MACROSCOPIC DIFFUSION ON ROUGH SURFACES*

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Abstract. We consider diffusion on rough and spatially periodic surfaces. The macroscopic diffusion tensor **D** is determined by averaging the local fluxes over the unit cell. **D** is proved to be the unit tensor for macroscopically isotropic surfaces. For general surfaces, an asymptotic analysis is applied, when the ratio of the oscillation amplitude to the size of the unit cell is a small parameter ε. The microscopic field is determined up to $O(\varepsilon^6)$ in analytical form and an algorithm is derived to calculate higher order terms. We also deduce general analytical formulae for **D** up to $O(\varepsilon^6)$ and derive an algorithm to compute **D** as a series in ε^2.

Key words. Laplace operator on surface, macroscopic diffusion tensor, composite material

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1. Introduction.

Diffusion on surfaces has important applications in several fields and it has attracted attention for a long time ([1, 2, 3, 4, 5] among many others); however, in these references, attention is mostly focused on the interaction between the diffusing atom and the underlying solid lattice. In a different field of applications, the phenomenon of surface conduction plays a role in electrolytes; it is presently explained [6] by diffusion of ions within the Stern layer.

In both situations, real surfaces are expected to be rough and the major purpose of the present paper is to study diffusion on a rough surface S, a phenomenon governed by the following equations [7]

$$\nabla_{\mathcal{S}} \cdot \mathbf{j} = 0, \qquad \mathbf{j} = -D\nabla_{\mathcal{S}} c, \tag{1.1}$$

where $\nabla_{\mathcal{S}}$ is the surface gradient operator, $\mathbf{j}$ the local flux, c the solute concentration, and D the molecular diffusion coefficient. For sake of simplicity, D is constant and normalized to 1. The macroscopic diffusion was introduced in [8] where it is called the surface capacity. General analysis of flow and transport on surfaces is presented in [9]. The purpose of the present paper is to describe local fields on periodical surfaces and to determine the macroscopic diffusion in analytic form.

The surface gradient operator and the Laplace equation on surfaces are detailed in Section 2. In Section 3, diffusion is studied on doubly periodic surfaces by asymptotic analysis; the ratio of the oscillation amplitude to the size of the unit cell is assumed to be equal to a small parameter ε. We derive the local concentration in the surface in Theorem 3.1 up to $O(\varepsilon^4)$.

In Section 4 we investigate the macroscopic diffusion tensor when the representative cell is a square. An isomorphism is defined which relates diffusion on surfaces and conductivity of special composite materials (for instance, polycristals). The main results of Section 4 are summarized by the two properties

THEOREM 1.1. *Let the representative cell be a square. Then,* $\det \mathbf{D} = D^2 = 1$.

COROLLARY 1.2. *Let the representative cell be a square and the surface be macroscopically isotropic. Then,* $\mathbf{D}$ *is the unit tensor* $\mathbf{I}$.

The proof parallels a Matheron's formula [10, p.122] and the well-known Dykhne-Keller manipulations for composite materials [11, 12, 13].

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Section 5 is devoted to the determination of the effective diffusion tensor **D** of the general surface up to $O(\varepsilon^6)$. In Section 6, we study square representative cells. First, a general algorithm is derived to calculate **D** in analytical form up to $O(\varepsilon^{2n+2})$ for a given number n. Second, the general form of **D** is represented up to $O(\varepsilon^6)$ in terms of the Fourier series and a general algorithm is derived for higher order terms. Examples of determination of **D** up to $O(\varepsilon^{22})$ are given for some surfaces. The symbolical algorithm is detailed in the Appendix.

2. Gradient operator and Laplace equation on surfaces. In the present section, we derive the Laplace operator on a surface $\mathcal{S}$ in a form convenient for our purposes. Let the surface $\mathcal{S}$ be defined as the function

$$z = f(x,y), \quad \text{or} \quad \mathbf{r}(x,y) = \big(x, y, f(x,y)\big), \qquad (x,y) \in Q \tag{2.1}$$

in the space $\boldsymbol{R}^3$ where Q is a simply connected domain with piece-wise smooth boundaries. (x, y, z) is an orthonormal system of coordinates. We assume that the function $f(x,y)$ has continuous second derivatives in the closure of Q.

The gradient operator $\nabla_{\mathcal{S}}$ on $\mathcal{S}$ has the form [7]

$$\nabla_{\mathcal{S}} c = (\mathbf{I} - \mathbf{n}\mathbf{n}^\top) \cdot \nabla c, \tag{2.2}$$

where the function $c(x,y,z)$ is continuously differentiable in the vicinity of $\mathcal{S}$; $\mathbf{I}$ is the identity operator; $\nabla c := \left(\frac{\partial c}{\partial x}, \frac{\partial c}{\partial y}, \frac{\partial c}{\partial z}\right)^\top$, where $^\top$ denotes the transpose operator; the normal unit vector $\mathbf{n}$ can be expressed as follows $\mathbf{n} = \frac{\nabla f}{\delta} = \frac{1}{\delta}(f_x, f_y, -1)^\top$; $\delta := \left(1 + f_x^2 + f_y^2\right)^{1/2}$. Here, the dyadic $\mathbf{n}\mathbf{n}^\top$ is given by

$$\mathbf{n}\mathbf{n}^\top = \frac{1}{\delta^2} \begin{bmatrix} f_x^2 & f_x f_y & -f_x \\ f_x f_y & f_y^2 & -f_y \\ -f_x & -f_y & 1 \end{bmatrix}.$$

One can write the gradient in the expanded form

$$\nabla_{\mathcal{S}} c = \frac{1}{\delta^2} \begin{bmatrix} 1 + f_y^2 & -f_x f_y & f_x \\ -f_x f_y & 1 + f_x^2 & f_y \\ f_x & f_y & f_x^2 + f_y^2 \end{bmatrix} \begin{bmatrix} \frac{\partial c}{\partial x} \\ \frac{\partial c}{\partial y} \\ \frac{\partial c}{\partial z} \end{bmatrix}. \tag{2.3}$$

Let us apply (2.3) to the surface $z = f(x,y)$. Instead of the concentration $c(x,y,z)$, it is convenient to use the function $\phi(x,y) = c(x,y,f(x,y))$. Then, (2.3) becomes

$$\nabla_{\mathcal{S}} \phi = \frac{1}{\delta^2} \begin{bmatrix} 1 + f_y^2 & -f_x f_y \\ -f_x f_y & 1 + f_x^2 \\ f_x & f_y \end{bmatrix} \nabla_{xy} \phi\,, \tag{2.4}$$

where $\nabla_{xy} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right)^\top$. Let us introduce the matrix

$$\mathbf{K} = \frac{1}{\delta^2} \begin{bmatrix} 1 + f_y^2 & -f_x f_y \\ -f_x f_y & 1 + f_x^2 \end{bmatrix}. \tag{2.5}$$

Then, the first two components of (2.3) can be written as a two-dimensional vector

$$\mathbf{q} = \mathbf{K} \nabla_{xy} \phi\,. \tag{2.6}$$

$\mathbf{q}$ denotes the two components in the $(x, y)-$plane of the opposite of the flux on the surface $\mathcal{S}$. The formula (2.6) will be used for calculating the effective diffusivity tensor. The Laplace operator on the surface $\mathcal{S}$ is given by the following formula [16]

$$\triangle_{\mathcal{S}}\phi = \frac{1}{\delta}\,\nabla_{xy}\cdot\left(\delta\,\mathbf{K}\,\nabla_{xy}\phi\right)\,. \tag{2.7}$$

Here, $\mathbf{K}$ can be considered as the contravariant metric tensor of $\mathcal{S}$. To prove this, we first consider the vector-function $\mathbf{r}(x, y) = \big(x, y, f(x, y)\big)$ from (2.1) which determines the surface $\mathcal{S}$. Next we contract the covariant metric tensor

$$\mathbf{M} = \begin{bmatrix} \mathbf{r}_x\cdot\mathbf{r}_x & \mathbf{r}_x\cdot\mathbf{r}_y \\ \mathbf{r}_x\cdot\mathbf{r}_y & \mathbf{r}_y\cdot\mathbf{r}_y \end{bmatrix} = \begin{bmatrix} 1+f_x^2 & f_xf_y \\ f_xf_y & 1+f_y^2 \end{bmatrix} \tag{2.8}$$

and calculate the determinant δ^2. The contravariant metric tensor is constructed as the inverse matrix of (2.8). $\mathbf{M}^{-1}$ is equal to $\mathbf{K}$ defined by (2.5).

It follows from (2.7) that the Laplace equation can be written as follows

$$\frac{1}{\delta}\,\nabla_{xy}\cdot\left(\delta\,\mathbf{K}\,\nabla_{xy}\phi\right)\; = 0 \tag{2.9}$$

or in an expanded form

$$\begin{aligned} &\left(1-\frac{f_x^2}{\delta^2}\right)\phi_{xx} + \left(1-\frac{f_y^2}{\delta^2}\right)\phi_{yy} - \frac{2f_xf_y}{\delta^2}\,\phi_{xy} \\ &\qquad - \frac{1}{\delta^4}\left[\Big(1+f_y^2\Big)f_{xx} - 2f_xf_yf_{xy} + \Big(1+f_x^2\Big)f_{yy}\right]\Big(f_x\phi_x + f_y\phi_y\Big) = 0\,. \end{aligned} \tag{2.10}$$

3. Asymptotic expansion and boundary value problem for general cells. In the following, the surface $\mathcal{S}$ is assumed to be spatially periodic with a unit cell whose projection on the xy–plane is Q. For our purpose, it is sufficient to consider the case where the domain Q is a rectangle $\Big\{\,(x, y)\in\boldsymbol{R}^2:\ |x| < \lambda_1/2,\ |y| < \lambda_2/2\,\Big\}$ with sides λ_1 and λ_2 and of area $\lambda_1\lambda_2$. When an external concentration gradient $\overline{\nabla c} = (-1, 0)$ is applied along the x–direction, the concentration $c(x, y, z)$ satisfying equations (1.1) on the surface $\mathcal{S}$ must verify the following periodicity conditions

$$\begin{aligned} &c(x+\lambda_1, y, z) - c(x, y, z) = \lambda_1, && \nabla_{\mathcal{S}}c(x+\lambda_1, y, z) = \nabla_{\mathcal{S}}c(x, y, z), \\ &c(x, y+\lambda_2, z) = c(x, y, z), && \nabla_{\mathcal{S}}c(x, y+\lambda_2, z) = \nabla_{\mathcal{S}}c(x, y, z). \end{aligned} \tag{3.1}$$

The conditions (3.1) must be fulfilled at the edges of the surface located on the planes $x = \pm\frac{\lambda_1}{2}$, $y = \pm\frac{\lambda_2}{2}$. Then (1.1) and (3.1) are considered as a conjugation problem on $\mathcal{S}$.

