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Exact solution of the reaction–diffusion problem for a particle generating band on a surface by Riemann–Hilbert matching

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Abstract. The existence of a class of exact solutions for diffusion–reaction problems is demonstrated for the example of a band. The method may be applied to any particle source which can be analytically mapped to a band (or a disc) situated on an infinite plane. A simple asymptotic expression for the experimentally measurable collector efficiency (current–current response function) has been found.

1. Introduction

The diffusion–reaction problem for particle generating sources on an infinite supporting surface arises in a number of physical and chemical contexts. Among important applications are the description of electrochemical micro-electrode sensors [1] and molecular electronic devices [2]. Progress in research with these and similar devices has been impeded by the lack of an exact description of the corresponding diffusion–reaction processes. Computer simulations [3] may not lead directly to accurate results due to the presence of singularities when the particle source dimensions tend to zero. An additional computational problem is connected with the presence of non-analyticity in the supporting surface reaction rate constant. This latter problem arises because particles generated (starting at $t = 0$) at the electrode surface will migrate to infinity as $t \to \infty$ if the supporting surface is inert. However, in the case of particle absorption on an infinite plane, even if this is infinitely slow all the particles will eventually be absorbed.

The diffusion problem for a generating band situated on an inert plane in the limit of zero band width, and/or as $t \to \infty$, has recently been analysed by Szabo *et al* [4]. They have shown that the long-time limit of this diffusion current is described by the asymptotics of the solution for a hemi-cylinder on an inert plane (which could easily be reduced to the classical solution for a cylinder [5]) by setting the radius to one quarter of the band width. We have subsequently shown [6], using the zero-range potential approach, that this result is of a very general nature. Due to dominating singularities when the source dimensions tend to zero, the asymptotics for electrodes of different shapes, both on inert and reacting planes, can be described by the solutions for a disc or for a band by adjusting one length scale parameter only. The applicability of this approximation to solutions of the Helmholtz equation in a halfspace has been developed by the St Petersburg University school [7].

In this paper we give an exact solution for a prototypical diffusion–reaction problem for a zero-height band (on which particles are generated) situated on a reacting infinite plane (see figure 1). The relationship of this problem to the description of redox reactions on micro-electrodes is described in appendix 1. As a method of solution we have used Riemann–Hilbert matching in the absence of time inversion ($t \to -t$) symmetry [8]. An

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analogous approach could be used for a generating disc on a surface and for all other geometries which can be analytically mapped to a band or a disc on an infinite plane. The work presented in this paper can be considered as an extension of the approach of Marshall and Watson [9a] and Keinz [9b] from one to two spatial dimensions.

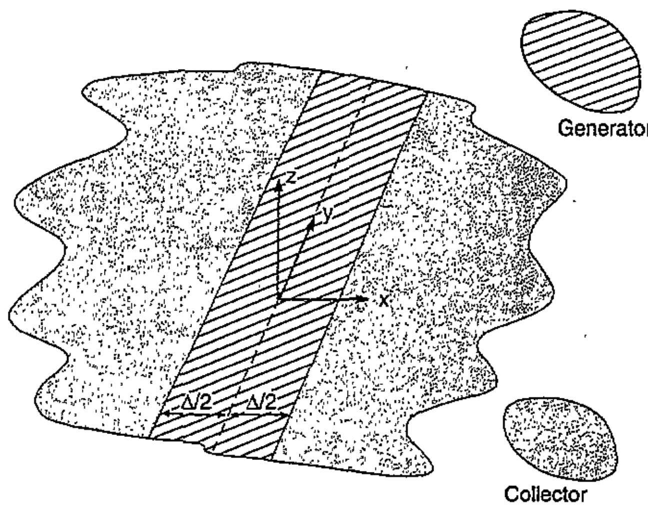

Figure 1. The geometry of the problem.

The paper is organized as follows. In section 2 we express the basic equations. In section 3 these equations are transformed into a solvable Riemann–Hilbert problem. In section 4 the singular integrals resulting from the solution of the Riemann–Hilbert problem are transformed into non-singular forms in which they can be numerically calculated and compared with experimentally measurable time-Fourier-transforms of densities and currents. In section 5 the nature of the singularities of the exact solution are made clear and asymptotic expressions are given in a form useful for analysis of experimental data. In the concluding section we discuss the reasons for the relative simplicity of the asymptotics for the collection efficiency, the relationship of our results to those results obtained in the zero range potential approximation [6], and possible generalizations.

2. Description of the problem

The geometry is as in figure 1. The concentration of particles $\rho(x, z, t)$ obeys the diffusion equation

$$\frac{\partial \rho}{\partial t} = D\left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2}\right) \tag{1}$$

as $\rho(x, z, t)$ is assumed to be independent of the coordinate y. In what follows we will calculate currents and other observable quantities per unit interval in the y direction. We seek a solution subject to the following boundary and initial conditions:

$$\begin{aligned}
&k_1\rho - D\frac{\partial\rho}{\partial z} = \theta(t)A \qquad \text{for } z=0\ |x| < \frac{\Delta}{2} \\
&k_2\rho - D\frac{\partial\rho}{\partial z} = 0 \qquad \text{for } z=0\ |x| > \frac{\Delta}{2} \\
&\rho(x,z,t) \to 0 \qquad \text{for } \sqrt{x^2+z^2} \to \infty\ k_2 > 0 \\
&\rho(x,z,t) = 0 \qquad \text{for } t = 0
\end{aligned} \tag{2}$$

where $\theta(t)$ is the step function, Δ is the band width (figure 1), k_1 and k_2 are surface reaction constants for $|x| < \Delta/2$ and $|x| > \Delta/2$ respectively, and A is a constant source per unit surface area, the meaning of which is indicated in the appendix 1 for the electrochemical situation. The problem has only the trivial solution $\rho \equiv 0$ for $A = 0$ or $\Delta = 0$.

