1166 Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1166—1172, July, 2001

# Method for the calculation of the species balance in the reaction zone

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A class of processes for which the problem of species balance can be solved without using any assumptions concerning the mechanism of the chemical event of the reaction was found in the problem of species balance in the reaction zone. The mathematical statement of the problem in this case was discussed; it was shown that the solution is mainly determined by the system geometry. The method for reducing the problem to determination of the probability of species entering the chemical event zone is substantiated; this can be done by the Green function method.

**Key words:** reaction zone, species balance, Green function, quasi-steady-state processes, chemical event.

The problem of species balance in the zone of elementary event of a reaction is of paramount importance for the investigation of diverse chemical,[1] radiation,[2] electrokinetic,[3] and other processes. The balance of species, *viz.*, reactants, products, and, perhaps, a catalyst, in the chemical event zone is determined by numerous factors of different natures. Depending on the model invoked to consider the process, these data may include the number of transalational degrees of freedom of species, one- or multi-species character of the reaction, the finiteness or infinity of the rate of chemical event, the continuity or discontinuity of the species flow, and other factors. Due to the diversity of processes whose description relies on the species balance in the chemical event zone, no unified approach to the mathematical formulation of these problems is available.

The following typical qualitative formulation can serve as an example of a kinetic problem that refers to a chemical reaction proceeding by a mechanism of intermediate adsorption complexes and is based on the species balance in the reaction zone. It is characteristic of a whole class of processes that follow the mechanism of intermediate adsorption complexes on the surface active sites, namely, metal ionization (*e.g.*, iron in water) and electrodeposition (*e.g.*, zinc on iron) and a broad range of reactions with heterogeneous catalysis.[4]

Let us consider the area near an isolated active site arranged on the flat solid surface of a component of the heterogeneous system. The surface adjoins the medium (either gas or liquid) containing species of an adsorbable surface-active component. The concentration of this component varies as a function of the coordinate. We assume that an adsorbate species that either has entered some area of capture of the active site as a result of bulk diffusion or has crossed an imaginary border on the surface as a result of surface diffusion is adsorbed on this site. This yields an intermediate adsorption complex on the surface; subsequently, it either decomposes due to the departure of ligands upon desorption or lateral diffusion, so that the complex-forming atom returns to the former quantum-mechanical state, or, alternatively, it can be detached from the surface as a result of reaction and passes to the gas/liquid phase.

Let us consider a steady-state process in which the rate of adsorption on the active sites of species coming from the bulk of the gas/liquid phase and migrating *via* surface diffusion is equal to the total rate of desorption to the gas/liquid phase and over the surface plus the rate of the reaction of species with the surface *via* the surface activated complex (SAC).

This typical statement of the kinetic problem can be further detailed[5] in accordance with specific features of the above-noted processes.

It follows from the most general considerations that the species balance at any instant of time can be described by a general equation of the form

$$d\theta/dt = -\theta(t)w^{\mathrm{out}}(t) + [\theta_{\max} - \theta(t)]w^{\mathrm{in}}(t), \qquad (1)$$

where $\theta$ is the number of species in the reaction zone* or the degree of filling of the reaction zone, normally defined as the ratio of the occupied volume** to the total volume (with $\theta_{\max} \equiv 1$); $w^{\mathrm{in}}$ and $w^{\mathrm{out}}$ are the probabilities of species arrival to and departure from the reaction zone, respectively, per unit time. Note that the ways of definition of $w^{\mathrm{in}}$ and $w^{\mathrm{out}}$ are different in kind:

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* The term "reaction zone" is used in this paper in the microscopic sense and is identified with the chemical event zone.

** The volume can be described both by a continuous value and by a discrete value, for example, in the case where it characterizes a countable set of the landing sites for the reactants on which the chemical event in a heterogeneous system occurs.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1112—1117, July, 2001.

1066-5285/01/5007-1166 $25.00 © 2001 Plenum Publishing Corporation

the definition of $w^{\text{out}}$ is related to the simulation of the mechanism of the chemical event, whereas the $w^{\text{in}}$ value is mainly (or exclusively) related to the geometry of the problem.

