Some Laws of a System With a Constant Amount of Energy

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Abstract:
In this paper, different relationships and functional dependences of a system with a constant energy \( U=\text{const} \), have been analyzed. The combinatorial nature of this analysis enables the conclusion that a family of entropy curves \( \sigma(N, U) \), for \( U=\text{const} \), have an envelope. The envelope theory is very important for consideration of long & short range order of statistic thermodynamic systems. Since, we analyzed a system for \( U=\text{const} \), we could explain some non-continual properties of a material. Like an example of this statement, we observed the situation, which is caused by anomaly filling of electronic orbits during the transfer from d to f elements.

Keywords: Functional dependence, Family of curves, Law of equipartial distribution of energy equilibrium, Electronic orbits, d- elements, f- elements

1. Introduction

The high level of structural complexity of sintering materials demands permanent development of contemporary models, which have to give deep insight into structural changes occurring in the system during the sintering process [1-2]. The structural changes inside the observed systems, together with the analogous ones in quantum physics and statistical mechanics [3], make it possible for us to get close to the full nature of the transport process from the viewpoint of different equilibrium properties [4-6]. The process of sintering is controlled by diffusion, and this process demands special attention in the analysis of the sintering process [7]. The approach to a material, as a well ordered particle system, formed by plenty subsystems, which are in the state of the equilibrium, has been the first step in our analysis. The parameters of these systems are \( N \) - the number of particle, \( U \) – the system energy, and \( l \) – the number of available states or levels. Permanent rearranging of particles per system levels and entropy changes \( \sigma(U, N) \) as consequences of rearranging effects, allowed formation of an entropic diffusion model, which showed the parallelism between the process of the long and short distance order in a particular stage of the sintering process. The characters of equilibrium states expressed through the laws of the equipartial distribution of particles for systems with \( N=\text{const} \), and the laws of equipartial distribution of the energy for the system with \( U=\text{const} \) and interdependence of these states gave a better view into the nature of the transport processes and mechanisms of making equilibrium. These laws control

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the level of state occupancy in the system. Also, these distributions are statistically dominant in the system [8-15].

All these conclusions have a very strong mathematical background based on partitions and compositions. These two related combinatorial objects have a host of interesting applications and properties in our analysis of equilibrium processes in thermodynamical systems. Specific ways of composition presentations through a curve family showed the envelope existence. The envelope is a straight line. The envelope slope is proportional to the log \( l \), where \( l \) is the composition order. The envelope divides the space into two parts. One contains the composition curves, and the second one is where composition curves don’t exists [16].

The mentioned characteristics of compositions, and their analogous with the processes of particle rearranging in systems with \( N=\text{const.} \), indicated that this conclusion can be applied to these systems too. But in this case the envelope has a full physical meaning. The character of systems with a constant amount of energy i.e. \( U=\text{const.} \), is a little bit different concerning the system parameters as now we analyze the functional dependence \( \sigma(N, U) \).

**Analysis**

As we mentioned above, the starting point of our analysis have been mathematical definitions of partitions and compositions [17].

**Definition 1.** Let \( n \in \{N\} \) be an integer (\( n \geq 1 \)). A partition of \( n \) is a representation of \( n \) as a sum of integer values, not considering the order of terms in this sum

\[
n = n_1 + n_2 + n_3 + \ldots + n_k \quad n \geq 1 \quad (i=1,2,\ldots,k) \quad (1)
\]

where the numbers \( n_i \), are called parts of a partition or summands [17].

An integer \( n \) can be presented as a sum of \( k \) nonnegative numbers, i.e. \( n \geq 0 \). This combinatorial object is well known as a composition

**Definition 2.** A composition of \( n \) is a particular arrangement of non negative integers \([n_1, n_2, \ldots, n_k]\), that sum up to \( n \), and whose total number is

\[
C_k(n) = \binom{n + k - 1}{k - 1} = \frac{(n + k - 1)!}{n!(k - 1)!} \quad (2)
\]

In the next step we found all possible compositions of the system with the number of available levels \( k \) for a total system energy \( U \) in the form

\[
U = n_1 + 2n_2 + 3n_3 + \ldots + kn_k \quad (4)
\]

where the \( n_i \) is the number of particles per system level and

\[
N_i = n_1 + n_2 + \ldots + n_k \quad (5)
\]

Also, for each composition set we computed \( \Omega \), i.e. the multinomial coefficient [17].

\[
\Omega = \frac{N!}{N_1!N_2!\ldots N_l!} = \frac{(N_1 + N_2 + \ldots + N_l)!}{N_1!N_2!\ldots N_l!} = \frac{N!}{\prod_{i=1}^{l} N_i!} \quad (6)
\]

All necessary computations of values \( m \) and, and appropriate compositions sets is achieved by available software organized into modules [18]. These modules are distributed in particular menus and subroutines. The values of the multinomial coefficient are computed on the base of precise values of factorial functions, where due to restricted system ability we used \( \sigma = \log \Omega \) instead of the value of \( \Omega \). In the next step, we repeated the same procedure as we used in the analysis of the system with \( N=\text{const.} \). So, we mapped all compositions sets \((n_1, n_2, \ldots, n_k)\) by ordered pairs \((N_i, \sigma)\) for \( U=\text{const.} \). Also, among all these sets, we had more than one composition set with the same value of \( N_i \) defined by (5), and like in the case of
system with \( N = \text{const} \) among all sets \((N_i, \sigma)\) with identical values of \( N_i \), the set with the greatest value of \( \sigma \), i.e. \( \sigma_{\text{max}} \) is selected and presented in the plane \( N_0\sigma \).