It follows from Section 2 that the same problem can be stated in terms of the function $\phi(x, y) := c(x, y, f(x, y))$ with the following boundary conditions

$$\begin{aligned} &\phi(\frac{\lambda_1}{2}, y) - \phi(-\frac{\lambda_1}{2}, y) = \lambda_1, && \frac{\partial\phi}{\partial x}(\frac{\lambda_1}{2}, y) = \frac{\partial\phi}{\partial x}(-\frac{\lambda_1}{2}, y), \\ &\phi(x, \frac{\lambda_2}{2}) = \phi(x, -\frac{\lambda_2}{2}), && \frac{\partial\phi}{\partial y}(x, \frac{\lambda_2}{2}) = \frac{\partial\phi}{\partial y}(x, -\frac{\lambda_2}{2}). \end{aligned} \tag{3.2}$$

The problem (2.10,3.2) is a standard jump problem on the torus represented by the rectangle Q with identified opposite sides for the elliptic equation (2.10). There are various methods to solve such problems. The most popular ones are the method of integral equations [15] and the method of finite elements [9]. However, they give only numerical results. Here, a perturbation method based on asymptotic analysis will be used. Computations of the integrals are avoided and the solution of the problem (2.10,3.2) is derived in an explicit form.

We assume that the sides λ_1 and λ_2 of the rectangle Q are sufficiently large in comparison to the amplitude A of the oscillation of the surface. A is supposed to be of order 1; hence, the ratio $\frac{A}{\lambda_1}$ is characterized by the small parameter $\varepsilon = \frac{2\pi}{\lambda_1}$. We also assume that λ_1 and λ_2 have the same scale, i.e., the parameter $\omega = \frac{\lambda_1}{\lambda_2}$ is of order $O(\varepsilon^0)$. Let us make a change of variables in the function $f(x, y)$ from (2.1) and equate it to $h(\xi, \eta)$, where the function $h(\xi, \eta)$ is defined for $|\xi| \leq \pi$, $|\eta| \leq \frac{\pi}{\omega}$; the new variables $\xi = \varepsilon x$, $\eta = \varepsilon y$ are the so called fast variables. We assume that $h(\xi, \eta)$ is doubly periodic, i.e., $h(\xi + 2\pi, \eta) = h(\xi, \eta) = h(\xi, \eta + \frac{2\pi}{\omega})$ and it is twice differentiable in the closure of Q. The small oscillation of the surface in terms of $h(\xi, \eta)$ means that the absolute values of h_ξ, h_η, $h_{\xi\xi}$, $h_{\xi\eta}$, $h_{\eta\eta}$ are of smaller order than λ_1 and λ_2 since

$$\begin{aligned} &f_x = \varepsilon h_\xi, && f_y = \varepsilon h_\eta, && \\ &f_{xx} = \varepsilon^2 h_{\xi\xi}, && f_{xy} = \varepsilon^2 h_{\xi\eta}, && f_{yy} = \varepsilon^2 h_{\eta\eta}. \end{aligned} \tag{3.3}$$

Theorem 3.1. *The problem (2.10,3.2) has a unique solution up to an arbitrary additive constant. This solution is represented in the form*

$$\phi(x, y) = x + \varepsilon \Phi(\xi, \eta) + O(\varepsilon^2)\,, \tag{3.4}$$

where $\Phi(\xi, \eta)$ is a periodic solution of the problem

$$\Phi_{\xi\xi} + \Phi_{\eta\eta} = h_\xi (h_{\xi\xi} + h_{\eta\eta})\,. \tag{3.5}$$

The proof of the theorem is standard and it is based on the asymptotic analysis applied to the problem (2.10,3.2).

Remark 1. An explicit form of the function Φ can be given through Green's function for a rectangle Q (see [15]). We do not write it here, because another formula in Section 6 which is considerably simpler, will be used.

Remark 2. The asymptotic analysis applied to the problem (2.10,3.2) can be extended to higher terms $O(\varepsilon^m)$, where $m \geq 3$. We shall do it in Section 6 for the case $\lambda_1 = \lambda_2$.

4. Diffusion tensor. The square cell. Diffusion on the surfaces is described at the large scale by a second order macroscopic diffusion tensor

$$\mathbf{D} = \begin{bmatrix} D_{xx} & D_{xy} \\ D_{xy} & D_{yy} \end{bmatrix},$$

which is understood as follows. First, we note that the macroscopic diffusion in the z–direction is absent, since $\mathcal{S}$ is periodic in x and y, and hence the macroscopic tensor $\mathbf{D}$ has only x– and y–components. Locally, the surface $\mathcal{S}$ (x and y belong to the cell Q) has a unit diffusion coefficient. Let $\mathcal{S}$ be substituted by the plane domain Q.

The macroscopic tensor $\mathbf{D}$ can be shown to be defined by the surface integral

$$\mathbf{D} \cdot \overline{\nabla c} = \frac{1}{\lambda_1 \lambda_2} \iint\limits_{\mathcal{S}} \mathbf{q}\, d\sigma_{\mathcal{S}} = \frac{1}{\lambda_1 \lambda_2} \iint\limits_{Q} \mathbf{q}\, \delta\, dxdy\,, \tag{4.1}$$

where the imposed gradient is equal to the vector $\overline{\nabla c}$. The opposite $\mathbf{q}$ of the local flux is defined by (2.6), and corresponds to $\overline{\nabla c}$. Let us recall that $\delta = \sqrt{1 + f_x^2 + f_y^2}$. The tensor $\mathbf{D}$ is symmetric as it should from general principles [17]. Note that the definition (4.1) is consistent with the definition of the surface capacity [8].

The Laplace equation (2.9) can be considered as a two-dimensional elliptic equation with respect to the potential $\phi(x, y)$, which derives conductivity of the plane composite material with the local conductivity tensor $\mathbf{\Lambda} := \delta\,\mathbf{K}$. Then the vector $-\delta\,\mathbf{q}$ can be treated as a flux in the composite material, and the tensor $\mathbf{D}$ from (4.1) as the effective conductivity tensor. Therefore, we have created an isomorphism between the diffusion on the surface $\mathcal{S}$ and the conduction in the composite material represented by the cell Q with the local conductivity tensor $\mathbf{\Lambda}$. Let us study this tensor

$$\mathbf{\Lambda} = \frac{1}{\delta}\begin{bmatrix} 1 + f_y^2 & -f_x f_y \\ -f_x f_y & 1 + f_x^2 \end{bmatrix}. \tag{4.2}$$

The eigenvalues of $\mathbf{\Lambda}$ are δ and δ^{-1}. Hence, the tensor $\mathbf{\Lambda}$ in the principal axes becomes

$$\mathbf{\Lambda} = \begin{bmatrix} \delta & 0 \\ 0 & \delta^{-1} \end{bmatrix}.$$

The local conductivities along the principal axes are δ and δ^{-1}. Let

$$\mathbf{\Lambda}_e \sim \begin{bmatrix} \sigma_1 & 0 \\ 0 & \sigma_2 \end{bmatrix}$$

denote the effective conductivity tensor corresponding to the local tensor $\mathbf{\Lambda}$.

For the rest of this section, we assume that Q is a square cell. Following Matheron [10], we rotate the cell Q of the composite material (of the surface) by 90°. Then, for the new structure the conductivity tensor in the principal axes becomes

$$\mathbf{R}^* \sim \begin{bmatrix} \delta^{-1} & 0 \\ 0 & \delta \end{bmatrix}.$$

Let us consider another composite material defined by the resistivity tensor $\mathbf{R}^*$, i.e., δ^{-1} and δ denote the local resistances along the principal axes. Hence, conductivity is changed into resistivity and vice versa. Since conductivity is the inverse of resistivity, the conductivity tensor $\mathbf{\Lambda}^*$ corresponding to the resistivity tensor $\mathbf{R}^*$ in the principal axes becomes

$$\mathbf{\Lambda}^* \sim \begin{bmatrix} \delta & 0 \\ 0 & \delta^{-1} \end{bmatrix}.$$

The effective conductivity tensor $\mathbf{\Lambda}_e^*$ has the same form as $\mathbf{\Lambda}_e$, since the local tensors have the same form. Rotate the cell by 90° backward. Hence, the effective resistivity tensor of the original composite material is obtained

$$\mathbf{R}_e \sim \begin{bmatrix} \sigma_2 & 0 \\ 0 & \sigma_1 \end{bmatrix}.$$

Using the relation between the conductivity and resistivity coefficients, we arrive at the fundamental formula

$$\sigma_1\,\sigma_2 = 1\,.$$

Therefore, the effective conductivity tensor $\mathbf{\Lambda}_e$ (the macroscopic diffusion tensor $\mathbf{D}$) in the principal axes becomes

$$\mathbf{D} \sim \begin{bmatrix} \sigma_1 & 0 \\ 0 & \sigma_1^{-1} \end{bmatrix}.$$

Then the invariant $\det \mathbf{D}$ is always equal to unity for the square cell (Theorem 1.1 from Section 1)

$$\det \mathbf{D} = D_{xx} D_{yy} - D_{xy}^2 = 1\,. \tag{4.3}$$

There is a surprising consequence of (4.3) for a macroscopically isotropic surface, namely $\sigma_1 = \sigma_1^{-1}$ or $\sigma_1 = 1$, i.e., the macroscopic diffusion tensor for isotropic surfaces with a square unit cell is always equal to the unit tensor (Corollary from Section 1).

