Dynamics of the reaction-diffusion system $A + B \to 0$ with input of particles

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We study dynamics of filling of an initially empty finite medium by diffusing particles $A$ and $B$, which arise on the surface upon dissociation of $AB$ molecules, impinging on it with a fixed flux density $I$, and desorb from it by the reaction $A + B \to AB \to 0$. We show that once the bulk diffusivities differ ($p = D_A/D_B < 1$), there exists a critical flux density $I_c(p)$, above which the relaxation dynamics to the steady state is qualitatively changed: on time dependences of $c_A/c_e$ ($c_e$ being the steady state concentration at $t \to \infty$) a maximum appears, the amplitude of which grows both with $I$ and with $D_B/D_A$ ratio. In the diffusion-controlled limit $I \gg I_c$ at $p \ll 1$ the reaction ”selects” the universal laws for the particles number growth $N_A = N_B \propto t^{1/4}$ and the evolution of the surface concentrations $c_{As} \propto t^{-1/4}, c_{Bs} \propto t^{1/4}$, which are approached by one of the two characteristic regimes i) and ii) with the corresponding hierarchy of the intermediate power-law asymptotics. In the first of these $c_{As}$ goes through a comparatively sharp $\max(c_{As}/c_e) \propto t^{1/6}$, the amplitude of which is $p$-independent, in the second one $c_{As}$ goes through a plateau-like $\max(c_{As}/c_e) \propto p^{-1/4}$, the amplitude of which is $I$-independent. We demonstrate that on the main filling stage the evolution of the $N(t)/N_e, c_{As}(t)/c_e$ and $c_{Bs}(t)/c_e$ trajectories with changing $p$ or $J$ between the limiting regimes i) and ii) is unambiguously defined by the value of the scaling parameter $K = p^{3/2}J$ ($J$ being the reduced flux density) and is described by the set of scaling laws, which we study in detail analytically and numerically. In conclusion, we analyze specific features of the long-time relaxation dynamics and calculate exactly the relaxation rate $\omega(p, J)$.

I. INTRODUCTION

For the last decade the reaction-diffusion system $A + B \to 0$, where unlike species $A$ and $B$ diffuse and irreversibly react in the bulk of a $d$-dimensional substrate, has acquired the status of one of the most popular objects in nonequilibrium statistical physics [1]. Two situations have been investigated most intensively: (i) dynamics of the $A + B \to 0$ annihilation in an infinite system with initially homogeneously (randomly) and equinomically distributed reactants, in which below the critical dimension $d_c = 4$ a dynamical clustering develops (fluctuation-induced like-particle domains formation) and, as a result, an anomalous reaction deceleration arises (Ovchinnikov and Zeldovich, 1978 [2], Toussaint and Wilczek, 1983 [3]); (ii) behaviour of the dynamic reaction front in an infinite system with initially spatially separated reactants (Galfi and Racz, 1988 [4]), and structure of the steady state front in a finite system, at the ends of which are injected equal currents of $A$'s and $B$’s particles (Ben-Naim and Redner, 1992 [5], Cornell and Droz, 1993 [6]).

Recently, we have shown [6], that in another wide class of RD system, where reaction and diffusion are spatially separated ( i.e. reaction proceeds on the surface and the medium and diffusion proceeds in its bulk ) the interplay between reaction and diffusion acquires qualitatively new features and leads to the threshold self-organizing dynamics of the $A + B \to 0$. It has been found that once particles $A$ and $B$ diffuse at different mobilities from the bulk of finite medium onto the surface and die on it by the reaction $A + B \to 0$, there should exist some threshold difference in the initial numbers of $A$ and $B$ particles , $\Delta c_e$ above which the process of their death , instead of usual deceleration, starts to accelerate autocatalytically. Moreover, it has been demonstrated [6] that in the diffusion-controlled limit $\Delta \to \infty$ a new critical phenomenon develops in the system - annihilation catastrophe, which arises as a result of self-organizing explosive growth (drop) of the surface concentrations of, respectively, slow and fast particles (concentration explosion) and manifests itself in the form of an abrupt singular jump in the desorption flux relaxation rate. In the limit of strong difference of diffusivities the annihilation catastrophe leads to the phenomenon of abrupt disappearance of the flux (flux breaking effect), which may pretend to be one of the most dramatic manifestations of the reaction-diffusion interplay.

The aim of this paper is, in contrast to the pure annihilation problem $A + B \to 0$, to consider dynamics of filling of an initially empty finite medium by diffusing particles $A$ and $B$, which arise on the surface upon dissociation of $AB$ molecules, impinging on it with a fixed flux density $I$, and desorb from it by the reaction $A + B \to AB \to 0$. We assume that the density of the input flux $J$ is not too large and (or) the reaction rate constant is sufficiently large so that in the process of filling up to the steady state the surface coverages by adatoms $A_{ads}$ and $B_{ads}$ remain small enough and, therefore, the reflection of $AB$ molecules from the occupied sites can be neglected. In addition, we assume that the particles exchange rates between the surface and the subsurface layer are great, and already at early stages of diffusion into the bulk a quasiequilibrium
is reached between the surface and the subsurface layer. Finally, we assume that in our 2d-reaction + 3d-diffusion problem diffusion smooths out lateral fluctuations and, hence, planar distribution of A’s and B’s particles is sustained mesoscopically uniform, so that 1) the desorption flux density may be described by the mean-field expression and 2) the problem can effectively be considered as one dimensional. In the framework of these assumptions we formulate a closed system of nonlinear boundary value diffusion problems, which we then investigate in detail analytically and numerically.

II. MODEL

Let the both surfaces $X = \pm \ell$ of an initially empty infinitely extended slab of thickness $2\ell$ be hit with a fixed-densit $I$ flux of AB molecules, which dissociate on unoccupied sites to atadoms $A_{ads}$ and $B_{ads}$ with probability 1. Adatoms $A_{ads}$ and $B_{ads}$ migrate along the surface and either, on running into one another, irreversibly desorb by the reaction $A_{ads} + B_{ads} \rightarrow AB \rightarrow 0$ or diffuse into the bulk, gradually filling it to some steady state concentration $c_c(I)$ (Fig.1). Because of planar spatial homogeneity (see below), the bulk diffusion flux must be directed normally to the surface plane, that is, the problem is effectively one dimensional. The boundary conditions for the bulk diffusion equations

$$\partial t c_i = D_i \partial x^2 c_i \quad (i = A, B)$$

(1)

and in the subsurface layer

$$a_i c_i = I_i^b - I_i^D \bigg| _{s}.$$ (3)

Here $\rho_i$ is the surface concentration of $i$-atadoms $(cm^{-2})$, $c_i = c_i \big|_{x=\ell}$ is the concentration of $i$-particles in the subsurface layer $(cm^{-2})$, $a$ is the lattice parameter, $I^a$ and $I^d$ are adsorption and desorption flux densities, $I^b = I^a - I^d = \Gamma_i^s \rho_i - \Gamma_i^b c_i \theta_0$ is the surface-to-subsurface layer flux density, where $\Gamma_i^s$ and $\Gamma_i^b$ are the rate constants of $i$-particles transition from the surface into the subsurface layer and back, respectively, $\theta_0 = 1 + \theta_A - \theta_B$ is the fraction of vacant sites on the surface, which we take to be close to unity ($\theta_0 \ll 1$), $(I^b)^D = D_i \partial x c_i \big|_{x=\ell}$ is the diffusion flux density at the surface (by symmetry, we consider the interval $[0, \ell]$ only with the condition $\partial x c_i \big|_{x=0} = 0$). We assume that the subsurface layer - surface barrier is not much different from the diffusion barrier in the bulk $(\Gamma_i^b \sim D_i/a)$, and probability of the atadoms transition to the subsurface layer is much greater than probability of their desorption $(\Gamma_i^b \gg I^a)$. Then, prior to desorbing, the particles multiply go to the subsurface layer and back, and already at early stages of diffusion into the bulk a quasiequilibrium must be established between the surface and the subsurface layer, $\rho_i \approx f_i c_i$, where $f_i = \Gamma_i^b/\Gamma_i^s$ is the surface segregation coefficient. Moreover, if the surface segregation is not enough strong (at elevated temperatures usually $f \sim (1 - 10^2)$), and the system size is quite large, $\ell \gg f_i$, then at comparatively short (in $\ell^2/D_i$ scale) times $f_i \ll t^D_f = \sqrt{D_i \ell} \ll \ell$, when the number of particles in the bulk (per surface unit) $N_i = f_i c_i dX \sim c_i \sqrt{D_i \ell}$ much exceeds that on the surface $f_i c_i$, the capacities of the subsurface layer $(I^D |_{s} = I^b)$ and of the surface $(f_i c_i |_{s} \ll I^D |_{s})$ may be neglected, therefore conditions (2) and (3) are degenerated to the following

$$N_i = I_i^D |_{s} = I^a - I^d.$$ (4)

According to Refs. [10], [11], and [12], in a distributed d-dimensional system $A + B \rightarrow 0$ with injection of A and B particles, with their difference being strictly conserved (correlated landing), a critical (marginal) dimensionality, above which no fluctuation-induced segregation of A and B occurs, equals $d_c = 2$ (2d-reaction + 2d-diffusion). It is to be expected that in our case (2d-reaction + 3d-diffusion) 3d-diffusion smoothes out lateral fluctuations, and a planar distribution of A and B particles is sustained mesoscopically uniform. So, the desorption flux density may be described by the mean-field expression $I^d = k_{PA} B D_B$. From the condition $I^b = I^a - I^d$ it follows

$$\rho_i = f_i c_i \theta_0 [1 + (I^a - I^d)/(I^a + 1/I^b)],$$

(5)

therefore, taking $I^a - I^d \ll I^a$, we obtain

$$I^d = \kappa c_A c_B \theta_0^2 [1 + (I^a - I^d)(1/I^A + 1/I^B)]$$

(6)

where $\kappa = k_f A B$ is the effective reaction rate constant $(cm^3/s)$. The above requirement $I^a, I^d \ll I^a$ imposes on the concentrations limitations $I^a/\Gamma_A^s \ll c_A \ll \Gamma_b^s/\kappa, I^b \ll c_B \ll \Gamma_b^s/\kappa$, the lower boundary of which defines the conditions for the crossover to the subsurface layer-surface quasiequilibrium regime. Restrictions on the flux densities $I^d, I^a \ll \Gamma_b^s \Gamma_A^b / \kappa$ follow herefrom. Taking into account the reflection from occupied sites, we write $I^a = \theta_0^2$ to obtain $I^a - I^d = \theta_0^2 (I^a - \kappa c_A c_B)$, where factor $\chi = [1 + \theta_0 ((\kappa/\Gamma_B^s) c_A + (\kappa/\Gamma_A^s) c_B)]^{-1} \approx 1$. So, after a short-term transient stage $t \gg t_{tr} = \max(f_i^D/D_i)$ the boundary conditions take the form

$$N_i = D_i \partial x c_i |_{s} = \chi_0^2 (I - \kappa c_A c_B),$$

(7)

where $1 - \chi_0^2 = 1$. We assume that on a transient stage the desorption can be neglected, i.e. $t_{tr} \ll t_q$, where $t_q$ is a characteristic time at which the desorption flux becomes comparable with the input flux $I^d \sim I$. Using then the Laplace transform, at $t < t_q, I^D_f = \ell^2/D_i$ one can easily obtain the complete solution of (1)-(3),
where from at $t \gg t_{is}$ (here $t_{is} = D_i/(\Gamma_i)^2$ and $t_{is} = f_i^2/D_i$) it follows

