EVALUATION OF THE ENERGY CARRIERS' MOTION MECHANISMS DURING A TRANSIENT IN OPEN THERMODYNAMIC SYSTEMS

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Abstract. Based on the early proposed general approach to quantitative describing a transient in an open thermodynamic system, normal and anomalous diffusion processes were analyzed. The analysis was conducted by approximating the approach-based time dependencies of relative average energy carriers' velocity with the corresponding ones deduced from the general relation for the time effects on the average displacement of the carriers in the course of the transport processes. It was shown analytically that any diffusion process (normal or anomalous one) should be considered as a combination of two alternative ones: "positive" and "negative" diffusion. The diffusion process types corresponding to each of the early specified transient development modes were revealed. It was shown that the real beginning of any of the transient modes does not correspond to the time moment $t = 0$, but to a time $t < 0$, the specific value of which is defined by the relevant approach relations. It was revealed that beginnings of the both modes of a transient are provided by the normal diffusion mechanism which is the positive and negative one for the 1st and 2nd mode, respectively. It was shown also further development of super-diffusion processes during both transient modes.

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Among the processes, an unobserved yet energy carrier motion super-diffusion mechanism is predicted to develop during the initial stage of the 2^{nd} transient mode in the thermodynamic systems consisted of interacting point-like energy carriers. Finishing stages of the both transient modes develop as the negative and positive super-diffusion, respectively for 1^{st} and 2^{nd} modes. The negative diffusion development on any stage of a transient in an open thermodynamic system was attributed to the interacting energy carriers' inhomogeneous spatial distribution formation during the preceding stages of such a transient.

Keywords: transient processes, an open thermodynamic system, normal and anomalous diffusion, point-like and line-type interacting energy carriers.

1. INTRODUCTION

Transient stochastic processes in open thermodynamic systems are a wide class of natural and industrial nonequilibrium stochastic ones [1–4] whose specific feature is the existence of time moments corresponding to their beginning and finishing. According to such criterion, in fact the all-transport processes in nature have to be considered as nonstationary or transient ones, including the evolution of our Universe [2–4]. However, there is only small number of scientific researches devoted to quantitative analysis of the transient processes within the full-time range of their development. The main reason for this is difficulties of the quantitative accounting for the basic features of the different transient stages within the frame of a single theoretical approach. Meantime, a variant of such an approach was proposed recently [5–7], with its successful application to in-depth analysis of the macroplastic deformation of polycrystalline metals [7], as well as to describing the evolution of the observable part of our Universe [8]. Some basic features of the plastic deformation mechanisms were also revealed by the approach application with good accordance with the available experimental data [7]. However, there is a lack of detailed information yet about: – the general applicability of the approach to quantitative description of the known kinds of traditional transport phenomena such as diffusion and heat transfer, as well as – the energy transferring mechanisms during the two early revealed transient development modes in an open thermodynamic system.

So, the article aims to obtain, within the frame of the early proposed single general approach, more detailed data regarding the energy carriers motion during a transient in an open thermodynamic system based on the known features of basic transport processes, specifically: - to evaluate quantitatively an ability of the approach to model the known types of diffusion [2,3] and – to reveal the diffusion process types, predominantly corresponding each of the early specified transient development modes [5–7].

2. MAIN RESULTS PRESENTATION

As it well known [2,3], the main characteristic used to describe a diffusion process is the average squared distance $\overline{r}^2$, which an object transferring a mass or an energy passes with time t through a corresponding thermodynamic system being under an action of a respective constant gradient. According to the well-known notions [2], there are, particularly the following main types of such transport processes: normal, super and sub diffusion which are characterized by the shown below, general relation $\overline{r}^2 = At^{\alpha}$ with the following levels of the corresponding constants: A is a constant related to the corresponding transport process characteristics such as diffusion coefficient, thermal conductivity etc; $\alpha = 1$, $\alpha > 1$, $\alpha < 1$. On the other hand, proceeding from the general approach [5, 6] for analyzing a transient in an open thermodynamic system, we have the general relation for the average velocity of an energy carrier in such a system: $\overline{V}_a = V_1\,(1 - P_2) + V_2 P_2$, where $V_1 = 0$ is the carrier velocity in its initial i.e., fully immovable state, $V_2 = V_{\max} = \text{const}$ – is the carrier velocity being in the state of its unhampered motion in a thermodynamic system; $P_2 = P(t)$ is a time dependent probability for the carrier to be in its unhampered moving state. So, the relative average velocity of the energy carrier, according to the early proposed approach may be expressed as:

$$\overline{V}_a(t)/V_{\max} = P_2(t). \tag{1}$$

Based on the above general relation for $\overline{r}^2$, we can also obtain the corresponding formula for the average velocity of the diffusing object:

$$\overline{V(t)} = d\overline{r}/dt = \mp\,(\alpha/2)\,(\sqrt{A})t^{(\alpha/2)-1} \quad \overline{V(t)} = \text{Const}\cdot t^{\gamma} \quad \gamma = (\alpha/2) - 1. \tag{2}$$

