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The influence of the transmission coefficient of the boundary on the diffusion in a solid surrounded by vacuum

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The calculations leading to the differential equations of statistical kinematics inside a solid and near the boundary between a solid and vacuum are given. The influence of the transmission coefficient of the boundary on the concentration of the diffusing material in solids is taken into account by introducing the length of extrapolation expressed by the polynomial of arbitrary order depending on the needed accuracy. The obtained length of extrapolation is influenced not only by the diffusion parameters and the boundary's characteristic feature but also by the initial distribution of concentration and by the time of diffusion. The presence of an external force is neglected. The numerical calculation for the planar diffusion of hydrogen in a palladium monocrystal is given as an example. The present method may be particularly useful for diffusion in thin layers and membranes, or when the detailed information on the distribution of diffusing material near the boundary between a solid and vacuum is needed.

1. Introduction

The measurements of the diffusion coefficients and the different models of the diffusion mechanism in solids are the subjects of many investigations. The diffusion coefficient is defined by the Fick law. Unfortunately the Fick equation leads to the so called "paradox of diffusion" and it is not valid far from the stationary state. Now we shall present a derivation of the new diffusion equation for solids which is free from the above mentioned paradox. It is believed that the statistical distribution functions of the length of jumps of the diffusing particle and of the times between the consecutive jumps describe the diffusion process in a proper way. Thus, that process depends on the statistical distribution moments. The differential equation, which will be called the equation of statistical kinematics in solids (SKS equation), is based on the balance of events, namely, jumps or collisions. At the stationary state our results tend to the Fick law. In the general case a better fit to the experimental data is available.

The properties of the surface layer of the examined medium differ from those inside the medium due to the lattice deformations and chemical adsorbers on the surface. In the classical approach there exists the boundary condition in the form of the length of extrapolation. The classical length of extrapolation depends on the transmission coefficient $\langle q \rangle$ of the boundary and on the mean length of jump $\langle \lambda \rangle$. That length of extrapolation does not depend on the diffusion coefficient and can be only applied for the steady state. We shall present another boundary condition using the classical concept of the length of extrapolation. Our event depends not only on all the parameters of diffusion but also on the initial condition and on the time of diffusion. The obtained boundary condition is applicable far from the steady state.

By comparison of the solution of our equation with the experimental data one can verify the diffusion models and, consequently, predict the values of the concentration of the diffusing substance more precisely than in the case of the classical approach.

2. Equation of statistical kinematics for solids

In the former paper [13] we have presented a solution of the SKS equation. The SKS equation itself was obtained in [12]. Here we give a more comprehensive derivation which gives more insight into the basic idea of that formulation of the diffusion process.

We take into consideration the motion of the projection of the diffusing particle on the x axis. The trajectory of that projection may have different shapes as shown in figure 1. The circles in figure 1 mark there the characteristic points of the trajectory, namely the points of jumps in a solid or the points of collisions (local maxima of curvature) in a gas and plasma. The characteristic points form the ensemble of events which will be used in our subsequent considerations.

We denote the length of distance x between two consecutive characteristic points by λ and the corresponding interval of time t by Δt. For liquids Δt is the sum of the time T during which the migrating particle is at rest in the position of equilibrium between two consecutive jumps and of the time τ of flight to the next position of equilibrium

$$\Delta t = T + \tau. \tag{1}$$

For solids we may assume

$$\Delta t = T. \tag{2}$$

The Δt and λ are the random variables. Next we assume that the sense of the x axis agrees with that of the more probable direction of motion. We introduce an additional random quantity σ characterized by the following statistical distribution

$$f_1(\sigma) = K_-\delta(\sigma + 1) + \left[1 - (K_- + K_+)\right]\delta(\sigma) + K_+\delta(\sigma - 1), \tag{3}$$

where $\delta(\sigma)$ is Dirac's delta function, K_+ is the probability that the diffusing particle moves in the positive direction along the x axis while jumping and K_- is the probability that it jumps in the negative one. We have

$$\langle \sigma^{2r} \rangle = K_+ + K_-, \qquad \langle \sigma^{2r-1} \rangle = K_+ - K_-, \tag{4}$$

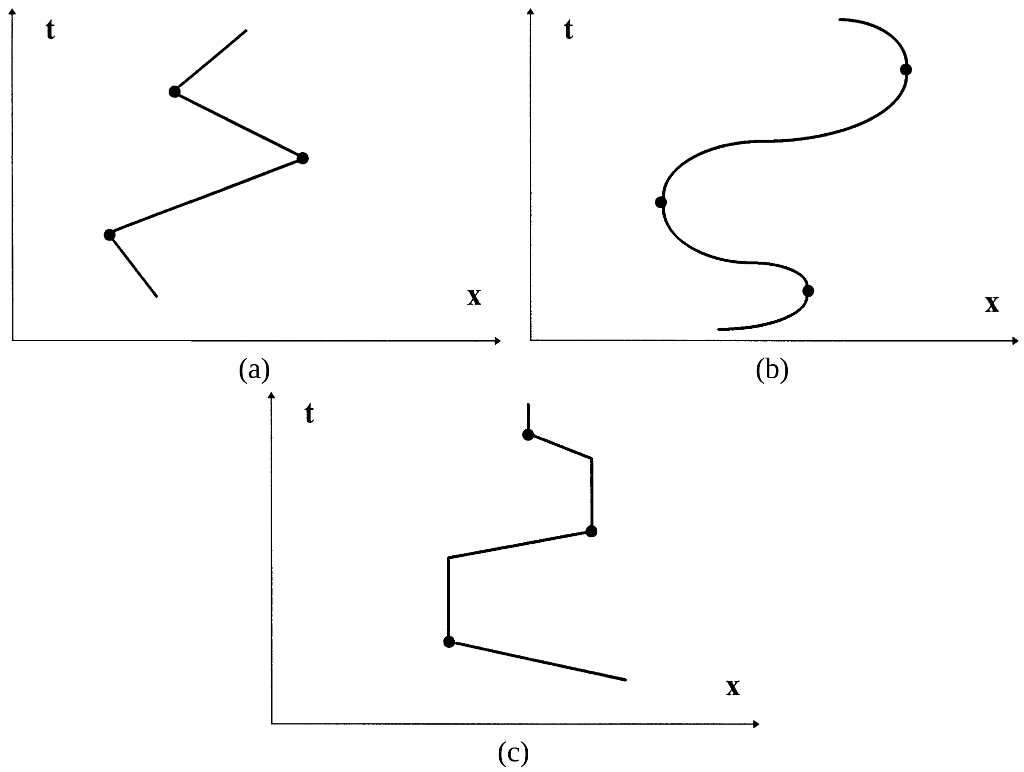

Figure 1. The different shapes of the trajectory of the projection of the diffusing particle on the x axis: (a) in an ideal gas, (b) in a real gas or plasma, (c) in a liquid. The circles mark the characteristic points.

where $r = 1, 2, \ldots$, and $\langle\sigma\rangle$ denotes the expectation value of σ. The random variable σ expresses the fact that the projection of the diffusing particle on the x axis can move in either the positive or negative direction or it can rest while the diffusing particle is moving in the plane normal to the x axis. The last possibility is not realized when $K_+ + K_- = 1$. Then we denote

$$\Delta x = \sigma\lambda. \tag{5}$$

Now we can draw the set of the surface elements S_n^m in the kinematic plane t, x (figure 2), where

$$S_n^m = (t_{m+1} - t_m)(x_{n+1} - x_n), \quad t_m = m\Delta t + c_1,\ x_n = n\Delta x + c_2, \tag{6}$$

m, n are integers and c_1, c_2 are arbitrary constants. These surface elements are the random variables. For the given Δt and Δx each characteristic point (connected with the values of Δt and λ) which lies in the rectangle S_n^{m+1} has its predecessor in one of the rectangles S_{n-1}^m, S_n^m and S_{n+1}^m. Therefore we can balance the events. We shall call the area of the four elements S_n^{m+1}, S_{n-1}^m, S_n^m and S_{n+1}^m the conservation of events or the balance area. Now we have two systems of co-ordinates: the discontinuous co-ordinates m, n and the continuous co-ordinates t, x. Moreover, the n axis can