\[
N_i = N_i^{(0)} \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{t_{is}}{\ell} \right)^{1/2} + \cdots \right],
\]

\[
c_{is} = c_{is}^{(0)} \left[ 1 - \frac{\sqrt{\pi}}{2} \left( \frac{t_{is}}{\ell} \right)^{1/2} + \cdots \right],
\]

\[
\rho_i = f_i c_{is} \left[ 1 + \frac{\sqrt{\pi}}{2} \left( \frac{t_{is}}{\ell} \right)^{1/2} + \cdots \right],
\]

where $N_i^{(0)} = It$ and $c_{is}^{(0)} = 2D_i^{3/2}$ are the solutions of (1), (4) with the initial conditions $c_i(X, 0) = 0$ at $\chi_0^2 = 1$ and $D^4/I \to 0$. From (5) it is seen that the influence of the transient stage rapidly decays in time. So, we are mainly interested here in the system’s behavior of the transient stage rapidly decays in time. Therefore in the steady state ($t \gg t_{tr}$) we shall take $c_i(X, 0) = 0$ as the initial condition for (1), (4). According to (5), the condition $t \sim \ell^2/(D_A D_B) \ll 1$ is reduced to the requirement $t \ll \ell^2/(D_A D_B)$, whence it follows $I \ll \sqrt{D_A D_B}/\kappa l_{tr}$. Introducing the index \(^H H^\circ\) (heavy) for the slower diffusing species and the index \(^L L^\circ\) (light) for the faster one, taking $\chi_0^2 = 1$ and going to dimensionless variables, we finally come to the boundary value diffusion problem

\[
\frac{\partial h}{\partial \tau} = \nabla^2 h, \quad \frac{\partial l}{\partial \tau} = (1/p)\nabla^2 l, \quad (6a)
\]

\[
\nabla h \big|_s = (1/p)\nabla l \big|_s = J - h_s l_s, \quad (6b)
\]

with the conditions of symmetry $\nabla(h, l) \big|_{x=0} = 0$ and the initial conditions $h(x, 0) = l(x, 0) = 0$. Here $h(x, \tau) = c_{is}^H/c_s$ and $l(x, \tau) = c_{is}^L/c_s$ are the reduced flux densities, $J = I/I_s$ is the reduced flux density, $\tau = D_H t/\ell^2$ is the nondimensional time, $p = D_H/D_L \ll 1$ is the ratio of species diffusivities, $I_s = \kappa c_s^H = (D_H/\sqrt{\kappa})^2$ and $c_s = D_H/\ell l$ are the characteristic flux density and concentration scales, from which the relaxation dynamics to the steady-state becomes diffusion-controlled (in the reaction-controlled regime the both species are distributed uniformly $c_s = N/\ell = I t/\ell$, so, from the condition $t_{tr} \sim \sqrt{D_A D_B}$ is reduced to the requirement $t_{tr} \ll \ell^2/(D_A D_B)$. By comparing $t_{tr}$ with the characteristic diffusion time of heavy species $t_{D} \sim \ell^2/D_H$, we obtain $s = (D_H/\sqrt{\kappa})^2$).

According to (5), with an accuracy to a negligibly small capacity of the surface layer ($\tau \gg t_{tr}$) we have $s = (D_H/\ell^2)^2$, \(d_i = f_i/\ell \ll 1\), equal amounts (per surface unit) of $H$ and $L$ particles diffuse into the bulk $N_H = N_L = N$, therefore in the steady state ($\tau \to \infty$)

\[
h_e = l_e = N_e = \sqrt{J},
\]

where $N = N/N_e$ is the reduced number of particles and $N_e = c_e \ell = D_H/\kappa$ is the characteristic scale of the number of particles. In dimensionless variables requirement $1 - \chi < \ll 1$ with account of $I^0 \sim D_0/\ell$ leads to the conditions $h_s \ll I^0 l/\ell D_H \sim p^{-1}(\ell/a)$ and $l_s \ll I^0 l/\ell D_L \sim \ell/a$ whence there follows a limitation on the reduced flux density $l_e = \sqrt{J} \ll \ell/a$ and, therefore, $J \ll J^0 \sim (\ell/a)^2$. The requirement $\theta_1 \sim a^2 \rho_i \ll 1$ leads to the conditions $h_s \ll (\kappa/a^2 D_H)_{D_H}^2$ and $l_s \ll (\kappa/a^2 D_L)_{D_L}^2$, whence by assuming $d_H \sim d_L$ we obtain $\rho \sim J^0 \sim (\kappa/a^2 D_H)^2 d_H^2$. Finally, the requirement $\tau_{tr} \sim (1/J \sqrt{p})$ leads to the condition $\rho \sim \rho^0 \sim d_H^2/\sqrt{p}$. In macroscopic systems the quantities $J^0_x$ and $J^0_y$ are very large (for example at $\ell \sim 10^{-1} \text{cm}$ and $f_H \sim f_L \sim 10$ a we have $J^0_x \sim 10^{14}$ and $J^0_y \sim 10^{12}/\sqrt{p}$). At temperatures of intensive desorption $(\kappa/a^2 D_H \geq 1)$ the quantity $J^0_y$ is as large. So, the reduced flux density $J$ can, formally, be taken as being unlimitedly variable.

### III. TRANSITION IN RELAXATION DYNAMICS

At a high enough density of the input flux, $J$, a quasi-equilibrium $J^q = h_s l_s \sim J$ should be established well before the particles distribution in the bulk becomes uniform. In view of the fact that at $p < 1$ there must be $l_s < h_s$, this means $h_e h_s > 1$, i.e. at sufficiently large $J$ the $H$ particles surface concentration should initially grow to some maximum $h_s^M > h_e$ and then, as a result of diffusion into the bulk, relax asymptotically to its steady state value, $h_e$, from above. We thus conclude that at $p < 1$ there ought to exist a critical flux density $J_c(p)$, above which the relaxation character is qualitatively changed. In this section we give a linear analysis of the long-time relaxation dynamics, in terms of which we find the relaxation rate $\omega(J, p)$ and the exact value of $J_c(p)$.

We introduce the new variables $\hat{h} = h_e - h, \hat{l} = l_e - l$ and $\bar{n} = N_e - N$. Then, instead of (6) we have

\[
\frac{\partial \hat{h}}{\partial \tau} = \nabla^2 \hat{h}, \quad \frac{\partial \hat{l}}{\partial \tau} = (1/p)\nabla^2 \hat{l}, \quad (7a)
\]

\[
\nabla \hat{h} \big|_s = (1/p)\nabla \hat{l} \big|_s = -\sqrt{J}(\hat{h}_s + \hat{l}_s) + \hat{h}_s \hat{l}_s \quad (7b)
\]

with $\nabla(\hat{h}, \hat{l}) \big|_{x=0} = 0$. In a long-time limit $\hat{h}, \hat{l} \sim \tau \to \infty \to 0$ the nonlinear term may be neglected, so by satisfying (7), we find the leading terms of the long-time relaxation in the form

\[
\hat{h} = A_H \cos(\sqrt{\omega}x)e^{-\omega \tau}, \quad \hat{l} = A_L \cos(\sqrt{\omega}x)e^{-\omega \tau}, \quad (8)
\]

where $A_H = (\sqrt{p} \sin(\sqrt{\omega}/\sin(\sqrt{\omega}))A_H$, and the relaxation rate $\omega(p, J)$ is defined by the least positive root of the equation

\[
\omega(p, J) = 0.
\]
\[ \cot \sqrt{\omega} = \sqrt{\frac{\omega}{J}} - \sqrt{p \cot \sqrt{\rho \omega}} \]  

(9)

It follows from (8) that long-time asymptotics of surface concentrations as a function of the particles number \( \hat{n} = \int_0^1 h dx = \int_0^1 \omega dx \) has the form

\[ \hat{h}_s |_{\hat{n} \to 0} = (\sqrt{\omega} \cot \sqrt{\omega})\hat{n}, \hat{l}_s |_{\hat{n} \to 0} = (\sqrt{\rho \omega} \cot \sqrt{\rho \omega})\hat{n}, \]  

(10)

whence

\[ r_s = \frac{\hat{h}_s}{l_s} |_{\hat{n} \to 0} = \frac{\cot \sqrt{\omega}}{p \cot \sqrt{\rho \omega}} = -1 + \frac{\omega}{J_p} \tan(\sqrt{\rho \omega}). \]  

(11)

According to (9), with growing \( J \) the relaxation rate is increased from \( \omega = 2\sqrt{J} \) in the reaction-controlled limit \( \sqrt{\omega} \ll 1 \)

\[ \omega = 2\sqrt{J}(1 - \frac{1}{3} p \sqrt{\omega} + \cdots), \quad \sqrt{J} \ll 1 \]

to a maximal

\[ \omega = \omega_m(p)(1 - b(p)/\sqrt{\omega} + \cdots), \quad \sqrt{J} \gg 1 \]

in the diffusion-controlled limit \( \sqrt{J} \gg 1 \), the maximal relaxation rate \( \omega_m(p) \) growing herewith from

\[ \omega_m(1) = \pi^2/4 \]

at \( p \to 1 \) to

\[ \omega_m(0) = 4.1158... \]

at \( p \to 0 \) \( b(p) \) changes from \( b(1) = 1 \) to \( b(0) = 1.348... \). So, in accord with (9),(10), we conclude that at \( p < 1 \) there exists a critical relaxation rate \( \omega_c = \pi^2/4 \), which is reached at a critical flux density

\[ J_c = \frac{\pi^2}{4p} \tan^2(\pi\sqrt{p}/2), \]  

(12)

above which the quantity \( \hat{h}_s \) reverses its sign \((+ \to -)\), i.e. the character of the surface concentration relaxation of \( H \) particles qualitatively changes: at \( J < J_c \) the \( h_s \) value grows to \( h_c \) monotonously, whereas at \( J > J_c \) the value of \( h_s \) reaches initially a maximum and then relaxes to \( h_c \) from above (Fig.2). According to (11), as \( J \) grows, the ratio \( r_s = \hat{h}_s/l_s |_{\hat{n} \to 0} \) is changed from 1 at \( \sqrt{J}/J_c \ll 1 \)

\[ r_s = 1 - \frac{2}{3} \sqrt{J}(1 - p) + \cdots, \quad \sqrt{J}/J_c \ll 1 \]

to -1 at \( \sqrt{J}/J_c \gg 1 \)

\[ r_s = -1 + \frac{\omega_m}{J_p} \tan(\sqrt{\rho \omega_m}), \quad \sqrt{J}/J_c \gg 1 \]

as is illustrated for \( p = 0.1 \) in Figs.3 and 4, the first of which demonstrates the dependences of \( r_s \) on \( J/J_c \), calculated from (9), (11), the second one demonstrates the time dependences of \( h_s/h_c \) and \( l_s/l_c \) at \( J = J_c \) and \( J = 10^3 \), numerically calculated from (6).

Eqs. (10) and (11) carry no information on the initial conditions, so they, clearly, remain valid at any initial number of particles \( N_H(0) = N_L(0) = N(0) \) and at their arbitrary initial distribution. In this case, according to (11), if the initial distribution is uniform, and \( \hat{n} > 0 \), i.e. the initial particles number is less than the steady state one, then \( J > J_c \) the \( h_s \) value passes a maximum and relaxes to the steady state level from above, whereas if the initial distribution is uniform, and \( \hat{n} < 0 \), i.e. the initial particles number is greater than the steady state one, then \( J > J_c \) the \( h_s \) value passes a minimum and relaxes to the steady state level from below.