Taking simultaneous Fourier transforms of equation (1) with respect to x and t we find the equation

$$\mathrm{i}\omega\tilde{\rho}(p,z,\mathrm{i}\omega) = D\left(\frac{\partial^2\tilde{\rho}((p,z,\mathrm{i}\omega))}{\partial z^2} - p^2\tilde{\rho}(p,z,\mathrm{i}\omega)\right) \tag{3a}$$

which has the solutions

$$\tilde{\rho}(p,z,\mathrm{i}\omega) = \exp[\mp\sqrt{p^2+(\mathrm{i}\omega/D)}z]\tilde{\rho}(p,\mathrm{i}\omega) \tag{3b}$$

where $\tilde{\rho}(p,\mathrm{i}\omega)$ is to be determined by the enforcement of the boundary and initial conditions. The function $\rho(x,z,t)$ satisfying (1) and decreasing as $z \to \infty$ can thus be represented in terms of the Fourier integrals

$$\begin{aligned}
\rho(x,z,t) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\rho(x,z,\mathrm{i}\omega)\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}\omega \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}\omega\int_{-\infty}^{\infty}\exp[(-\sqrt{p^2+(\mathrm{i}\omega/D)}z]\mathrm{e}^{-\mathrm{i}px}\tilde{\rho}(p,\mathrm{i}\omega)\,\mathrm{d}p.
\end{aligned} \tag{4}$$

The (distribution valued) generalized function $\tilde{\rho}(p,\mathrm{i}\omega)$ satisfies the conditions

$$\tilde{\rho}^*(p,\mathrm{i}\omega) = \tilde{\rho}(-p^*,(\mathrm{i}\omega)^*) \qquad \lim_{p\to\infty}|p\tilde{\rho}(p,\mathrm{i}\omega)| \leqslant \text{constant} \tag{5}$$

corresponding to the fact that the concentration $\rho(x,y,t)$ is a real finite function. The initial condition at $t = 0$ will be satisfied by (4) because all singularities of $\tilde{\rho}(\mathrm{i}\omega, p)$ as a function of ω will be located in the upper half-plane of the complex variable ω and it is possible, for $t \leqslant 0$, to close the integral over $\mathrm{d}\omega$ in (4) by the integral contour over an infinite semi-circle in the lower complex half-plane.

We require that the square root $\sqrt{q^2+\mathrm{i}\omega/D}$ as a function of the complex variable q be confined on the Riemann sheet where

$$k_{1,2} + D\sqrt{q^2+\frac{\mathrm{i}\omega}{D}} \neq 0 \qquad \mathrm{Re}\sqrt{p^2+\frac{\mathrm{i}\omega}{D}} > 0 \qquad (\mathrm{Im}\,p = 0). \tag{6}$$

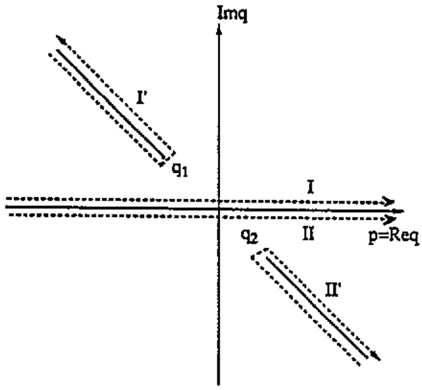

Figure 2. The singularity structure of the integrands of integrals in the text. The points $q_1 = \mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}}$ and $q_2 = -\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}}$ are the endpoints of square root cuts. The cut along the real axis is determined by the behaviour of the factor $\mathrm{e}^{\psi(q)}$: $\mathrm{e}^{\psi(p+\mathrm{i}\varepsilon)} = \gamma(p)\mathrm{e}^{\psi(p-\mathrm{i}\varepsilon)}$ for real p. There are additional poles in some integrands. The contours I, I′, II and II′ are utilized in the developments described in the text.

We choose the square root cuts running (see figure 2) from

$$\pm\,\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}} \qquad \text{to} \qquad \pm\,\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}} \times \infty. \tag{7}$$

The inequality (6) guarantees that expression (4), for $\rho(x, z, t)$, decreases as $z \to \infty$ and the boundary condition at $z \to \infty$ is satisfied. The boundary condition at $z = 0$ can be rewritten as

$$\begin{aligned}
\theta\left(\frac{\Delta^2}{4} - x^2\right) &\int \left(k_1 + D\sqrt{p^2 + \frac{\mathrm{i}\omega}{D}}\right) \tilde{\rho}(p, \mathrm{i}\omega)\mathrm{e}^{-\mathrm{i}px}\,\mathrm{d}p + \theta\left(x^2 - \frac{\Delta^2}{4}\right) \\
&\times \int \left(k_2 + D\sqrt{p^2 + \frac{\mathrm{i}\omega}{D}}\right) \tilde{\rho}(p, \mathrm{i}\omega)\mathrm{e}^{-\mathrm{i}px}\,\mathrm{d}p \\
&= \int \left(k_2 + D\sqrt{p^2 + \frac{\mathrm{i}\omega}{D}}\right) \tilde{\rho}(p, \mathrm{i}\omega)\mathrm{e}^{-\mathrm{i}px}\,\mathrm{d}p - \theta\left(\frac{\Delta^2}{4} - x^2\right) \\
&\times (k_2 - k_1)\sqrt{2\pi}\,\rho(x, 0, \mathrm{i}\omega) \\
&= \theta\left(\frac{\Delta^2}{4} - x^2\right) \frac{\sqrt{2\pi}\,A}{2\pi\mathrm{i}(\omega - \mathrm{i}\varepsilon)}
\end{aligned} \tag{8}$$

where we have substituted (4) into (2) and used the expression for the Fourier transform of the step function $\theta(t)$:

$$\theta(t) = \frac{1}{2\pi\mathrm{i}} \int \mathrm{e}^{\mathrm{i}\omega t} \frac{\mathrm{d}\omega}{\omega - \mathrm{i}\varepsilon} \qquad \varepsilon \to +0. \tag{9}$$

The problem is thus reduced to the construction of $\tilde{\rho}(p, \mathrm{i}\omega)$ satisfying (8) and (5). In the next section we show that such a construction can be performed by finding the solution of the Riemann–Hilbert matching problem.

3. Formulation and solution of the Riemann–Hilbert matching problem

We first seek the solution of equation (8) on the interval $x > -\frac{\Delta}{2}$ and will later use the symmetry about the inversion $x \to -x$ to continue the solution to the interval $x < -\frac{\Delta}{2}$.

The function $\tilde{\rho}(p, \mathrm{i}\omega)$ may be represented in the two forms

$$\begin{aligned}\tilde{\rho}(p,\mathrm{i}\omega) &= \frac{1}{k_1 + D\sqrt{p^2+(\mathrm{i}\omega/D)}}\mathrm{e}^{\mathrm{i}p\Delta/2}\left\{f_1(p,\mathrm{i}\omega) + \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)(p-\mathrm{i}\varepsilon)}\right\}\\ &= \frac{1}{k_2 + D\sqrt{p^2+(\mathrm{i}\omega/D)}}\mathrm{e}^{\mathrm{i}p\Delta/2}\\ &\quad\times\left\{f_2(p,\mathrm{i}\omega) + \frac{k_2+\sqrt{D\mathrm{i}\omega}}{k_1+\sqrt{D\mathrm{i}\omega}}\frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)(p-\mathrm{i}\varepsilon)}\right\}.\end{aligned} \tag{10}$$

The boundary conditions (8) will be satisfied for $x \geqslant -\frac{\Delta}{2}$ if the (unknown) functions $f_1(q,\mathrm{i}\omega)$ and $f_2(q,\mathrm{i}\omega)$, *considered now as functions of the complex variable* q, have singularities only in the lower and the upper half of the complex plane respectively. This follows from Cauchy's theorem after closing the integration paths over $\mathrm{d}p$ in (8) by semi-circles in upper and lower complex half-planes for $x > \frac{\Delta}{2}$ and $|x| < \frac{\Delta}{2}$ respectively.