Consider an example which illustrates the physical essence of Theorem 1.1. Let the surface be cylindrical and its generator parallel to the x–axis (see Figure A.1). The unit cell Q is a square of side 1; however, the length of the arc of circle is l.

First, the imposed gradient $\overline{\frac{\partial c}{\partial x}}$ is parallel to the x–axis. Then, the total flux of solute is equal to $-lD\overline{\frac{\partial c}{\partial x}}$. Second, the imposed gradient is along the y-axis; the corresponding flux is given by $-\frac{D}{l}\overline{\frac{\partial c}{\partial y}}$.

Hence, these relations can be summarized by $D_{xx} = lD$ and $D_{yy} = \frac{D}{l}$; therefore we get $D_{xx}D_{yy} = D^2$. In words, the longer length in one direction implies a smaller conductivity; but, when it is viewed from another direction, it offers a larger surface and thus a larger conductivity.

5. Diffusion tensor for a general cell at low order. In the previous section, we have obtained an exact result for diffusion on isotropic surfaces. For general surfaces represented by a square cell, formula (4.3) has been deduced. We now proceed to discuss general surfaces represented by a rectangular cell. In order to determine $\mathbf{D}$ from (4.1), it is sufficient to consider diffusion under two external fields in the x– and y–directions, separately. Let us first choose the x–direction; then, we can determine the two components of the diffusion tensor

$$\left(D_{xx}, D_{xy}\right) = \frac{1}{\lambda_1\lambda_2}\iint\limits_{\mathcal{S}} \mathbf{q}\, d\sigma_{\mathcal{S}} = \frac{1}{\lambda_1\lambda_2}\iint\limits_{Q} \mathbf{q}\,\delta\, dxdy, \tag{5.1}$$

where the vector $\mathbf{q}$ is defined by (2.6). Substituting (2.5), (2.6) into (5.1), we obtain

$$D_{xx} = \frac{1}{\lambda_1\lambda_2}\iint\limits_{Q} \frac{1}{\sqrt{f_x^2+f_y^2+1}}\left(\left(f_y^2+1\right)\frac{\partial\phi}{\partial x} - f_x f_y \frac{\partial\phi}{\partial y}\right) dxdy. \tag{5.2}$$

The component D_{xy} is calculated as follows

$$D_{xy} = \frac{1}{\lambda_1\lambda_2}\iint\limits_{Q} \frac{1}{\sqrt{f_x^2+f_y^2+1}}\left(-f_x f_y\frac{\partial\phi}{\partial x} + \left(f_x^2+1\right)\frac{\partial\phi}{\partial y}\right) dxdy. \tag{5.3}$$

The function $\phi(x,y)$ from (5.2,5.3) is solution of the problem (2.10,3.2).

Let us apply the formulae (5.2) and (5.3) to the first order approximation. Substitution of (3.4) into (5.2,5.3) yields

$$D_{xx} = 1 - \varepsilon^2\frac{\omega}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi/\omega}^{\pi/\omega}\left(\frac{1}{2}\left(h_\xi^2 - h_\eta^2\right) - \Phi_\xi\right) d\xi d\eta + O(\varepsilon^4)\,,$$

Apply the Green formula

$$\iint\limits_{G} (\Phi)_\xi d\xi d\omega = \int\limits_{\partial G} \Phi d\omega \tag{5.4}$$

and use the periodicity of Φ to obtain

$$D_{xx} = 1 - \varepsilon^2 \frac{\omega}{8\pi^2} \int\limits_{-\pi}^{\pi} \int\limits_{-\pi/\omega}^{\pi/\omega} \left(h_\xi^2 - h_\eta^2\right) d\xi d\eta + O(\varepsilon^4) \,. \tag{5.5}$$

Similar arguments yield the formulae

$$D_{xy} = \varepsilon^2 \frac{\omega}{\pi^2} \int\limits_{-\pi}^{\pi} \int\limits_{-\pi/\omega}^{\pi/\omega} h_\xi h_\eta \, d\xi d\eta + O(\varepsilon^4) \,, \tag{5.6}$$

$$D_{yy} = 1 + \varepsilon^2 \frac{\omega}{8\pi^2} \int\limits_{-\pi}^{\pi} \int\limits_{-\pi/\omega}^{\pi/\omega} \left(h_\xi^2 - h_\eta^2\right) d\xi d\eta + O(\varepsilon^4) \,. \tag{5.7}$$

In terms of f, (5.5–5.7) take the form

$$\mathbf{D} = \begin{bmatrix} 1 - \frac{1}{2\lambda_1\lambda_2} \iint\limits_Q \left(f_x^2 - f_y^2\right) dxdy & -\frac{1}{\lambda_1\lambda_2} \iint\limits_Q f_x f_y \, dxdy \\ -\frac{1}{\lambda_1\lambda_2} \iint\limits_Q f_x f_y \, dxdy & 1 + \frac{1}{2\lambda_1\lambda_2} \iint\limits_Q \left(f_x^2 - f_y^2\right) dxdy \end{bmatrix} + O(\lambda_1^{-m}\lambda_2^{-n}), \tag{5.8}$$

where $m + n = 4$.

The formulae (5.5–5.8) have the following interpretation in the space $\mathcal{L}_2$ endowed by the scalar product and the norm

$$\langle F, G \rangle = \frac{\omega}{4\pi^2} \int\limits_{-\pi}^{\pi} \int\limits_{-\pi/\omega}^{\pi/\omega} F(\xi,\eta)\, G(\xi,\eta)\, d\xi d\eta \,, \qquad \|F\|^2 = \langle F, F \rangle. \tag{5.9}$$

For instance, (5.5–5.7) can be written as

$$\mathbf{D} = \mathbf{I} - \varepsilon^2 \begin{bmatrix} -\frac{1}{2}\left(\|h_\xi\|^2 - \|h_\eta\|^2\right) & \langle h_\xi, h_\eta \rangle \\ \langle h_\xi, h_\eta \rangle & \frac{1}{2}\left(\|h_\xi\|^2 - \|h_\eta\|^2\right) \end{bmatrix} + O(\varepsilon^4) \,. \tag{5.10}$$

The formula (5.10) is valid up to $O(\varepsilon^4)$ in terms of the fast variables. Let us deduce a higher order formula for $\mathbf{D}$ using the function $\Phi(\xi,\eta)$ from Theorem 3.1. For the definiteness, consider the component D_{xx}. (3.4) can be further expanded as

$$\phi(x,y) = x + \varepsilon\Phi(\xi,\eta) + \varepsilon^2\phi_2(\xi,\eta) + \varepsilon^3\phi_3(\xi,\eta) + O(\varepsilon^4) \,, \tag{5.11}$$

where ϕ_2 and ϕ_3 are unknown functions. Substitution of (5.11) into (5.2) yields

$$D_{xx} = \frac{\omega}{4\pi^2} \int\limits_{-\pi}^{\pi} \int\limits_{-\pi/\omega}^{\pi/\omega} \Bigg(1 - \varepsilon^2\Big(\frac{1}{2}(h_\xi^2 - h_\eta^2) - \Phi_\xi\Big) + \varepsilon^3(\phi_2)_\xi + \tag{5.12}$$

$$\varepsilon^4\Big((\phi_3)_\xi - \frac{1}{2}(h_\xi^2 - h_\eta^2)\Phi_\xi - h_\xi h_\eta \Phi_\eta + \frac{1}{2}(h_\xi^2 + h_\eta^2)(\frac{3}{4} - h_\eta^2)\Big)\Bigg) d\xi d\eta + O(\varepsilon^5) \,.$$

First, we note that application of the Green formula (5.4) cancels the unknown functions ϕ_2 and ϕ_3. Hence, (5.12) becomes

$$D_{xx} = \frac{\omega}{4\pi^2} \int_{-\pi}^{\pi} \int_{-\pi/\omega}^{\pi/\omega} \Big(1 - \frac{\varepsilon^2}{2}(h_\xi^2 - h_\eta^2) + \tag{5.13}$$

$$\varepsilon^4 \Big(-\frac{1}{2}(h_\xi^2 - h_\eta^2)\Phi_\xi - h_\xi h_\eta \Phi_\eta + \frac{1}{8}\big(3h_\xi^4 + 2h_\xi^2 h_\eta^2 - h_\eta^4\big)\Big)\Big)\, d\xi d\eta + O(\varepsilon^6)\,.$$

Here, $O(\varepsilon^5)$ was changed into $O(\varepsilon^6)$, because it can be shown that $\mathbf{D}$ is an even function of ε. The formula (5.13) can be written as follows

$$\begin{aligned} D_{xx} = 1 + \frac{\varepsilon^2}{2}\big(\|h_\xi\|^2 - \|h_\eta\|^2\big) + \varepsilon^4 \Big(\frac{1}{8}\big(3\|h_\xi^2\|^2 + 2\langle h_\xi^2, h_\eta^2\rangle - \|h_\eta^2\|^2\big) \\ - \frac{1}{2}\big(h_\xi^2 - h_\eta^2\,, \Phi_\xi\big) - \big(h_\xi h_\eta\,, \Phi_\eta\big)\Big) + O(\varepsilon^6)\,. \end{aligned} \tag{5.14}$$

Recall that $|\nabla h|^2 = h_\xi^2 + h_\eta^2$. (5.14) shows that calculation of D_{xx} up to $O(\varepsilon^6)$ requires only the knowledge of function $\Phi(\xi,\eta)$ from Theorem 3.1. The same is true for the tensor $\mathbf{D}$.