In the present paper the main attention will be focused on the behavior of the surface concentrations and the growth dynamics of the particles number in the diffusion-controlled limit \( J \gg J_c \), which is of greatest interest. As at \( \omega \tau > 1 \) deviations from the steady state become exponentially small then, clearly, in the diffusion-controlled limit the main nonlinear kinetic effects evolve in times \( \tau \ll 1 \) when the diffusion of \( H \) particles proceeds, actually, into a semi-infinite medium. In the next Section we shall consider the dynamics of behavior of \( h_s, l_s \) and \( N \) at \( \tau \ll 1 \), taking into account the reflection from the boundary \( x = 0 \), and then, in Section V, we shall come back to an analysis of the long-time relaxation and obtain expressions for the \( A_t(J,p) \) amplitudes.

IV. DIFFUSION OF H PARTICLES INTO A SEMI-INFINITE MEDIUM \((\tau \ll 1)\).

By applying the Laplace transform \( \hat{f}(s) = \hat{L} f(\tau) = \int_0^{\infty} e^{-st} f(\tau) d\tau \) to Eqs. (6), one can easily obtain a formal solution of problem (6) in the form

\[ \hat{h}(x,s) = \hat{h}_s \cosh(x \sqrt{s}/c) \cosh \sqrt{s}/c, \quad \hat{l}(x,s) = \hat{l}_s \cosh(x \sqrt{sp}/c) \cosh \sqrt{sp}/c \]  

(13)

with the boundary conditions (6b), which, can, for convenience, be represented as

\[ \hat{N} = \hat{h}_s \frac{\tanh \sqrt{s}}{\sqrt{s}}, \quad \frac{l_s \tanh \sqrt{sp}}{\sqrt{sp}} \]

(14)

and

\[ \hat{N} = \frac{J}{s^2} - s^{-1} \hat{L}(h_s l_s). \]  

(15)

The system of equations (14) and (15) comprehensively defines the behavior of \( N(\tau), h_s(\tau), \) and \( l_s(\tau) \) which, in turn, define the evolution of spatial particles distribution via Eqs.(13). In the limit of our interest here \( \tau \ll 1 \) the first of Eqs.(14) is reduced to

\[ \frac{\hat{N}}{\sqrt{s}} = \frac{\hat{h}_s}{\sqrt{s}}(1 - 2e^{-2\sqrt{s}} + \cdots), \]  

(16)
where in expansion of \( \tanh \sqrt{s} \) in power-series of \( e^{-2\sqrt{s}} \)
the leading term \( O(e^{-1/\tau}) \), which takes into account the
contribution of reflection from the boundary \( x = 0 \), is
retained. The second characteristic time \( \tau_L = p \), at which
the diffusive length \( L \) of particles becomes equal to the
system’s size, separates two temporal regions, \( \tau \ll p \) and
\( \tau \gg p \), within which the growth dynamics of the particles
number is qualitatively different. Within \( \tau \ll p \) the \( L \)
particles diffusion proceeds, actually, into a semi-infinite
medium, and from (14) we have

\[
\dot{\hat{N}} = \frac{\dot{i}_s}{\sqrt{sp}} (1 - 2e^{-2\sqrt{s}} + \cdots).
\]

(17)

In the opposite limit, \( \tau \gg p \), the \( L \) particles distribution
becomes practically uniform, and from (14) it follows

\[
\dot{\hat{N}} = \frac{\dot{i}_s}{\sqrt{sp}} \left( 1 - \frac{1}{3}sp + \cdots \right),
\]

(18)

where in expansion of \( \tanh \sqrt{s} \) in power-series of \( \sqrt{sp} \)
the leading term \( O(p/\tau) \) is retained, which in the case of
the power growth \( l_s \propto \tau^n \) leads to the law

\[
N = l_s \left[ 1 - \frac{n}{3} \left( \frac{p}{\tau} \right) + \cdots \right].
\]

(19)

In what follows, we shall consider the dynamics of
crossover from the adsorption-controlled regime to the
diffusion-controlled one first in the limit of \( \tau \ll p \), when
\( H \) and \( L \) particles diffuse into a semi-infinite medium,
then in the limit \( p \ll \tau \ll 1 \), when \( H \) particles diffuse
to a semi-infinite medium at a uniform \( L \) particles dis-
tribution.

A. Diffusion of \( H \) and \( L \) particles into a semi-infinite
medium (\( \tau \ll p \)).

On neglecting the reflection from the boundary \( x = 0 \),
we have from (16) and (17)

\[
\dot{h}_s = \frac{\dot{i}_s}{\sqrt{p}} = \dot{\hat{N}} \sqrt{s}.
\]

(20)

The system of equations (15) and (20) is reduced to
the nonlinear integral equation that cannot be solved in
the general form. Our aim will be, starting with (20),
to obtain asymptotics for the solution of (15)-(17) in
the limits of \( J^D \big|_s \simeq J \gg J^d \) (adsorption-controlled regime)
and \( J^d \simeq J \gg J^D \big|_s \) (diffusion-controlled regime).

1. Adsorption-controlled regime (\( \tau \ll p, \tau_s \))

By assuming \( N = J\tau \), i.e. by neglecting the contribu-
tion of desorption, from (20) we obtain

\[
h_s = l_s/\sqrt{p} = (2/\sqrt{\pi})J\sqrt{\tau},
\]

whence it follows that the adsorption-controlled
asymptotics has the form

\[
h_s = \frac{2}{\sqrt{\pi}} J\sqrt{\tau}(1 + g_H),
\]

\[
l_s = \frac{2}{\sqrt{\pi}} J\sqrt{\tau}(1 + g_L),
\]

(21)

\[
N = J\tau(1 + g_N),
\]

where \( g_i \ll 1 \). Thus, the condition of smallness of des-
orption flux is \( J^d = h_s l_s = (4/\pi)p J^2 \sqrt{p} \tau \ll J \), whence it
follows that it takes place at \( \tau \ll \tau_q = 1/J^2 \).
Substituting the expression for \( J^d \) into (15), we obtain

\[
\dot{\hat{N}} = J\tau(1 - \frac{2}{\pi} \frac{\tau}{\tau_q} + \cdots).
\]

Substituting further this expression into (16) and (17), with an accuracy to
the leading terms, we finally obtain

\[
\dot{h}_s = \frac{\dot{i}_s}{\sqrt{p}} = \frac{8}{3\pi} \left( \frac{\tau}{\tau_q} \right) + 2\sqrt{\pi} \text{erfc} \frac{1}{\sqrt{\tau}} + \cdots,
\]

\[
\dot{l}_s = \frac{\dot{i}_s}{\sqrt{p}} = \frac{8}{3\pi} \left( \frac{\tau}{\tau_q} \right) + 2\sqrt{\pi} \text{erfc} \frac{1}{\sqrt{\tau}} \cdots,
\]

(22)

\[
\dot{g}_N = -\frac{2}{\pi} \left( \frac{\tau}{\tau_q} \right) + \cdots,
\]

where the function \( \text{erfc}(\eta) = e^{-\eta^2}/\sqrt{\pi} - \eta \text{erf}(\eta) \)
at \( \eta \gg 1 \) has the asymptotic form \( e^{-\eta^2}(1 - 3/2\eta^2 +
\cdots)/2\sqrt{\pi}\eta^3 \).

2. Diffusion-controlled regime (\( \tau_q \ll \tau \ll p \)).

In this limit, by neglecting the contribution of the transient
region, i.e. by assuming \( \tau_q \to 0 \), from (20) and (15) we have

\[
h_s = l_s/\sqrt{p}, \quad h_s l_s = J,
\]

whence we find \( h_s = h_s p^{-1/4}, l_s = l_s p^{1/4} \), and,
subsequently, according to (20), we obtain \( N = 2\sqrt{J}/p\sqrt{p}^{-1/4}\sqrt{\tau} \) and, hence, \( J^D \big|_s = J((2\pi)^{1/2}/\sqrt{\tau}) \). Thus, the
diffusion-controlled asymptotics has the form

\[
h_s = h_s p^{-1/4}(1 + \lambda_H),
\]

\[
l_s = l_s p^{1/4}(1 + \lambda_L),
\]

(23)

\[
N = \frac{2}{\sqrt{\pi}} N_s p^{-1/4} \sqrt{\tau}(1 + \lambda_N),
\]
where \( \lambda \ll 1 \). Substituting (23) into Eqs. (15), (16), and (17), we find that, asymptotically, \( \lambda_H \) and \( \lambda_L \) are connected by relationships

\[
\lambda_H - \lambda_L = -2 \left( \text{erfc} \left( \frac{p}{\sqrt{\tau}} \right) - \text{erfc} \left( \frac{1}{\sqrt{\pi}} \right) \right) + \cdots,
\]

\[
\lambda_H + \lambda_L = -\frac{1}{\sqrt{\pi}} \left( \frac{\tau_q}{\tau} \right)^{1/2} + \cdots,
\]

whence, with taking account of (16) and (17), we finally obtain

\[
\lambda_H = -\frac{1}{2\sqrt{\pi}} \left( \frac{\tau_q}{\tau} \right)^{1/2} - \text{erfc} \left( \frac{p}{\sqrt{\tau}} \right) + \text{erfc} \left( \frac{1}{\sqrt{\pi}} \right),
\]

\[
\lambda_L = -\frac{1}{2\sqrt{\pi}} \left( \frac{\tau_q}{\tau} \right)^{1/2} + \text{erfc} \left( \frac{p}{\sqrt{\tau}} \right) - \text{erfc} \left( \frac{1}{\sqrt{\pi}} \right),
\]

\[
\lambda_N = -\frac{\sqrt{\pi}}{4} \left( \frac{\tau_q}{\tau} \right)^{1/2} - \sqrt{\pi} \left( \text{ierfc} \left( \frac{p}{\sqrt{\tau}} \right) + \text{ierfc} \left( \frac{1}{\sqrt{\pi}} \right) \right),
\]

where complementar error function \( \text{erfc}(\eta) = 1 - \text{erf}(\eta) \) at \( \eta \ll 1 \) has the asymptotics \( e^{-\eta^2} (1 - 1/2\eta^2 + \cdots)/\sqrt{\pi}. \)

B. Diffusion of H particles into a semi-infinite medium at uniform distribution of L particles \((p \ll \tau \ll 1)\).

By neglecting the H particles reflection from the boundary \( x = 0 \) and nonuniformity of the distribution of L particles, from (16) and (18) we have

\[
\hat{N} = \hat{l}_s = \hat{h}_s/\sqrt{\pi}.
\]

Evidently, the character of the crossover onto regime (25) depends on the \( \tau_q/\tau_L \) relation. In the region of \( \tau_q \ll \tau_L \) regime (25) is realized after a quasiequilibrium \( h_s \ll J \) has been reached, whereas in the opposite limit, \( \tau_L \ll \tau_q \), the crossover to regime (25) occurs directly at the initial stage when the desorption can yet be neglected.