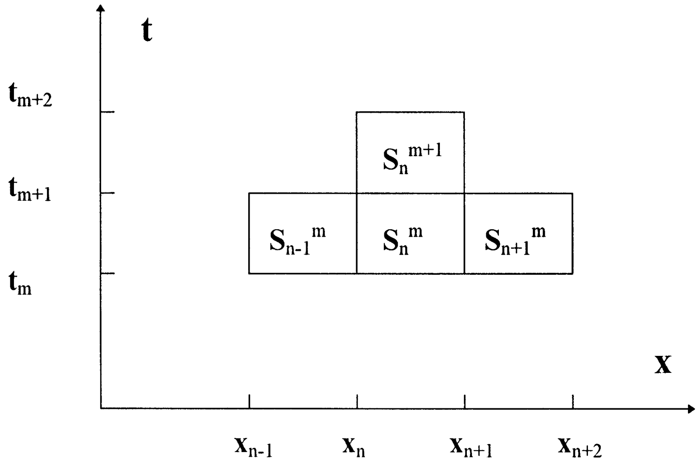

Figure 2. The area of the balance of events for $\sigma = 1$.

be parallel, antiparallel or perpendicular to the x axis due to the random variable σ. We see, that only four points $(m+1, n)$, $(m, n-1)$, (m, n) and $(m, n+1)$ are necessary to form the balance area in the co-ordinates m, n. In the co-ordinates t, x each point (m, n) is represented by the element S_n^m which is a random quantity. For the continuous statistical distribution of Δt and λ the whole balance area is filled by the characteristic points (figure 2), which form a continuous ensemble. For the discrete statistical distribution of Δt and λ the balance area is covered by a discrete ensemble of events (figure 3). When Δt is a constant, the balance area reduces itself to two segments parallel to the x axis (figure 4). When λ has a constant value, the balance area reduces itself to three segments parallel to the t axis (figure 5). Only for constant values of Δt and λ, when the variability of these quantities is neglected, each point (m, n) is explicitly represented by one point (t, x), because the other points of the element S_n^m are free from the events; S_n^m is empty except one point. For this case the balance area consists of four points: (t_m, x_{n-1}), (t_m, x_n), (t_m, x_{n+1}) and (t_{m+1}, x_n) (figure 6) in the co-ordinates t, x. We see that each of the cases considered above is connected with different geometric structure of the balance area. We think that this structure brings the information on the fundamental features of the diffusion phenomenon and should be reflected in the form of the differential equation describing the process here considered.

Let $C(t, x, \Delta t, \lambda)\,\mathrm{d}t\,\mathrm{d}x\,\mathrm{d}(\Delta t)\,\mathrm{d}\lambda$ be the average number of events inside the intervals $(t, t+\mathrm{d}t)$ and $(x, x+\mathrm{d}x)$. These events lie at the distances included in the intervals $(\Delta t, \Delta t + \mathrm{d}(\Delta t))$ along the t axis and $(\lambda, \lambda + \mathrm{d}\lambda)$ along the x axis from their predecessors. The average value of the function $C(t, x, \Delta t, \lambda)$ in the element S_n^m for the given realization of σ, Δt and λ is as follows:

$$\frac{1}{\Delta t \Delta x} \int_{t_m}^{t_{m+1}} \int_{x_n}^{x_{n+1}} C(t, x, \Delta t, \lambda)\,\mathrm{d}x\,\mathrm{d}t.$$

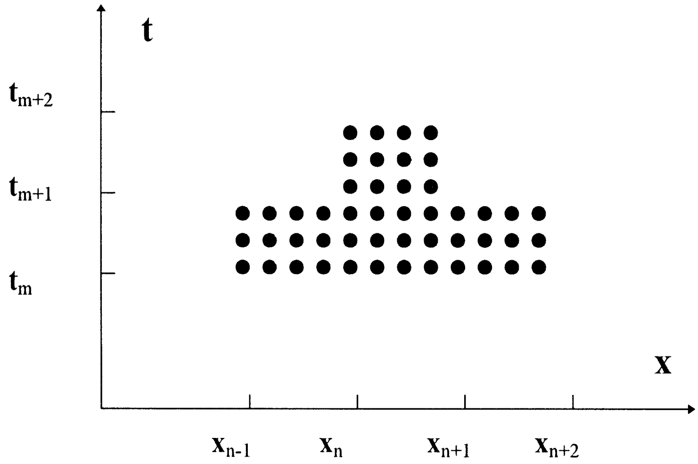

Figure 3. The possible positions of the characteristic points in the balance area for the discrete statistical distributions of Δt and λ and for $\sigma = 1$. Here $j = 3$ and $l = 4$.

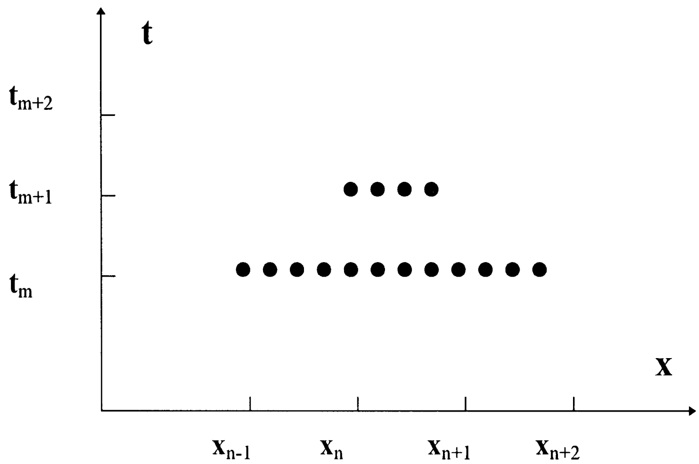

Figure 4. The possible positions of the characteristic points in the balance area for constant Δt and for $\sigma = 1$. The statistical distribution of λ is discrete. Here $j = 1$ and $l = 4$.

We assume, that the above expression remains finite when $\sigma = 0$. The value of the concentration of events that we can ascribe to the point (m, n) is

$$C_n^m = \int_\lambda \int_{\Delta t} \int_\sigma \left[\frac{1}{\Delta t \Delta x} \times \int_{t_m}^{t_{m+1}} \int_{x_n}^{x_{n+1}} C(t, x, \Delta t, \lambda)\, \mathrm{d}x\, \mathrm{d}t \right] f_1(\sigma)\, \mathrm{d}\sigma\, \mathrm{d}(\Delta t)\, \mathrm{d}\lambda. \tag{7}$$

Now we can write the equation of the conservation of events:

$$C_n^{m+1} = K_+ C_{n-1}^m + \left[1 - (K_- + K_+)\right] C_n^m + K_- C_{n+1}^m. \tag{8}$$

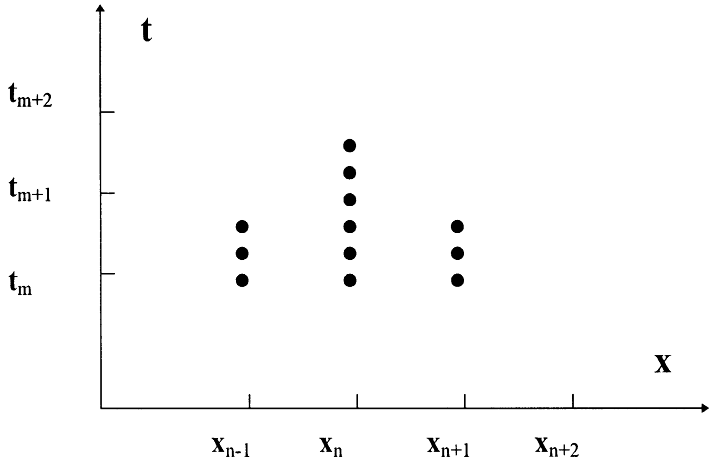

Figure 5. The possible positions of the characteristic points in the balance area for constant λ and for $\sigma = 1$. The statistical distribution of Δt is discrete. Here $j = 3$ and $l = 1$.