The $\theta$ value is the primary and direct characteristics of the species balance in the zone of the elementary chemical event. In microscopic consideration of the processes in the reaction zone, $\theta$ takes on a discrete set of values, and in macroscopic consideration, it assumes a continuous set of values. In the latter case, description of the species balance requires a certain thoroughness because the chemical event of the process involves a discrete number of micro-species and one has to be able to pass from this number to the $\theta$ value in the macroscopic approach as a whole. This problem can be solved in different ways. One method is as follows:[6] the $\langle\theta\rangle$ value, representing the degree of site coverage $\theta(t)$ averaged over the ensemble of landing sites in the heterogeneous problem is used instead of $\theta(t)$ in equations of type (1) and in associated equations. This can be done most easily when no exchange-correlation effects among the landing sites are involved; in physical interpretation, this is matched by a relatively low concentration of sites in the system.

Using the approach proposed previously,[6] it is possible to calculate the $\theta$ value for several practically important situations, for steady-state and quasi-steady-state macroscopic processes, and as an integral characteristics of a macroscopic process throughout the whole process duration. The latter case is especially interesting because it does not require the simulation of the mechanism of the chemical event of the reaction, *i.e.*, it is rather general. The degree of filling of the reaction area can be calculated using the method of Green functions of mathematical physics; this is the subject of this work.

## Special cases of the species balance equation

Let us consider the zone of a chemical event of a reaction in the absence of exchange-correlation effects in the whole macroscopic system. We will use Eq. (1) for time instants sufficiently great for the relaxation processes in the system to become exponentially small: $t \gg t_r$. Under these conditions, replacing $\theta$ by the mean value over all the reaction zones of the system and using hereinafter $\theta$ to imply the mean value, gives Eq. (1) in the form

$$-\theta w^{\text{out}}(t) + (1 - \theta)w^{\text{in}}(t) = 0;$$

from this we determine the species balance for quasi-steady-state processes

$$\theta = \frac{w^{\text{in}}(t >> t_r)}{w^{\text{in}}(t >> t_r) + w^{\text{out}}(t >> t_r)}. \tag{2a}$$

On the basis of physical considerations, the time dependence of $\theta$ should be weak. For steady-state processes, we obtain

$$\theta(\infty) = \lim_{t\to\infty} w^{\text{in}}(t)/[w^{\text{in}}(t) + w^{\text{out}}(t)]\,. \tag{2b}$$

Now we will approach Eq. (1) in a different way. The equation will be written in the form

$$\mathrm{d}\theta/\mathrm{d}t = -\theta(t)[w^{\text{out}}(t) + w^{\text{in}}(t)] + w^{\text{in}}(t),$$

integrated over time from 0 to $\infty$, and transformed to the form

$$\bar{\theta} = \left\{\int_0^{+\infty} w^{\text{in}}(t)\mathrm{d}t - [\theta(\infty) - \theta(0)]\right\}\Big/\left[1 + \int_0^{+\infty} w^{\text{in}}(t)\mathrm{d}t\right]. \tag{3}$$

It is evident that the $\bar{\theta}$ value in Eq. (3) is identical to neither $\theta$ nor $\theta(\infty)$ in Eqs. (2); it characterizes the species balance in the reaction zone and refers to the process as a whole rather than to a particular point in time, as in relation (2). Thus, $\bar{\theta}$ is a quantitative measure of the degree of occupancy of the active sites during the reaction, which allows a quantitative comparison of various processes from this standpoint (which is especially significant for the problems related to catalysis[1,4]).

Let us consider the $\theta(\infty) - \theta(0)$ difference. It can be considered small in those cases where the reactant concentration in the reaction zone is relatively low; this can be true due to a number of factors present either altogether or separately, namely, a relatively low background concentration of reactants and a relatively low rate of supply of the process participants (this corresponds to relatively low probability $w^{\text{in}}(t)$ for $t \to 0$) and, conversely, high rate of the removal of the process participants from the reaction zone (corresponds to relatively high probability $w^{\text{out}}(t)$ for $t \to 0$). Thus, the equation of the form

$$\bar{\theta} = \left[\int_0^{+\infty} w^{\text{in}}(t)\mathrm{d}t\right]\Big/\left[1 + \int_0^{+\infty} w^{\text{in}}(t)\mathrm{d}t\right] \tag{4}$$

corresponds to a whole class of processes, which includes, in particular, quasi-steady-state processes.