Let us introduce a single function $f(q)$ of the complex variable q (the $\mathrm{i}\omega$ dependence will be understood) such that

$$\begin{aligned} &f(q) = f_1(q,\mathrm{i}\omega) && \text{for } \operatorname{Im} q > 0\\ &f(q) = f_2(q,\mathrm{i}\omega) && \text{for } \operatorname{Im} q < 0\\ &f(p+\mathrm{i}\varepsilon) = f_1(p,\mathrm{i},\omega) &&\\ &f(p-\mathrm{i}\varepsilon) = f_2(p,\mathrm{i}\omega) && \varepsilon \to +0, \text{with } p \text{ real}\end{aligned} \tag{11}$$

this being the essence of the Riemann–Hilbert method [8]. According to (10), the function $f(q)$ must have a cut on the real axis $p = \operatorname{Re} q$ with the discontinuity satisfying the relation

$$\gamma(p)f(p-\mathrm{i}\varepsilon) - f(p+\mathrm{i}\varepsilon) = \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)p}\left(1-\frac{\gamma(p)}{\gamma(0)}\right) \tag{12}$$

where the functions

$$\gamma(q) = \frac{k_1 + D\sqrt{q^2+(\mathrm{i}\omega/D)}}{k_2 + D\sqrt{q^2+(\mathrm{i}\omega/D)}} \qquad \ln\gamma(q) \qquad \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)q}\left(1-\frac{\gamma(q)}{\gamma(0)}\right) \tag{13}$$

are analytic functions of the complex variable q in the strip near the real axis where

$$\left|q^2 + \frac{\mathrm{i}\omega}{D}\right| > 0 \tag{14}$$

provided that the logarithmic branch cuts do not intersect the boundary of the strip. The branch of $\ln\gamma(q)$ is chosen so that on the real axis $\operatorname{Im}(q) = 0$, $\operatorname{Re}(q) = p$ and

$$\ln\gamma(p) \to 0 \qquad \text{as } |p| \to \infty. \tag{15}$$

Equation (12) has the form of a classical Riemann–Hilbert matching problem [8]. In order to solve (12) we introduce an auxiliary function $F(q)$ [8]:

$$F(q) = f(q)\mathrm{e}^{-\psi(q)}$$
$$\psi(q) = \frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p)}{p-q}\,\mathrm{d}p. \tag{16}$$

Using the well known symbolic relation

$$\frac{1}{p'-p\pm\mathrm{i}\varepsilon} = \frac{p}{p'-p} \pm \pi\mathrm{i}\delta(p'-p) \qquad \varepsilon\to+0 \text{ for real } p \text{ and } p' \tag{17}$$

(12) can be rewritten as

$$\begin{aligned} B(p) &\equiv F(p-\mathrm{i}\varepsilon) - F(p+\mathrm{i}\varepsilon) \\ &= \frac{\sqrt{2\pi}A(1-(\gamma(p)/\gamma(0)))}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)p}\frac{1}{\sqrt{\gamma(p)}}\exp\left[-\frac{p}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p')}{p'-p}\,\mathrm{d}p'\right] \\ &= \frac{\sqrt{2\pi}A(1-(\gamma(p)/\gamma(0)))}{(2\pi\mathrm{i})^2(\omega-\mathrm{i}\varepsilon)p}\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\mathrm{d}p'\frac{\ln\gamma(p')}{p'-p-\mathrm{i}\varepsilon}\right]. \end{aligned} \tag{18}$$

If the constant A was equal to zero and, correspondingly, $B(p) = 0$, then the function $F(q)$ could be analytically continued to the entire complex plane and in accordance with (5) would be a real constant. Correspondingly equation (18) has the unique (up to a constant C) solution

$$F(q) = C - \frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\mathrm{d}p\frac{B(p)}{p-q} \tag{19}$$

and according to (16)

$$f(q) = \left(C - \frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\mathrm{d}p\frac{B(p)}{p-q}\right)\mathrm{e}^{\psi(q)}. \tag{20}$$

The constant $C \equiv C(\mathrm{i}\omega)$ is to be determined from the symmetry condition

$$\left.\frac{\partial\rho(x,0,\mathrm{i}\omega)}{\partial x}\right|_{x=0} = -\mathrm{i}\sqrt{2\pi}\int_{-\infty}^{\infty}p\tilde{\rho}(p,\mathrm{i}\omega)\,\mathrm{d}p = 0 \tag{21}$$

after introducing expression (10) for $\tilde{\rho}(p,\mathrm{i}\omega)$ into (21) and with $f(q)$ determined by (20). Condition (21) allows us to construct the solution of our problem symmetrically about the inversion $x\to -x$ (see also the note before (29)).

4. Expression of $\rho(x, 0, \mathrm{i}\omega)$ through nonsingular integrals

The substitution of (20) into (10) with the subsequent enforcement of condition (21) provides the formal solution of the problem in terms of singular integrals. In order to analyse approximations that are valid in different limiting cases and to perform numerical calculations it is useful to transform these integrals into non-singular integrals. The standard method used to achieve this transformation is contour distortion in the complex plane, which in some cases even allows us to find expressions of the relevant integrals in terms of elementary functions. The method is illustrated in appendix 2. It follows from (10), (19), (20) and the results of appendix 2 that

$$\tilde{\rho}(p, \mathrm{i}\omega) = \frac{\mathrm{e}^{\mathrm{i}p\Delta/2}}{k_1 + D\sqrt{p^2 + (\mathrm{i}\omega/D)}}\left\{C \exp\left[\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p')\,\mathrm{d}p'}{p' - p - \mathrm{i}\varepsilon}\right] + \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega - \mathrm{i}\varepsilon)p - \mathrm{i}\varepsilon}\left(\frac{\gamma(p)}{\gamma(0)}\right)\right\}$$

$$= \frac{\mathrm{e}^{\mathrm{i}p\Delta/2}}{k_2 + D\sqrt{p^2 + (\mathrm{i}\omega)/D}}\left\{\frac{C}{\sqrt{\gamma(p)}}\left(\frac{D\mathrm{i}p + \sqrt{D\mathrm{i}\omega - k_1^2}}{\sqrt{D\mathrm{i}\omega - k_1^2}}\right)^{\frac{k_1}{4\sqrt{D\mathrm{i}\omega}}} \times \left(\frac{D\mathrm{i}p + \sqrt{D\mathrm{i}\omega - k_2^2}}{\sqrt{D\mathrm{i}\omega - k_2^2}}\right)^{-\frac{k_2}{4\sqrt{D\mathrm{i}\omega}}} + \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2\gamma(0)(\omega - \mathrm{i}\varepsilon)(p - \mathrm{i}\varepsilon)}\right\}. \tag{22}$$