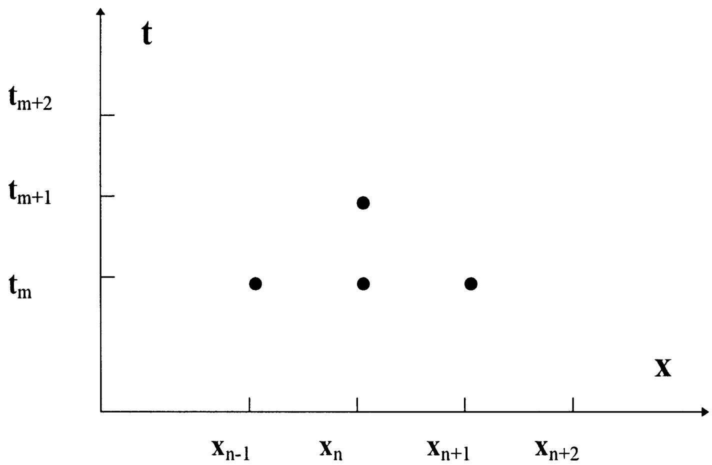

Figure 6. The possible positions of the characteristic points in the balance area for constant Δt and λ and for $\sigma = 1$. Here $j = 1$ and $l = 1$.

Only these particles which collide or jump in one of the elements S_{n-1}^m, S_n^m or S_{n+1}^m can have the next collision (or jump) in the element S_n^{m+1}. This is the essential sense of equation (8). The form of equation (8) is like a form of master equation in the co-ordinates m, n. When $K_- = K_+ = K$ equation (8) can be written as follows:

$$\frac{C_n^{m+1} - C_n^m}{\Delta t} = K\frac{\Delta x^2}{\Delta t}\frac{(C_{n+1}^m - C_n^m) - (C_n^m - C_{n-1}^m)}{\Delta x^2}. \tag{9}$$

Let $\Delta t \to 0$ and $\Delta x \to 0$ while $K(\Delta x^2/\Delta t) = D$ remains constant. The above condition means that: (1) the variabilities of the quantities Δt and λ are neglected, (2) the balance area reduces itself to its edge point. We see that in this case the Fick equation can be obtained from equation (9) in a direct way. Therefore, we think that the differential SKS equation will turn into the Fick equation for constant Δt and λ when the concentration of the diffusing substance and its derivatives will be taken in the edge point of the balance area and without the external force ($\langle\sigma\rangle = 0$).

Now we assume that

$$C(t, x, \Delta t, \lambda) = C(t, x) f(\Delta t, \lambda) \tag{10}$$

and

$$f(\Delta t, \lambda) = f_2(\Delta t) f_3(\lambda). \tag{11}$$

It means that: (1) the statistical distribution of Δt and λ does not depend on t and x, (2) the function of the statistical distribution of the random variables Δt and λ can be written in the multiplicative form. The first of these requirements may be fulfilled when there is no transport process except self-diffusion in the examined medium. Consequently, the differential equation has constant coefficients. Our second requirement means that the random variables Δt and λ are statistically independent. The additional limitation of the proposed model of diffusion is connected with the assumption that the random variables Δt and λ are statistically independent of the sense of motion along the x axis (see formula (7)).

We can only say that due to these assumptions the Fick equation can be obtained from the SKS equation when all terms of equation (8) are expressed by the function $C(t, x)$ and its derivatives taken in the edge point of the balance area. As that equation agrees with the majority of the experimental data, we may think that our second requirement is fulfilled.

The quantity $C(t, x)\,\mathrm{d}x$ gives the average number of events (jumps or collisions) inside the interval $(x, x + \mathrm{d}x)$ at the moment t. We assume, that $C(t, x)\,\mathrm{d}x$ is proportional to the amount of the diffusing substance in that interval. Hence, we can interpret $C(t, x)$ as the concentration of the diffusing material. Then we can write

$$C_n^m = \langle W_n^m \rangle, \tag{12}$$

where

$$\langle W_n^m \rangle = \int_\lambda \int_{\Delta t} \int_\sigma W_n^m f_1(\sigma) f_2(\Delta t) f_3(\lambda)\,\mathrm{d}\sigma\,\mathrm{d}(\Delta t)\,\mathrm{d}\lambda \tag{13}$$

and

$$W_n^m = \frac{1}{\Delta t \Delta x} \int_{t_m}^{t_{m+1}} \int_{x_n}^{x_{n+1}} C(t, x)\,\mathrm{d}t\,\mathrm{d}x, \tag{14}$$

or

$$W_n^m = \frac{1}{\Delta t \Delta x} \int_0^{\Delta t} \int_0^{\Delta x} C(t_m + u, x_n + v)\,\mathrm{d}u\,\mathrm{d}v.$$

The form of the trajectory of the diffusing particle in a solid ($\Delta t = T$) should be properly reflected in the operator relating $C(t_m + u, x_n + v)$ and $C(t_m, x_n)$. The step of u is represented by the action of the operator

$$\sum_{a=0}^{\infty} \frac{u^a}{a!} \frac{\partial^a}{\partial t^a}$$

when applied to the function $C(t_m, x_n)$. Similarly, we represent the step of v by

$$\sum_{b=0}^{\infty} \frac{v^b}{b!} \frac{\partial^b}{\partial x^b}.$$

Thus,

$$C(t_m + u, x_n + v) = \sum_{a,b=0}^{\infty} \frac{u^a v^b}{a!b!} C(t_m, x_n)_{t^a x^b}, \tag{15}$$

where we use the notation

$$\frac{\partial^{a+b}}{\partial t^a \, \partial x^b} f(t, x) = f(t, x)_{t^a x^b}. \tag{16}$$

Introducing equation (15) into equation (14) we obtain

$$W_n^m = \sum_{a,b=0}^{\infty} \frac{\Delta t^a \Delta t^b}{(a+1)!(b+1)!} C(t_m, x_n)_{t^a x^b}. \tag{17}$$

Starting from here we will use throughout this paper the following approximation:

$$W_n^m = C(t_m, x_n) + \frac{\Delta t}{2} C(t_m, x_n)_t + \frac{\Delta x}{2} C(t_m, x_n)_x + \frac{\Delta t \Delta x}{4} C(t_m, x_n)_{tx}. \tag{18}$$

The presence of the mixed derivative $C(t_m, x_n)_{tx}$ reflects the fact that in our scheme the diffusing particle is allowed to pass from the point (t_m, x_n) to the point (t_{m+1}, x_{n+1}) only through the points (t_{m+1}, x_n) or (t_m, x_{n+1}).

For solids we assume that the statistical distributions of Δt and λ are discrete, i.e.,

$$\Delta t = jT_0 \tag{19}$$

and

$$\lambda = l\lambda_0, \tag{20}$$

where λ_0 is the constant length of the elementary jump, T_0 is the constant period of oscillations of the diffusing particle in its equilibrium position and j, l are integers being the random variables. When $f_2(j) = \delta(j - 1)$ we put $\langle \Delta t \rangle$ instead of T_0; when

$f_3(l) = \delta(l-1)$ we replace λ_0 by $\langle\lambda\rangle$. Now for solids W_n^m takes the following form in the first approximation:

$$W_n^m = C(t_m, x_n) + \frac{1}{2}(j-1)T_0 C(t_m, x_n)_t + \frac{1}{2}\sigma(l-1)\lambda_0 C(t_m, x_n)_x + \frac{1}{4}\sigma(j-1)(l-1)T_0\lambda_0 C(t_m, x_n)_{tx}. \tag{21}$$

In the earlier paper [12] dealing with diffusion in solids we have recently detected some minor numerical errors in numbers representing the factors in W_n^m, therefore the coefficients of the differential equations (but not the equations themselves) have to be slightly corrected. These errors have no influence on the general conclusions in [13].