1. Adsorption-controlled regime \((p \ll \tau \ll \tau_s)\).

By assuming \( N = J\tau \), i.e. by neglecting the contribution of desorption, from (25) we have

\[
N = l_s = J\tau, \quad h_s = (2/\sqrt{\pi})J^{3/2}/\tau,
\]

whence it follows that the adsorption-controlled asymptotics has the form

\[
h_s = \frac{2}{\sqrt{\pi}} J^{3/2}/(1 + \Delta_H),
\]

\[
l_s = J(1 + \Delta_L),
\]

\[
N = J(1 + \Delta_N).
\]

According to (26), the condition of smallness of the desorption flux takes now the form \( J^d = h_s l_s \approx (2/\sqrt{\pi}) J^{3/2}/\tau \ll J \), whence it follows that it is realized at times \( \tau \ll \tau_s = J^{-2/3} \). So, under the conditions of uniform distribution of L particles, there appears a new characteristic time scale \( \tau_s = J^{-2/3} \) in the vicinity of which the crossover from the adsorption-controlled to the diffusion-controlled regime occurs. Using the exact series expansion in particular points

\[
\text{coth} \sqrt{sp} = \frac{1}{\sqrt{sp}} \sum_{n=1}^{\infty} \frac{\sqrt{sp}}{sp + (\pi n)^2},
\]

we find from (14)

\[
\hat{l}_s = \hat{N} \left\{ 1 + \frac{1}{3} sp - 2 \sum_{n=1}^{\infty} \frac{(sp/\pi n)^2}{sp + (\pi n)^2} \right\},
\]

and, therefore, in the limit \( \tau/\tau_s \to 0 \) we have exactly

\[
l_s = J(1 + \frac{1}{3} (p/\tau) - \frac{6}{\pi^2} \sum_{n=1}^{\infty} n^{-2} e^{-\frac{\pi n^2}{2}} \),
\]

whence it is seen that the addition to (19) becomes negligibly small \( O(e^{-\pi^2}) \) already at \( \tau \sim p \). Substituting the expression for \( J^d \) into (15), we obtain \( N = J(1 - \frac{1}{\sqrt{\pi}} (p/\tau_s)^{3/2} + \cdots) \). Substituting then this expression into (16) and (28), respectively, we finally find

\[
\Delta_H = -\frac{3\sqrt{\pi}}{8} \left( \frac{\tau}{\tau_s} \right)^{3/2} + 2\sqrt{\pi} \text{ierfc} \left( \frac{1}{\sqrt{\pi}} \right) + \cdots,
\]

\[
\Delta_L = \frac{1}{3} \left( \frac{p}{\tau} \right) - \frac{4}{5\sqrt{\pi}} \left( \frac{\tau}{\tau_s} \right)^{3/2} + \cdots,
\]

\[
\Delta_N = -\frac{4}{5\sqrt{\pi}} \left( \frac{\tau}{\tau_s} \right)^{3/2} + \cdots.
\]

2. Diffusion-controlled regime \((p, \tau_s \ll \tau \ll 1)\)

By neglecting the contribution of the transient region, i.e. by taking \( p, \tau_s \to 0 \) and assuming that \( h_s \) changes by the power law \( h_s \sim \tau^n \), from (25) and (15) we have

\[
N = l_s = \gamma(n) h_s \sqrt{\tau}, \quad h_s l_s = J,
\]

where \( \gamma(n) = \Gamma(n + 1)/\Gamma(n + 3/2) \) and \( \Gamma(n) \) is the gamma function. From (30) it immediately follows \( n =

Indeed, let $\nu$ which contradicts the condition (33). Thus, we finally obtain the diffusion-controlled asymptotics in the form
\[ h_s = h_c \beta^{-1} \tau^{-1/4} (1 + \phi_H), \]
\[ l_s = l_c \beta^{1/4} (1 + \phi_L), \]
\[ N = N_c \beta^{-1} (1 + \phi_N). \]

Substituting (32) into (15) and (18) and taking $\phi_i \ll 1$ we find that, asymptotically, $\phi_H, \phi_L,$ and $\phi_N$ are connected by the relationships
\[ \phi_H + \phi_L = -\frac{\beta}{4} \left( \frac{\tau}{\bar{s}} \right)^{3/4} + \cdots \] (33)
and
\[ \phi_N = \phi_L - \frac{1}{12} \left( \frac{\bar{p}}{\bar{s}} \right) + \cdots. \] (34)

Substituting then (32) into Eq.(16), we come to the equation
\[ \beta^2 \mathcal{L}(\phi_N \tau^{1/4}) = s^{-1/2} \mathcal{L}(\phi_H / \tau^{1/4}) - \frac{2\Gamma(3/4)}{s^{3/4}} e^{-2\sqrt{s}}, \] (35)
which, on neglecting the contribution of $H$ particles reflection from the boundary $x = 0$, takes the form
\[ \beta^2 \mathcal{L}(\tilde{\phi}_N \tau^{1/4}) = s^{-1/2} \mathcal{L}(\tilde{\phi}_H / \tau^{1/4}). \] (36)

Assuming that $\tilde{\phi}_i$ decay asymptotically in time by the power-law
\[ \tilde{\phi}_i = C_i / \tau^{\nu_i} + \cdots, \] (37)
where $C_i(p, \tau_s) \to 0$ as $p, \tau_s \to 0$, from (33),(34) and (36) it can easily be shown that the exponents $\nu_i \geq 3/4$. Indeed, let $\nu_H < 3/4$. Then, from (36) it follows that $\nu_L = \nu_H$, and the coefficients $C_L$ and $C_H$ have like signs, which contradicts the condition (33). Thus, $\nu_i \geq 3/4$ which suggests that in contrast to the diffusion-controlled asymptotics (23), the sign and value of the $C_L$ and $C_H$ are governed by all the prehistory of transition to the asymptotics (31) and can be calculated only numerically. In the next sections we shall discuss the behavior of $\phi_L$ and $\phi_H$ in more detail and demonstrate that it is quite nontrivial. We now consider the contribution into $\phi_i$ due to the reflection of $H$ particles from the boundary $x = 0$. According to (33) and (34), in the limit $p, \tau_s \to 0$ we have $\phi_H = -\phi_L = -\phi_N = \phi^{(0)}$.

Substituting $\phi^{(0)}$ into Eq.(35), we obtain
\[ \beta^2 \mathcal{L}(\phi^{(0)} \tau^{1/4}) = \frac{2\Gamma(3/4)}{s^{3/4}} e^{-2\sqrt{s}} - s^{-1/2} \mathcal{L}(\phi^{(0)} / \tau^{1/4}). \] (38)

It is easy to check that the inverse Laplace transform of the solution of Eq.(38) ought to have the form
\[ \phi^{(0)} = \frac{2\Gamma(5/4)}{\sqrt{s}} \tau^{3/4} e^{-1/\tau} (1 + g), \] (39)
where
\[ g = c_1/2 \tau^{1/2} + c_1 \tau + c_3/2 \tau^{3/2} + \cdots. \]

Substituting Eq.(39) into (38) and equilizing the coefficients at the same $s$ powers, we finally find
\[ c_1/2 = -\frac{1}{\beta^2}, c_1 = -\frac{15}{16} + \frac{1}{\beta^4}, c_3/2 = \frac{1 - c_1}{\beta^2}. \]

C. Two characteristic paths of the crossover to the diffusion-controlled regime with uniform $L$ particle distribution.

According to subsections A) and B), depending on the relation of three characteristic times $\tau_L = p, \tau_q$, and $\tau_s$, the crossover to the diffusion-controlled regime with uniform $L$ particles distribution proceeds by one of the two qualitatively different scenarios. One of these is realized in the limit $\tau_q \ll p \ll 1$, when at first, a quasiequilibrium between the input and desorption fluxes is established in the system (crossover $A_1 \to A_2$ at $\tau \sim \tau_q$), following which the $L$ particles distribution becomes uniform (crossover $A_2 \to B_2$ at $\tau \sim p$). In this case, the surface concentrations $h_s, l_s,$ and particle number $N$ go, respectively, through the following chains of power-law asymptotics:
\[ h_s : \ \tau^{1/2} \to \tau^0 \to \tau^{-1/4}, \]
\[ l_s : \ \tau^{1/2} \to \tau^0 \to \tau^{1/4}, \]
\[ N : \ \tau^{-1} \to \tau^{1/2} \to \tau^{-1/4}. \] (40)

The second scenario is realized in the limit $p \ll \tau_s \ll 1$, when at first the $L$ particles distribution becomes uniform (crossover $A_1 \to B_1$ at $\tau \sim p$), whereupon a quasiequilibrium is established between the input and desorption fluxes (crossover $B_1 \to B_2$ at $\tau \sim \tau_s$). In this case, $h_s, l_s,$ and $N$ go, respectively, through the following chains of power-law asymptotics:
\[ h_s : \ \tau^{1/2} \to \tau^{-1/4}, \]
\[ l_s : \quad \tau^{1/2} \to \tau \to \tau^{1/4}, \quad (41) \]
\[ N : \quad \tau \to \tau^{1/4}. \]

It can easily be shown from Eqs. (13) that at each of the given power-law asymptotics, \( h_s \propto \tau^n, \tau \ll 1 \), the spatial distribution of \( H \)-particles changes, on neglecting the contribution of the transient regions, by the law
\[
h(x, \tau) = h_s F_n \left( \frac{1-x}{2\sqrt{\tau}} \right), \quad (42)\]

where
\[
F_n(\xi) = \begin{cases} 
\pi^{1/2} \text{erfc}(\xi), & n = 1/2 \\
\text{erfc}(\xi), & n = 0 \\
\frac{2^{1/4} \Gamma(3/4)}{\sqrt{\pi}} e^{-\xi^2/2} D_{-1/2}(\sqrt{2}\xi), & n = -1/4.
\end{cases}
\]

Here \( D_{\nu}(z) \) is the function of parabolic cylinder which at \( z \gg 1 \) has the asymptotics \( D_{\nu}(z) \sim e^{-z^{1/4}} z^{\nu [1+\nu(\nu-1)/2z^2+\ldots]} \). The spatial distribution of \( L \)-particles at asymptotics \( l_s \propto \tau^n, \tau \ll p \) with \( n = 1/2, 0 \) has exactly the same form, except for the substitution \( \tau \to \tau/p \).