Let us consider an elementary example of surface

$$f(x,y) = \sin\frac{2\pi x}{\lambda_1}\sin\frac{2\pi y}{\lambda_2}\,, \qquad |x| \le \frac{\lambda_1}{2}\,,\ |y| \le \frac{\lambda_2}{2}\,.$$

Then,

$$h(\xi,\eta) = \sin\xi\,\sin\omega\eta\,, \qquad |\xi| \le \pi\,,\ |\eta| \le \frac{\pi}{\omega}\,,$$

where ω is recalled to be equal to λ_1/λ_2. The Poisson equation (3.5) becomes

$$\Phi_{\xi\xi} + \Phi_{\eta\eta} = -(1+\omega^2)\cos\xi\,\sin\xi\,\sin^2\omega\eta\,. \tag{5.15}$$

It is easily seen that the function

$$\Phi(\xi,\eta) = \frac{1}{16}\sin 2\xi\,\big(1 + \omega^2 - \cos 2\omega\eta\big)$$

is doubly periodic and satisfies (5.15). D_{xx} is deduced from (5.14) as

$$D_{xx} = 1 + \frac{\varepsilon^2}{8}(1-\omega^2) + \frac{\varepsilon^4}{512}(21 - 8\omega^2 - 13\omega^4) + O(\varepsilon^6)\,.$$

Along similar lines, we obtain

$$\begin{aligned} D_{xy} &= 0\,, \\ D_{yy} &= 1 + \frac{\varepsilon^2}{8}(\omega^2 - 1) + \frac{\varepsilon^4}{512}(21\omega^4 - 8\omega^2 - 13) + O(\varepsilon^6)\,. \end{aligned}$$

One can see that $D_{xx}D_{yy} = 1$ up to $O(\varepsilon^6)$ and that it verifies Theorem 1.1.

Remark 3. Note that when ω is replaced by ω^{-1}, D_{xx} is not replaced by D_{yy}. This is due to the fact that when (λ_1,λ_2) is replaced by (λ_2,λ_1), ω is replaced by ω^{-1} and ε is multiplied by a factor λ_1/λ_2.

6. Diffusion tensor for square cells at higher orders.

6.1. General. Let us discuss anisotropic surfaces in the present section. Consider the case $\lambda_1 = \lambda_2 = \lambda$ where calculations become easier since it is possible to avoid calculations of the integrals and to deduce analytical formulae for the tensor $\mathbf{D}$ of higher order in $\varepsilon = \frac{2\pi}{\lambda}$. According to the general scheme given in Section 3, we solve the surface Laplace equation on the surface with the following boundary conditions

$$\begin{aligned} &\phi(\frac{\lambda}{2}, y) - \phi(-\frac{\lambda}{2}, y) = \lambda, && \frac{\partial \phi}{\partial x}(\frac{\lambda}{2}, y) = \frac{\partial \phi}{\partial x}(-\frac{\lambda}{2}, y), \\ &\phi(x, \frac{\lambda}{2}) = \phi(x, -\frac{\lambda}{2}), && \frac{\partial \phi}{\partial y}(x, \frac{\lambda}{2}) = \frac{\partial \phi}{\partial y}(x, -\frac{\lambda}{2}), \end{aligned} \tag{6.1}$$

by using the fast variables $\xi = \varepsilon x$, $\eta = \varepsilon y$, where $\varepsilon = \frac{2\pi}{\lambda}$. Hence, ω is equal to one. We decompose $\phi(x, y)$ onto slow and fast components

$$\phi(x, y) = F_0(x, y) + F(\varepsilon x, \varepsilon y).$$

It is known from Theorem 3.1 that $F_0(x, y) = x$. We are looking for $F(\xi, \eta)$ in the form of an expansion

$$F(\xi, \eta) = \sum_{k=1}^{\infty} \varepsilon^k \phi_k(\xi, \eta).$$

Then,

$$\phi(x, y) = \sum_{k=-1}^{\infty} \varepsilon^k \phi_k(\xi, \eta), \tag{6.2}$$

where $\phi_{-1}(\xi, \eta) = \xi$, $\phi_0(\xi, \eta) = 0$; the unknown functions ϕ_k $(k = 1, 2, \ldots)$ are periodic in the square $(-\pi, \pi) \times (-\pi, \pi)$, i.e., $\phi_k(\xi + \pi, \eta) = \phi_k(\xi, \eta + \pi) = \phi_k(\xi, \eta)$.

Let us rewrite (2.9) as an expansion in ε in terms of the fast variables. First, we introduce the matrices

$$\mathbf{P} = \begin{bmatrix} h_\xi^2 & h_\xi h_\eta \\ h_\xi h_\eta & h_\eta^2 \end{bmatrix}, \qquad \mathbf{I} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

In order to calculate (5.1) and (5.3), we rewrite the vector $\mathbf{q}$ in terms of the fast variables

$$\mathbf{q} = \delta\, \mathbf{K} \nabla_{xy} \phi = \frac{1}{\delta} (\mathbf{I} + \varepsilon^2 \mathbf{P}) \nabla_{xy} \phi. \tag{6.3}$$

Here, in agreement with (6.2)

$$\nabla_{xy} \phi = \sum_{k=0}^{\infty} \varepsilon^k \nabla \phi_{k-1}, \tag{6.4}$$

since $\nabla_{xy} = \varepsilon \nabla$, where $\nabla = \left(\frac{\partial}{\partial \xi}, \frac{\partial}{\partial \eta} \right)^{\mathsf{T}}$ is the gradient in the fast variables. Using

(6.3) and (6.4), we obtain

$$\begin{aligned} \mathbf{q} = \frac{1}{\delta}(\mathbf{I}+\varepsilon^2\mathbf{P})(\varepsilon\nabla\phi) = \nabla\phi_{-1}+ \\ +\sum_{n=1}^{\infty}\varepsilon^{2n}\left(\nabla\phi_{2n-1}+\sum_{m=1}^{n}A_m H^{m-1}\big((2m-1)H\mathbf{I}-2m\mathbf{P}\big)\nabla\phi_{2n-2m-1}\right)+ \\ +\sum_{n=1}^{\infty}\varepsilon^{2n+1}\left(\nabla\phi_{2n}+\sum_{m=1}^{n}A_m H^{m-1}\big((2m-1)H\mathbf{I}-2m\mathbf{P}\big)\nabla\phi_{2n-2m}\right), \end{aligned} \tag{6.5}$$

where

$$A_m = \frac{(-1)^m(2m-3)!!}{(2m)!!} \qquad \text{and} \qquad H := |\nabla h|^2 = h_\xi^2 + h_\eta^2. \tag{6.6}$$

We put $n!! = 1$ for all $n \le 0$. Applying the operator ∇_{xy} to (6.5), we obtain the Laplace operator on $\mathcal{S}$ as a series in the powers of ε

$$\begin{aligned} \delta\,\Delta_{\mathcal{S}}\phi = \nabla_{xy}\cdot(\delta\,\mathbf{K}\nabla_{xy}\phi) = \varepsilon^2\nabla\cdot\big(\frac{1}{\delta}\,(\mathbf{I}+\varepsilon P)\nabla\phi\big) = \\ \sum_{n=1}^{\infty}\varepsilon^{2n+1}\left(\Delta\phi_{2n-1}+\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m-1})\right) \\ +\sum_{n=1}^{\infty}\varepsilon^{2n+2}\left(\Delta\phi_{2n}+\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m})\right), \end{aligned} \tag{6.7}$$

where the linear operator $\mathcal{L}_m$ acts on the scalar function $\phi(\xi,\eta)$ as follows

$$\begin{aligned} \mathcal{L}_m(\phi) = (2m-1)H^m\Delta\phi \\ + mH^{m-1}\big((2m-1)\nabla H\cdot\nabla\phi - 2\nabla\cdot(\mathbf{P}\nabla\phi)\big) \\ - 2m(m-1)H^{m-2}\nabla H\cdot(\mathbf{P}\nabla\phi)\,, \end{aligned} \tag{6.8}$$

where Δ is the Laplace operator in the fast variables. The Laplace equation $\Delta_{\mathcal{S}}\phi = 0$ holds if and only if the coefficient of every power of ε is equal to zero. This implies that we have reduced the Laplace equation to the two separate cascades of Poisson equations

$$\Delta\phi_{2n-1} = -\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m-1})\,, \tag{6.9}$$

$$\Delta\phi_{2n} = -\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m})\,, \tag{6.10}$$

where $n = 1, 2, \dots$.

One can see that (6.10) becomes

$$\Delta\phi_{2n} = 0\,, \qquad n = 1, 2, \dots\,, \tag{6.11}$$

since the initial term ϕ_0 is equal to zero. It follows from the Liouville's theorem for the class of doubly periodic functions [18] that $\phi_{2n} = \mathsf{constant}$ for $n = 1, 2, \dots$.

Let us write the first two equations of (6.9)

$$\begin{aligned}
\Delta\phi_1 &= h_\xi\left(h_{\xi\xi}+h_{\eta\eta}\right),\\
\Delta\phi_3 &= \frac{1}{2}\big(h_\xi^2-h_\eta^2\big)\big((\phi_1)_{\xi\xi}-(\phi_1)_{\eta\eta}\big)+2h_\xi h_\eta(\phi_1)_{\xi\eta}\\
&\quad+\big(h_{\xi\xi}+h_{\eta\eta}\big)\big(h_\xi(\phi_1)_\xi+h_\eta(\phi_1)_\eta\big)\\
&\quad-\frac{1}{2}\,h_\xi\left(h_\xi^2\big(3h_{\xi\xi}+h_{\eta\eta}\big)+h_\eta^2\big(h_{\xi\xi}+3h_{\eta\eta}\big)+4h_\xi h_\eta h_{\xi\eta}\right).
\end{aligned}\tag{6.12}$$

One can see that ϕ_1 satisfies a Poisson equation with a known right-hand part; ϕ_3 satisfies a Poisson equation with a right-hand part depending on $\nabla\phi_1$ and so on. Therefore, the cascade (6.9) is correct, i.e., each function is determined by the previous ones.