The expression for the constant C in terms of the non-singular integrals that follow from (21) and (10) after the contour distortions shown on figure 2, and a change of the integration variables, has the form

$$C = -\frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega - \mathrm{i}\varepsilon)\gamma(0)}\int_1^{\infty}\mathrm{d}p\exp\left[-\sqrt{\frac{\mathrm{i}\omega}{D}}\frac{\Delta}{2}p\right]\frac{\sqrt{p^2-1}}{k_2^2 + D\mathrm{i}\omega(p^2-1)} \times \left[\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}}\int_1^{\infty}\mathrm{d}p\exp\left[-\sqrt{\frac{\mathrm{i}\omega}{D}}\frac{\Delta}{2}p\right]\frac{p\sqrt{p^2-1}\exp[\psi(\mathrm{i}\sqrt{\mathrm{i}\omega/D}p)]}{(\sqrt{D\mathrm{i}\omega}p - \sqrt{D\mathrm{i}\omega - k_1^2})}\right]^{-1}. \tag{23}$$

The explicit expression for the factor $\exp[\psi(\mathrm{i}\sqrt{\mathrm{i}\omega/D}p)]$ in (23) is calculated in appendix 2.

By a Fourier transform of (22) it is possible to find the integral representations for the experimentally measurable quantity $\rho(x, z, \mathrm{i}\omega)$. For $z = 0$ we find from (22), with the help of the contour distortion, that

$$\rho(x, 0, \mathrm{i}\omega) = \frac{1}{\sqrt{2\pi}}\int_1^{\infty}\mathrm{d}p\exp\left[\mathrm{i}p\left(\frac{\Delta}{2} - |x|\right)\right]\tilde{\rho}(p, \mathrm{i}\omega)$$

$$= \frac{A}{2\pi\mathrm{i}(k_1 + \sqrt{D\mathrm{i}\omega})\omega} + \frac{2D\mathrm{i}\omega}{\sqrt{2\pi}}\int_1^{\infty}\mathrm{d}p\exp\left[-\sqrt{\frac{\mathrm{i}\omega}{D}}\left(\frac{\Delta}{2} - |x|\right)p\right]\sqrt{p^2-1}\frac{1}{k_1^2 + D\mathrm{i}\omega(p^2-1)} \times \left\{C\exp\left[\psi\left(\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}}p\right)\right] + \frac{\sqrt{2\pi}A\gamma(p)}{(2\pi\mathrm{i})^2\gamma(0)\omega p}\right\} \qquad \text{for } |x| < \frac{\Delta}{2}, |\omega| > 0$$

$$\rho(x, 0, \mathrm{i}\omega) = \frac{2D\mathrm{i}\omega}{\sqrt{2\pi}}\int_{-1}^{-\infty}\mathrm{d}p\exp\left[-\sqrt{\frac{\mathrm{i}\omega}{D}}\left(\frac{\Delta}{2} - |x|\right)p\right]\frac{\sqrt{p^2-1}}{k_2^2 + D\mathrm{i}\omega(p^2-1)}$$

$$\times\left\{C\exp\left[\psi\left(\mathrm{i}\sqrt{\frac{\mathrm{i}\omega}{D}}p\right)\right]+\frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2\gamma(0)\omega p}\right\}\qquad\text{for } |x|>\frac{\Delta}{2},\ |\omega|>0 \tag{24}$$

where the expressions for C and $\exp[\psi(\mathrm{i}\sqrt{\mathrm{i}\omega/D}p)]$ are given by (23), (A12) and (A14). The relatively simple non-singular integral representations (24) for $\rho(x,0,\mathrm{i}\omega)$ allows us to describe the most common experimental situations where concentrations and currents are measured on the plane $z=0$.

5. Asymptotics

For applications, especially in the case of small Δ, it is important to calculate the asymptotics in the long-time limit

$$\Delta\sqrt{\frac{1}{Dt}}\to 0 \tag{25}$$

which corresponds in terms of time-Fourier-transforms to the limit of the dimensionless width $\tilde{\Delta}$ going to zero:

$$\tilde{\Delta}=\Delta\sqrt{\frac{|\omega|}{D}}\to 0. \tag{26}$$

It is also important to understand the behaviour of the solution as $k_2\to +0$.

In this section we give a direct derivation of the asymptotic solution of our problem using a method analogous to the zero-range approximation of wave scattering theory [7, 10]. The starting point is the relation

$$\rho(p,\mathrm{i}\omega)=\frac{1}{k_2+D\sqrt{p^2+(\mathrm{i}\omega/D)}}\left[\frac{\sqrt{2\pi}A\sin\frac{1}{2}\Delta p}{2\pi^2\mathrm{i}(\omega-\mathrm{i}\varepsilon)p}\right.$$
$$\left.+(k_2-k_1)\frac{1}{\sqrt{2\pi}}\int_{-\Delta/2}^{\Delta/2}\mathrm{e}^{\mathrm{i}px}\rho(x,0,\mathrm{i}\omega)\,\mathrm{d}x\right] \tag{27}$$

which follows from the Fourier transform of (8). Since in the limit $\tilde{\Delta}\to 0$ the function $\rho(x,0,\mathrm{i}\omega)$ on the interval $|x|<\frac{\Delta}{2}$ becomes constant up to terms of the first order in $\tilde{\Delta}$, it is possible to replace, approximately, $\rho(x,0,\mathrm{i}\omega)$ under the integral in (27) by its value $\rho(0,0,\mathrm{i}\omega)$ at $x=0$. This leads to the equation

$$\tilde{\rho}(p,\mathrm{i}\omega)=\frac{\sin\frac{1}{2}\Delta p}{(k_2+D\sqrt{p^2+(\omega/D)})p}\left[\frac{\sqrt{2\pi}A}{2\pi^2\mathrm{i}(\omega-\mathrm{i}\varepsilon)}+(k_2-k_1)\sqrt{\frac{2}{\pi}}\rho(0,0,\mathrm{i}\omega)\right] \tag{28}$$

which is correct up to terms of the order of $\tilde{\Delta}^2$. The value of $\rho(0,0,\mathrm{i}\omega)$ is defined by the self consistency condition†

$$\rho(0,0,\mathrm{i}\omega)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{\rho}(p,\mathrm{i}\omega)\,\mathrm{d}p=\frac{1}{\pi\mathrm{i}}\left[\frac{\sqrt{2\pi}A}{(2\pi)^{3/2}\mathrm{i}(\omega-\mathrm{i}\varepsilon)}+(k_2-k_1)\rho(0,0,\mathrm{i}\omega)\right]p$$

† Note that relations (27) can also be used as the starting point as an alternative to the method based on (21) for the continuation of the expression for $\rho(x,z,\mathrm{i}\omega)$ from the interval $x>-\Delta/2$ to the whole real x-axis.