By comparing the paired ratios of the characteristic times \( \tau_L, \tau_q, \) and \( \tau_s \), we find
\[
\frac{\tau_L}{\tau_q} = \left( \frac{\tau_L}{\tau_s} \right)^{3/2} = \left( \frac{\tau_q}{\tau_q} \right)^{3} = K = p^{3/2} J, \quad (43)
\]

whence it is seen that the character of the system’s evolution is governed by the value of the parameter \( K = p^{3/2} J \): at any \( p \) and \( J \) relation in the limit \( K \gg 1 \) the system evolves in accord with the chains of asymptotics (40), whereas in the opposite limit, \( K \ll 1 \), the system evolves in accord with the chains of asymptotics (41). On neglecting the reflection of \( H \) particles from the boundary \( x = 0 \), one can easily see that in the limit \( K \to \infty(\tau_s/p \to 0) \) the only characteristic time scale is defined by the quantity \( p \), therefore, as suggested by (23) and (32), the behavior of \( h_s \) and \( l_s \) should have the scaling form
\[
h_s/h_e = p^{-1/4} w_H(\tau/p), \quad l_s/l_e = p^{1/4} w_L(\tau/p), \quad (44)
\]

where the scaling functions \( w_\nu(\zeta) \) have asymptotics \( w_{H,L}(\zeta) \approx (\beta \zeta^{1/4})^{\pm 1} \) at \( \zeta \gg 1 \). Indeed, substituting (44) into (14) and (15) and going to the Laplace transform with respect to the reduced time \( \zeta = \tau/p \to s \), in the limit \( K \to 0 \) we find
\[
\hat{L}(v_Hv_L) = s^{-1}(1-s^2 \hat{v}_L), \quad \hat{v}_L = \hat{v}_L \sqrt{s},
\]

whence it immediately follows \( \tilde{v}_i = v_i(\tau/\tau_s) \) and, hence, \( \hat{\tilde{v}}_i = \hat{v}_i(\tau/\tau_s) \). In the opposite limit, \( K \to 0(\tau_s \to 0) \), the only characteristic time scale is defined by the quantity \( \tau_s \), therefore, in accord with (27) and (32), the behavior of \( h_s \) and \( l_s \) should have the scaling form
\[
h_s/h_e = J^{1/6} v_H(\tau/\tau_s), \quad l_s/l_e = J^{-1/6} v_L(\tau/\tau_s), \quad (45)
\]

where the scaling functions \( v_i(\zeta) \) have asymptotics \( v_H(\zeta) \approx 2\sqrt{\zeta/\pi}, v_L(\zeta) \approx \zeta \) at \( \zeta \ll 1 \) and \( v_{H,L} \approx (\beta \zeta^{1/4})^{\pm 1} \) at \( \zeta \gg 1 \). Indeed, substituting (45) into (14) and (15) and going to the Laplace transform with respect to the reduced time \( \zeta = \tau/p \to s \), in the limit \( K \to 0 \) we find
\[
\hat{L}(v_Hv_L) = s^{-1}(1-s^2 \hat{v}_L), \quad \hat{v}_L = \hat{v}_L \sqrt{s},
\]

whence it immediately follows \( \tilde{v}_i = v_i(\tau/\tau_s) \) and, hence, \( \hat{\tilde{v}}_i = \hat{v}_i(\tau/\tau_s) \).

From (45) it follows that in the limit \( K \to 0 \) the crossover to the diffusion-controlled regime is characterized by a comparatively sharp maximum of \( h_s/h_e \), the height of which depends solely on \( J \) and changes with growing \( J \) by the law
\[
h_s/M/h_e = b_H J^{1/6}, \quad (46)
\]

In the opposite limit \( K \to \infty \), according to (23),(44), a maximum of \( h_s/h_e \) is degenerated to an extended plateau, of which the height depends on \( p \) alone
\[
h_s/M/h_e = p^{-1/4}, \quad (47)
\]

and the extension, defined as the ratio of the times, which bound the region \( \lambda_H \leq \epsilon \ll 1 \), grows with \( J \) as \( \propto K \epsilon^2 / \ln(1/\epsilon) \).

In the next subsections we give the results of a detailed numerical study of the dynamics of the system in question, enabling one to gain a complete picture of evolution of \( h_s, l_s, \) and \( N \) "trajectories" between two limiting regimes (40) and (41).

### D. Numerical calculations

The numerical integration of equations (6) was performed by means of the implicit discretization scheme of increased accuracy with an additional "fictitious" node at the surface. The scheme allowed performing the calculations in the system with strong difference in species diffusivities with an accuracy down to \( 10^{-3}\% \) (see below). The space and time steps were changed within the ranges \( \delta x \sim 3 \times 10^{-4} \pm 3 \times 10^{-6} \) and \( \delta t \sim 10^{-4} \pm 10^{-11} \), respectively, with the number of time steps being \( 10^5 \pm 10^6 \). The evolution dynamics of \( h_s(\tau), l_s(\tau), \) and \( N(\tau) \) was studied in the ranges of \( p = 10^{-10} \pm 1 \) and \( J = 10^{-1} \pm 10^{12} \).

1. Kinetic diagrams \( p - J - \tau \)

Fig. 5(a) illustrates the time dependences \( h_s(\tau)/h_e, l_s(\tau)/l_e, \) and \( N(\tau)/N_e, \)
calculated numerically at a fixed flux density \( J = 10^8 \) for \( p \) values ranging from 1 to \( 10^{-9} \) (the arrows show the directions of shift of the corresponding trajectories at a change of \( p \) from \( p = 1 \) (bold curves) to \( p = 10^{-9} \) (bold curves)). One can clearly see the whole set of power-law asymptotic regions (40),(41) of \( h_s, l_s, \) and \( N \) trajectories and the character of their evolution as \( p \) (and, hence, \( K \)) are decreased from the values corresponding to the limiting regime (40) \( (p \gg 5 \times 10^{-6}, K > 1) \) to those of (41) \( (p \ll 5 \times 10^{-6}, K \ll 1) \) where the dependences of the trajectories on \( p \) dissapears and they asymptotically approach those shown in bold lines. In accord with (46) and (47), as \( p \) decreases, the plateau on the curves \( h_s(\tau)/h_e \) is transformed to a comparatively sharp maximum, the height of which depends only on \( J \). At all \( p \ll 1 \) the \( h_s/h_e, l_s/l_e, \) and \( N/N_e \) trajectories come to the universal asymptotics \( (\beta r^{1/4})^{\mp 1} \) (31). Herewith, as seen from Fig.5a and will be demonstrated in detail in what follows, the \( h_s(\tau)/h_e \) trajectories always come to the asymptotics \( (\beta r^{1/4})^{-1} \) only from above, whereas the \( l_s(\tau)/l_e \) trajectories always come to the asymptotics \( \beta r^{1/4} \) only from below.

By defining the boundaries of the asymptotic regions so that within their confines the condition

\[
\max \{|\delta_n|, |d\delta_n/d\ln \tau|\} \leq 0.01 \quad (48)
\]

shall hold (here \( \delta_n \equiv \{\phi_i, \lambda_i, \Delta_i, \phi_i, \sigma_i\}, \sigma_i \) describes the exponential relaxation to the steady state according to Eqs.(69)), we have carried out an extensive numerical study of the positions of the corresponding boundaries for \( J = 10^8 \) and \( p \) values, ranging from 1 to \( 10^{-10} \) (we have calculated and analyzed trajectories for 100 values of \( p \), 10 for each order). Figs.5b and c show the kinetic \( p - \tau \) diagrams of the regions of the power-law asymptotics and steady state (shaded by light gray) for the \( h_s(\tau)/h_e \) and \( l_s(\tau)/l_e \) trajectories, respectively. In Fig.5c by dark gray is distinguished the \( \beta r^{1/4} \) asymptotic region for the \( N(\tau)/N_e \) trajectories of the growth of the particles number. From Figs.5b,c it is seen that the dashed lines of the characteristic times \( \tau_p, \tau_s, \tau_L = p \) and \( \tau_H \) divide the \( p - \tau \) plane into several segments, confining the regions of the power-law asymptotics \( \tau^n \) with \( n = 1/2, 0, 1 \) and \( \mp 1/4 \). The boundaries of these regions go in parallel with the lines of the corresponding characteristic times, in accord with Eqs. (22), (24), (29), (39), (44) and (45). The \( \tau_p, \tau_s, \) and \( \tau_L \) lines intersect in the point \( K = 1 \) \( (\tau_p = \tau_s = \tau_L = 4.64158 \times 10^{-6}) \), shown by filled circle, in accord with Eq.(43). As the \( n = 1/2, 0, 1 \) region boundary positions are described by Eqs. (22), (24) and (26), we shall focus mainly on the \( n = \mp 1/4 \) region boundary positions.

From Figs.5b,c it is seen that, in accord with (44), at \( p \gg 5 \times 10^{-6}(K > 1) \) the left-hand boundaries of the \( n = \mp 1/4 \) regions go in parallel with the \( \tau_L \) line down to the point of intersection of left- and right-hand boundaries of \( n = 0 \) regions \( (p \approx 2 \times 10^{-3}, K \approx 5 \times 10^3) \) where the plateau on the \( h_s \) and \( l_s \) trajectories disappears. Above this point the \( h_s/h_e \) and \( l_s/l_e \) approach the \( (\beta r^{1/4})^{\mp 1} \) asymptotics simultaneously and, which is important, this occurs at \( \tau \approx p \), i.e. long before the \( L \) particles distribution in the bulk becomes uniform (left boundary of the \( n = 1/4 \) region shaded by dark gray in Fig.5c). Such synchronization of the trajectories directly follows from Eqs.(33) and (44), according to which in the scaling limit \( K \rightarrow \infty \) \( (\tau_s/p \rightarrow 0) \) \( w_H w_L = 1 \) and \( \phi_H = -\phi_L \). In the opposite limit \( p \ll 5 \times 10^{-6}(K \ll 1) \) the left boundaries of \( n = \mp 1/4 \) regions become parallel to the \( \tau_s \) line in the vicinity of the intersection point of \( n = 1/2 \) boundary (Fig.5b) with the \( \tau_L \) line \( (p \approx 3 \times 10^{-7}, K \approx 2 \times 10^{-2}) \), in accord with Eq.(45). Below this point (i) the behavior of \( h_s(\tau) \) obeys the scaling law (45), i.e. it ceases to be dependent on \( p \) and (ii) the boundaries of \( n = 1/4 \) regions of growth of \( l_s(\tau) \) and \( N(\tau) \) merge, i.e. by the instant of the transition to asymptotics \( \beta r^{1/4} \) the distribution of \( L \) particles becomes uniform. Essentially, that in this region of \( p \) and \( K \) the behavior of \( h_s \) and \( l_s \) becomes strongly asymmetric: the transition of the \( h_s/h_e \) trajectories to \( (\beta r^{1/4})^{-1} \) asymptotics takes place well before the \( l_s/l_e \) trajectories reach the \( \beta r^{1/4} \) asymptotics. Below the point \( p \approx 2 \times 10^{-9}, K \approx 10^{-5} \) where on the kinetic diagram of Fig.5c there appears the \( n = 1 \) region, the merging of the \( l_s(\tau) \) and \( N(\tau) \) trajectories takes place already on the stage of the adsorption-controlled regime, beyond which the \( l_s(\tau) \) trajectory ceases to be \( p \)-independent.