Based on the definitions [2, 3] of the above types of diffusion together with the corresponding intervals of the α- values, we may write:

$$\begin{array}{ll} \gamma = -0.5 \text{ – normal diffusion} & (\alpha = 1) \\ \gamma > -0.5 \text{ – super-diffusion} & (\alpha > 1) \\ \gamma < -0.5 \text{ – sub-diffusion} & (\alpha < 1) \end{array}\;. \tag{3}$$

Besides, proceeding from the definitions (2) of the above constant quantities: $\text{Const} = \mp\,(\alpha/2)\,(\sqrt{A})$, and the γ, we shall have from the expressions

(2):

$$\overline{V}(t) = (\mp\sqrt{A})(t^{\gamma}) \mp \gamma\sqrt{A}(t^{\gamma}). \tag{4}$$

As it follows from the formula (4), any diffusion process (normal or anomalous one) may be considered in general as a combination of the two alternative processes: "positive" and "negative" diffusion [9, 10]. In view of the relevant mechanisms involved, it evidently means that during any diffusion process there should be energy carriers which move in opposed directions in an open thermodynamic system under the same external conditions: from the system volumes corresponding bigger energy – to the ones having lower energy and vice-versa. So, based on relation (4), it is easy to see that the existing, widely used relations to model any known types of the diffusion phenomena, allows development of "positive" and "negative" diffusion, which was also grounded theoretically [11,12], but not taken into account by the relevant models having been developed [2,4].

Besides, the formula (4) may be rewritten in the form:

$$\begin{array}{l} \overline{V}(t)/V_{\max} = ((\mp 1) \mp \gamma)(\sqrt{A}/V_{\max})(t^{\gamma}) \\ \overline{V}(t)/V_{\max} = K(t^{\gamma}) \end{array}, \tag{5}$$

where $K = ((\mp 1) \mp \gamma)\sqrt{A}/V_{\max}$.

Concerning the "negative" diffusion inevitably involved in the general form of the diffusion relation (2), (4) or (5), it should be noticed that according to the theoretical results [10–12], its development is possible in heterogeneous thermodynamic systems, due to, evidently, additional locally acting energy or mass gradients.

According to the aim of the article, let us approximate the time dependencies $\overline{V}_a(t)/V_{\max}$, calculated according to the formula (1) for the both modes, by the relations of the type (5). Evidently, that full or partial coincidence of the time dependencies calculated using the formula (1) with the curves defined by the relation (5) or (4), which correspond to well-clarified mechanisms of the energy transfer, provides physically grounded evaluation of the predominant mechanisms acting during the early defined transient development mode.

Some main results, obtained in the course of the current analysis are shown on Fig. 1, 2. Calculated approach-based time dependences of the relative average carrier velocity in the course of 1$^{\text{st}}$ and 2$^{\text{nd}}$ [5, 6] transient development modes are shown in Fig. 1. As the main relevant features of the obtained results the following ones should be emphasized: – non-monotonic character of the approach-based time dependencies contrary to the typically used ones to model diffusion processes; – non-zero energy carrier average velocity at the