Let us consider the method for calculation of the probability $w^{\text{in}}$ of species entering the reaction zone. Further analysis will be restricted to the frameworks of the approach corresponding to Eq. (4). Consideration of the possible mechanisms of the chemical event of the process and determination of the probabilities $w^{\text{out}}$ that the species will leave the reaction zone in conformity with Eq. (2b) is beyond the scope of this study.

## The probability that species will enter the zone of the chemical event

Assume that there is the known Green function $G(\mathbf{r}_M,\mathbf{r}_P,t)$ for one-species outer diffusion problem with a zero first-kind boundary condition at the edge of the elementary event zone; the condition corresponds to the absorption or attachment of the incoming species, and an initial condition of form $G(\mathbf{r}_M,\mathbf{r}_P,t=0) = \psi(\mathbf{r}_0 - \mathbf{r}_P)$, where $\mathbf{r}_0$ is the species position at $t = 0$, $\mathbf{r}_M$ and $\mathbf{r}_P$ are the coordinates of points $M$ and $P$. The probability density ($W$) is expressed as the integral over the range of definition of the problem $\Omega$

$$W(\mathbf{r}_M,\mathbf{r}_0,t) = \int\limits_{\Omega} G(\mathbf{r}_M,\mathbf{r}_P,t)\psi(\mathbf{r}_0 - \mathbf{r}_P)\mathrm{d}^3\mathbf{r}_P. \qquad (5)$$

The expression for the probability that one neutral species will pass through the boundary of the reaction zone $\Gamma$ in unit time has the form[7]

$$\mathrm{d}W_{\mathrm{in}}(\mathbf{r}_M,\mathbf{r}_0,t)/\mathrm{d}t = D|\nabla_M W(\mathbf{r}_M,\mathbf{r}_0,t)|\|_{\Gamma}, \qquad (6)$$

where $D$ is the diffusion coefficient.

In order to calculate the probability that a species will get inside the reaction zone, it is necessary to average relation (6) over the initial coordinates using the concentration of species $n(\mathbf{r})$ in the region $\Omega$ and then to integrate over the boundary of the region $\Gamma$

$$w^{\mathrm{in}}(t) = \int\limits_{\Gamma}\mathrm{d}S\int\limits_{\Omega}[\mathrm{d}W_{\mathrm{in}}(\mathbf{r},\mathbf{r}_0,t)/\mathrm{d}t]n(\mathbf{r}_0)\mathrm{d}^3r_0. \qquad (7)$$

The distribution of concentrations about the reaction zone has to be known on the basis of some data. In the case where determination of the species balance is a component part of a more general diffusion problem, $n(\mathbf{r})$ should be calculated together with the probability that a species will enter the reaction zone. This can be done, for example, by a self-consistent procedure realized as iterations, both the distribution of concentrations and the species balance being calculated at each iteration step.

In the next section, we present the calculation performed by this method in the quadratures of species balance in the zone of elementary event of a surface electrochemical reaction. This example reflects in full measure characteristic features of the method in question.

## Species balance in the zone of a chemical event in a surface electrochemical reaction

In the physical process under consideration[6] (see the typical qualitative formulation of the problem given above), the reaction zone is a hemisphere with the radius $r_S$ centered at the origin of coordinates. The species are distributed in some way in the half-space $\Omega = \{r > r_S, z > 0\}$ confined by the ensemble of points $\Sigma = \{r > r_S, z = 0\}$ and by the boundary of the reaction zone $\Gamma = S \cup L$, where $S = \{r = r_S, z > 0\}$ and $L = \{r = r_S, z = 0\}$. The species diffuse in the half-space $\Omega$; they are able to penetrate into the reaction zone through the boundary $S$, to stick to the boundary $\Sigma$, to diffuse along it, to penetrate into the reaction zone through boundary $L$, or to leave $\Sigma$ and return to the half-space $\Omega$.

