law of thermodynamics to the statistical concept proposed by Boltzmann. In fact, this relationship argues on the basis of all possible modes of energy consumption in the same way that certain components appear as independent components. Although to apply the Boltzmann entropy equation is very difficult at the systems with interacting particles with no much freedom, the novel presented approach has not this problem since it is written using the macroscopic components energy of the system, as shown in Figure 5.

Eq. (26) has the same base with the Boltzmann entropy equation, and can establish a novel quasi-static definition of entropy. Energy components of the system are the basis of this novel definition, and therefore, can mainly decrease the volume of the needed calculations in comparison with the Boltzmann entropy equation, in particular in configurationally systems. Finally, K_{MS} is a universal coefficient, and can be determined from experiments or other methods.

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