Now we need to express all the terms of equation (8) by the derivatives of the function $C(t,x)$ taken at the edge point of the balance area. We should introduce the information about the geometric proportions of the balance area to the calculation. So we go to the edge point step by step, each step is connected with the separate expansion of $C(t,x)$ in the Taylor series

$$C(t_m, x_n) = \sum_{a=0}^{\infty} \frac{\Delta x^a}{a!} C(t_m, x_{n-1})_{x^a}, \tag{22}$$

$$C(t_m, x_{n+1}) = \sum_{a,b=0}^{\infty} \frac{\Delta x^{a+b}}{a!b!} C(t_m, x_{n-1})_{x^{a+b}}, \tag{23}$$

$$C(t_{m+1}, x_n) = \sum_{a,b=0}^{\infty} \frac{\Delta t^a \Delta x^b}{a!b!} C(t_m, x_{n-1})_{t^a x^b}. \tag{24}$$

Introducing the above expressions together with (4), (5), (12), (13) and (17) into equation (8) we obtain the general differential equation. That equation contains the derivatives of the function $C(t,x)$ taken in the edge point of the balance area. Its form depends on the assumed forms of the statistical distribution functions $f_1(\sigma)$, $f_2(\Delta t)$ and $f_3(\lambda)$. Limiting the play of the series indices to two values 0 and 1, we obtain the following differential equation as the first approximation of the general equation:

$$C_t + A' C_{t^2} + B_1' C_x + B_2' C_{tx} - B_3' C_{x^3} + B_4' C_{t^2 x} - B_5' C_{tx^3} - D_1' C_{x^2} + D_2' C_{tx^2} + D_3' C_{t^2 x^2} = 0, \tag{25}$$

where

$$A' = \left(\langle j^2\rangle - \langle j\rangle\right)\frac{T_0}{2\langle j\rangle},$$

$$B_1' = \frac{\langle\sigma\rangle^2\langle l\rangle\lambda_0}{\langle j\rangle T_0},$$

$$B_2' = \frac{1}{2}\langle\sigma\rangle\left(3\langle l\rangle - 1 + \langle\sigma\rangle\langle l\rangle\frac{\langle j\rangle - 1}{\langle j\rangle}\right)\lambda_0,$$

$$B_3' = \frac{1}{4}\langle\sigma\rangle\big(\langle\sigma^2\rangle - \langle\sigma\rangle\big)\big(\langle l^3\rangle - \langle l^2\rangle\big)\frac{\lambda_0^3}{\langle j\rangle T_0},$$
$$B_4' = \frac{1}{4}\langle\sigma\rangle\frac{\langle j^2\rangle - \langle j\rangle}{\langle j\rangle}\big(3\langle l\rangle - 1\big)T_0\lambda_0,$$
$$B_5' = \frac{1}{8}\langle\sigma\rangle\big(\langle\sigma^2\rangle - \langle\sigma\rangle\big)\frac{\langle j\rangle - 1}{\langle j\rangle}\big(\langle l^3\rangle - \langle l^2\rangle\big)\lambda_0^3,$$
$$D_1' = \frac{1}{2}\langle\sigma^2\rangle\big[\langle\sigma^2\rangle\langle l^2\rangle - \langle\sigma\rangle\big(2\langle l^2\rangle - \langle l\rangle\big)\big]\frac{\lambda_0^2}{\langle j\rangle T_0},$$
$$D_2' = \frac{1}{4}\langle\sigma^2\rangle\left\{2\big(\langle l^2\rangle - \langle l\rangle\big) - \frac{\langle j\rangle - 1}{\langle j\rangle}\big[\langle\sigma^2\rangle\langle l^2\rangle - \langle\sigma\rangle\big(2\langle l^2\rangle - \langle l\rangle\big)\big]\right\}\lambda_0^2,$$
$$D_3' = \frac{1}{4}\langle\sigma^2\rangle\frac{\langle j^2\rangle - \langle j\rangle}{\langle j\rangle}\big(\langle l^2\rangle - \langle l\rangle\big)T_0\lambda_0^2.$$

We see that the obtained above SKS equation contains the second order derivative with respect to time and the third order derivative with respect to distance. It agrees with the geometric proportions of the balance area which lasts $2\Delta t$ and has the length $3\Delta x$ (see figure 3).

Let $f_2(j) = \delta(j-1)$ and $\langle\sigma\rangle = 0$ (see figure 4). Now equation (25) takes the form

$$C_t - D_1' C_{x^2} + D_2' C_{tx^2} = 0. \tag{26}$$

The above equation was obtained by Cantello [1] and then by Mrygon and Wojtczak [8] from master equation.

Assuming the concentration in the form of Fourier series

$$C(t,x) = \sum_{p=0}^{\infty} A(p)\exp\big[-\alpha(p)t\big]\exp(\mathrm{i}px), \tag{27}$$

one obtains from Cantello equation the relaxation coefficient $\alpha(p)$ as follows:

$$\alpha(p) = \frac{p^2 D_1'}{1 - p^2 D_2'}. \tag{28}$$

According to the Cantello equation if $p^2 D_2' > 1$ then the amplitudes of concentration harmonics increase infinitely with time while the external forces are absent ($\langle\sigma\rangle = 0$). Such effect contradicts the energy conservation principle and it is not observed. Therefore the Cantello equation leads to a very substantial paradox.

When $f_2(j) = \delta(j-1)$, $f_3(l) = \delta(l-1)$ and $\langle\sigma\rangle = 0$ we obtain the Fick equation (see figure 6)

$$C_t - D_1' C_{x^2} = 0 \tag{29}$$

with its known paradox

$$\alpha(p) = p^2 D_1' \tag{30}$$

and $\lim_{p\to\infty} \alpha(p) = \infty$. The above result agrees with equation (9). We see that the orthodox equations with their failures can be obtained from equation (8) in the edge point of the area of the conservation of events. Moreover, it is possible only under condition that the balance area has the length of one step Δt along time axis, i.e., $f_2(j) = \delta(j-1)$. When Δt varies randomly, the balance area has the length of two steps Δt along time axis and the derivative of the second order with respect to time must appear in the differential equation. Also in the coefficients of the differential equation must appear the first and the second moments of the statistical distribution function $f_2(j)$ (see $\langle j\rangle$ and $\langle j^2\rangle$ in equation (25)). We cannot agree with the orthodox approach based on the form of master equation which contains only the first derivative with respect to time [7,9]. Such form can be justified only when one neglects the random variability of Δt, i.e., for long time of diffusion, when the expansion into a Fourier series contains no more than a few harmonics.

Let us look once more on equation (25) for $\langle\sigma\rangle > 0$. Let $f_2(j) = \delta(j-1)$ and $f_3(l) = \delta(l-1)$. One may suppose that in this case equation (25) should turn into the classical Einstein–Fokker–Planck (EFP) equation. Actually we obtain, instead of the EFP equation, another equation,

$$C_t + B_1' C_x - D_1' C_{x^2} + B_2' C_{tx} = 0 \tag{31}$$

with the phase velocity of the waves of concentration

$$\beta(p) = \frac{B_1' - p^2 B_2' D_1'}{1 + p^2 B_2'^2}, \tag{32}$$

while the EFP equation does not contain the mixed derivative and it gives the phase velocity β independent of p. We can interpret this discrepancy in the following way. The EFP equation describes the drift with constant velocity of the crystal lattice together with the diffusing particles. In our model only the diffusing particles feel the action of an external force and the crystal lattice remains at rest with respect to the observer. The waves of concentration may interact with the lattice depending on the wave number p. In this paper we shall deal with the case $\langle\sigma\rangle = 0$.