Thus, the problem of balance determination is split into two components. One component implies diffusion of species in the bulk, while in the other one, they diffuse along the surface. Correspondingly, the probability that a species will penetrate into the reaction zone is represented as the sum

$$w^{\mathrm{in}}(t) = w_S^{\mathrm{in}}(t) + w_L^{\mathrm{in}}(t). \qquad (8)$$

Now we calculate $w_S^{\mathrm{in}}(t)$. The problem statement for the Green function $G(\mathbf{r}_M,\mathbf{r}_P,t)$ with allowance made for the axial symmetry has the form

$$\begin{cases} \mathrm{d}G/\mathrm{d}t = D\Delta G \\ G|_S = 0 \\ \nu_1 G|_{\Sigma} + \nu_2 \mathrm{d}G/\mathrm{d}z|_{\Sigma} = 0 \\ G|_{t=0} = \rho_P^{-1}\delta(\rho_0 - \rho_P)\delta(z_0 - z_P) \end{cases}, \qquad (9)$$

where $\mathbf{r}_0 = \{\rho_0,z_0\}$ is the position vector of a species for $t = 0$, $\mathbf{r}_P = \{\rho_P,z_P\}$ is the position vector of the mobile point $P$. Solution of problem (8) can be found by the reflection method[8] and has the form

$$G = \frac{1}{\left(2\sqrt{\pi Dt}\right)^3}\left[\exp\left(-\frac{r_{MP}^2}{4Dt}\right) - \exp\left(-\frac{r_P}{r_S}\frac{r_{MP_1}^2}{4Dt}\right) \pm \right.$$
$$\left. \pm\exp\left(-\frac{r_{MP_2}^2}{4Dt}\right) \mp \exp\left(-\frac{r_{P_2}}{r_S}\frac{r_{MP_3}^2}{4Dt}\right)\right], \qquad (10)$$

where $M$ is the fixed point of the Green function; the point $P_1$ is symmetric to $P$ relative to $S$, $P_2$ is symmetric to $P$ relative to $\Sigma$, $P_3$ is symmetric to $P_1$ relative to $\Sigma$; the upper sign (hereinafter) corresponds to the case where $\nu_1 = 0$, the lower sign implies $\nu_2 = 0$. The expressions for the Green function and the subsequent equations in the general case where $\nu_1\nu_2 \neq 0$ have a rather cumbersome form and, to make the consideration complete, they are presented in Appendix 1. As a brief remark, we would like to note that $G$ and its derivative are continuous within $\Omega$ together with its boundary.

According to Eq. (5), the distribution of probabilities in the half-space $\Omega$ equals

$$W(\mathbf{r},\mathbf{r}_0,t) = \frac{1}{4\pi^{1/2}(Dt)^{3/2}}\left\{I_0\left(\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{\rho^2+\rho_0^2}{4Dt}\right)\times\right.$$
$$\times\left[\exp\left(-\frac{(z-z_0)^2}{4Dt}\right) - \exp\left(-\frac{(z+z_0)^2}{4Dt}\right)\right]\pm$$
$$\pm I_0\left(\frac{r_S}{r_0}\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{r_0}{r_S}\frac{\rho^2+\rho_0^2 r_S^4/r_0^4}{4Dt}\right)\times$$
$$\left.\times\left[\exp\left(-\frac{r_0}{r_S}\frac{\left(z - z_0 r_S^2/r_0^2\right)^2}{4Dt}\right) - \exp\left(-\frac{r_0}{r_S}\frac{\left(z + z_0 r_S^2/r_0^2\right)^2}{4Dt}\right)\right]\right\}, \qquad (11)$$

where $\{\rho,z\}$ are the coordinates of the position vector $\mathbf{r}$ of the species, $I_0$ is the modified zero-order Bessel function, whose integral representation was used to derive Eq. (11). Equation (6) now acquires the form

$$\frac{\mathrm{d}W_{\mathrm{in}}\left[\mathbf{r}(\rho, z), \mathbf{r}_0(\rho_0, z_0), t\right]}{\mathrm{d}t} =$$
$$= D\sqrt{\left[\frac{\partial W(\rho, z; \rho_0, z_0; t)}{\partial \rho}\right]^2 + \left[\frac{\partial W(\rho, z; \rho_0, z_0; t)}{\partial z}\right]^2}, \quad (12)$$

where the expressions for partial derivatives were obtained by elementary differentiation of Eq. (11); they are presented in Appendix 2.