A Poisson equation has a unique solution in the class of doubly periodic functions up to an arbitrary additive constant. Since we need in the final formulae the flux, i.e., the derivatives of $\phi_k(\xi,\eta)$, it is useless to determine this arbitrary constant at each step of the cascade (6.9).

The components D_{xx} and D_{xy} by performing the integration in the fast variables can be calculated as follows

$$(D_{xx},D_{xy})^{\mathsf{T}}=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\delta\,\mathbf{q}\,d\xi d\eta\,,\tag{6.13}$$

where $\mathbf{q}$ has the form (6.5). Hence, (6.13) becomes

$$(D_{xx},D_{xy})^{\mathsf{T}}=(1,0)^{\mathsf{T}}+\sum_{n=1}^{\infty}\varepsilon^{2n}\sum_{m=1}^{n}A_m\big[(2m-1)\mathbf{b}_{n,m}-2m\,\mathbf{c}_{n,m}\big]\,,\tag{6.14}$$

where the vectors $\mathbf{b}_{n,m}$ and $\mathbf{c}_{n,m}$ are given by

$$\begin{aligned}
\mathbf{b}_{n,m}&=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}H^m\,\nabla\phi_{2n-2m-1}d\xi d\eta\\
\mathbf{c}_{n,m}&=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}H^{m-1}\,\mathbf{P}\nabla\phi_{2n-2m-1}d\xi d\eta\,,
\end{aligned}\tag{6.15}$$

and A_m, H are given by (6.6).

Let us represent the function h as a Fourier series

$$h(\xi,\eta)=\sum_{s,t}\Big(a_{st}\cos(s\xi+t\eta)+b_{st}\sin(s\xi+t\eta)\Big)\,.\tag{6.16}$$

We can assume in the representation (6.16) that s varies from 0 to $+\infty$, and that t varies from $-\infty$ to $+\infty$, because

$$a_{s,t}\cos(s\xi+t\eta)+b_{s,t}\sin(s\xi+t\eta)=a_{s,t}\cos(-s\xi-t\eta)-b_{s,t}\sin(-s\xi-t\eta)\,.$$

We can also take $b_{0,t}=0$ for $t\le 0$, since $b_{0,t}\sin t\eta=-b_{0,t}\sin(-t\eta)$. Moreover, we put $a_{00}=0$, since we shall only use derivatives of $h(\xi,\eta)$.

In order to apply the above algorithm to (6.16), we have to solve in each step of the cascade (6.12) a Poisson equation with a right hand side of the general form

$$\gamma(\xi,\eta) = \alpha\cos(s\xi + t\eta) + \beta\sin(s\xi + t\eta), \tag{6.17}$$

where α and β are constants. The terms (6.17) appear because of the following operations at each step of the cascade (6.9):

i) all partial derivatives of (6.17) have the form (6.17);
ii) the result of the multiplication of the terms (6.17) is also reduced to a linear combination of terms of the same type;
iii) the Poisson equation

$$\phi_{\xi\xi} + \phi_{\eta\eta} = \gamma(\xi,\eta)$$

has the unique solution

$$\phi(\xi,\eta) = -\frac{\gamma(\xi,\eta)}{s^2+t^2}, \tag{6.18}$$

Hence, this solution is of the same form as (6.17).

It is necessary to note that at each step of the cascade (6.9), the constant term with $s = t = 0$ never appears because the right hand side of (6.9) is a sum of derivatives of trigonometric functions. Hence, the denominator of (6.18) is never zero.

In order to calculate the integrals in (6.13), we represent the integrands as Fourier series. Then, $\frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi} p(\xi,\eta)\,d\xi d\eta$ is equal to the zeroth term of this series for any double periodical function $p(\xi,\eta)$. Hence, at each step we do not perform any direct integration, since it is reduced to arithmetic operations. The longest operation consists of reexpanding the trigonometric series.

6.2. Procedure to derive the second order terms. We shall use the expanded form of (6.13)

$$D_{xx} = 1 - \frac{\varepsilon^2}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi}\frac{1}{\sqrt{1+\varepsilon^2(h_\xi^2+h_\eta^2)}}\Big(h_\xi^2\big(1+\varepsilon^2(\phi_1)_\xi + \varepsilon^4(\phi_3)_\xi + \ldots\big) \tag{6.19}$$
$$+ h_\xi h_\eta\big(\varepsilon^2(\phi_1)_\eta + \varepsilon^4(\phi_3)_\eta + \ldots\big)\Big)\,d\xi\,d\eta := 1 + \sum_{k=1}^{\infty} D_{xx}^{(k)}\varepsilon^{2k}\,,$$

$$D_{xy} = -\frac{\varepsilon^2}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi}\frac{1}{\sqrt{1+\varepsilon^2(h_\xi^2+h_\eta^2)}}\Big(h_\xi h_\eta\big(1+\varepsilon^2(\phi_1)_\xi + \varepsilon^4(\phi_3)_\xi + \ldots\big) \tag{6.20}$$
$$+ h_\eta^2\big(\varepsilon^2(\phi_1)_\eta + \varepsilon^4(\phi_3)_\eta + \ldots\big)\Big)\,d\xi\,d\eta := \sum_{k=1}^{\infty} D_{xy}^{(k)}\varepsilon^{2k}\,.$$

If the expansion is limited up to the order $O(\varepsilon^6)$, (6.19) and (6.20) imply

$$\begin{aligned} D_{xx} &= 1 + \varepsilon^2 D_{xx}^{(1)} + \varepsilon^4 D_{xx}^{(2)} + O(\varepsilon^6)\,,\\ D_{xy} &= \varepsilon^2 D_{xy}^{(1)} + \varepsilon^4 D_{xy}^{(2)} + O(\varepsilon^6)\,, \end{aligned} \tag{6.21}$$

where

$$D_{xx}^{(1)} = -\frac{1}{8\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi}\left(h_\xi^2 - h_\eta^2\right) d\xi\, d\eta\,, \tag{6.22}$$

$$D_{xx}^{(2)} = \frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi}\Big(\frac{1}{8}\left(h_\xi^2 + h_\eta^2\right)\left(3h_\xi^2 - h_\eta^2\right) - \frac{1}{2}\left(h_\xi^2 - h_\eta^2\right)(\phi_1)_\xi - h_\xi h_\eta (\phi_1)_\eta\Big) d\xi\, d\eta\,, \tag{6.23}$$

$$D_{xy}^{(1)} = -\frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi} h_\xi h_\eta\, d\xi\, d\eta\,, \tag{6.24}$$

$$D_{xy}^{(2)} = \frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi}\Big(\frac{1}{2}\left(h_\xi^2 + h_\eta^2\right)h_\xi h_\eta - h_\xi h_\eta (\phi_1)_\xi + \frac{1}{2}\left(h_\xi^2 - h_\eta^2\right)(\phi_1)_\eta\Big) d\xi\, d\eta\,. \tag{6.25}$$

To calculate the integrals (6.22)-(6.25), we use the following Parseval formula for the scalar product (5.9)

$$\langle F, G\rangle = \frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi} F(\xi,\eta)G(\xi,\eta)\, d\xi\, d\eta = \frac{1}{2}\sum_{s,t}\Big(F_{st}^{(1)}G_{st}^{(1)} + F_{st}^{(2)}G_{st}^{(2)}\Big)\,, \tag{6.26}$$

where

$$F(\xi,\eta) = \sum_{s,t}\Big[F_{st}^{(1)}\cos(s\xi + t\eta) + F_{st}^{(2)}\sin(s\xi + t\eta)\Big]\,. \tag{6.27}$$

We recall that $F_{00}^{(1)} = 0$, $F_{st}^{(1)} = F_{st}^{(2)} = 0$ for $s < 0$ and $F_{0t}^{(2)} = 0$ for $t \le 0$. Application of (6.26) to (6.22) and (6.24) yields

$$\begin{aligned} D_{xx}^{(1)} &= -\frac{1}{4}\sum_{s,t}(s^2 - t^2)\Big(a_{st}^2 + b_{st}^2\Big)\,, \\ D_{xy}^{(1)} &= -\frac{1}{2}\sum_{s,t} st\Big(a_{st}^2 + b_{st}^2\Big)\,. \end{aligned} \tag{6.28}$$

The algorithm described in Section 6.1 implies

$$\begin{aligned} \phi_1(\xi,\eta) = \frac{1}{2}\sum_{s_1,t_1,s_2,t_2}\frac{s_1(s_2^2 + t_2^2)}{(s_1 - s_2)^2 + (t_1 - t_2)^2}\Big[& (a_1 b_2 + a_2 b_1)\cos\big((s_1 + s_2)\xi + (t_1 + t_2)\eta\big) \\ & - (a_1 a_2 - b_1 b_2)\sin\big((s_1 + s_2)\xi + (t_1 + t_2)\eta\big) \\ & - (a_1 b_2 - a_2 b_1)\cos\big((s_1 - s_2)\xi + (t_1 - t_2)\eta\big) \\ & - (a_1 a_2 + b_1 b_2)\sin\big((s_1 - s_2)\xi + (t_1 - t_2)\eta\big)\Big]\,. \end{aligned} \tag{6.29}$$