With account taken of the fact that the boundaries of the asymptotic regions are strongly related to the characteristic times \( \tau_L, \tau_s, \) and \( \tau_r \), one can easily get from Fig.5b,c the idea of how the kinetic diagrams evolve with changing density of the input flux \( J \). Indeed, as \( J \) grows, the point \( K = 1 \) should shift along the \( \tau_L \) line, as shown by arrows in Fig.5b,c, entailing the \( \tau_q \) and \( \tau_s \) lines. The \( \tau_q \) and \( \tau_s \) lines, shifting in parallel to themselves, should in turn entail the lines of the corresponding boundaries of the asymptotic regions, so that with growing \( J \) the \( n = 0, \mp 1/4 \) regions should expand in a self-similar manner, and the \( n = 1/2, 1 \) regions contract in a self-similar manner. From the conditions \( \tau_{-1/4} \approx \tau_r \) and \( \tau_{1/4} \approx \tau_r \), where \( \tau_{-1/4} = 5.855 \tau_r \) and \( \tau_{1/4} = 93.88 \tau_r \) are the positions of the left boundaries of regions \( n = -1/4 \) and \( n = 1/4 \) at \( K = 0 \) and \( \tau_r \approx 0.2 \) is the position of their right boundary associated with the influence of the \( H \) particles reflection from the boundary \( x = 0 \), one can conclude that the starting flux densities for the appearance of \( \tau_{-1/4} \) and \( \tau_{1/4} \) asymptotics are \( J_{-1/4} \approx 10^2 \) and \( J_{1/4} \approx 10^4 \), respectively. From Fig.5b,c it follows that the vertices of \( n = \mp 1/4 \) regions for the surface concentrations and the number of particles are in the points \( p_s \approx 0.1 \) and \( p_N \approx 2 \times 10^{-2} \), respectively. Thus, the \( J = \) limits of \( (\beta r^{1/4})^{\mp 1} \) asymptotics are defined by the following conditions:

\[
h_s : p < p_s \approx 0.1, J > J_{-1/4} \approx 10^2,
\]
\[
l_s : p < p_s \approx 0.1, J > J_{1/4} \approx 10^4,
\]
\[ N : p < p_N \approx 2 \times 10^{-2}, J > J_{1/4} \approx 10^4. \]

2. **Maximum of \( h_s \)**

Figs. 6a and b illustrates the behavior of the maximum of the surface \( H \) particles concentration, \( h_s^M / h_c, (a) \) and the time for which this maximum is reached, \( \tau_M, (b) \) as a function of growing \( J \). The curves are calculated numerically at fixed \( p = 10^{-3}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} \) and \( 10^{-6} \). It is seen that, in accord with (45), (46), at small \( K \ll 1 \) the calculated curves approach the \( p \)-independent power-law asymptotics (shown in the dashed lines)

\[ h_s^M / h_c = 0.7221 J^{1/6}, \quad \tau_M = 1.125 J^{-2/3}. \quad (49) \]

As \( J \) grows, the dependences of \( h_s^M / h_c \) and \( \tau_M \) on \( J \) deviate from the \( p \)-independent asymptotics (49) the earlier the large is \( p \), reaching at \( K \gg 1 \) the \( J \)-independent plateau (47) (as seen for the curves for \( p = 10^{-1} \) and \( p = 10^{-2} \)). Interestingly that at \( p \ll 1 \) the curves approach the power-law asymptotics (49) already at comparatively small flux densities \( J \approx 50 \), exceeding \( J_c \) by no more than an order of magnitude.

3. **Behavior of \( \phi_H \) and \( \phi_L \)**

We shall now consider the regularities of the behavior of transient terms \( \phi_H (\tau) \) and \( \phi_L (\tau) \), which characterize the kinetics of the transition of surface concentrations to the universal asymptotics \((\beta \tau^{1/4}) \pm 1\). Fig. 7 shows the dependences \( \phi_H (\tau)(a) \) and \( \phi_L (\tau)(b) \), calculated numerically at \( p = 10^{-4} \) for \( J \) values, ranging from \( J = 10^4 \) to \( J = 10^{12} \) (from \( K = 10^{-2} \) to \( K = 10^6 \), respectively). It is seen that (i) the \( \phi_H \) value at any \( K \) first crosses zero, changing the sign from - to +, then reaches a maximum and asymptotically approaches zero only from above; (ii) the \( \phi_L \) value at any \( K \) asymptotically approaches zero only from below, in this case, with \( K < 1 \) it occurs monotonously whereas with \( K > 1 \) the \( \phi_L \) value first crosses zero, changing the sign from + to -, then reaches in modulus a maximum, and only after this begins to approach zero; (iii) with a growth in \( J \) the \( \phi_H \) maximum is shifted left and its amplitude grows, whereas the \( |\phi_L| \) maximum is shifted right and its amplitude drops, so that at \( K > 10^6 \) the behavior of \( \phi_H (\tau) \) and \( \phi_L (\tau) \) becomes completely "symmetric", in agreement with (33), (44)

\[ \phi_H (\tau) = |\phi_L (\tau)|. \]

From Fig. 8 where are presented the sections of the dependences \( \phi_H (\tau) > 0(a) \) and \( \phi_L (\tau) < 0(b) \) replotted in double logarithmic coordinates, we find that at \( J > J_{1/4} \) the \( \phi_H \) and \( \phi_L \) values decrease at a sufficient distance from the \( \phi_H \) maximum by the power law (37) with the exponents \( \nu_H = \nu_L = 3/4 \)

\[ \phi_t = C_1 / \tau^{3/4} + \cdots \quad (50) \]

up to \( \tau \approx 0.1 \div 0.2 \) where a rapid growth of \( |\phi_t| \) begins due to the reflection of \( H \) particles from the boundary \( x = 0 \). At the growth stage the \( |\phi_t| \) dependences are seen to go exactly onto the bold \( \phi^{(0)} \) curve, calculated from Eq. (39). It is important to note that from Fig. 8 it directly follows that the error of numerical calculations does not exceed \( 10^{-3}\% \). According to Eq. (44) in the scaling limit \( K \to \infty \) from (50) and (33) it follows

\[ \tilde{\phi}_t = m_t^\infty (p / \tau)^{3/4} + \cdots, \]

where the coefficients \( m_\tau^\infty = -m_L^\infty \) are independent of \( J \) and \( p \). From the data of Fig. 8 we find at \( K > 10^6 \)

\[ m_H^\infty = m_L^\infty = 0.023 \quad (51) \]

and obtain for the maximum \( |\phi_t| \) and the time of its attaining \( \tau_t^m \)

\[ \phi_H^m = |\phi_L|^m \approx 0.00798, \quad \tau_t^m = 2.51p. \quad (52) \]

In Fig. 9 are plotted in double logarithmic coordinates the sections of the dependences \( \phi_H (\tau) > 0(a) \) and \( \phi_L (\tau) < 0(b) \), calculated numerically at a fixed flux density \( J = 10^6 \) for the \( p \) values, ranging from \( p = 10^{-2} \) to \( p = 10^{-6} \) (from \( K = 10^3 \) to \( K = 10^{-3} \), respectively). The both maxima, \( \phi_H^\infty \) and \( |\phi_L|^M \), are seen to shift towards smaller \( \tau \) with decreasing \( p \), herewith the \( \phi_H \) maximum amplitude decreases, whereas the \( |\phi_L| \) maximum amplitude increases, and at \( K < 1 \) it disappears. At \( p \ll p_s \) the \( \phi_H (\tau) \) and \( \phi_L (\tau) \) dependences decay at a distance from \( \phi_H^\infty \) by the power law (50), converging to the \( p \)-independent trajectories at \( p \approx 10^{-6} (K \approx 10^{-3}) \). According to Eq. (45) in the scaling limit \( K \to 0 \) from (50) and (33) it follows

\[ \phi_H^\infty = m_t^0 (\tau_s / \tau)^{3/4} + \cdots, \]

where the \( p- \) and \( J- \)independent coefficients \( m_t^0 \) should satisfy the condition

\[ m_H^0 + m_L^0 = -\beta / 4 = -0.29068. \quad (53) \]

From the data of Fig. 9, in accord with (53), we find at \( K < 10^{-3} \)

\[ m_H^0 = 0.014, \quad m_L^0 = -0.305 \quad (54) \]

and obtain for the \( \phi_H^\infty \) maximum and the time of its attaining \( \tau_t^m \)

\[ \phi_H^\infty = 0.00108, \quad \tau_t^m = 17.3 \tau_s. \quad (55) \]
E. Scaling and universality

So far the main attention has been focused on the limiting regimes $K \ll 1$ and $K \gg 1$ and on specific features of the crossover between these regimes at a change in $J$ for $p = \text{const.}$ or at a change in $p$ for $J = \text{const.}$ We shall now show that at $\tau \ll 1$, when the $H$ particles reflection from the boundary $x = 0$ can be neglected, the behavior of $h_s, l_s$, and $N$ is described by the scaling laws

$$h_s = h_e p^{-1/4} W_H(K, T),$$

$$l_s = l_e p^{-1/4} W_L(K, T),$$

$$N = N_e p^{-1/4} W_N(K, T),$$

where $T = \tau/p$ and the scaling functions $W_i(K, T)$ depend on the only parameter $K = p^{3/2}/J$. Indeed, going to the Laplace transform with respect to the reduced time $T \to s$, on substituting (56) into Eqs.(14) and (15) and neglecting the terms, related to the $H$ particles reflection from the boundary $x = 0$, we easily find

$$W_N = \frac{\hat{W}_H}{\sqrt{s}} = \frac{\hat{W}_L}{\sqrt{s}} \tanh \sqrt{s},$$

$$\hat{W}_N = \frac{\sqrt{K}}{s^3} \left(1 - s \hat{L}(W_H W_L)\right),$$

whence it follows $W_i = W_i(K, T)$. In agreement with the results of Sections IVA and B, the asymptotic behavior of the scaling functions $W_i(K, T)$ on the power-law portions of the $h_s, l_s$, and $N$ trajectories have the following form:

A) Diffusion of $H$ and $L$ particles into a semi-infinite medium ($T \ll 1$).

1. Adsorption-controlled regime ($T \ll 1, 1/K$).

$$W_H = \frac{2}{\sqrt{\pi}} \sqrt{K} T \left(1 - \frac{8}{3\pi} K T + \cdots\right),$$

$$W_L = \frac{2}{\sqrt{\pi}} \sqrt{K} T \left(1 - \frac{8}{3\pi} K T + T e^{-1/T} + \cdots\right),$$

$$W_N = T \sqrt{K} \left(1 - \frac{2}{7} K T + \cdots\right).$$

2. Diffusion-controlled regime ($1/K \ll T \ll 1$).

$$W_{H,L} = 1 - \frac{1}{2\sqrt{\pi K T}} \mp \text{erf} \left(\frac{1}{\sqrt{T}}\right) + \cdots,$$

$$W_N = 2 \sqrt{\frac{1}{T \pi}} \left(1 - \frac{1}{T} \sqrt{\frac{\pi}{K T}} - \sqrt{\pi \text{erf} \frac{1}{\sqrt{T}}} + \cdots\right).$$

B) Diffusion of $H$ particles into a semi-infinite medium at uniform distribution of $L$ particles ($1 \leq T \leq 1/p$).

1. Adsorption-controlled regime ($T \ll 1, 1/K^{2/3}$).

$$W_H = \frac{2}{\sqrt{\pi}} \sqrt{K} T \left(1 - \frac{3\sqrt{\pi}}{8} K T^{3/2} + \cdots\right),$$

$$W_L = T \sqrt{K} \left(1 + \frac{1}{3T} - \frac{3\sqrt{\pi}}{8} K T^{3/2} + \cdots\right),$$

$$W_N = T \sqrt{K} \left(1 - \frac{4}{5\sqrt{\pi}} K T^{3/2} + \cdots\right).$$

2. Diffusion-controlled regime ($T \gg 1, 1/K^{2/3}$).

$$W_{H,L} = (\beta T^{1/4})^{-1} (1 + m_{H,L}(K) T^{-3/4} + \cdots),$$

$$W_N = \beta T^{1/4} \left(1 - \frac{1}{12T} + m_L(K) T^{-3/4} + \cdots\right).$$

According to Eqs.(56), at arbitrary changes in $J$ and $p$, with $K = \text{const.}$ retained, the scaling functions are the universal functions of the reduced time, $W_i(T)$, and the $h_s, l_s, l_e$, and $N/N_e$ trajectories are shifted by a factor

$$p^{3/4} = (J/K)^{+1/6}.$$

So, the boundaries of the power-law asymptotic regions, the $W_H$ and $|\phi_i|$ maxima, the times at which they are attained, $T_M$ and $T_m$, and the $m_i$ coefficients are unambiguous functions of the parameter $K$. Their behavior will be considered in what follows.