By substituting expression (12) into Eq. (7), we have

$$\int\limits_0^{+\infty} w_S^{\mathrm{in}}(t)\mathrm{d}t = r_S^2 \iint\limits_{\Omega} \rho_0 n(\rho_0, z_0)\mathrm{d}z_0\mathrm{d}\rho_0 \times$$
$$\times \int\limits_0^1 \mathrm{d}p \int\limits_0^{+\infty} \frac{\mathrm{d}W_{\mathrm{in}}\left[\mathbf{r}(r_S\sqrt{1-p^2}, r_S p), \mathbf{r}_0(\rho_0, z_0), t\right]}{\mathrm{d}t}\mathrm{d}t\ . \quad (13)$$

Now we shall calculate $w_L{}^{\mathrm{in}}(t)$. The problem statement for the Green function $G(\mathbf{r}_M, \mathbf{r}_P, t)$, where $\mathbf{r}_M$, $\mathbf{r}_P$ lie in the *xy* plane, with allowance for the axial symmetry of the system, has the form

$$\begin{cases} \mathrm{d}G/\mathrm{d}t = D\Delta G \\ G|_L = 0 \\ G|_{t=0} = \rho_P^{-1}\delta(\rho_0 - \rho_P) \end{cases}.$$

The reflection method gives the Green function

$$G = \frac{1}{4\pi Dt}\left[\exp\left(-\frac{r_{MP}^2}{4Dt}\right) - \exp\left(-\frac{\rho_P}{r_S}\frac{r_{MP_1}^2}{4Dt}\right)\right], \quad (14)$$

where $\rho_P$ is the coordinate of the position vector $\mathbf{r}_P$. The probability distribution in the Σ plane equals

$$W(\mathbf{r}, \mathbf{r}_0, t) = \frac{1}{2Dt}\left\{I_0\left(\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{\rho^2 + \rho_0^2}{4Dt}\right) - \right.$$
$$\left. - I_0\left(\frac{\rho r_S}{2Dt}\right)\exp\left[-\frac{1}{4Dt}\left(\frac{\rho^2\rho_0}{r_S} + \frac{r_S^3}{\rho}\right)\right]\right\}.$$

In this case, Eq. (6) takes on the form

$$\frac{\mathrm{d}W_{\mathrm{in}}\left[\mathbf{r}(\rho), \mathbf{r}_0(\rho_0), t\right]}{\mathrm{d}t} = D\left|\frac{\partial W(\rho, \rho_0, t)}{\partial \rho}\right|\Bigg|_{\rho = r_S} =$$
$$= \frac{1}{4Dt^2}\left\{\exp\left(-\frac{r_S^2 + \rho_0^2}{4Dt}\right)\left[\rho_0 I_1\left(\frac{r_S\rho_0}{2Dt}\right) - r_S I_0\left(\frac{r_S\rho_0}{2Dt}\right)\right] - \right.$$
$$\left. - \exp\left[-\frac{r_S(\rho_0 + r_S)}{4Dt}\right]\left[\left(\frac{r_S}{2} - \rho_0\right)I_0\left(\frac{r_S^2}{2Dt}\right) + r_S I_1\left(\frac{r_S^2}{2Dt}\right)\right]\right\}. \quad (15)$$

Substitution of expression (15) into Eq. (7) gives

$$\int\limits_0^{+\infty} w_L^{\mathrm{in}}(t)\mathrm{d}t = r_S \int\limits_{r_S}^{+\infty} \rho_0 n_S(\rho_0)\mathrm{d}\rho_0 \times$$
$$\times \int\limits_0^{+\infty} \frac{\mathrm{d}W_{\mathrm{in}}\left[\mathbf{r}(\rho), \mathbf{r}_0(\rho_0), t\right]}{\mathrm{d}t}\mathrm{d}t\ , \quad (16)$$

where $n_S(\rho)$ is the two-dimensional concentration distribution in the Σ plane.