The integral (6.23) is calculated by means of (6.26). After tedious calculations, we obtain

$$D_{xx}^{(2)} = \frac{1}{64}\Bigg(\sum_{\substack{s_4=s_1-s_2+s_3\\ t_4=t_1-t_2+t_3}}{}' \alpha_1 A_1 + \sum_{\substack{s_4=s_1+s_2-s_3\\ t_4=t_1+t_2-t_3}}{}' \alpha_1 A_2 \\ + \sum_{\substack{s_4=-s_1+s_2-s_3\\ t_4=-t_1+t_2-t_3}}{}' \alpha_1 A_3 + \sum_{\substack{s_4=-s_1-s_2-s_3\\ t_4=-t_1-t_2-t_3}}{}' \alpha_1 A_4 + \sum_{\substack{s_4=s_1-s_2+s_3\\ t_4=t_1-t_2+t_3}}{}' \alpha_2 A_5 \\ + \sum_{\substack{s_4=s_1+s_2+s_3\\ t_4=t_1+t_2+t_3}}{}' \alpha_2 A_6 + \sum_{\substack{s_4=-s_1+s_2+s_3\\ t_4=-t_1+t_2+t_3}}{}' \alpha_2 A_7 + \sum_{\substack{s_4=-s_1-s_2+s_3\\ t_4=-t_1-t_2+t_3}}{}' \alpha_2 A_8 \Bigg), \tag{6.30}$$

where

$$\alpha_1 = \Big[t_1 t_2 \Big(3s_3^3 s_4 + s_3 s_4 (7s_4^2 + 3t_3^2 + 4t_3 t_4 + 7t_4^2) \\ - t_3 t_4 (s_4^2 + (t_3+t_4)^2) + s_3^2 (10 s_4^2 - t_4(t_3 - 4t_4)) \Big) \\ + s_1 \Big(-8 s_3 t_2 (t_3+t_4)(s_4^2 + t_4^2) + s_2 \Big(3s_3^2 s_4 - s_3 s_4 (s_4^2 - 3t_3^2 - 4t_3 t_4 + t_4^2) \\ - t_3 t_4 (s_4^2 + (t_3+t_4)^2) + s_3^2 (2s_4^2 - t_4(t_3+4t_4)) \Big) \Big) \Big] \Big/ \Big[(s_3+s_4)^2 + (t_3+t_4)^2 \Big],$$

$$\alpha_2 = \Big[t_1 t_2 \Big(3s_3^3 s_4 + s_3 s_4 (7s_4^2 + 3t_3^2 - 4t_3 t_4 + 7t_4^2) \\ - t_3 t_4 (s_4^2 + (t_3-t_4)^2) - s_3^2 (10 s_4^2 + t_4(t_3 + 4t_4)) \Big) \\ + s_1 \Big(8 s_3 t_2 (t_3-t_4)(s_4^2 + t_4^2) + s_2 \Big(3s_3^2 s_4 - s_3 s_4 (s_4^2 - 3t_3^2 + 4t_3 t_4 + t_4^2) \\ - t_3 t_4 (s_4^2 + (t_3-t_4)^2) - s_3^2 (2s_4^2 + t_4(t_3-4t_4)) \Big) \Big) \Big] \Big/ \Big[(s_3-s_4)^2 + (t_3-t_4)^2 \Big],$$

$$\begin{aligned}
A_1 &= -a_1\Big(a_2(a_3a_4 - b_3b_4) - b_2(a_3b_4 + b_3a_4)\Big) - b_1\Big(a_3(a_2b_4 + b_2a_4) + b_3(a_2a_4 - b_2b_4)\Big),\\
A_2 &= a_1\Big(a_2(a_3a_4 - b_3b_4) + b_2(a_3b_4 + b_3a_4)\Big) + b_1\Big(a_3(a_2b_4 - b_2a_4) + b_3(a_2a_4 + b_2b_4)\Big),\\
A_3 &= -a_1\Big(a_2(a_3a_4 - b_3b_4) + b_2(a_3b_4 + b_3a_4)\Big) + b_1\Big(a_3(a_2b_4 - b_2a_4) + b_3(a_2a_4 + b_2b_4)\Big),\\
A_4 &= a_1\Big(a_2(a_3a_4 - b_3b_4) - b_2(a_3b_4 + b_3a_4)\Big) - b_1\Big(a_3(a_2b_4 + b_2a_4) + b_3(a_2a_4 - b_2b_4)\Big),\\
A_5 &= a_1\Big(a_2(a_3a_4 + b_3b_4) - b_2(a_3b_4 - b_3a_4)\Big) + b_1\Big(a_3(a_2b_4 + b_2a_4) - b_3(a_2a_4 - b_2b_4)\Big),\\
A_6 &= -a_1\Big(a_2(a_3a_4 + b_3b_4) + b_2(a_3b_4 - b_3a_4)\Big) - b_1\Big(a_3(a_2b_4 - b_2a_4) - b_3(a_2a_4 + b_2b_4)\Big),\\
A_7 &= a_1\Big(a_2(a_3a_4 + b_3b_4) + b_2(a_3b_4 - b_3a_4)\Big) - b_1\Big(a_3(a_2b_4 - b_2a_4) - b_3(a_2a_4 + b_2b_4)\Big),\\
A_8 &= -a_1\Big(a_2(a_3a_4 + b_3b_4) - b_2(a_3b_4 - b_3a_4)\Big) + b_1\Big(a_3(a_2b_4 + b_2a_4) - b_3(a_2a_4 - b_2b_4)\Big).
\end{aligned}$$

There are some conventions assumed in the sums from (6.30). For instance, the first sum $\sum\nolimits'_{\substack{s_4=s_1-s_2+s_3\\t_4=t_1-t_2+t_3}}$ denotes that s_1, s_2 and s_3 vary from 0 to $+\infty$; t_1, t_2 and t_3 vary from $-\infty$ to $+\infty$; moreover, $s_4 = s_1 - s_2 + s_3$, $t_4 = t_1 - t_2 + t_3$. Finally, the terms with $(s_3 \pm s_4)^2 + (t_3 \pm t_4)^2 = 0$ are excluded from α_1 and α_2.

6.3. Numerical examples.

6.3.1. Example 1. Let us consider an example where the surface $\mathcal{S}$ is given by the function (see Figure A.2)

$$h(\xi, \eta) = \sin \xi \sin 2\eta = \frac{1}{2}\Big(\cos(\xi - 2\eta) - \cos(\xi + 2\eta)\Big) . \tag{6.31}$$

Then, application of the algorithm yields the following formula for $\mathbf{D}$

$$D_{xx} = \frac{1 + 9.49508\,\varepsilon^2 + 33.0992\,\varepsilon^4 + 52.0167\,\varepsilon^6 + 36.1186\,\varepsilon^8 + 8.71534\,\varepsilon^{10}}{1 + 9.12008\,\varepsilon^2 + 30.1069\,\varepsilon^4 + 43.9516\,\varepsilon^6 + 27.7049\,\varepsilon^8 + 5.97388\,\varepsilon^{10}} ,$$

$$D_{xy} = 0 , \qquad D_{yy} = D_{xx}^{-1} . \tag{6.32}$$

Here, we apply the Padé approximation $(10, 10)$ which provides an approximation up to $O(\varepsilon^{22})$ to the polynomial form of D_{xx} obtained by the algorithm from Subsection 6.1. The last two equalities from (6.32) are obtained by straightforward computations up to $O(\varepsilon^{22})$ and they numerically confirm Theorem 1.1. The components of the tensor $\mathbf{D}$ (6.32) for $0 \le \varepsilon \le 1$ are presented as function on ε in Figure A.3. The tensor ellipse of $\mathbf{D}$ [14] is presented in Figure A.4.

6.3.2. Example 2. Consider another example when the surface $\mathcal{S}$ is given by the function (see Figure A.5)

$$h(\xi, \eta) = \cos(3\xi - \eta) - \frac{3}{4}\cos(\xi - 3\eta) + \frac{1}{2}\cos(\xi + 3\eta) - \frac{1}{4}\cos(3\xi + \eta) . \tag{6.33}$$

In this case, we obtain

$$D_{xx} = \frac{1 + 65.0538\,\varepsilon^2 + 1442.10\,\varepsilon^4 + 12868.4\,\varepsilon^6 + 40773.5\,\varepsilon^8 + 25197.8\,\varepsilon^{10}}{1 + 65.5538\,\varepsilon^2 + 1471.43\,\varepsilon^4 + 13418.5\,\varepsilon^6 + 44493.4\,\varepsilon^8 + 32159.0\,\varepsilon^{10}} , \tag{6.34}$$

$$D_{xy} = \frac{1.875\,\varepsilon^2 + 104.697\,\varepsilon^4 + 1881.82\,\varepsilon^6 + 11724.5\,\varepsilon^8 + 15838.8\,\varepsilon^{10}}{1 + 65.5259\,\varepsilon^2 + 1509.92\,\varepsilon^4 + 14484.6\,\varepsilon^6 + 51634.2\,\varepsilon^8 + 37182.9\,\varepsilon^{10}} , \tag{6.35}$$

$$D_{yy} = \frac{1 + 75.2283\,\varepsilon^2 + 1968.17\,\varepsilon^4 + 20570.5\,\varepsilon^6 + 70022.0\,\varepsilon^8 + 46386.5\,\varepsilon^{10}}{1 + 74.7283\,\varepsilon^2 + 1930.49\,\varepsilon^4 + 19610.8\,\varepsilon^6 + 61118.0\,\varepsilon^8 + 30072.0\,\varepsilon^{10}} . \tag{6.36}$$

We apply here the Padé approximation $(10, 10)$. The components of the tensor $\mathbf{D}$ (6.34) are presented inn Figure A.3. The tensor ellipse of $\mathbf{D}$ is presented in Figure A.6.