More interesting results can be achieved at the centre point of the balance area. We pass from the edge point (t_m, x_{n-1}) to the centre point (t_m, x_n) by one step of $-\Delta x$:

$$C(t_m, x_{n-1}) = \sum_{a=0}^{\infty} \frac{(-\Delta x)^a}{a!} C(t_m, x_n)_{x^a}. \tag{33}$$

We obtain the following differential equation in the first approximation:

$$\begin{aligned} &C_t + AC_{t^2} + B_1 C_x + B_2 C_{tx} + B_3 C_{x^3} + B_4 C_{t^2 x} - B_5 C_{tx^3} - B_6 C_{t^2 x^3} \\ &\quad - D_1 C_{x^2} - D_2 C_{tx^2} - D_3 C_{t^2 x^2} + D_4 C_{x^4} + D_5 C_{tx^4} = 0, \end{aligned} \tag{34}$$

where

$$A = \big(\langle j^2\rangle - \langle j\rangle\big)\frac{T_0}{2\langle j\rangle},$$

$$B_1 = \frac{\langle\sigma\rangle^2\langle l\rangle\lambda_0}{\langle j\rangle T_0},$$

$$B_2 = \frac{1}{2}\langle\sigma\rangle\left(\langle l\rangle - 1 + \langle\sigma\rangle\langle l\rangle\frac{\langle j\rangle - 1}{\langle j\rangle}\right)\lambda_0,$$

$$B_3 = \frac{1}{4}\langle\sigma\rangle\big[\langle\sigma^2\rangle\big(\langle l^3\rangle + \langle l^2\rangle\big) - \langle\sigma\rangle\big(3\langle l^3\rangle - \langle l^2\rangle\big)\big]\frac{\lambda_0^3}{\langle j\rangle T_0},$$

$$B_4 = \frac{1}{4}\langle\sigma\rangle\frac{\langle j^2\rangle - \langle j\rangle}{\langle j\rangle}\big(\langle l\rangle - 1\big)T_0\lambda_0,$$

$$B_5 = \frac{1}{4}\langle\sigma\rangle\left\{2\big(\langle l^3\rangle - \langle l^2\rangle\big) - \frac{1}{2}\frac{\langle j\rangle - 1}{\langle j\rangle}\big[\langle\sigma^2\rangle\big(\langle l^3\rangle + \langle l^2\rangle\big) - \langle\sigma\rangle\big(3\langle l^3\rangle - \langle l^2\rangle\big)\big]\right\}\lambda_0^3,$$

$$B_6 = \frac{1}{4}\langle\sigma\rangle\big(\langle l^3\rangle - \langle l^2\rangle\big)\frac{\langle j^2\rangle - \langle j\rangle}{\langle j\rangle}T_0\lambda_0^3,$$

$$D_1 = \frac{1}{2}\langle\sigma^2\rangle\big(\langle\sigma^2\rangle\langle l^2\rangle + \langle\sigma\rangle\langle l\rangle\big)\frac{\lambda_0^2}{\langle j\rangle T_0},$$

$$D_2 = \frac{1}{2}\langle\sigma_2\rangle\left[2\langle l^2\rangle + \frac{\langle j\rangle - 1}{2\langle j\rangle}\big(\langle\sigma^2\rangle\langle l^2\rangle + \langle\sigma\rangle\langle l\rangle\big)\right]\lambda_0^2,$$

$$D_3 = \frac{1}{2}\langle\sigma^2\rangle\langle l^2\rangle\frac{\langle j^2\rangle - \langle j\rangle}{\langle j\rangle}T_0\lambda_0^2,$$

$$D_4 = \frac{1}{4}\langle\sigma^2\rangle\big(\langle\sigma^2\rangle - \langle\sigma\rangle\big)\big(\langle l^4\rangle - \langle l^3\rangle\big)\frac{\lambda_0^4}{\langle j\rangle T_0},$$

$$D_5 = \frac{1}{8}\langle\sigma^2\rangle\big(\langle\sigma^2\rangle - \langle\sigma\rangle\big)\big(\langle j\rangle - 1\big)\big(\langle l^4\rangle - \langle l^3\rangle\big)\frac{\lambda_0^4}{\langle j\rangle}.$$

The above SKS equation plays here a similar role as the EFP equation plays for the orthodox approach. It is evident that the passage from the edge point (t_m, x_{n-1}) to the centre point (t_m, x_n) generates the derivative of the fourth order with respect to distance. Thus we see, that the order of the differential equation depends on the point of tangency of the solution of that equation to the solution of equation (8).

When $\langle\sigma\rangle = 0$, equation (34) takes the form

$$C_t + AC_{t^2} - D_1C_{x^2} - D_2C_{tx^2} - D_3C_{t^2x^2} + D_4C_{x^4} + D_5C_{tx^4} = 0 \qquad (35)$$

and the corresponding relaxation coefficient is

$$\alpha(p) = \frac{1 + p^2D_2 + p^4D_5 - (\Delta)^{1/2}}{2(A + p^2D_3)}, \qquad (36)$$

where

$$\begin{aligned}\Delta = 1 + 2p^2(D_2 - 2AD_1) + p^4\bigl(D_2^2 + 2D_5 - 4AD_4 - 4D_1D_3\bigr) \\ + 2p^6(D_2D_5 - 2D_3D_4) + p^8D_5^2.\end{aligned} \tag{37}$$

It can be seen that

$$\lim_{p\to\infty} \alpha(p) = \frac{D_2}{2D_3}, \tag{38}$$

so equation (35) is free from the paradox of diffusion.

When $f_2(j) = \delta(j-1)$ (see figure 4), equation (35) gives

$$C_t - D_1C_{x^2} - D_2C_{tx^2} + D_4C_{x^4} = 0. \tag{39}$$

The above equation corresponds to the Cantello equation and is free from its paradox:

$$\alpha(p) = \frac{p^2D_1 + p^4D_4}{1 + p^2D_2}. \tag{40}$$

We see that $\alpha(p) > 0$ for all p. We have $\lim_{p\to\infty} \alpha(p) = \infty$ but here it does not contradict to the assumed conditions, because now Δt is constant and λ may be arbitrary long.

For the case shown in figure 6, equation (35) turns into

$$C_t - D_1C_{x^2} - D_2C_{tx^2} = 0. \tag{41}$$

The relaxation coefficient obtained from the above equation is as follows:

$$\alpha(p) = \frac{p^2D_1}{1 + p^2D_2} \tag{42}$$

and

$$\lim_{p\to\infty} \alpha(p) = \frac{D_1}{D_2}. \tag{43}$$

Equation (41) corresponds to the Fick equation and is free from the diffusion paradox (for constant Δt and constant λ the relaxation coefficient α should be limited for all p). The coefficients D_1 and D_2 in equation (41) contain $\langle\sigma^2\rangle$, λ_0^2 and $\langle\Delta t\rangle$. Interpreting the experimental data according to equation (41) one can determine two from three those quantities. Our approach allows one to obtain more information from the experiment than the orthodox approach does.

3. Boundary conditions

The simplest boundary condition used for transparent barrier (i.e., barrier characterized by the transmission coefficient equal to one) when the concentration of the diffusing atoms outside the sample equals zero is the condition of Dirichlet,

$$C(t,0) = C(t,L) = 0, \tag{44}$$

where L is the length of the specimen.

In the case of diffusion in gases or when neutrons diffuse in solids (i.e., when the mean free path of the diffusing particles is not considered as an infinitesimal quantity) another boundary condition for transparent barriers is used. It has the form

$$C(t,-d) = C(t, L+d) = 0, \tag{45}$$

where d is the length of extrapolation.