Equations (13) and (16) in combination with expressions (4) and (8) complete the solution of the problem of the species balance in the reaction zone.

Thus, in this work, we described a fairly general approach to the solution of the problem in the species balance in the zone of an elementary chemical event of a reaction. A class of processes has been found, namely, quasi-steady-state processes, for which the problem of the species balance can be solved without invoking any assumptions concerning the mechanism of the chemical event in the reaction zone. The balance of species in this case is mainly determined by the geometric properties of the system, the problem being actually reduced to determination of the probability of species entering the chemical act zone and is solved by the Green function method.

The difference between the approach proposed here and conventional macroscopic analysis of the balance is that in this case, there is no need to take into account diffusion, migration, and surface diffusion of the reaction products. This is based on the fact that the probability of their removal from the reaction zone is equal to unity throughout the whole process (unlike the probability that the reactants will enter the reaction zone, which substantially differs from unity). Thus, for quasi-steady-state processes, the description of the corresponding systems is markedly simplified.

## Appendix 1. Green function and probability distribution in the Ω half-space in the general case where $\nu_1\nu_2 \neq 0$

Let us consider $M(x,y,z)$ and $P(\xi,\eta,\zeta)$, *i.e.*, the fixed and mobile points of the Green function, respectively. Then the Green function, similar to Eq. (10), in the general case where $\nu_1\nu_2 \neq 0$ has the form

$$G = \frac{1}{\left(2\sqrt{\pi Dt}\right)^3}\left\{\exp\left(-\frac{r_{MP}^2}{4Dt}\right) - \exp\left(-\frac{r_P}{r_S}\frac{r_{MP_1}^2}{4Dt}\right) + \exp\left(-\frac{r_{MP_2}^2}{4Dt}\right) - \exp\left(-\frac{r_{P_2}}{r_S}\frac{r_{MP_3}^2}{4Dt}\right) + \right.$$

$$+\,2\frac{\nu_1}{\nu_2}\int\limits_{-\infty}^{-\varsigma}\mathrm{d}\hat{\varsigma}\exp[-(\nu_1/\nu_2)(\varsigma+\hat{\varsigma})]\left[\exp\left(-\frac{(x-\xi)^2+(y-\eta)^2+(z-\hat{\varsigma})^2}{4Dt}\right)-\right.$$

$$\left.\left.-\exp\left(-\frac{\sqrt{\xi^2+\eta^2+\hat{\varsigma}^2}}{r_S}\,\frac{\left(x-\dfrac{\xi r_S^2}{\xi^2+\eta^2+\hat{\varsigma}^2}\right)^2+\left(y-\dfrac{\eta r_S^2}{\xi^2+\eta^2+\hat{\varsigma}^2}\right)^2+\left(z-\dfrac{\hat{\varsigma} r_S^2}{\xi^2+\eta^2+\hat{\varsigma}^2}\right)^2}{4Dt}\right)\right]\right\}.$$

The probability distribution in the $\Omega$ half-space is then equal to

$$W(\mathbf{r},\mathbf{r}_0,t)=\frac{1}{4\pi^{1/2}(Dt)^{3/2}}\left\{2\frac{\nu_1}{\nu_2}\left[I_0\left(\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{\rho^2+\rho_0^2}{4Dt}\right)T_1(z,z_0,t)-T_2(\rho,z,\rho_0,z_0,t)\right]+\right.$$

$$+\,I_0\left(\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{\rho^2+\rho_0^2}{4Dt}\right)\left[\exp\left(-\frac{(z-z_0)^2}{4Dt}\right)-\exp\left(-\frac{(z+z_0)^2}{4Dt}\right)\right]+$$