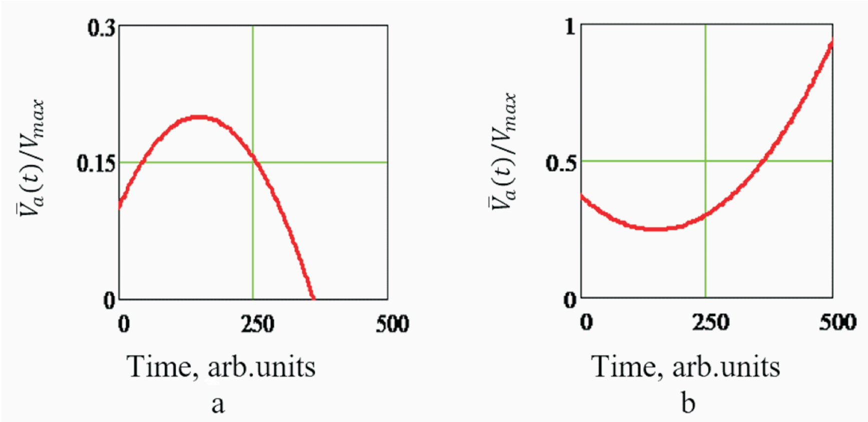

Fig. 1. Time dependencies of the relation $\overline{V}_a(t)/V_{\max}$ for the 1st (a) and 2nd (b) mode of a transient development in an open thermodynamic system. Parameter values for the calculated curves [5–7]: (a) $t_1^* = 130$; $P_{21}^* = 3$; (b) $t_2^* = 130$; $P_{22}^* = 30$

time moment ($t = 0$) corresponding conventional beginning each mode of a transient development. The term "conventional beginning" is used to designate of time moment corresponding to reaching a nominal, further unchangeable, according to the above definition, value of an acting energy gradient. Evidently that, just at a time moment of an energy gradient real application to an open thermodynamic system, the level of the gradient has to be much lower (practically zero) than the nominal one value due to, at least the limited speed of an energy exchange in nature. Meantime, hereafter such a low energy gradient level increases with time, until reaching the nominal value by the time t = 0 corresponding the "conventional beginning" a transient. Besides, due to existence of internal structure defects in real thermodynamic systems, some of the defects provide lower resistance for the carrier's motion than the others. As the relevant examples, high angle grain boundary effects in the course of polycrystal macroplastic deformation and heterogeneous phase transformations should be considered [5, 13]. So, during the above time interval of the nominal acting energy gradient reaching, there should be increasing number or probability P2(t) to appear of the carriers being in the moving state with the maximum velocity until this number or the probability P2(t), gets the value P2(0) corresponding macroscopically detectable beginning of a transient development. The value of the corresponding velocity, at the time moment $t = 0$, according to [5,6], depends on the thermodynamic system or the approach parameters and may be numerically evaluated using the approach. Proceeding from the above, one may conclude that real beginning of a transient development in an open thermodynamic system does not correspond to the time moment $t = 0$, but to a time $t < 0$, the specific value of which may be defined using the relevant relations given in [5–7].

Now, let us consider some variants of the approximation (See Fig. 2) for the approach-based time dependencies shown on Fig. 1. As it seen from the Fig. 2a, the both stages ($t < t_1^*$ and $t > t_1^*$) of the 1$^{\text{st}}$ mode of a transient development can be approximated by using a number of relations of a general type:

$$V(t)/V_{\max} = Bt\beta + C, \tag{6}$$

where: B, β, C are constants and as it may be concluded from the definitions (2) and (5): $B \equiv K$, $\beta \equiv \gamma$.

It should be noted that equation (6) is different from the linear equation (5), analytically deduced from the above general relation for the time dependence of an energy carrier displacement during a diffusion process. The difference is the existence of the absolute term C in the expression (6). Evidently that the term C characterizes a relative level of the energy carrier velocity reached by the time moment $t = 0$, that is not taken into account by the relations (2), (4) or (5). Particularly, for the beginning ($t < t_1^*$) stage of the 1-st mode we used: $B > 0$, $0 < \beta \leq 1$, $C < 1$ (see curves 2, 3) and $B < 0$, $\beta > 0$, $C < 1$ for the finishing ($t > t_1^*$) stage of the mode (see curve 4). Taking into account the data given in Fig. 2a, together with the relations (2) and (3), it may be seen that: $\alpha > 2$ for the both stages of the 1$^{\text{st}}$ mode of a transient development. According to the known definitions [1] together with the relations (3), it should be concluded that the 1$^{\text{st}}$ mode of a transient develops by the super-diffusion mechanism (curves 1–4). The main difference between the beginning ($t < t_1^*$) and finishing ($t > t_1^*$) stages is development of the positive and negative diffusion processes, respectively. It is also important to note that numerical values of C for all calculated approximating curves are less than 1, that is in agreement with the above constant definition.