Smoluchowski [10] calculated the value of the length of extrapolation $d_c = 0.707\langle\lambda\rangle$, where $\langle\lambda\rangle$ is the length of the mean free path of the diffusing particles. He dealt with the distribution of temperature near the boundary between gas and solid but his result can be applied to diffusion. In the contemporary monograph [4] the length of linear extrapolation is applied to the diffusion of neutrons and it is quoted as $d_c = 0.7\langle\lambda\rangle$. When one wants to take into account the fact that the barrier may have different degrees of transparency one should use the following form of the length of linear extrapolation [3]

$$d_c = 0.71\bigl(2 - \langle q\rangle\bigr)\langle\lambda\rangle/\langle q\rangle, \tag{46}$$

where q is the random variable equal to 1 (when the diffusing particle penetrates through the barrier) or 0 (when the diffusing particle rebounds from the barrier). Thus $\langle q\rangle$ is the expectation value of q and has a meaning of the coefficient of transmission. For $\langle q\rangle = 0$ the boundary condition (46) leads to the condition of Neumann ($\nabla C(t,0) = \nabla C(t,L) = 0$). The classical length of extrapolation can be applied only to steady state. It does not depend on the initial distribution of concentration and on the time of diffusion. The features of the medium are characterized only by $\langle\lambda\rangle$ and $\langle q\rangle$; the coefficient of diffusion does not enter equation (46).

The boundary condition in the form of the length of extrapolation is still used – see equation (2.6.1) in [5], where d_c is written as follows:

$$d_c = \frac{1+R}{1-R}\frac{2}{3}\langle\lambda\rangle. \tag{47}$$

Here $R = 1 - \langle q\rangle$ is the effective reflection coefficient. For $R = 0$ we obtain the result of Smoluchowski with accuracy to the numerical factor.

A similar boundary condition was given by Crank [2] and now by the authors of [6], where in the point $x = 0$ it has the form

$$\frac{\mathrm{d}C}{\mathrm{d}x} - KC = 0. \tag{48}$$

Here K may be considered as the reciprocal of the length of extrapolation. Two cases are considered in [6]: (1) $K = 0$ for the Neumann boundary condition ($\langle q\rangle = 0$), and (2) $K = \infty$ for the Dirichlet condition. The last case means that the authors of [6] assume $d_c = 0$ for $\langle q\rangle = 1$. This assumption cannot be thought as an exact one from the times of Smoluchowski.

The above mentioned results were obtained within the orthodox approach.

The balance of events near the boundary between solid and vacuum was considered in [11]. Unfortunately, the results obtained in [11] are not correct because of the error in [12] mentioned earlier.

If the barrier between solid and vacuum lies at the point x_{n+1} then the element S_{n+1}^{m} is absent in the balance area because it lies outside the examined medium. Thus the probability that a particle which jumps (with the given values of j and l) inside element S_n^m will not have the next jump inside element S_n^{m+1} is $\langle q\rangle K_+ + K_-$, so the balance of events leads to the following equation:

$$C_n^{m+1} = K_+ C_{n-1}^{m} + \big[1 - \big(\langle q\rangle K_+ + K_-\big)\big] C_n^m. \tag{49}$$

Under the same conditions as formerly one can obtain the differential equation from equation (49) in the point (t_m, x_{n-1}) as follows:

$$\begin{aligned} &C_t + A^{*,} C_{t^2} + B_1^{*,} C_x + B_2^{*,} C_{tx} + B_3^{*,} C_{t^2x} \\ &\quad + D_1^{*,} C_{x^2} + D_2^{*,} C_{tx^2} + D_3^{*,} C_{t^2x^2} + E^* C = 0, \end{aligned} \tag{50}$$

where

$$\begin{aligned}
A^{*,} &= \big(\langle j^2\rangle - \langle j\rangle\big)\frac{T_0}{2\gamma},\\
B_1^{*,} &= \langle\sigma\rangle\big\{\langle\sigma^2\rangle\big[2\langle l\rangle + \langle q\rangle\big(3\langle l\rangle - 1\big)\big]\\
&\quad - \langle\sigma\rangle\big[2\big(2\langle l\rangle - 1\big) - \langle q\rangle\big(3\langle l\rangle - 1\big)\big]\big\}\frac{\lambda_0}{4\gamma T_0},\\
B_2^{*,} &= \langle\sigma\rangle\big\{2\langle j\rangle\big(3\langle l\rangle - 1\big) + (1/2)\big(\langle j\rangle - 1\big)\big[\langle\sigma^2\rangle\big[2\langle l\rangle + \langle q\rangle\big(3\langle l\rangle - 1\big)\big]\\
&\quad - \langle\sigma\rangle\big[2\big(2\langle l\rangle - 1\big) - \langle q\rangle\big(3\langle l\rangle - 1\big)\big]\big]\big\}\frac{\lambda_0}{4\gamma},\\
B_3^{*,} &= \langle\sigma\rangle\big(\langle j^2\rangle - \langle j\rangle\big)\big(3\langle l\rangle - 1\big)\frac{T_0\lambda_0}{4\gamma},\\
D_1^{*,} &= \langle\sigma^2\rangle\big[\langle\sigma^2\rangle\big(1 + \langle q\rangle\big) - \langle\sigma\rangle\big(1 - \langle q\rangle\big)\big]\big(\langle l^2\rangle - \langle l\rangle\big)\frac{\lambda_0^2}{4\gamma T_0},\\
D_2^{*,} &= \langle\sigma^2\rangle\Big\{2\langle j\rangle + \frac{1}{2}\big(\langle j\rangle - 1\big)\big[\langle\sigma^2\rangle\big(1 + \langle q\rangle\big)\\
&\quad - \langle\sigma\rangle\big(1 - \langle q\rangle\big)\big]\Big\}\big(\langle l^2\rangle - \langle l\rangle\big)\frac{\lambda_0^2}{4\gamma},\\
D_3^{*,} &= \langle\sigma^2\rangle\big(\langle j^2\rangle - \langle j\rangle\big)\big(\langle l^2\rangle - \langle l\rangle\big)\frac{\lambda_0^2 T_0}{4\gamma},\\
E^* &= \big[\langle\sigma^2\rangle\langle q\rangle - \langle\sigma\rangle\big(2 - \langle q\rangle\big)\big]\frac{1}{2\gamma T_0},\\
\gamma &= \langle j\rangle + \frac{1}{4}\big(\langle j\rangle - 1\big)\big[\langle\sigma^2\rangle\langle q\rangle - \langle\sigma\rangle\big(2 - \langle q\rangle\big)\big].
\end{aligned}$$

Equation (50) is the differential equation of statistical kinematics near the boundary between solid and vacuum (SKSB equation) taken at the edge point of the balance area (the point (t_m, x_{n-1})). Now the presence of the barrier in the point x_{n+1} breaks the symmetry of the balance area and the consideration of the differential terms at the point x_n is not applicable.

4. Length of extrapolation

Farther on we shall use equation (34) because it is free from the paradox of diffusion. Equation (50) plays the role of the boundary condition for equation (34). Since the distance between the point x_n and the boundary equals $l\lambda_0$ we shall consider equations (34) and (50) in the point $x_b = L - \langle l \rangle \lambda_0$. We assume that $K_+ = K_-$ and $\langle \sigma \rangle = 0$, i.e., both directions of jumping along the x axis have the same probability (an external force is absent).

Equation (50) gives

$$C(t, x_b) = -\frac{1}{E^*}\big(C_t + A^{*\prime} C_{t^2} + D_1^{*\prime} C_{x^2} + D_2^{*\prime} C_{tx^2} + D_3^{*\prime} C_{t^2x^2}\big). \tag{51}$$

We know the solution of the SKS equation under the boundary condition (44) (in [13]) and we can find the values of $C_t,\ C_{t^2},\ C_{x^2},\ C_{tx^2}$ and $C_{t^2x^2}$ in the point x_b – thus the value of $C(t, x_b)$ is attainable from equation (51). Of course this value does not represent the actual concentration inside the sample. It is only a fictitious quantity introduced for approximate determination of the length of extrapolation. Next we expand the concentration into the Taylor series:

$$C(t, x_b + \delta x) = \sum_{i=0}^{\infty} \frac{(\delta x)^i}{i!} C(t, x_b)_{x^i}. \tag{52}$$

We end the summation of the series with $i = i_{\max}$ depending on the needed accuracy and we seek such value of δx for which $C(t, x_b + \delta x) = 0$. In the simplest case of linear extrapolation we have $C(t, x_b) + \delta x C(t, x_b)_x = 0$ and

$$\delta x = -\frac{C(t, x_b)}{C(t, x_b)_x}. \tag{53}$$

Here $C(t, x_b)$ is calculated from equation (51) and $C(t, x_b)_x$ is calculated from the solution of equation (35) under the boundary condition (44).