$$\times \int_{-\infty}^{\infty} \frac{\mathrm{d}p}{p} \frac{\mathrm{e}^{\mathrm{i}p\frac{\Delta}{2}}}{k_2 + D\sqrt{p^2 + (\mathrm{i}\omega/D)}} = \left[\frac{A\sqrt{2\pi}}{2\pi \mathrm{i}(\omega - \mathrm{i}\varepsilon)} + (k_2 - k_1)\rho(0,0,\mathrm{i}\omega) \right]$$
$$\times \left[\frac{1}{k_2 + \sqrt{D\mathrm{i}\omega}} + \frac{2\sqrt{D\mathrm{i}\omega}}{\pi} \int_1^{\infty} \frac{\mathrm{d}p\sqrt{p^2-1}}{p} \frac{\exp\left[-\sqrt{\frac{\mathrm{i}\omega}{D}}\frac{\Delta}{2}p\right]}{k_2^2 + D\mathrm{i}\omega(p^2-1)} \right] \tag{29}$$

where in the last equality we have made the now familiar integral contour distortion taking into account the pole at $p = \mathrm{i}\varepsilon$ in the integrand. The asymptotic expression (A19) for the integral in (29) is found in appendix 3. After substitution of (A19) into (36) we find, finally, that

$$\rho(0,0,\mathrm{i}\omega) \underset{\Delta\to 0}{=} -\frac{A\sqrt{\mathrm{i}\omega/D}\,\Delta}{2\pi \mathrm{i}\omega} \left[\frac{\mathrm{i}k_2}{D\mathrm{i}\omega\sqrt{D\mathrm{i}\omega - k_2^2}} \ln \frac{k_2 + \mathrm{i}\sqrt{D\mathrm{i}\omega - k_2^2}}{k_2 - \mathrm{i}\sqrt{D\mathrm{i}\omega - k_2^2}} \right.$$
$$\left. + \frac{k_2^2}{2D\mathrm{i}\omega(D\mathrm{i}\omega - k_2^2)} \left(\gamma - 1 + \ln \frac{\Delta\sqrt{\mathrm{i}\omega/D}}{4} \right) + \mathrm{O}(\tilde{\Delta}^2 \ln \tilde{\Delta}) \right]$$
$$\text{for } k_2 > 0,\ \omega > 0 \tag{30a}$$

where γ is Euler's constant. In the process of deriving equation (30*a*) the following exact cancellation takes place:

$$\frac{1}{|k_2| - \sqrt{D\mathrm{i}\omega}} - \frac{1}{k_2 - \sqrt{D\mathrm{i}\omega}} = 0 \qquad \text{for } k_2 > 0.$$

For $k_2 < 0$ these terms do not cancel each other and the formal introduction of (A18) into (29) leads to the qualitatively different result

$$\rho(0,0,\mathrm{i}\omega) \underset{\tilde{\Delta}\to 0}{=} \frac{\sqrt{2\pi}A}{2\pi \mathrm{i}(\omega - \mathrm{i}\varepsilon)} \frac{(|k_2| + D\mathrm{i}\omega)^2 - 2k_1\sqrt{D\mathrm{i}\omega}}{k_2} \qquad \text{for } k_2 < 0. \tag{30b}$$

According to (30), $\rho_0(0,0,\mathrm{i}\omega)$ depends non-analytically on both $\tilde{\Delta}$ at k_2 with singularities at $\Delta = 0$, and $k_2 = 0$. The non-analytical dependence on k_2 is the result of the absence of particle sinks at $x > |\Delta/2|$ in the system when $k_2 \leqslant 0$.

As an important example of the theory, we analyse the asymptotics for the experimentally measurable quantity $\Psi(\omega)$, the so-called collector efficiency, for the Fourier components

$$\Psi(\omega) = \left| \frac{j_2(\omega)}{j_1(\omega)} \right| \tag{31}$$

where $j_1(\omega)$ and $j_2(\omega)$ are the time-Fourier-transforms of currents measured at the generator and collector planes ($z = 0$) for $|x| < \Delta/2$ and $|x| > \Delta/2$ respectively, as shown in figure 1:

$$j_1(\omega) = \frac{2}{\sqrt{2\pi}} \int_0^{\Delta/2} \mathrm{d}x \int D\sqrt{p^2 + \frac{\mathrm{i}\omega}{D}} \mathrm{e}^{-\mathrm{i}px} \tilde{\rho}(p, \mathrm{i}\omega)\,\mathrm{d}p$$
$$= \frac{A\Delta}{\sqrt{2\pi}2\pi \mathrm{i}(\omega - \mathrm{i}\varepsilon)} - 2k_1 \int_0^{\Delta/2} \rho(x, 0, \mathrm{i}\omega)\,\mathrm{d}x$$
$$j_2(\omega) = \frac{2}{\sqrt{2\pi}} \int_{\Delta/2}^{\infty} \mathrm{d}x \int D\sqrt{p^2 + \frac{\mathrm{i}\omega}{D}} \mathrm{e}^{-\mathrm{i}px} \tilde{\rho}(p, \mathrm{i}\omega)\,\mathrm{d}p$$
$$= -\frac{2k_2}{\sqrt{2\pi}} \int_{\Delta/2}^{\infty} \mathrm{d}x \int \mathrm{e}^{-\mathrm{i}px} \tilde{\rho}(p, \mathrm{i}\omega)\,\mathrm{d}p. \tag{32}$$

After substituting $\rho(0,0,\mathrm{i}\omega)$ for $\rho(x,0,\mathrm{i}\omega)$ on the interval $|x| \leqslant \Delta/2$ we find from (32), up to terms of

$$\mathrm{O}(\tilde{\Delta}^2)\text{and }\mathrm{O}(\tilde{\Delta}^2\ln\tilde{\Delta}) \tag{33}$$

that for $k_2 > 0$ and $|\omega| > 0$ the currents $j_{1,2}(\omega)$ are equal to

$$j_1(\omega) = \frac{\Delta}{2}\left(\frac{A}{2\pi\mathrm{i}\omega} - 2k_1\rho(0,0,\mathrm{i}\omega)\right)$$

$$j_2(\omega) = -\frac{k_2}{\sqrt{2\pi}}\left[\left(\int_{-\infty}^{\infty} - \int_{-\Delta/2}^{\Delta/2}\right)\mathrm{d}x\int \mathrm{d}p\,\mathrm{e}^{-\mathrm{i}px}\frac{\sin\frac{1}{2}\Delta p}{p\left(k_2 + D\sqrt{p^2+\frac{\mathrm{i}\omega}{D}}\right)}\left(\frac{A}{2\pi^2\mathrm{i}(\omega-\mathrm{i}\varepsilon)}\right.\right.$$
$$\left.\left. +2(k_2-k_1)\frac{\rho(0,0,\mathrm{i}\omega)}{\sqrt{2\pi}}\right)\right] = -\frac{\frac{1}{2}\Delta k_2}{k_2+\sqrt{D\mathrm{i}\omega}}\left(\frac{A}{2\pi\mathrm{i}\omega} + 2(k_2-k_1)\rho(0,0,\mathrm{i}\omega)\right) \tag{34}$$