7. Conclusion. The main purpose of this paper was to obtain analytical formulae for the macroscopic diffusion tensor of surfaces. We derived a boundary value problem for the Laplace operator (2.10). We applied an asymptotic analysis to study the boundary problem and deduced approximate analytical formulae. We proved Theorem 3.1, where the local field is determined up to $O(\varepsilon^2)$ in terms of the function $\Phi(\xi, \eta)$ satisfying a Poisson equation. For a square representative cell, an analytical form of this function (6.29) was obtained. The results of the calculation of the local field were applied to the determination of the macroscopic diffusion tensor $\mathbf{D}$. First,

D was proved to be the unit tensor for isotropic surfaces. A general algorithm to calculate higher order terms was constructed which is based on a cascade of Poisson equations. In particular, analytical formulae for **D** were deduced. The tensor **D** was computed up to $O(\varepsilon^{22})$ for two particular surfaces.

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Appendix.

Almost all manipulations of this paper have been performed with *Mathematica*® in interactive (or semi-automatic) mode. Use of *Mathematica*® allows us to create a constructive algorithm to solve the small parameter method in closed symbolic form. In particular, the cascade (6.9) and the solver of the Poisson equation (6.18) have been constructed in symbolic form. The operators have been constructed not only to simplify manipulations, but to write solutions of the boundary value problems and the macroscopic tensor in symbolic form.

The present section gives some of the key ideas. First, we expand possibilities of *Mathematica*® by introducing auxiliary definitions which significantly reduce the computational cost.

One example (see Section 6) is presented as follows. First, we introduce auxiliary definitions

(*i*) the double factorial

```
In[1]:= Off[General::"spell",RuleDelayed::"rhs"];
In[2]:= Unprotect[Factorial2];
        Factorial2[n_/;n<=0]= 1;
        Protect[Factorial2];
```

(*ii*) the operator which simplifies trigonometrical polynomials

```
In[3]:= TrigCollect[expr_]:= Collect[expr//TrigReduce,_Cos|_Sin];
```

(*iii*) the nabla operator acting on scalars and vectors

```
In[4]:= Del[φ_List?VectorQ/;Length[φ]==2]:=D[φ⟦1⟧,ξ]+D[φ⟦1⟧,η];
        Del[φ_]:= {D[φ,ξ],D[φ,η]};
```

(*iv*) the Laplace operator

```
In[5]:= Δ[φ_][ξ_Symbol,η_Symbol]:= D[φ[ξ,η],{ξ,2}]+D[φ[ξ,η],{η,2}];
```

We construct the solver of the Poisson equation with periodic boundary conditions

```
In[6]:= Poisson[expr_Plus,args:{__Symbol}]:= Poisson[#,args]&/@expr;
        Poisson[a_ expr_,{ξ_Symbol,η_Symbol}]:=
          a Poisson[expr,{ξ,η}]/;FreeQ[a,ξ]∧FreeQ[a,η];
        Poisson[expr:(Sin|Cos)[s_ (ξ_|η_)],
                {ξ_Symbol,η_Symbol}]:= -expr/s^2;
        Poisson[expr:(Sin|Cos)[s_ ξ_ + t_ η_],
                {ξ_Symbol,η_Symbol}]:= -expr/(s^2+t^2);
```

The integrator of trigonometrical polynomial over the unit cell can be expressed as

```
In[7]:= TrigIntegrate[expr_]:=
          Collect[expr//TrigReduce,_Cos|_Sin]/._Cos|_Sin_→0;
```

Let us consider an example of surface described by the equation (see Subsection 6.3.2)

```
In[8]:= h[ξ_,η_]:=Cos[3ξ-η]-(3/4)Cos[ξ-3η]+(1/2)Cos[ξ+3η]-(1/4)Cos[3ξ+η];
```

According to the algorithm, we introduce the functions

```
In[9]:= H[ξ_Symbol,η_Symbol]= D[h[ξ,η],ξ]^2 + D[h[ξ,η],η]^2//TrigCollect;
        H[ξ_Symbol,η_Symbol,m_/;m<=0]= 1;
        H[ξ_Symbol,η_Symbol,m_]:= Block[
          {result= H[ξ,η,m-1]H[ξ,η]//TrigCollect},
          DownValues[H]= Prepend[DownValues[H],
            H[ξ_Symbol,η_Symbol,m]:>Evaluate[result]];
          result];
```

and the matrix

```
In[10]:= P[ξ_Symbol,η_Symbol]= {
            {  D[h[ξ,η],ξ]^2,  -D[h[ξ,η],ξ] D[h[ξ,η],η]  },
            { -D[h[ξ,η],ξ] D[h[ξ,η],η],  D[h[ξ,η],η]^2  }
          }//TrigCollect;
```

We are now ready to create a cascade of Poisson equations. Coefficients of the surface gradient are introduced by

```
In[11]:= CG[m_]:= CG[m]= (-1)^m (2m-3)!!/(2m)!!;
```

The coefficients of the Laplace operator are given by

```
In[12]:= CLap_m_[ξ_Symbol,η_Symbol]:= (2m-1) H[ξ,η,m] Δ[φ][ξ,η] +
         +m H[ξ,η,m-1]((2m-1)∇H[ξ,η]·∇φ[ξ,η] - 2∇(P[ξ,η]·∇φ[ξ,η])s)+
         -2m(m-1) H[ξ,η,m-2] ∇H[ξ,η]·(P[ξ,η]·∇φ[ξ,η]);
```

The right hand side of Poisson equation is written as follows

```
In[13]:= RHS_n_[ξ_Symbol,η_Symbol]:= - Sum[CG[m]CLap_m[φ_(2n-2m-1)][ξ,η], {m,1,n}];
```

Introduce the potential ϕ_{-1} and the potentials with even indices as zeros

```
In[14]:= φ_-1[ξ_Symbol,η_Symbol]:= ξ;
         φ_?EvenQ[ξ_Symbol,η_Symbol]= 0;
```

Coefficients of the expansion of the potential in series of ε have the form

```
In[15]:= φ_n_?OddQ[ξ_Symbol,η_Symbol]:= φ_n[ξ_Symbol,η_Symbol]=
           TrigCollect[Poisson[RHS_(n+1)/2[φ][ξ,η]//TrigCollect,{ξ,η}]];
```

The gradient of the potential is given by

```
In[16]:= Φ[n_,m_]:= Φ[n,m]= TrigCollect[ ∇φ_(2n-2m-1)][ξ,η] ];
```

We now are ready to compute the macroscopic diffusion tensor. We introduce the integrals

```
In[17]:= IH[n_,m_]:= IH[n,m]= H[ξ,η,m]Φ[n,m]//TrigIntegrate;
         IP[n_,m_]:= IP[n,m]= H[ξ,η,m-1](P[ξ,η]·Φ[n,m])//TrigIntegrate;
```

The first two components of the macroscopic tensor are calculated by

```
In[18]:= xD[0]= {1,0};
           xD[n_]:= xD[n]= Sum[CG[m]((2m-1)IH[n,m]-2m IP[n,m]), {m,1,n}];
```

The first two components of the macroscopic tensor, for instance up to ε^6 are calculated by the following expression

```
In[19]:= ({Dxx,Dxy}= Σ_{n=0}^{3} xD[n]ε^{2n} + O[ε]^8)//TableForm
Out[19]//TableForm=
```

$$1-\frac{\varepsilon^2}{2}+\frac{441\varepsilon^4}{128}-\frac{82409\varepsilon^6}{2048}+O[\varepsilon]^8$$

$$\frac{15\varepsilon^2}{8}-\frac{2325\varepsilon^4}{128}+\frac{3855\varepsilon^6}{16}+O[\varepsilon]^8$$

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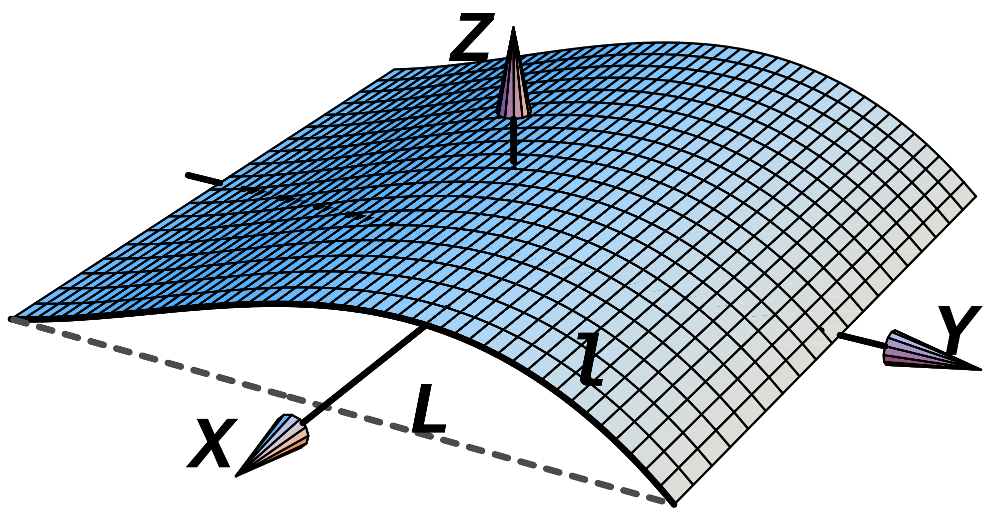

FIG. A.1. *Cylindrical surface.*

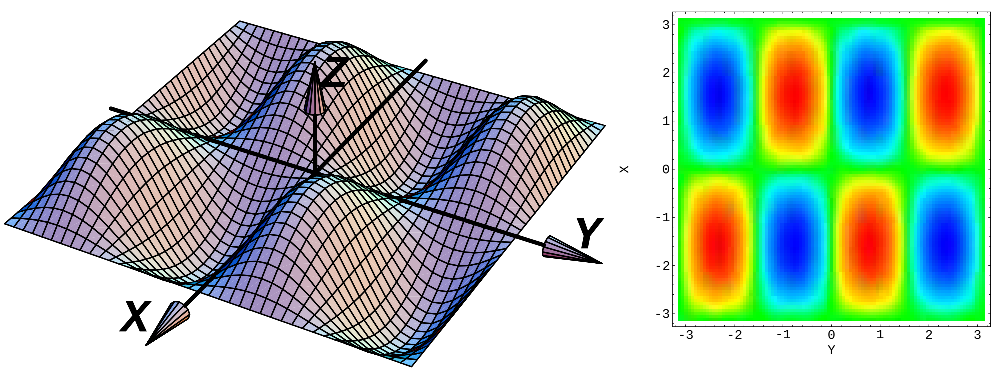

FIG. A.2. *Example 1. The surface $\mathcal{S}$ defined by* (6.31).