Now the length of linear extrapolation is found:

$$d^{(0)} = \delta x - \langle l \rangle \lambda_0. \tag{54}$$

Then we obtain the new value $L^{(1)} = L + 2d^{(0)}$ and repeat the calculation till $d^{(n+1)} - d^{(n)} \approx 0$. At last we assume that $d^{(n+1)}$ is the wanted value of d. We see that our length of extrapolation depends not only on the coefficients of diffusion and on the transmission coefficient of the boundary but also on the initial distribution of concentration $C(0,x)$ and on the time of diffusion t. The length of extrapolation should depend on time in order to reproduce the initial distribution of concentration for $t = 0$. The last dependence vanishes for long times when the expansion of concentration into the Fourier series approximates to the first term.

5. Example of hydrogen diffusion in palladium

Let us look on diffusion of hydrogen in a palladium monocrystal. We assume that an external force is absent and $\langle\sigma\rangle = 0$. We shall use the results of our former work [13]. Let us introduce the initial distribution of concentration:

$$C(0,x) = C_0 H(x)\bigl[1 - H(x-L)\bigr], \tag{55}$$

where

$$H(z) = \begin{cases} 1 & \text{for } z > 0, \\ 0 & \text{for } z < 0, \end{cases}$$

is the Heaviside function, L is the length of sample and C_0 is the initial concentration of hydrogen in palladium.

We assume $T_0 = 1$, $\langle j^2\rangle = 2\langle j\rangle^2$, $\langle j\rangle = 1600$ (what corresponds to a diffusion temperature of about 345 K [14]), lattice constant $a = 1$, $L = 10$ and $C_0 = 1$.

We want to obtain the length of linear extrapolation d for two directions of hydrogen diffusion in palladium lattice and for different values of the transmission coefficient $\langle q\rangle$. The dependence of d on the diffusion time t will be shown also.

(a) Let the x axis be parallel to the [100] direction. For this case we have $\langle l^r\rangle = 1$ for arbitrary r, $\lambda_0 = 1/2$ and $\langle\sigma^2\rangle = 2/3$. The corresponding solution of the SKS equation (35) with boundary condition (44) is now given by the function

$$C_1(t,x) = \frac{4C_0}{\pi}\sum_{k=0}^{\infty}\frac{1}{2k+1}\exp[-\alpha_1 t]\sin\left(\frac{2k+1}{L}\pi x\right), \tag{56}$$

where

$$\alpha_1 = \frac{1 + p^2 D_2 - \sqrt{\Delta_1(p)}}{2(A + p^2 D_3)}$$

is a function of k by

$$\Delta_1(p) = 1 + 2p^2(D_2 - 2AD_1) + p^4\bigl(D_2^2 - 4D_1 D_3\bigr),$$

$$p = \frac{\pi}{L}(2k+1).$$

This solution differs from that given in [13] because for the revised values of the coefficients in the SKS equation we have $\Delta_1(p) > 0$ for all values of p.

(b) Let the x axis be parallel to the [110] direction. Now we have $\langle l\rangle = 1.2$, $\langle l^2\rangle = 1.6$, $\langle l^3\rangle = 2.4$, $\langle l^4\rangle = 4$, $\lambda_0 = \sqrt{2}/4$ and $\langle\sigma^2\rangle = 5/6$. The corresponding solution of the SKS equation with boundary condition (44) is given by the function [13]

$$C_2(t,x) = \frac{4C_0}{\pi}\left\{\sum_{k=0}^{k_1'} \frac{1}{2k+1}\exp[-\alpha_2 t]\sin\left(\frac{2k+1}{L}\pi x\right) + \sum_{k=k_1'+1}^{k_2'} \frac{1}{2k+1}\exp[-\alpha_3 t]\sin\left(\frac{2k+1}{L}\pi x\right)\cos(\omega t) + \sum_{k=k_2'+1}^{\infty} \frac{1}{2k+1}\exp[-\alpha_2 t]\sin\left(\frac{2k+1}{L}\pi x\right)\right\}, \tag{57}$$

where $k_1' = 3$, $k_2' = 32$ and

$$\alpha_2 = \frac{1 + p^2 D_2 + p^4 D_5 - \sqrt{\Delta_2(p)}}{2(A + p^2 D_3)},$$
$$\alpha_3 = \frac{1 + p^2 D_2 + p^4 D_5}{2(A + p^2 D_3)},$$
$$\omega = \frac{\sqrt{\Delta_2(p)}}{2(A + p^2 D_3)},$$
$$\Delta_2(p) = 1 + 2p^2(D_2 - 2AD_1) + p^4\left[D_2^2 + 2D_5 - 4(AD_4 + D_1 D_3)\right] + 2p^6(D_2 D_5 - 2D_3 D_4) + p^8 D_5^2.$$

The values of k_1' and k_2' differ from those given in [13] because now we use the revised values of the coefficients in the SKS equation.

The values of the length of linear extrapolation d calculated in the way presented in the preceding chapter for the cases (a) and (b) and for different diffusion times t and transmission coefficients $\langle q \rangle$ are given in tables 1 and 2.

One can see that for $\langle q \rangle = 1$ the length of linear extrapolation $d < 0$. It means that in this case the surface of a crystal is free from the diffusing material. For $\langle q \rangle \to 0$ the length of linear extrapolation d tends to infinity – it agrees with the classical boundary condition for reflecting boundary (Neumann condition) $C(t,0)_x = C(t,L)_x = 0$.

Table 1
The values of the length of extrapolation d after n steps of iteration for the diffusion time $t = 10^7$. The number of decimal digits reflects numerical accuracy of the results.

	[100]		[110]	
	$\langle q \rangle = 1$	$\langle q \rangle = 10^{-2}$	$\langle q \rangle = 1$	$\langle q \rangle = 10^{-2}$
d	−0.488359	0.24217	−0.412266	0.2773
n	3	9	3	9

Table 2
The values of the length of extrapolation d after n steps of iteration for the diffusion time $t = 10^5$. The series (56) and (57) were summed up to $k = 50$. Further increase of k does not change the results within the range of assumed numerical accuracy.

	[100]		[110]	
	$\langle q \rangle = 1$	$\langle q \rangle = 10^{-2}$	$\langle q \rangle = 1$	$\langle q \rangle = 10^{-2}$
d	-0.484216	0.758471	-0.410438	0.51931
n	3	4	3	5

The application of the length of extrapolation may be illustrated as follows. For the given value of the transmission coefficient $\langle q \rangle$ we find the length of extrapolation $d^{(0)}$ and the extrapolated length of sample $L^{(1)} = L + 2d^{(0)}$. This value should be introduced to the wave number p instead of L, i.e., $L^{(1)}$ influences the values of the exponential and trigonometric functions forming our solutions $C_1(t, x)$ or $C_2(t, x)$. The term C_0 remains the same as formerly. One has to control the values of k_1' and k_2' which may be changed. As one may see the function Δ_2 changes its sign for k_1 and k_2 – the values of k_1' and k_2' are the highest integers which are not higher than k_1 and k_2, respectively. For the value $L^{(1)}$ we find new value $d^{(1)}$ and so on, until $d^{(n+1)} - d^{(n)} \simeq 0$. One can see in tables 1 and 2 that the lower is $\langle q \rangle$ and the longer is t the higher ordered approximation should be used (n grows).