In respect to the 2$^{\text{nd}}$ mode (see Fig. 2b), the best fitting the curve obtained by the approach application (curve 1) and approximating dependencies is provided by applying relations of the type (6) with naturally different from the above constant values. Particularly, as well as for the 1$^{\text{st}}$ mode, the 2$^{\text{nd}}$ mode time dependence may be divided into two stages: beginning (at $t < t_2^*$) and finishing (at $t > t_2^*$) one. As it seen from the Fig. 2b, in the close vicinity of the point $t = 0$ the best fitting for the approach-based dependence (curve 1) is reached using the approximating one having the following constant values:

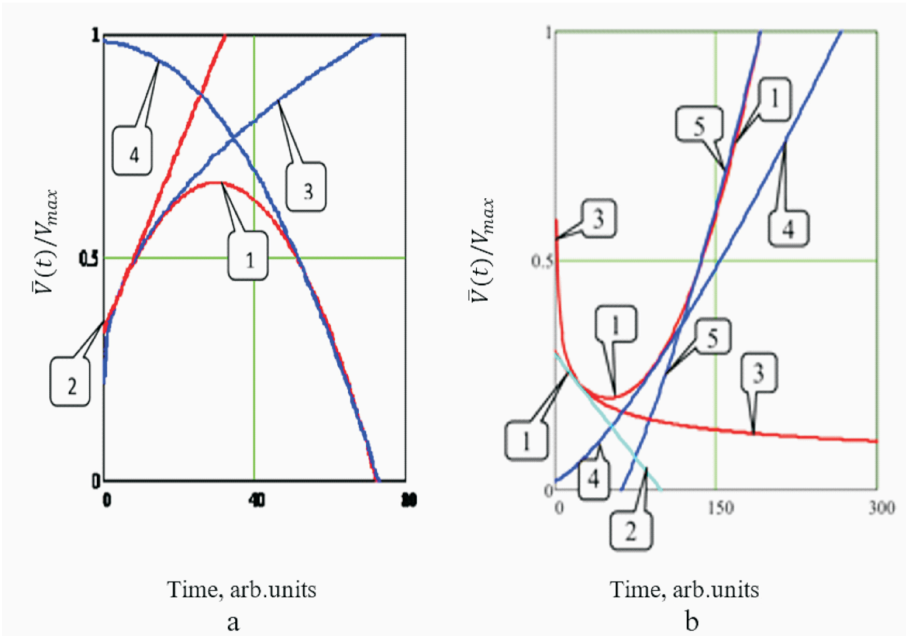

Fig. 2. Time dependencies of the relations $\overline{V}(t)/V_{\max}$ calculated according to the investigated approach for the 1-st (a) and 2-nd (b) mode (curves 1) together with their approximation by the dependencies (curves 2 – 5) based on the relation (6) for the diffusion processes. Values of the constants for the used approximating curves: ***(a)*** *curve 2*: $B = 0.021$, $\beta = 1$, $C = 0.33$; *curve 3*: $B = 0.1$, $\beta = 0.48$, $C = 0.22$; *curve 4*: $B = -1.43 \cdot 10^{-4}$, $\beta = 2.06$, $C = 0.98$; ***(b)*** *curve 2*: $B = -0.003$, $\beta = 1$, $C = 0.295$; *curve 3*: $B = 0.59$, $\beta = -0.3$, $C = 0$; *curve 4*: $B = 6.9 \cdot 10^{-4}$, $\beta = 1.3$, $C = 0.15$; *curve 5*: $B = 7.4 \cdot 10^{-5}$, $\beta = 1.55$, $C = 0$ (See text for details)

$B < 0$, $\beta = 1$, $C < 1$ (curve 2). During the further evolution of the velocity relation $\overline{V}(t)/V_{\max}$, until $t = t_2^*$, the above linear form of the approximating expression becomes a power one with the constant values: $B > 0$, $0 < \beta \leq 1$, $C < 1$ (curve 3). Taking into account the relations (3), it should be concluded that the main diffusion mechanism for the 2-nd transient mode within the time interval $0 < t < t_2^*$ is the super-diffusion one with $2 < \alpha < 4$, which begins as negative diffusion, but continues as positive one. Hence, two consequences may be formulated: – during the 2-nd mode, the energy carriers also have to move with non-zero average velocity at the transient conventional beginning time moment ($t = 0$); – a mechanism of the mode macroscopically detected initial development is complex one that includes negative and positive super-diffusion processes. A joint, consistent with the above conclusions, explanation of the results is that in the course of the 2^{nd} mode, as well as for the 1^{st} mode, carriers motion also actually begins before the time $t = 0$, i.e. – at the time moment $t < 0$, the specific value of which can be defined by the approach expressions. As it was noted above, in result of the motion, formation of inhomogeneous spatial distributions of the carriers is possible by the time point ($t = 0$) due to the carriers' interactions and internal structure defects presence in real open thermodynamic systems. This notion is directly confirmed by the results obtained earlier in [6], where periodic variations of the 2^{nd} transient development mode parameters were shown to exist and the local interacting carrier configurations appearance was physically grounded for the case of crystal dislocations. So, the local effects of the energy carriers' interaction during a diffusion process have to provide the carriers negative diffusion behavior. It should be noted that such type of a transport phenomenon is not experimentally observed yet in thermodynamic systems with diffusion or heat transfer behavior of non-interacting mass or energy carriers. Meantime, such kind of the carriers' average velocity evolution is typical, particularly, in plastically deformed polycrystal line metals where the deformation starts by moving highly mobile grain boundary dislocations which gradually loss their initial increased velocity due to the corresponding obstacles self-formation [13]. A possible explanation of the above difference in the carriers' behavior in corresponding open thermodynamic systems: mass or heat transfer ones and plastically deformed crystalline solids, is distinction in the spatial configuration of the carriers themselves, respectively, point-like (electrons, ions, atoms, molecules etc.) and interacting one dimensional, line-type (dislocations etc.) ones.