and accordingly (30a)

$$\Psi(\omega) \underset{\tilde{\Delta}\to 0}{=} \frac{k_2}{k_2+\sqrt{D\mathrm{i}\omega}}\left\{1 + 2k_2\Delta\left[\frac{\mathrm{i}k_2}{D\mathrm{i}\omega\sqrt{D\mathrm{i}\omega - k_2^2}}\ln\frac{k_2+\mathrm{i}\sqrt{D\mathrm{i}\omega-k_2^2}}{k_2-\mathrm{i}\sqrt{D\mathrm{i}\omega-k_2^2}}\right.\right.$$
$$\left.\left. + \frac{k_2^2}{2D\mathrm{i}\omega(D\mathrm{i}\omega-k_2^2)}\left(\gamma - 1 + \ln\frac{\Delta\sqrt{\mathrm{i}\omega}}{8}\right)\right]\right\} + \mathrm{O}(\tilde{\Delta}^2) \tag{35}$$

thus recovering the result of [6].

6. Conclusions

The exact solution of the chosen reaction–diffusion problem has a rather complex structure reflecting the singular character of the dynamics itself. The most complicated (and informative) is the transition interval from small t (large ω), when all concentrations are almost the same as at $t = 0$ and it is possible to use perturbation theory, to large t (small ω). At the same time the expression for the collector efficiency $\Psi(\omega)$ is, at least in the asymptotic limit, relatively simple and independent of the generator constant k_1. This independence has an important practical implication: by measuring $\Psi(\omega)$ it is possible to find the constant k_2 experimentally, avoiding the influence of the noise connected with the smallness of the generator size. There are two reasons for this simplicity. First, $\Psi(\omega)$ is a causal response function obeying a dispersion relation. It is clear from the results of appendix 1 that the current j_2 is a causal response to the current j_1 with the Fourier component $j_2(\omega)$ proportional to $j_1(\omega)$. Second, the structure of asymptotics can be inferred from the simple zero-range potential approximation discussed in section 5. The present calculations allow an understanding of the limits of validity of such an approximation and also allow the calculation of the constant itself for the chosen geometry. This is important because the approach based on the zero-range potential approximation can yield simple asymptotic expressions not only for a band or disc, but also in the cases of regular or random arrays of sources with complicated geometries, zero and non-zero heights and with different diffusion laws for different chemical species [6]. The only parameters in such approximate expressions characterizing the geometry of an individual source are 'effective widths' Δ_{eff} (or, in the case of sources with finite dimensions in all directions, 'effective radii'). For example, in the case of a source in the form of a semi-cylinder with radius R, on the surface the parameter Δ_{eff} is equal, in accordance with [4], to $4R$.

For practical applications it is important that the zero-range approximation can provide not only the main diffusion asymptotics $t \to \infty$ when all variables with the dimension of time are less than t, but is also valid for the time interval

$$\frac{\Delta^2}{D} < t < \frac{\Delta}{k_i} \tag{36}$$

where $k_i (i = 1, \ldots, n)$ are the, possibly different, reaction constants for n sources and sinks on the plane.

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Appendix 1

We will discuss the most simple realistic example of one-reversible redox reaction. The first electrode El_1—the generator—is a strip with the width Δ and the second electrode El_2—the collector—occupies the remaining part of the infinite surface (see figure 1). The oxidation–reduction reaction

$$A_0 + \mathrm{El}_i \underset{\kappa_{-i}}{\overset{\kappa_i}{\leftrightarrows}} \mathrm{El}_i + A_{\mathrm{R}} \qquad i = 1, 2 \tag{A1}$$

takes place only on the surfaces $i = 1, 2$ where A_{O} and A_{R} are a redox couple with concentrations $C_{\mathrm{O}}(x, z, t)$ and $C_{\mathrm{R}}(x, z, t)$, and κ_i and κ_{-i} are the direct and reverse surface reaction rate constants (per unit electrode surface) at electrode $\mathrm{El}_i (i = 1, 2)$. The constants κ_i and κ_{-i} in electrochemical systems are dependent on the potential drop which can depend on time and differ on different electrodes. We will suppose that at $t \leqslant 0$ the system is in equilibrium, which means that

$$\left.\begin{array}{l} C_{\mathrm{O}}(x, y, 0) = C_{\mathrm{O}}^0 \qquad C_{\mathrm{R}}(x, y, 0) = C_{\mathrm{R}}^0 \\ \kappa_i C_{\mathrm{O}}^0 = \kappa_{-i} C_{\mathrm{R}}^0 \\ \kappa_1 = \kappa_2, \kappa_{-1} = \kappa_{-2} \end{array}\right\} t \leqslant 0. \tag{A2}$$

At the moment $t = 0$ the reaction constants at El_1 are changed and, correspondingly,

$$\begin{aligned} \kappa_1(t) &= \kappa_1(0) + \theta(t)\delta\kappa_1 \\ \kappa_{-1}(t) &= \kappa_{-1}(0) + \theta(t)\delta\kappa_{-1}. \end{aligned} \tag{A3}$$

The reaction constants at El_2 remain the same for all times. Concentrations C_{O} and C_{R} obey the diffusion equation and the equations of material balance on the surface (boundary conditions) which have the form

$$\left.\begin{aligned} D\frac{\partial C_{\mathrm{O}}}{\partial z} &= \kappa_{-1}C_{\mathrm{R}} - \kappa_1 C_{\mathrm{O}} \\ D\frac{\partial C_{\mathrm{R}}}{\partial z} &= \kappa_1 C_{\mathrm{O}} - \kappa_{-1}C_{\mathrm{R}} \end{aligned}\right\} \qquad z = 0,\ |x| < \frac{\Delta}{2}$$
$$\left.\begin{aligned} D\frac{\partial C_{\mathrm{O}}}{\partial z} &= \kappa_{-2}C_{\mathrm{R}} - \kappa_2 C_{\mathrm{O}} \\ D\frac{\partial C_{\mathrm{R}}}{\partial z} &= \kappa_2 C_{\mathrm{O}} - \kappa_{-2}C_{\mathrm{R}} \end{aligned}\right\} \qquad z = 0,\ |x| > \frac{\Delta}{2}. \tag{A4}$$