**Discussion**

On the basis of equations (5),(6), every distribution of particles inside the system with \( U = \text{const} \) and a limited number of available levels is presented by pairs \((N_i, \sigma)\). In further analysis a functional dependence \( \sigma_i = \log N_i \) for \( U = \text{const} \) is investigated with parallel observation of previous results concerning systems for \( N = \text{const} \). We analyzed the distribution of ordered pairs \((N_i, \sigma)\). On fig. 1, it is possible to notice the asymmetrical distribution of the pairs \((N_i, \sigma)\) in the plane \( N_0\sigma \). These distributions have a sharp maximum \( \sigma_{\text{max}} \) only if \( U = 0 \mod(l) \). This maximum corresponds to composition sets where the amounts of energy per system levels are equal or at least equal, i.e. \( n_1 \approx 2n_1 \approx 3n_1 \approx \ldots \approx kn_1 \). This fact like in the case of the system with \( N = \text{const} \), will be used to determine and to calculate the equation of envelopes of the system for \( U = \text{const} \). Also, according to fig.1, the values of \( \sigma_i \) start from the zero value only for the case where \( U = 0 \mod(l) \).

Analyzing graphical presentation of ordered pairs and their distribution in the plane \( N_0\sigma \), it can be seen that with an appropriate approximate function on the base of calculated data, just like in the case of the system with \( N = \text{const} \), a family of curves with parameter \( U \), may be obtained. Every curve from the family has one and only one appropriate value for the parameter \( U = \text{const} \). We are able to follow all curves, which presents a specific evaluative process in the system, by changing the parameter \( U_l \) in a specific space defined by \( U = \text{const} \). This condition may be expressed as \( F(N_i, \sigma) = 0 \), for \( U = \text{const} \).

**Fig.1** The family of curves for \( U = \text{const} \). \( l = 2 \) We noticed that the maximums (darker points) of the entropic distribution presented by the ordered pairs don’t belong to the envelope. The entropic values located on the envelope respond to the maximums of entropic distribution for \( N = \text{const} \) and \( l = 2 \).

Determination and calculation of the system envelope in this case was more complicated than the case for the system with \( N = \text{const} \). But, in the both cases we used the noticed fact about the properties of maximums and the fact that maximums of the observed system for \( N = \text{const} \). are located on the envelope of the curve family for the system with \( U = \text{const} \) and vice-versa for the same value of \( l \) (fig.2).
Fig. 2. The envelope of system curve family for $l=3$. Detailed analysis of the curve family allowed us to select the maximums and different envelope in the cases for the specific relations between the $U$ energy of the system and the $N$ number of system particles, and number of system levels-state for $N=0 \mod(3)$ (a), and $U=0 \mod(6)$ (d) and triple maximums for $N=0 \mod(3)$ (b and c), and $U=0 \mod(6)$ and $U=6 \mod(6)$ for $N=0 \mod(3)$ (b and c), and values of energy belong to the classes of numbers $6D+1$, $6D+2$, $6D+3$, and $6D+4$ and $6D+5$ (f).

This general conclusion about the content of the curve family envelope for both systems indicates that system states characterized by the maximum of disorder on the macro level and at the same time maximum ordered on the micro level are located on the envelope. In other words, the states located on the envelopes are characterized by the law of equipartition of energies and the law of the equipartition number of particles, respectively.

Generally, for the system with $l$ levels we can write that

$$U_1^l = U_2^l = \cdots = U_l^l \Leftrightarrow N_1^l E_1 = N_2^l E_2 = \cdots = N_l^l E_l \equiv U / l,$$

and:

$$N_1^l = 2N_2^l = 3N_3^l = \cdots = lN_l^l,$$

Where $U_1^l, U_2^l, ..., U_l^l$ present the energy per system level and $N_1^l, N_2^l, ..., N_l^l$ - present the number of particles per system levels. Superscript $l$ indicates that systems have $l$ available levels.
This condition and \((N = \sum_{i=1}^{l} N_i^l)\) give us:
\[
\sum_{i=1}^{l} N_i^l = \sum_{i=1}^{l} \frac{IN_i^l}{i} = IN_l\left[\frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{i}\right] = IN_l A_l = N, \tag{9}
\]
Equation (9) allows us to determine the value of \(N_i^l\), and all others values of \(N_i^l = \frac{IN_l^l}{i}\):
\[
N_1^l = \frac{N}{A_l}, \quad N_2^l = \frac{N}{2A_l}, \ldots, \quad N_i^l = \frac{N}{iA_l}, \quad \ldots, \quad N_l^l = \frac{N}{lA_l}, \tag{10}
\]
where \(A_i\) is a constant determined as:
\[
A_i = 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{i} + \cdots + \frac{1}{l} = \sum_{i=1}^{l} \frac{1}{i}, \tag{11}
\]
As we can see the values of \(A_i\) show a divergence character. But the values of \(A_i\) could be determined for the known values of the number system level. For \(l = 2, 3, 4, 5, 6, 7, 8\), the values of \(A_l = 3/2, 11/6, 25/12, 137/60, 49/20, 363/140, 761/280\) respectively. We could notice that this value increased by logarithm laws. (fig.3). If we put these results in (9) and use the Striling approximation we can obtain an equation of the curve family envelope in the form
\[
\sigma^l_N (U) \cong N^l \ln N^l - \sum_{i=1}^{l} N_i \ln N_i = 2A_i^l N_2 \ln 2A_i^l N_2 - \sum_{i=1}^{l} N_i \ln N_i \tag{12}
\]
After arranging and appropriate substitutions for \(N\) we obtain the final expression for the equation of the curve family envelope
\[
\sigma_N^{obv} (U) \cong \frac{U}{IE_0} \left[ \sum_{i=1}^{l} \frac{1}{i} \ln \left( \sum_{i=1}^{l} \frac{1}{i} \right) + \sum_{i=2}^{l} \frac{\ln i}{i} \right] = \frac{U}{IE_0} \left( A_i \ln A_i + \sum_{i=2}^{l} \frac{\ln i}{i} \right) \tag{13}
\]
Numerical computation for the \(l = 2, 3\ ..., and appropriate \(A_2, A_3 \ldots\) give us the first ten values of slope \(k_N^{obv} = 0.477386, 0.608009, 0.647113, 0.653288, 0.64588, 0.632603, 0.616902, 0.600422, 0.583979\), It could be seen that the values of the slope increase and for \(l = 5\) we have a maximum (fig.3.a). After that, we have a monotone decrease of \(k\) with an asymptotical approach to the zero value for large values of \(l\) (fig.3b). This law has a common character applied on the system and its subsystems too.

![Fig.3](https://example.com/fig3.png)

**Fig.3** The values of constant \(A_i\) and the slope \(k\) of the envelope versus the number of system levels for \(l=1-20\) with a noticable maximum for \(l=5\) (a) and for \(l=0-100\).
Now we could note here that a system reaches the equilibrium state by the process of rearrangement of particles per system levels. It is reflected through permanent particle transfer from lower to upper system levels.

Anomaly filing of electronic orbits during transfer of \( d \) to \( f \) elements could be analyzed by the properties of the system envelopes for \( U=\text{const} \). We already mentioned, that system states characterized by the maximum of disorder on the macro level and at the same time maximum ordered on the micro level are located on the envelope. During system analysis we noticed the existence of structural hierarchy of the observed system, i.e. structure of structure. It means that, we are able to select a subsystem with \( l = 2 \) levels, inside the system for \( l = 3 \). In the system for \( l = 4 \), we are able to select subsystems with \( l = 2 \) and \( l = 3 \) levels, etc. When the system reached the equilibrium state then all subsystems are in the equilibrium state too. For example, when a system with \( l = 7 \) reaches the equilibrium state, all subsystems for \( l = 2, 3, 4, 5, 6 \) have already reached the equilibrium state. Also, we are able to select systems whose parameters satisfy special relations in the sense of classes of numbers, congruence’s etc (fig.3). Based on this and the values of parameter \( k \) (slope of envelope) we concluded that inside the observed system, the subsystems for \( l = 2 \) reached the equilibrium states first, then subsystems for \( l = 3 \) and the subsystem for \( l = 4 \). In the case of the subsystem with \( l = 5 \) the situation is slightly different. The envelope slope in this case has a maximum (fig.3a). After that, we have a monotonic decrease of the values of \( k \) for \( l = 6, 7, \) etc. That means that the subsystem for \( l = 6 \), will reach the equilibrium state before the subsystem for \( l = 5 \). This observation could be used in some analysis of the configurational model of solids for explanation of the formation of a stable atomic configuration.

References

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**Abstract:** In the context of this work, certain functional dependencies of particle systems with a limited number of available states were examined under a constant energy. A specific method of their representation as a combinatorial nature of the presented analysis has clearly shown that the observed family of entropic curves \( \sigma(N, U) \), for \( U = \text{const} \), is characterized by an equation that is explicitly calculated. Based on this observation, in the light of our analysis, it is possible to give an explanation of certain discontinuous properties of the material. As an example, analyzed is the process of anomalous electron orbital filling during transfer between \( d \) and \( f \) elements.

**Keywords:** Functional dependence, family of curves, law of equipartition of energy, electron orbit, \( d \)-elements, \( f \)-elements.