As it follows from the curves 4 and 5 on Fig. 2b, the finishing stage of the 2^{nd} transient mode (at $t > t_2^*$) should be approximated using the formula (6) with values of the constants B and β which change within the intervals, respectively: $B > 0$, $1 < \beta < 2$ and $C \approx 0$. Hence, the interval of possible α variations on the stage is: $4 < \alpha < 6$. Based on the results, it may be concluded that on the finishing stage of the 2^{nd} mode, i.e., under the conditions $t > t_2^*$, a transient in an open thermodynamic system develops as a positive superdiffusion process with gradually increasing average velocity of energy carriers' motion. It is important to emphasize that numerical values for the C constant in all the considered cases are: $C < 1$, that is in agreement with the above physical definition of the quantity. Specific values of the constants for the dependences shown on Fig. 2 are given in the legend.

3. DISCUSSION

Proceeding from the above results obtained by the early developed approach application to analysis of the typical transport processes, the following general description of the process in an open thermodynamic system should be proposed.

At first, taking into account possibility of any type of the transient processes ("civilian" and "military ones) simultaneous development in our observable Universe [8, 13], synchronous time evolution of the 1^{st} and 2^{nd} transient modes have to be considered in the general case. Additionally, the same for the both modes carrier motion mechanism of normal diffusion at the time moment of a transient conventional beginning ($t = 0$) is revealed, that is in accordance with the basic notion of the developed approach about thermally-activated character of the transients in an open thermodynamic system [8]. Besides, also for the both modes, the special type of carriers' motion, preceding the macroscopically detected start of a transient in a thermodynamic system, is predicted in accordance with the well-known data concerned with heterogeneous phase transitions, polycrystal plastic deformation etc. [5 -7, 13]. It is also in agreement with the "negative" diffusion development just at the beginning of the 2^{nd} mode, that was explained by the foregoing appearance of inhomogeneous spatial distribution of the carriers, in analogy with mobile dislocations [6]. Proceeding from this, possibility of unobserved yet energy transfer mechanism is predicted to exist. Such super-diffusion mechanism develops as positive diffusion process but with decreasing with time average velocity of the carriers. The mechanism had been observed in the plastically deformed crystalline solids [7] and is expected to exist in thermodynamic systems consisting of interacting energy or mass carriers.

As to the finishing stages of the above modes' development, their features were defined as the negative and positive super diffusion, respectively, for the 1^{st} and 2^{nd} transient mode.

4. CONCLUSIONS

1. Based on the commonly accepted, general form of the expression describing time dependence of an average squared displacement of the mass or energy carriers in the course of a transport process, it is analytically shown that any diffusion process (normal or anomalous) should be considered as a combination of two alternative ones: "positive" and "negative" diffusion.
2. Real beginning of each of the transient modes development in an open thermodynamic system does not correspond to the time moment $t = 0$,

but to a time $t < 0$, the specific value of which may be defined using the relevant approach relations.

3. Beginnings of the both modes of a transient development are provided by the super-diffusion mechanism which is positive and negative one for the 1^{st} and 2^{nd} mode, respectively.
4. An unobserved yet energy carrier motion mechanism is predicted to develop during the initial stage of the 2^{nd} transient mode in open thermodynamic systems consisted of the interacting carriers.
5. Possible development of the specific interacting carriers motion mechanism during the initial stage of the 2^{nd} transient mode is grounded by observations of such mechanism in the systems formed by the line-type, one-dimension carriers.
6. Finishing stages of the both transient modes develop as the negative and positive super-diffusion, respectively for 1^{st} and 2^{nd} modes.

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