$$\left.+\,I_0\left(\frac{r_S}{r_0}\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{r_0}{r_S}\frac{\rho^2+\rho_0^2r_S^4/r_0^4}{4Dt}\right)\left[\exp\left(-\frac{r_0}{r_S}\frac{\left(z-z_0r_S^2/r_0^2\right)^2}{4Dt}\right)-\exp\left(-\frac{r_0}{r_S}\frac{\left(z+z_0r_S^2/r_0^2\right)^2}{4Dt}\right)\right]\right\},$$

where

$$T_1(z,z_0,t)=4\sqrt{Dt}\,\exp\left[Dt\left(\frac{\nu_1}{\nu_2}\right)^2-\frac{\nu_1}{\nu_2}(z+z_0)\right]\mathrm{Erfc}\left[\frac{z+z_0}{\sqrt{2Dt}}-\sqrt{2Dt}\,\frac{\nu_1}{\nu_2}\right],$$

$$T_2(\rho,z,\rho_0,z_0,t)=\int\limits_{z_0}^{+\infty}I_0\left(\frac{r_S}{\sqrt{\rho_0^2+q^2}}\frac{\rho\rho_0}{2Dt}\right)\exp\left[-\frac{\nu_1}{\nu_2}(z-q)\right]\times$$

$$\times\exp\left[-\frac{\sqrt{\rho_0^2+q^2}}{r_S}\frac{1}{4Dt}\left(\rho^2+\rho_0^2\frac{r_S^4}{(\rho_0^2+q^2)^2}+\left(z+q\frac{r_S^2}{\rho_0^2+q^2}\right)^2\right)\right]\mathrm{d}q\,.$$

## Appendix 2. Partial derivatives of the probability distribution function in the $\Omega$ half-space

Here, we present the expressions for the partial derivatives in Eq. (12) for all possible sorts of combinations of the $\nu_1$ and $\nu_2$ parameters.

In the case where $\nu_1 = 0$ or $\nu_2 = 0$, we have

$$\frac{\partial W\left[\mathbf{r}(\rho,z),\mathbf{r}_0(\rho_0,z_0),t\right]}{\partial\rho}=\frac{1}{8\pi^{1/2}(Dt)^{5/2}}\left\{\pm\left[\frac{r_S\rho_0}{r_0}I_1\left(\frac{r_S}{r_0}\frac{\rho\rho_0}{2Dt}\right)-\frac{r_0\rho}{r_S}I_0\left(\frac{r_S}{r_0}\frac{\rho\rho_0}{2Dt}\right)\right]\times\right.$$

$$\times\exp\biggl(-\frac{r_0}{r_S}\,\frac{\rho^2+\rho_0^2r_S^4/r_0^4}{4Dt}\biggr)\Biggl[\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z-z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)-\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z+z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)\Biggr]+$$

$$+\exp\biggl(-\frac{\rho^2+\rho_0^2}{4Dt}\biggr)\biggl[\exp\biggl(-\frac{(z-z_0)^2}{4Dt}\biggr)-\exp\biggl(-\frac{(z+z_0)^2}{4Dt}\biggr)\biggr]\biggl[\rho_0I_1\biggl(\frac{\rho\rho_0}{2Dt}\biggr)-\rho I_0\biggl(\frac{\rho\rho_0}{2Dt}\biggr)\biggr]\Biggr\},$$

$$\frac{\partial W\bigl[\mathbf{r}(\rho,z),\mathbf{r}_0(\rho_0,z_0),t\bigr]}{\partial z}=\frac{1}{8\pi^{1/2}(Dt)^{5/2}}\Biggl\{\pm\exp\biggl(-\frac{r_0}{r_S}\,\frac{\rho^2+\rho_0^2r_S^4/r_0^4}{4Dt}\biggr)I_0\biggl(\frac{r_S}{r_0}\,\frac{\rho\rho_0}{2Dt}\biggr)\frac{r_0}{r_S}\times$$

$$\times\Biggl[\biggl(z+z_0\frac{r_S^2}{r_0^2}\biggr)^2\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z+z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)-\biggl(z-z_0\frac{r_S^2}{r_0^2}\biggr)^2\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z-z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)\Biggr]+$$

$$+\exp\biggl(-\frac{\rho^2+\rho_0^2}{4Dt}\biggr)I_0\biggl(\frac{\rho\rho_0}{2Dt}\biggr)\biggl[(z+z_0)\exp\biggl(-\frac{(z+z_0)^2}{4Dt}\biggr)-(z-z_0)\exp\biggl(-\frac{(z-z_0)^2}{4Dt}\biggr)\biggr]\Biggr\}.$$