1. Behavior of $W_i(K, T)$ and kinetic diagrams $K - T$

Figs.10,11, and 12 show the plots $W_H = p^{1/4} h_s/h_e, W_L = p^{-1} l_s/l_e,$ and $W_N = p^{-1/4} N/N_e$ vs $T = \tau/p$ in the $K$ range from $K = 10^{-11/2}$ to $K = 10^{13/2}$ (upper panels), and the corresponding $K - T$ diagrams of the power-law asymptotic regions (lower panels), obtained by reploting the data of Fig.5 $(J = 10^6)$ for $\tau < \tau_c \approx 0.2$ in the corresponding scaling coordinates. It is seen that with the growing $K$ from $K \ll 1$, the $W_i(K, T)$ trajectories initially shift in a self-similar manner in accord with the scaling (45)

$$W_i(K, T) = K^{+1/6} v_i(K^{2/3} T), \quad K \to 0,$$

(note that for $W_L(K, T)$ this scaling takes place only at $T \gg 1$ whereas at $T \ll K^{-2/3}$, according to (28), the scaling $W_L(K, T) = \sqrt{K} u(T)$ takes place) and then at $K \gg 1$ they shift in a self-similar manner at "tails" of $T \ll 1$, in accord with the scaling
\[ W_{H,L}(\mathcal{K}, T) = \Lambda_s(\mathcal{K}T), \]  
\[ W_N(\mathcal{K}, T) = \mathcal{K}^{-1/2} \Lambda_N(\mathcal{K}T), \]

converging at \( \mathcal{K}T \to \infty \) to the universal (\( \mathcal{K} \) independent) trajectories (44)

\[ W_i(\mathcal{K}, T) = w_i(T), \quad \mathcal{K}T \to \infty. \]  

Fig.11 clearly demonstrates the evolution of the course of the \( W_L(\mathcal{K}, T) \) trajectories as a result of competition of two opposite tendencies: (i) growth acceleration of \( l_s \), associated with the reflection of \( L \) particles from the boundary \( x = 0 \) and (ii) growth deceleration of \( l_s \), associated with the establishment of quasiequilibrium \( J^d \approx J \), the former being dominant at any \( \mathcal{K} \) in the vicinity of \( T \approx 1 \), the latter in the vicinity of \( T \approx T_s = 1/\mathcal{K}^{2/3} \) at \( \mathcal{K} < 1 \) and in the vicinity of \( T \approx T_q = 1/\mathcal{K} \) at \( \mathcal{K} > 1 \), shifting with the growing \( \mathcal{K} \) towards \( T \to 0 \).

The general evolution picture of the power-law asymptotic regions with the growing \( \mathcal{K} \) between the limiting regimes (40) and (41) as well as of the \( \mathcal{K} \) and \( T \) regions, in the confines of which the crossovers between power-law asymptotics fit the scaling laws (63), (64), and (65), are demonstrated by the kinetic \( \mathcal{K} \to T \) diagrams on the lower panels of Figs. 10, 11, and 12. According to Eqs.(56), the given plots yield an exhaustive description of evolution of the \( h_s, l_s \), and \( N \) trajectories at the stage of the \( H \) particles diffusion into a semi-infinite medium at arbitrary \( J \) and \( p \) changes. In particular, at \( p = \text{const.} \), the given plots factually describe the evolution of the \( h_s, l_s \), and \( N \) trajectories with the growing density of the flux \( J \) up to \( T = T_r \), where \( T_r \approx 0.2/p \) is the time, beginning with which the reflection of \( H \) particles from the boundary \( x = 0 \) becomes essential.

2. Scaling of \( h^M_s \)

From Eqs.(56) it follows that at \( p < 1, J \gg J_s \), and \( \tau < \tau_r \), the \( p \) and \( J \) dependences of the \( h^M_s \) amplitude and the time \( \tau_M \), for which \( h_s \) reaches a maximum, should have the scaling form

\[ h^M_s = h_e p^{-1/4} M(\mathcal{K}), \quad \tau_M = p T_M(\mathcal{K}). \]  

In the limit of small \( \mathcal{K} \ll 1 \), according to (63),(46), and (49), the scaling \( M(\mathcal{K}) \) and \( T_M(\mathcal{K}) \) functions have the asymptotics

\[ M(\mathcal{K}) = 0.7221 K^{1/6}, \quad T_M(\mathcal{K}) = 1.125 \mathcal{K}^{-2/3}. \]  

In the opposite limit of large \( \mathcal{K} \gg 1 \) the quantity \( M(\mathcal{K}) \) reaches its limiting value \( M(\mathcal{K} \to \infty) = 1 \). By differentiating (60), in this limit we find

\[ M(\mathcal{K}) = \frac{2}{\ln 16 \mathcal{K}}, \]

whence it follows that \( M(\mathcal{K}) \) approaches 1 as \( 1 - M \propto \sqrt[4]{\ln \mathcal{K}/\mathcal{K}}, \) and a rapid drop of \( T_M(\mathcal{K}) \) transforms at \( \mathcal{K} \gg 1 \) to a slow logarithmic one. In Fig.12 are presented the numerical data of Fig.6 replotted in the scaling coordinates \( p^{1/4} h^M_e / h_e - \mathcal{K} \) and \( T_M / p \mathcal{K} \), respectively. It is seen, that in complete agreement with (62), the points, calculated for different \( p \) and \( J \) values, fit the scaling functions \( M(\mathcal{K}) \) and \( T_M(\mathcal{K}) \) which at small \( \mathcal{K} \ll 1 \) and large \( \mathcal{K} \gg 1 \) approach, respectively, asymptotics (67) and (68), shown in dashes.

3. Scaling of \( \phi^m_i \) and \( m_i \)

In Figs.13a and b are drawn, respectively, the \( |\phi^m_i| \) and \( T^m_i \) vs \( \mathcal{K} \) dependences derived from the data of Figs.8 and 9, and the analogous data for some other \( p \ll p_s \) and \( J > J_{1/4} \) values. The points, calculated in a broad range of \( p \) and \( J \), are seen to fit, in accord with (56), the scaling functions \( \phi^m_i(\mathcal{K}) \) and \( T^m_i(\mathcal{K}) \), which in the limit of small \( \mathcal{K} \ll 1 \) approach the asymptotics (55) (dashed lines)

\[ \phi^m_H = 0.00108, \quad T^m_H = 17.3 \mathcal{K}^{-2/3}, \]

and in the limit of large \( \mathcal{K} \gg 1 \) merge and approach the asymptotics (52) (dashed lines)

\[ |\phi^m_i| = 0.00798, \quad T^m_i = 2.51. \]

According to Eqs.(33),(50), and (56), at \( p \ll p_s \) and \( J > J_{1/4} \) in the range of \( T^m_H < T < T_r \) the \( \phi^m_i(\mathcal{K}, T) \) functions ought to asymptotically decay by the law

\[ \tilde{\phi}_i(\mathcal{K}, T) = m_i(\mathcal{K})/T^{3/4} + \cdots \]

with the coefficients \( m_i(\mathcal{K}) \), satisfying the condition

\[ m_H(\mathcal{K}) + m_L(\mathcal{K}) = -\beta/4 \sqrt{\mathcal{K}}. \]

In Fig.13c are drawn the \( \mathcal{K} \) dependences of \( m_H \) and \( |m_L| \), derived from the data of Figs. 8 and 9, and the analogous data for some other \( p \ll p_s \) and \( J > J_{1/4} \) values. The points, calculated in a broad range of \( p \) and \( J \), are seen to fit the scaling functions \( |m_i(\mathcal{K})| \), in which in the limit of small \( \mathcal{K} \ll 1 \) approach the asymptotics (54), (dashed lines)

\[ |m_i(\mathcal{K})| = m_i^{(0)}/\sqrt{\mathcal{K}}, \]

and in the limit of large \( \mathcal{K} \gg 1 \) approach the asymptotics (51) (dashed lines)
\[ \tilde{m}_H^m = -m_L^m = 0.023. \]

Figs. (7), (8), (9), and (14) give a complete picture of the crossovers to the universal \((\beta \tau)^{1/4}\) asymptotics in a broad range of \(0 < K < \infty\), the main features of which can be summarized as follows:

1) With growing \(K\) the \(\phi_H^p\) amplitude grows from the \(K\)-independent asymptotics (55) at \(K \approx 10^{-3}\) to the \(K\)-independent asymptotics (52) at \(K > 10^5\). The time of its attaining, \(T_H^m\), drops up to \(K \approx 1\) according to the \(p\)-independent asymptotics (55), reaching the \(I\)-independent asymptotics (52) in the same range of \(K > 10^5\).

2) With growing \(K\) at the critical point \(K_m = 3.0\) the \(|\phi_H^p|\) maximum appears, and its amplitude then drops to the \(K\)-independent asymptotics (52) at \(K > 10^5\). The time of its attaining, \(T_H^m\), grows and approaches the \(I\)-independent asymptotics (52) in the same range of \(K > 10^5\). In the second critical point \(K_c = 7.3\) the \(K > K_c\) region appears, within which the \(\phi_L\) curves cross zero, changing the sign herewith.

3) Surprisingly, in the narrow vicinity of the critical point \(K_m\) both the time \(T_H^m\) and the \(|m_H|\) coefficient approach the \(\phi\)-independent asymptotics (55) and (54), respectively, whereas the \(m_H\) coefficient approaches the \(I\)-independent asymptotics (51): the formers change within the \(K < K_m\) range as \(K^{-3/4}\) and \(K^{-1/2}\), respectively, the latter remains constant within the \(K > K_m\) range.

V. LONG-TIME RELAXATION DYNAMICS
\((\omega \tau > 1)\).

In the light of the results of the previous Section IV, we return, in conclusion, to the analysis of the long-time relaxation dynamics of \(h_s, l_s,\) and \(N\), which, according to Section III can be given as

\[ h_s = h_c(1 - \sigma_H), \]
\[ l_s = l_c(1 - \sigma_L), \]
\[ N = N_c(1 - \sigma_N), \]

where \(\sigma_H = \tilde{h}_s/h_c, \sigma_L = \tilde{l}_s/l_c,\) and \(\sigma_N = \tilde{n}/N_c\) at sufficiently large \(\omega \tau > 1\) decay by the law

\[ \sigma_i = A_i e^{-\omega \tau} (1 + O(e^{-\omega \tau})), \]

and the coefficients \(A_i\) are related as

\[ A_H = r_s A_L = A_N \sqrt{\omega} \cot \sqrt{\omega}. \]

By preserving in (8) the next-to-leading terms

\[ \tilde{l}_s = A_H \cos(\sqrt{\omega} x)e^{-\omega \tau} + B_H \cos(2\sqrt{\omega} x)e^{-2\omega \tau} + ..., \]

from Eq.(7) we easily find

\[ \sigma_i = A_i e^{-\omega \tau} (1 + B_i \sigma_N + ...), \]

where the coefficients \(B_i\) are defined from the relations

\[ B_H = \sqrt{p} \cot \sqrt{p} \cot \sqrt{2}/Q, \]
\[ B_L = \sqrt{p} \cot \sqrt{2} \omega \cot \sqrt{2p}/Q, \]
\[ B_N = \sqrt{p} \cot \sqrt{p} \cot \sqrt{\omega}/\sqrt{2Q}, \]

\[ Q = \cot \sqrt{2\omega} + \sqrt{p} \cot \sqrt{2p}/\sqrt{\omega}. \]