We have three cases: (1) $d > 0$, (2) $d < 0$, and (3) $d = 0$. The last case do not require any comment. For the second case the layers of thickness $|d|$ adjacent to the boundaries are free from the diffusing atoms. The illustrations of the cases (1) and (2) are given in figures 7–10. The anisotropy of diffusion shown in these figures was commented in [13]. Now we have $D_1^{[100]} \simeq 3.47 \times 10^{-5}$ and $D_1^{[110]} \simeq 4.34 \times 10^{-5}$. The relative difference between concentrations given by diffusion in [100] and [110] directions becomes smaller for shorter times when the concentrations are higher. The influence of the boundary's transmission coefficient $\langle q \rangle$ on the planar diffusion of hydrogen in a palladium monocrystal was considered by us as an example of application of our approach and the detailed discussion of the diffusion mechanism is not our aim.

6. Conclusions

In this paper the new approach to the diffusion problem is presented in detail. We find a particular area (called the balance area) where the principle of the conservation of events (jumps or collisions) is fulfilled in the kinematic plane t, x. That balance area is a random quantity. The equation of the balance of events allows one to obtain the differential equation which governs the diffusion process. The geometric structure of the balance area influences the form of the differential equation. That structure depends on the statistical distributions of the lengths of jumps λ and of the time intervals between them Δt. Particularly, the concentration derivative of the second

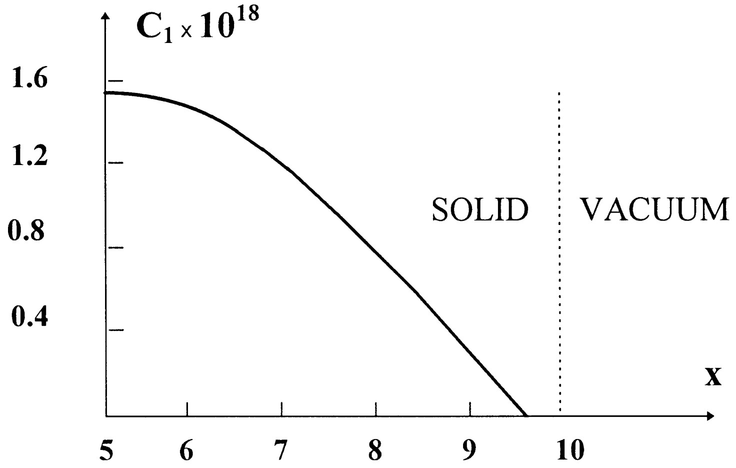

Figure 7. The dependence of the hydrogen concentration C_1 on the distance x in the palladium monocrystal. The x axis lies on the [100] direction. The time of diffusion $t = 10^7$ and the transmission coefficient of the boundary $\langle q \rangle = 1$. The additional information is given in the text of the paper.

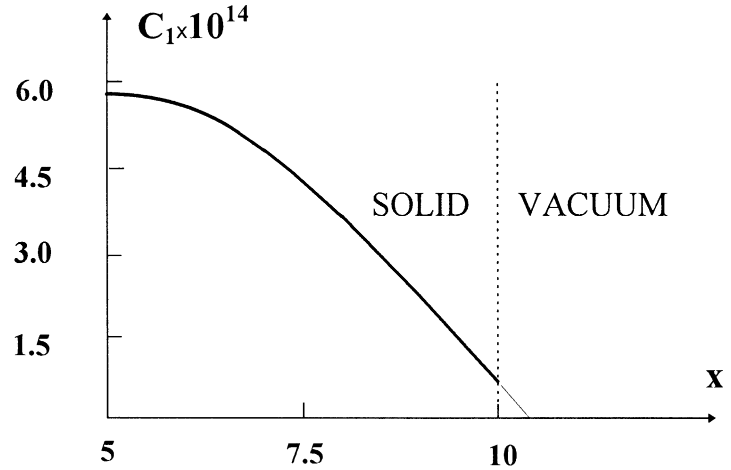

Figure 8. The dependence of the hydrogen concentration C_1 on the distance x in the palladium monocrystal. The transmission coefficient of the boundary $\langle q \rangle = 10^{-2}$. For additional information see figure 7.

order with respect to time must appear in the differential equation when one wants to take into account the random variability of Δt. The classical equations of Fick and of Cantello with their failures are obtained for constant Δt at the edge point of the balance area. The differential equation free from the "paradox of diffusion" (SKS equation) is available at the centre point of the balance area. The calculations are performed for the discrete statistical distributions of Δt and λ which characterize a solid.

The balance of events near the boundary between a medium and vacuum leads to another differential equation (SKSB equation) which, together with the SKS equation,

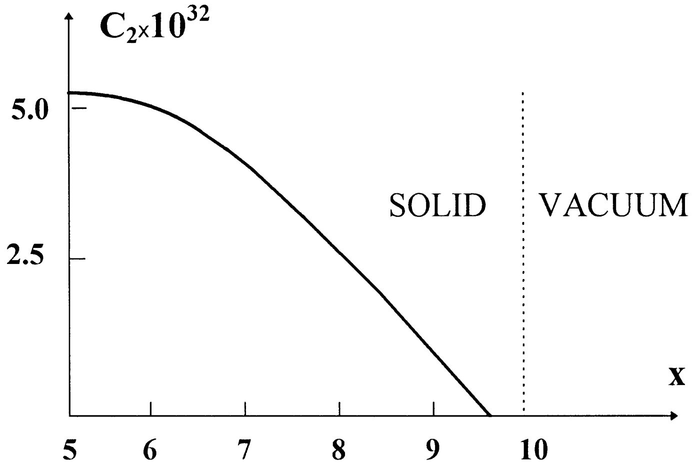

Figure 9. The dependence of the hydrogen concentration C_2 on the distance x in the palladium monocrystal. The x axis lies on the [110] direction. The time of diffusion $t = 10^7$ and the transmission coefficient of the boundary $\langle q \rangle = 1$. The additional information is given in the text of the paper.

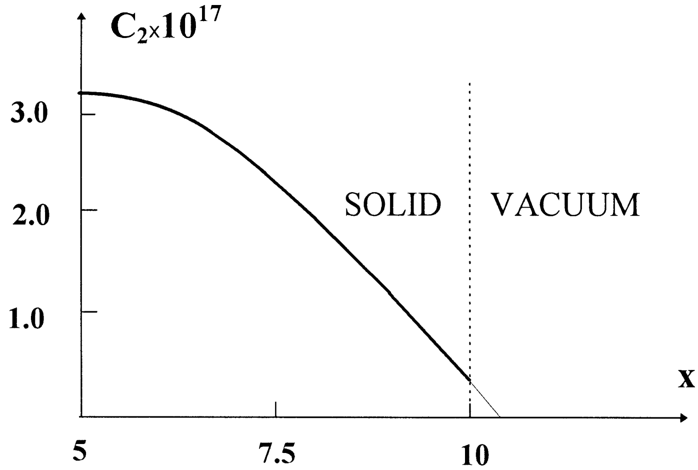

Figure 10. The dependence of the hydrogen concentration C_2 on the distance x in the palladium monocrystal. The transmission coefficient of the boundary $\langle q \rangle = 10^{-2}$. For more information see figure 9.

allows one to introduce the boundary condition using the concept of the length of extrapolation. Our length of extrapolation d depends not only on $\langle \lambda \rangle$ and on the transmission coefficient of the boundary $\langle q \rangle$ but also on all the parameters of diffusion and on the time t and it can be applied far from the stationary state contrary to the classical length of extrapolation d_c.

The obtained results may be particularly useful when the length of extrapolation cannot be treated as an infinitesimal quantity, i.e., for diffusion in thin layers and membranes or when the transmission coefficient of the boundary is very small. Our approach may serve as a reference to verify different mechanisms of atoms' migration by further inspection into the statistical distributions of Δt and λ. The SKS equation together with the boundary condition in the form of the SKSB equation give a new description of the diffusion phenomenon in solids which goes beyond the classical approach.

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