In the case where $\nu_1\nu_2 \neq 0$, we have

$$\frac{\partial W\bigl[\mathbf{r}(\rho,z),\mathbf{r}_0(\rho_0,z_0),t\bigr]}{\partial \rho}=\frac{1}{8\pi^{1/2}(Dt)^{5/2}}\Biggl\{\biggl[\frac{r_S\rho_0}{r_0}I_1\biggl(\frac{r_S}{r_0}\,\frac{\rho\rho_0}{2Dt}\biggr)-\frac{r_0\rho}{r_S}I_0\biggl(\frac{r_S}{r_0}\,\frac{\rho\rho_0}{2Dt}\biggr)\biggr]\times$$

$$\times\exp\biggl(-\frac{r_0}{r_S}\,\frac{\rho^2+\rho_0^2r_S^4/r_0^4}{4Dt}\biggr)\Biggl[\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z-z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)-\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z+z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)\Biggr]+$$

$$+\exp\biggl(-\frac{\rho^2+\rho_0^2}{4Dt}\biggr)\biggl[\exp\biggl(-\frac{(z-z_0)^2}{4Dt}\biggr)-\exp\biggl(-\frac{(z+z_0)^2}{4Dt}\biggr)\biggr]\biggl[\rho_0I_1\biggl(\frac{\rho\rho_0}{2Dt}\biggr)-\rho I_0\biggl(\frac{\rho\rho_0}{2Dt}\biggr)\biggr]+$$

$$+2\frac{\nu_1}{\nu_2}\biggl[T_1(z,z_0,t)\exp\biggl(-\frac{\rho^2+\rho_0^2}{4Dt}\biggr)\biggl(\rho_0I_1\biggl(\frac{\rho\rho_0}{2Dt}\biggr)-\rho I_0\biggl(\frac{\rho\rho_0}{2Dt}\biggr)\biggr)-\frac{\partial T_2}{\partial\rho}\biggr]\Biggr\},$$

$$\frac{\partial W\bigl[\mathbf{r}(\rho,z),\mathbf{r}_0(\rho_0,z_0),t\bigr]}{\partial z}=\frac{1}{8\pi^{1/2}(Dt)^{5/2}}\Biggl\{\exp\biggl(-\frac{r_0}{r_S}\,\frac{\rho^2+\rho_0^2r_S^4/r_0^4}{4Dt}\biggr)I_0\biggl(\frac{r_S}{r_0}\,\frac{\rho\rho_0}{2Dt}\biggr)\frac{r_0}{r_S}\times$$

$$\times\Biggl[\biggl(z+z_0\frac{r_S^2}{r_0^2}\biggr)^2\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z+z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)-\biggl(z-z_0\frac{r_S^2}{r_0^2}\biggr)^2\exp\biggl(-\frac{r_0}{r_S}\,\frac{\bigl(z-z_0r_S^2/r_0^2\bigr)^2}{4Dt}\biggr)\Biggr]+$$

$$+ \exp\left(-\frac{\rho^2+\rho_0^2}{4Dt}\right) I_0\left(\frac{\rho\rho_0}{2Dt}\right)\left[(z+z_0)\exp\left(-\frac{(z+z_0)^2}{4Dt}\right) - (z-z_0)\exp\left(-\frac{(z-z_0)^2}{4Dt}\right)\right] +$$

$$+ 2\frac{\nu_1}{\nu_2}\left[I_0\left(\frac{\rho\rho_0}{2Dt}\right)\exp\left(-\frac{\rho^2+\rho_0^2}{4Dt}\right)\frac{\partial T_1}{\partial z} - \frac{\partial T_2}{\partial \rho}\right]\Bigg\}.$$

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*Received July 26, 2000;*
*in revised form February 23, 2001*