The diffusion coefficient D is supposed to be constant and equal for both species A_{O} and A_{R}. Correspondingly, the sum $C_{\mathrm{O}} + C_{\mathrm{R}}$ remains constant:

$$C_{\mathrm{O}}(x,z,t) + C_{\mathrm{R}}(x,z,t) = C_{\mathrm{O}}^0 + C_{\mathrm{R}}^0 \tag{A5}$$

and we can only seek solutions for the quantity

$$\rho(x,z,t) = C_{\mathrm{O}}(x,z,t) - C_{\mathrm{O}}^0$$

which obey relations (1) and (2) in the text with

$$\begin{aligned} A &= \delta\kappa_{-1}C_{\mathrm{R}}^0 - \delta\kappa_1 C_{\mathrm{O}}^0 \\ k_1 &= \kappa_1 + \kappa_{-1} \\ k_2 &= \kappa_2 + \kappa_{-2}. \end{aligned} \tag{A6}$$

Appendix 2

In order to demonstrate the integration technique allowing transformation of the singular integrals of section 2 into non-singular integrals, we consider the expression for $F(\tilde{p} + \mathrm{i}\varepsilon)$. According to equations (17)–(19)

$$\begin{aligned} F(p+\mathrm{i}\varepsilon) &= C - \frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty} \mathrm{d}p' \frac{B(p')}{p'-p-\mathrm{i}\varepsilon} = C - \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega - \mathrm{i}A)}\int_{-\infty}^{\infty}\frac{\mathrm{d}p'}{p'-p-\mathrm{i}\varepsilon}\frac{1}{p+\mathrm{i}\varepsilon} \\ &\quad \times\left(\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p'')\,\mathrm{d}p''}{p''-p'-\mathrm{i}\varepsilon}\right] - \frac{1}{\gamma(0)}\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p'')\,\mathrm{d}p''}{p''-p'+\mathrm{i}\varepsilon}\right]\right) \\ &= C - \frac{\sqrt{2\pi}A}{(2\pi\mathrm{i})^2(\omega - \mathrm{i}A)}\frac{1}{p'+\mathrm{i}\varepsilon}\left(\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p'')\,\mathrm{d}p''}{p''-p'-\mathrm{i}\varepsilon}\right]\right. \\ &\quad \left. - \frac{1}{\gamma(0)}\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p'')\,\mathrm{d}p''}{p''-p'+\mathrm{i}\varepsilon}\right]\right) \\ &= C - \frac{A\sqrt{2\pi}}{(2\pi\mathrm{i})^2(\omega - \mathrm{i}\varepsilon)p}\exp\left[-\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p'')\,\mathrm{d}p''}{p''-p'-\mathrm{i}\varepsilon}\right]\left(\frac{1-\gamma(p)}{\gamma(0)}\right). \end{aligned} \tag{A7}$$

In (22) we have first shifted the factor p' in the dominator, $p' \to p' + \mathrm{i}\varepsilon$, taking into account that the integrand is non-singular at $p' = 0$ and have then closed the integration contours by infinite semi-circles in the upper half-plane (in the first term) and in the lower half-plane (in the second term) of the complex integration variable p'. The final result (A7) follows from Cauchy's theorem taking into account that in the corresponding closed domains the only singularities are poles. The factors

$$\mathrm{e}^{\psi(q)} = \exp\left[+\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p)\,\mathrm{d}p}{p-q}\right] \qquad \mathrm{Im}\,q \neq 0 \tag{A8}$$

entering (A7) and other expressions in the text can be calculated as follows. We find, using integration by parts and the symmetry $\gamma(p) = -\gamma(-p)$, that

$$\begin{aligned}\frac{\mathrm{d}\psi(q)}{\mathrm{d}q} = \frac{D}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}&\frac{p^2\,\mathrm{d}p}{(p^2-q^2)\sqrt{p^2+(\mathrm{i}\omega/D)}}\\ &\times\left(\frac{1}{k_1+D\sqrt{p^2+(\mathrm{i}\omega/D)}}-\frac{1}{k_2+D\sqrt{p^2+(\mathrm{i}\omega/D)}}\right)\\ &= \frac{Dq}{2\sqrt{q^2+(\mathrm{i}\omega/D)}}\left(\frac{1}{k_1+D\sqrt{q^2+(\mathrm{i}\omega/D)}}-\frac{1}{k_2+D\sqrt{q^2+(\mathrm{i}\omega/D)}}\right)\frac{\mathrm{i}\omega}{\mathrm{i}\pi}\\ &\times\int_1^{\infty}\frac{p^2\,\mathrm{d}p}{((\mathrm{i}\omega/D)p^2+q^2)\sqrt{p^2-1}}\\ &\times\left(\frac{k_1}{k_1^2+D\mathrm{i}\omega(p^2-1)}-\frac{k_2}{k_2^2+D\mathrm{i}\omega(p^2-1)}\right).\end{aligned} \tag{A9}$$

In the last equality (A9) we have made the contour distortion I $\to$ I$'$ (see figure 2) followed by an integration variable transformation. The remaining integral in (A9) can be transformed as

$$\begin{aligned}\frac{\mathrm{i}\omega}{\mathrm{i}\pi}\int_1^{\infty}&\frac{p^2\,\mathrm{d}p}{((\mathrm{i}\omega/D)p^2+q^2)\sqrt{p^2-1}}\frac{k_{1,2}}{k_{1,2}^2+D\mathrm{i}\omega(p^2-1)}\\ &= \frac{\mathrm{i}\omega}{2\pi\mathrm{i}}\frac{k_{1,2}}{\mathrm{i}}\int_{-\infty+\mathrm{i}\varepsilon}^{\infty+\mathrm{i}\omega}\frac{p^2\,\mathrm{d}p}{((\mathrm{i}\omega/D)p^2+q^2)\sqrt{1-p^2}(k_{1,2}^2+D\mathrm{i}\omega(p^2-1))}\end{aligned} \tag{A10}$$

where, on the right-hand side, the square root $\sqrt{1-p^2}$ as a function of p has a cut on the interval from -1 to $+1$, and $\sqrt{1-(p+\mathrm{i}\varepsilon)^2}$ is an asymmetric function of real p on this interval as $\varepsilon \to +0$. The integral (A10) can be performed by closing the integration contour in the upper complex half-plane:

$$\begin{aligned}\text{(A10)} = \frac{k_{1,2}D}{2}&\frac{2\sqrt{D/\mathrm{i}\omega}}{\sqrt{1+(D/\mathrm{i}\omega)q^2}}\frac{1}{k_{1,2}^2-D^2(q^2+(\mathrm{i}\omega/D))}\\ &+\frac{1}{2\mathrm{i}}\sqrt{\frac{\mathrm{i}\omega}{D}}\frac{\sqrt{1-(k_{1,2}^2/\mathrm{i}\omega)}}{((\mathrm{i}\omega/D)-(k^2/D^2))+q^2} \qquad \mathrm{Im}\,q > 0.\end{aligned} \tag{A11}$$