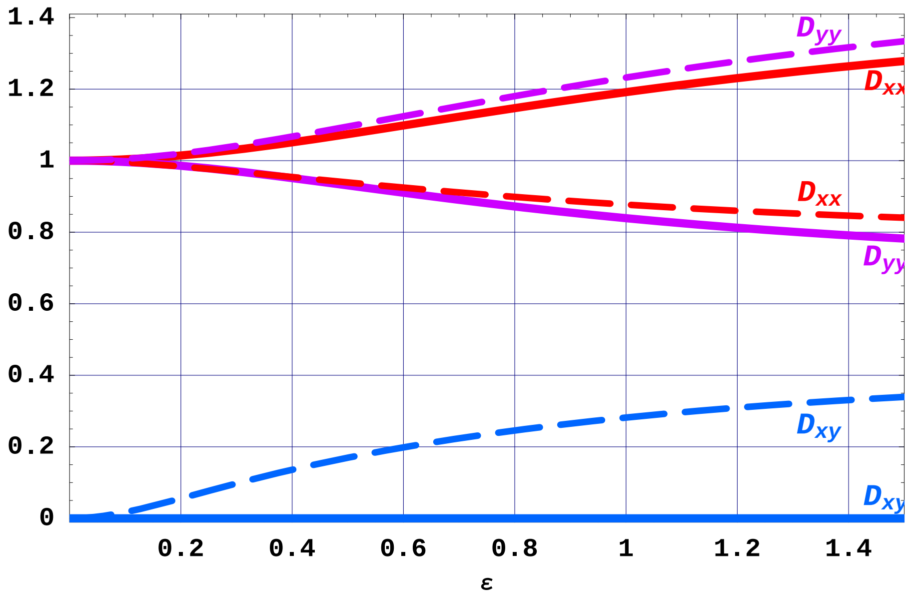

FIG. A.3. *Dependence of the tensor* $\mathbf{D}$ *components on* ε *for the surfaces defined by* (6.31) *(solid lines) and by* (6.33) *(broken lines).*

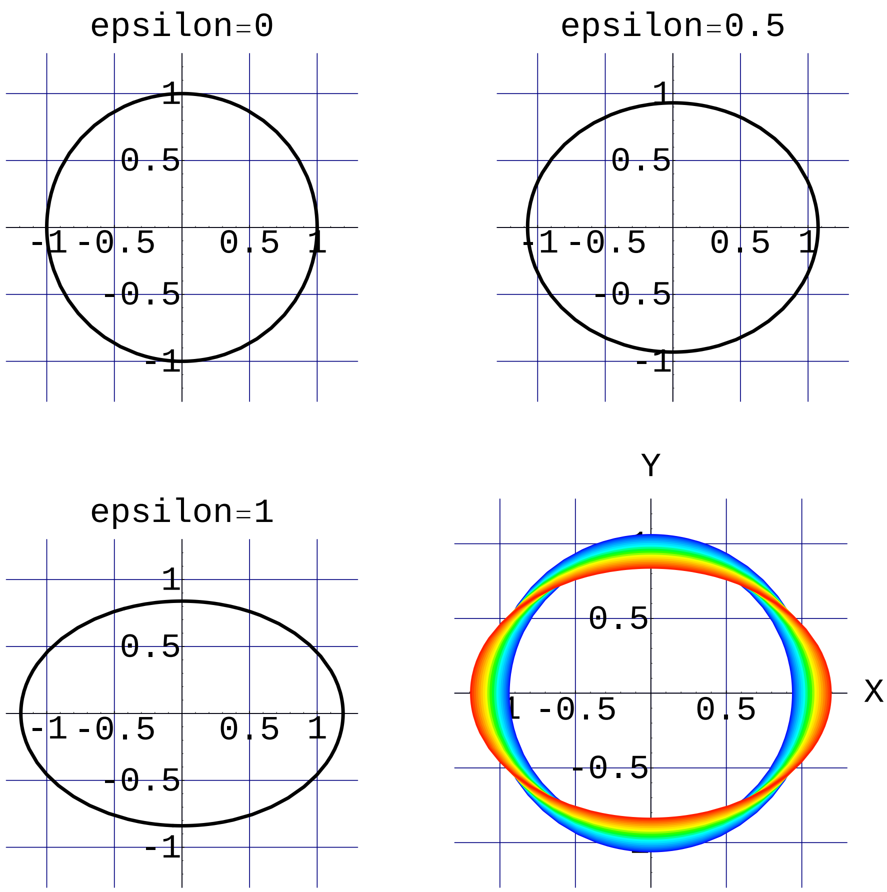

Fig. A.4. *Example 1. Dependence of the tensor* $\mathbf{D}$ *on* ε *for the surface defined by* (6.31)*:* $\varepsilon = 0, 0.5, 1$ *in the first three pictures and for all* ε $(0 \leq \varepsilon \leq 1)$ *in the last picture.*

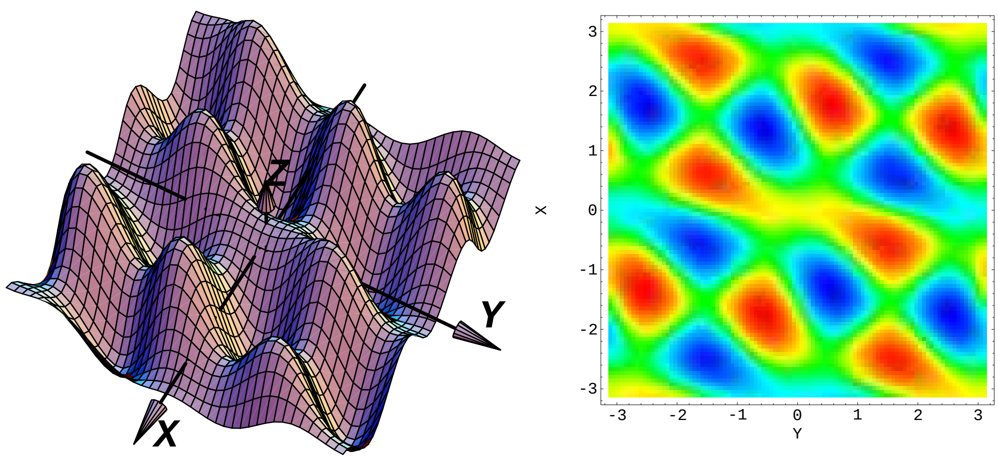

FIG. A.5. *Example 2. The surface $\mathcal{S}$ defined by* (6.33).

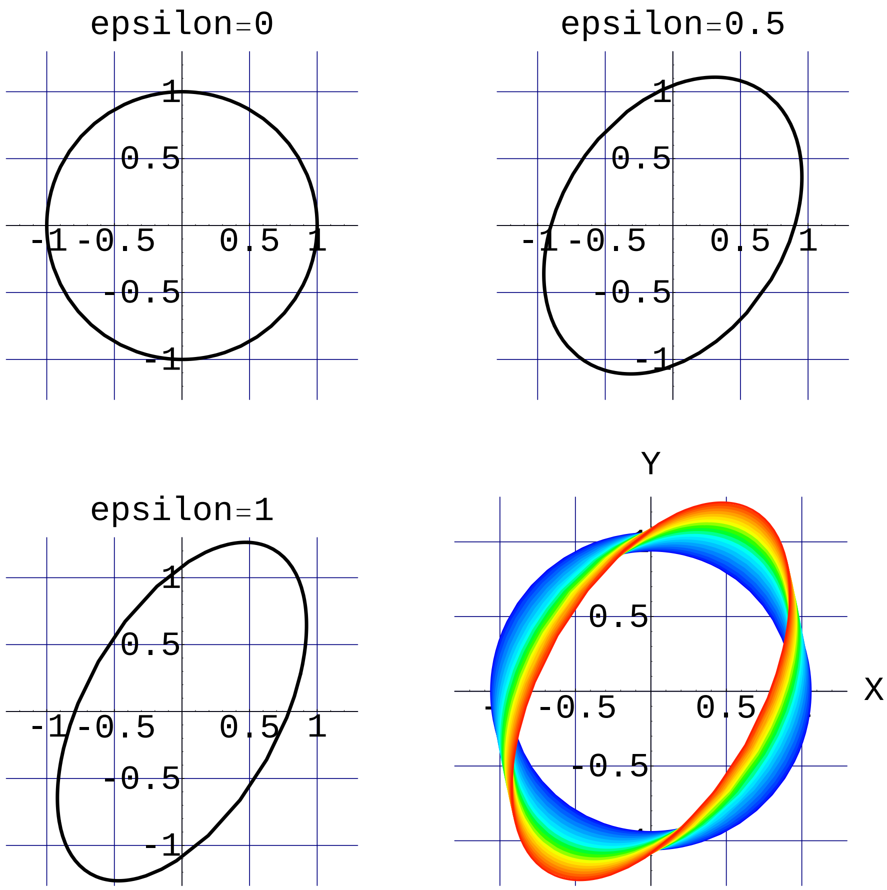

FIG. A.6. *Example 2. Dependence of the tensor* $\mathbf{D}$ *on* ε *for the surface defined by* (6.33).