By substituting now (69) into (14) and (15) and introducing the designation \(D = \sigma_H \sigma_L\), after having excluded \(\sigma_H(s)\) and \(\sigma_N(s)\), we find

\[ \sigma_L(s) = \frac{\sqrt{s} - (1 - sD(s))}{s \sqrt{\sin \sqrt{p}/\sqrt{p} \cot \sqrt{p} \sqrt{s} + \sqrt{s}/J}}. \]

In accord with the results of Section III, the main pole of Eq.(72) \((s = -\omega)\) defines the relaxation rate \(\omega\) as the least positive root of (9) and yields the relaxation "amplitude" \(A_L\) in the form

\[ A_L = A_{L0} (1 + \frac{1}{2} \omega \hat{D}(-\omega)) \]

where

\[ A_{L0} = \frac{4 \sqrt{p}/\omega \cot \sqrt{2}/Q}{\sin^{-2} \sqrt{\omega} + p \sin^{-2} \sqrt{p}/\omega + 1/\sqrt{J}}. \]

and \(\hat{D}(-\omega) = \int_0^\infty \sigma_H \sigma_L e^{\omega \tau} d\tau\). In the diffusion-controlled limit of our concern here, \(J \rightarrow \infty\), the coefficients \(B_i\) change from \(B_N = B_L = B_H - 1 = 0.1079...\) at \(p \rightarrow 0\) to \(B_i \rightarrow 0\) at \(p \rightarrow 1\), therefore given that the next after the main root of (9) is an order of magnitude above, we conclude that down to \(\tau \sim \omega^{-1}\) the asymptotic behavior of \(\sigma_L\) has the form \(\sigma_L = A_L e^{-\omega \tau} (1 + B_L \sigma_N + ...) \approx A_L e^{-\omega \tau}\). By matching this asymptotics at \(\tau = \omega^{-1}\) with that of (32), which for \(p \ll 1\) assumes the form

\[ \sigma_L = (1 - \beta \tau^{1/4}(1 + \phi_L)) \approx 1 - \beta \tau^{1/4}, \]

in the limit \(p \rightarrow 0\) we find

\[ A_L \approx e(1 - \beta/\omega^{1/4}) \approx 0.5. \]

From (73) and (75) it follows that at \(p \rightarrow 0\) the quantity \(\hat{D}(-\omega) \sim -0.1\) and the difference of \(A_L\) from \(A_{L0}\) does not exceed 20%. Obviously, with the growing \(p\) this difference can only go down, therefore by assuming in the first approximation \(A_L \approx A_{L0}\) and extrapolating the \(D \sim -A_{L0}^2 e^{-2\omega \tau}\) asymptotics down to \(\tau = 0\)
with the results of the calculation from the expressions
\[ \sigma_L(\tau) \approx 4(1 - \frac{1}{2} A_L^2) \]
which, according to the numerical data, differ from the exact values by no more than 1 – 2% for any \( p \).

Fig.15 gives, as an illustration, the time dependences \( \sigma_H(\tau) \) and \( \sigma_L(\tau) \), calculated numerically at \( J = 10^6 \) for \( p = 10^{-4}, 0.5 \) and at \( J = 10^8 \) for \( p = 0.9 \) and compared with the results of the calculation from the expressions \( \sigma_i = A_i e^{-\omega \tau} \), (9), (76) and (74). The excellent agreement between the numerical and analytical data is evident.

FIG. 1. Schematic illustration of the processes of dissociation, desorption, surface migration and diffusion into the bulk in the system \( A + B \rightarrow 0 \) with input of \( A \) and \( B \) particles. \( l_A^2 = \sqrt{D_A t} \) and \( l_B^2 = \sqrt{D_B t} \) are the diffusion lengths of \( A \)'s and \( B \)'s particles, respectively.

FIG. 2. Time dependences \( h_s(\tau)/h_{c_e} \), calculated numerically at flux densities \( J = 1, J_c = 7.250031, 10^2, 10^4 \), and \( 10^6 \) (bottom to top) for \( p = 0.1 \).

FIG. 3. Dependence of \( r_s \) on \( \sqrt{J/J_c} \), calculated from Eq.(5) for \( p = 0.1 \). Left and right insets demonstrate the specific features of relaxation of surface concentrations at small \( J \ll J_c \) and large \( J \gg J_c \), respectively.

FIG. 4. Time dependences \( h_s(\tau)/h_e \) and \( l_s(\tau)/l_e \), calculated numerically at \( J = J_c \) (open circles) and \( J = 10^4 \) (filled circles) for \( p = 0.1 \).

FIG. 5. (a) Time dependences \( h_s(\tau)/h_e \), \( l_s(\tau)/l_e \), and \( N(\tau)/N_c \), calculated numerically at \( p = 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8} \), and \( 10^{-9} \) for \( J = 10^6 \) (the arrows point to the displacement directions of the corresponding trajectories at a change in \( p \) from \( p = 1 \) to \( p = 10^{-9} \)). The trajectories for \( p = 1 \) and \( p = 10^{-9} \) are shown in bold lines; (b), (c) Kinetic \( p - \tau \) diagrams of the regions of power-law asymptotics and of steady state (shaded by light gray) for \( h_s(\tau)/h_e \) (b) and \( l_s(\tau)/l_e \) (c) trajectories calculated numerically at \( J = 10^6 \) according to condition (48). The characteristic times \( \tau_H = 1, \tau_L = p, \tau_N = 1/J\sqrt{p} \) and \( \tau_a = 1/J^{2/3} \) are shown in dashed lines. The intersection point of \( \tau_L, \tau_N \), and \( \tau_s = 1/J(\sqrt{\tau} + \sqrt{p}) \) is marked off by filled circle. The arrow shows the direction of displacement of this point along the \( \tau_s \) line with the growing flux density \( J \). In Fig.5c the \( \beta \tau^{-3/4} \) asymptotic region for the \( N(\tau)/N_c \) trajectories is distinguished by dark gray.

FIG. 6. Dependences of \( h_s(\tau)/h_e \) (a) and \( \tau_M \) (b) on \( J \), calculated numerically at \( p = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} \) (bottom to top and top to bottom in (a) and (b), respectively). Dashed lines show the asymptotics (49).

FIG. 7. Time dependences \( \phi_H(\tau) \) (a) and \( \phi_L(\tau) \) (b), calculated numerically at \( p = 10^{-5} \) for \( J = 10^4, 10^6, 10^8, 10^9, 10^{10}, 10^{11} \), and \( 10^{12} \) (right to left).

FIG. 8. Data of Fig.7 for sections \( \phi_H > 0 \) (a) and \( \phi_L < 0 \) (b) replotting in double logarithmic scale. Dashed lines show the slope of \(-3/4\). Bold lines show the \( \phi^0 \) curve, calculated from Eq.(39).

FIG. 9. Time dependences \( \phi_H(\tau) \) (a) and \( |\phi_L(\tau)| \) (b) for sections \( \phi_H > 0 \) and \( \phi_L < 0 \), respectively, calculated numerically at \( J = 10^6 \) for \( p = 10^{-2n+3} \) with \( n = 3, 4, 5, 6, 7, 8 \), and 9(right to left). Dashed lines show the slope of \(-3/4\). Bold lines show the \( \phi^0 \) curve, calculated from Eq.(39).
FIG. 10. (a) Scaling functions $W_H(K,T)$, derived from the data of Fig.5a ($p$ from $p = 10^{-1}$ to $10^{-9}$, $\tau \leq 0.2$) by replotting in scaling coordinates $p^{1/4}h_c/h_e$ vs $T = \tau/p$. (b) Kinetic $K-T$ diagram of the regions of power-law asymptotics of $W_H(K,T)$, derived from the data of Fig.5b ($\tau \leq 0.2$) by replotting in scaling coordinates $K = p^{3/2}J$ vs $T = \tau/p$. Note the different scale on the $T$ axis in (a) and (b).

FIG. 11. (a) Scaling functions $W_L(K,T)$, derived from the data of Fig.5a ($p$ from $p = 10^{-1}$ to $10^{-9}$, $\tau \leq 0.2$) by replotting in scaling coordinates $p^{-1/4}h_c/h_e$ vs $T = \tau/p$. (b) Kinetic $K-T$ diagram of the regions of power-law asymptotics of $W_L(K,T)$, derived from the data of Fig.5c ($\tau \leq 0.2$) by replotting in scaling coordinates $K = p^{3/2}J$ vs $T = \tau/p$. As contrasted from Fig.5c, the regions with $n = 1/2$ and $n = 1$ are added. Note the different scale on the $T$ axis in (a) and (b).

FIG. 12. (a) Scaling functions $W_N(K,T)$, derived from the data of Fig.5a ($p$ from $p = 10^{-1}$ to $10^{-9}$, $\tau \leq 0.2$) by replotting in scaling coordinates $p^{-1/4}N/N_e$ vs $T = \tau/p$. (b) Kinetic $K-T$ diagram of the regions of power-law asymptotics of $W_N(K,T)$, derived from the data of Fig.5c ($\tau \leq 0.2$) by replotting in scaling coordinates $K = p^{3/2}J$ vs $T = \tau/p$. As contrasted from Fig.5c, the regions with $n = 1/2$ and $n = 1$ are added. Note the different scale on the $T$ axis in (a) and (b).

FIG. 13. (a) Collapse of the dependences of $h_c^H/h_c$ on $J$ from Fig.6a to the scaling function $M(K)$ in scaling coordinates $p^{1/4}h_c^H/h_e$ vs $K = p^{3/2}J$. Dashed lines show the asymptotics (67) and (68). (b) Collapse of the dependences of $\tau_M$ on $J$ from Fig.6b to the scaling function $T_M(K)$ in scaling coordinates $\tau_M/p$ vs $K = p^{3/2}J$. Dashed lines show the asymptotics (67) and (68).

FIG. 14. Collapse of calculated numerically for $p = 10^{-4}$ (circles) and $p = 10^{-5}$ (diamonds) dependences $|\phi_L^m(J)|$, $T_L^m(J)$, and $|m_L(J)|$, and calculated numerically for $J = 10^6$ (stars) and $J = 10^9$ (squares) dependences $|\phi_L^m(p)|$, $T_L^m(p)$, and $|m_L(p)|$ to scaling functions $|\phi_L^m(K)|$ (a), $T_L^m(K)$ (b), and $|m_L(K)|$ (c), respectively. Filled symbols stand for $i = H$, open symbols stand for $i = L$. In Fig.14a,b filled circle $m$ marks off the point $K_m = 3.0$ with which the $K \geq K_m$ region begins where a maximum on the $|\phi_L|$ curves appears. Open circle $c$ marks off the point $K_c = 7.3$ with which the region $K \geq K_c$ of crossing of the $\phi_L$ curve with zero begins. Dashed lines show the asymptotics (52) and (55)(a),(b), and (54) and (51)(c).

FIG. 15. Time dependences $|\sigma_H(\tau)|$ (filled circles) and $\sigma_L(\tau)$ (open circles), calculated numerically at $p = 10^{-4}$ and $p = 0.5$ for $J = 10^6$ and at $p = 0.9$ for $J = 10^9$ (for the sake of clarity, the data are given beginning with $\tau = 10^{-4}$). Straight bold lines show $|\sigma_H(\tau)|$ and $\sigma_L(\tau)$, calculated from the equations $\sigma_i = A_i e^{-\omega^\tau}$, (9), (76), and (74).
(a) $h_s / h_e$ vs $J$

(b) $\tau M$ vs $J$

- $1/6$
- $-2/3$
\[ \frac{p^{1/4} h_s^M}{h_e} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]

\[ \frac{\tau_p}{\rho} \]