After the introduction of (A11) into (A9) and the integration over dq we find that

$$\mathrm{e}^{\psi(q)} = \sqrt{\gamma(q)\frac{(k_2 - D\sqrt{(\mathrm{i}\omega/D)+q^2})(k_1 - \sqrt{D\mathrm{i}\omega})}{(k_1 - D\sqrt{(\mathrm{i}\omega/D)+q^2})(k_2 - \sqrt{D\mathrm{i}\omega})}}$$

$$\times \left(\frac{k_1^2 - D^2((\mathrm{i}\omega/D)+q^2)}{k_2^2 - D^2((\mathrm{i}\omega/D)+q^2)}\frac{k_2^2 - D^2\mathrm{i}\omega}{k_2^2 - D^2\mathrm{i}\omega}\frac{\left(\sqrt{D\mathrm{i}\omega - k_1^2} - \mathrm{i}Dq\right)\left(\sqrt{D\mathrm{i}\omega - k_2^2} + \mathrm{i}Dq\right)}{\left(\sqrt{D\mathrm{i}\omega - k_1^2} + \mathrm{i}Dq\right)\left(\sqrt{D\mathrm{i}\omega - k_2^2} - \mathrm{i}Dq\right)}\right)^{1/4}$$

$$\operatorname{Im} q < 0. \tag{A12}$$

In deriving (A12) we have taken into account that

$$\psi(\mathrm{i}\varepsilon) = \frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\ln\gamma(p)}{p - \mathrm{i}\varepsilon} = \tfrac{1}{2}\gamma(0). \tag{A13}$$

The value of the factor $\mathrm{e}^{\psi(q)}$ for $\operatorname{Im} q < 0$ can be found from (A12) with the help of the equality

$$\psi(-q) = -\psi(q). \tag{A14}$$

Appendix. 3

To calculate the asymptotics of the integral

$$\begin{aligned} J(\tfrac{1}{2}\Delta, k_2) &= \int_1^{\infty}\frac{\mathrm{d}p\sqrt{p^2-1}}{p}\frac{\exp[-\sqrt{(\mathrm{i}\omega/D)}\frac{1}{2}\Delta p]}{k_2^2 + D\mathrm{i}\omega(p^2-1)} \\ &= \int_0^{\infty}\frac{\mathrm{d}\alpha(\cosh^2\alpha - 1)}{\cosh\alpha}\frac{\exp[-\sqrt{(\mathrm{i}\omega/D)}\frac{1}{2}\Delta\cosh\alpha]}{k_2^2 + D\mathrm{i}\omega(\cosh^2\alpha - 1)} \end{aligned} \tag{A15}$$

we divide it into three parts:

$$\begin{aligned} J(\tfrac{1}{2}\Delta, k_2) = {} & \frac{1}{D\mathrm{i}\omega - k_2^2}\int_0^{\infty}\frac{\mathrm{d}\alpha\exp-[\sqrt{(\mathrm{i}\omega/D)}\frac{1}{2}\Delta\cosh\alpha]}{\cosh\alpha} \\ & - \frac{k_2^2}{2(D\mathrm{i}\omega - k_2^2)D\mathrm{i}\omega}\Bigg[\exp-[\sqrt{(\mathrm{i}\omega/D)}\tfrac{1}{2}\Delta\sqrt{1-(k_2^2/D\mathrm{i}\omega)}] \\ & \times\int_0^{\infty}\frac{\mathrm{d}\alpha\exp-[\sqrt{(\mathrm{i}\omega/D)}\frac{1}{2}\Delta(\cosh\alpha - \sqrt{1-(k_2^2/D\mathrm{i}\omega)})]}{\cosh\alpha - \sqrt{1-(k_2^2/D\mathrm{i}\omega)}} \\ & + \exp[\sqrt{(\mathrm{i}\omega/D)}\tfrac{1}{2}\Delta\sqrt{1-(k_2^2/D\mathrm{i}\omega)}] \\ & \times\int_0^{\infty}\frac{\mathrm{d}\alpha\exp-[\sqrt{(\mathrm{i}\omega/D)}\frac{1}{2}\Delta(\cosh\alpha + \sqrt{1-(k_2^2/D\mathrm{i}\omega)})]}{\cosh\alpha + \sqrt{1-(k_2^2/D\mathrm{i}\omega)}}\Bigg]. \end{aligned} \tag{A16}$$

The integrals in (A16) have the form

$$\tilde{J}(\tfrac{1}{2}\Delta, a) = \int_0^\infty \frac{\mathrm{d}\alpha \exp[-\sqrt{(\mathrm{i}\omega/D)}\tfrac{1}{2}\Delta(\cosh\alpha + a)]}{\cosh\alpha + a} \qquad a = 0, \pm\sqrt{1 - (k_2^2/D\mathrm{i}\omega)} \tag{A17}$$

and are equal [11] to

$$\tilde{J}(\tfrac{1}{2}\Delta, a) = \frac{1}{\mathrm{i}\sqrt{1-a^2}} \ln \frac{1 + a + \mathrm{i}\sqrt{1-a^2}}{1 + a - \mathrm{i}\sqrt{1-a^2}} - \sqrt{\frac{\mathrm{i}\omega}{D}} \int_0^{\Delta/2} \mathrm{d}x\, K_0\left(\sqrt{\frac{\mathrm{i}\omega}{D}}x\right) \exp[-\sqrt{(\mathrm{i}\omega/D)}\tfrac{1}{2}\Delta a x]. \tag{A18}$$

Introducing (A17) into (A16) and letting $\tilde{\Delta} \to 0$ we find

$$\begin{aligned} J(\tfrac{1}{2}\Delta, k_2) \underset{\tilde{\Delta}\to 0}{=} &\frac{\pi}{2} \frac{1}{\sqrt{D\mathrm{i}\omega} + |k_2|} + \frac{\pi \mathrm{i}}{2}\sqrt{\frac{\mathrm{i}\omega}{D}}\Delta \frac{|k_2|}{D\mathrm{i}\omega\sqrt{D\mathrm{i}\omega - k_2^2}} \\ &\times \ln \frac{|k_2| + \mathrm{i}\sqrt{D\mathrm{i}\omega - k_2^2}}{|k_2| - \mathrm{i}\sqrt{D\mathrm{i}\omega - k_2^2}} + \frac{k_2^2\sqrt{(\mathrm{i}\omega/D)}\tfrac{1}{2}\Delta}{(D\mathrm{i}\omega - k_2^2)D\mathrm{i}\omega}\left(\ln\frac{\Delta\sqrt{\mathrm{i}\omega/D}}{4} + \gamma - 1\right) \\ &+ \mathrm{O}\left(\left(\left|\frac{k_2\Delta}{2}\right| + \tilde{\Delta}^2\right)^2\right) \end{aligned} \tag{A19}$$

where we have used the asymptotics [11] of the Bessel function $K_0(x)$ for small x:

$$K_0(x) \underset{x\to 0}{=} -\left(\ln\frac{x}{2} + \gamma\right)(1 + \mathrm{O}(\mathrm{x}^2))$$

γ being Euler's constant.

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