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Macroscopic diffusion on rough surfaces

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We consider diffusion on rough and spatially periodic surfaces. The macroscopic diffusion tensor $\mathbf{D}$ is determined by averaging the local fluxes over the unit cell. $\mathbf{D}$ 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 formulas for $\mathbf{D}$ up to $O(\varepsilon^6)$ and derive an algorithm to compute $\mathbf{D}$ as a series in ε^2.

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I. INTRODUCTION

Diffusion on surfaces influences many dynamical processes and therefore has important applications in several fields. A first example is surface conduction, which plays a role in electrolytes; it is presently explained by the diffusion of ions within the Stern layer which is of molecular thickness [1]. Another field is related to dynamical processes involving chemisorbates on solid surfaces; it has attracted attention for a long time (Refs. [2–4] among many others) and it has seen explosive growth in the past ten years. Several reviews have been published starting with the classical one in Ref. [5] and they are recommended to the reader since they cover different aspects of the domain [6–8]. Besides the experimental studies (see Refs. [4], [9], [10] and the references therein), a number of theoretical and numerical studies was simulated in the recent years. If some of them are more theoretical in character and use as a starting point the Green-Kubo response function formalism [11], most of them are based on Monte Carlo calculations [12–17].

Most of these numerical studies deal with situations where the surface is not an atomic plane and thus contains certain defects of some sort. These defects can be geometrical such as linear steps on an otherwise plane surface [12], or of chemical nature such as quenched impurities [16]. These defects are thus local in character, in the sense that they are of atomic dimensions.

However, to the best of our knowledge, there is no study on the influence of large scale defects on surface diffusion, such as surface roughness; on real surfaces, roughness is likely to exist on all scales. It will be the major purpose of this paper to describe the local concentration fields on such surfaces and to determine the macroscopic diffusion tensor in an analytic form.

On large scales, surface diffusion on a rough surface S is governed by the following equations [18]:

$$\nabla_{\mathcal{S}}\cdot \mathbf{j}=0, \quad \mathbf{j}=-D\nabla_{\mathcal{S}}c, \tag{1}$$

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; this value may be distinct of the atomic value on a perfect surface and may take into account the various impurities and defects that any real surface contains. The macroscopic diffusion was introduced in Ref. [19], where it is called the surface capacity. A general analysis of flow and transport on surfaces is presented in Ref. [20].

This paper is organized as follows. The surface gradient operator and the Laplace equation on surfaces are detailed in Sec. II. In Sec. III, diffusion is studied on doubly periodic surfaces by an 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 2 up to $O(\varepsilon^4)$.

In Sec. IV 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, polycrystals). The main results of Sec. IV are summarized by the two properties

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

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

The proof parallels a Matheron's formula (Ref. [21], p. 122) and the well-known Dykhne-Keller manipulations for composite materials [22–24].

Section V is devoted to a determination of the effective diffusion tensor $\mathbf{D}$ of the general surface up to $O(\varepsilon^6)$. In Sec. VI, we study square representative cells. A general algorithm is derived to calculate $\mathbf{D}$ in an analytical form up to $O(\varepsilon^{2n+2})$ for a given number n. Examples of determination of $\mathbf{D}$ up to $O(\varepsilon^{22})$ are given for some surfaces. Finally, it will be shown in Sec. VII that this general approach is useful for studying surface diffusion on the atomic scale when suitable changes are made.

Technical details are gathered in Ref. [25] available at the Electronic Physics Auxiliary Service. It is divided into two parts; the first one contains the derivation of the procedure to derive the second order terms, and the second one the symbolic algorithm.

II. 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

$$z=f(x,y) \quad \text{or} \quad \mathbf{r}(x,y)=(x,y,f(x,y)) \quad (x,y)\in Q \tag{2}$$

in the space $\mathbf{R}^3$ where Q is a simply connected domain with piecewise 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 [18]

$$\nabla_{\mathcal{S}}c=(\mathbf{I}-\mathbf{n}\mathbf{n}^{\mathsf{T}})\cdot\nabla c, \tag{3}$$

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

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

One can write the gradient in the expanded form

$$\nabla_{\mathcal{S}}c=\frac{1}{\delta^2}\begin{bmatrix} 1+f_y^2 & -f_xf_y & f_x \\ -f_xf_y & 1+f_x^2 & f_y \\ f_x & f_y & f_x^2+f_y^2\end{bmatrix}\begin{bmatrix}\dfrac{\partial c}{\partial x}\\ \dfrac{\partial c}{\partial y}\\ \dfrac{\partial c}{\partial z}\end{bmatrix}. \tag{4}$$

Let us apply Eq. (4) 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 Eq. (4) becomes

$$\nabla_{\mathcal{S}}\phi=\frac{1}{\delta^2}\begin{bmatrix} 1+f_y^2 & -f_xf_y \\ -f_xf_y & 1+f_x^2 \\ f_x & f_y\end{bmatrix}\nabla_{xy}\phi, \tag{5}$$

where $\nabla_{xy}=(\partial/\partial x,\partial/\partial y)^{\mathsf{T}}$. Let us introduce the matrix

$$\mathbf{K}=\frac{1}{\delta^2}\begin{bmatrix} 1+f_y^2 & -f_xf_y \\ -f_xf_y & 1+f_x^2\end{bmatrix}. \tag{6}$$

Then, the first two components of Eq. (5) can be written as a two-dimensional vector

$$\mathbf{q}=\mathbf{K}\nabla_{xy}\phi. \tag{7}$$

$\mathbf{q}$ denotes the two components in the (x,y) plane of the opposite of the flux on the surface $\mathcal{S}$. Formula (7) will be used for calculating the effective diffusivity tensor. The Laplace operator on the surface $\mathcal{S}$ is given by the following formula [26]:

$$\Delta_{\mathcal{S}}\phi=\frac{1}{\delta}\nabla_{xy}\cdot(\delta\mathbf{K}\nabla_{xy}\phi). \tag{8}$$

Here, $\mathbf{K}$ can be considered as the contravariant metric tensor of $\mathcal{S}$. To prove this, we first consider the vector-function $\mathbf{r}(x,y)=(x,y,f(x,y))$ from Eq. (2) which determines the surface $\mathcal{S}$. Next we contract the covariant metric tensor

$$\mathbf{M}=\begin{bmatrix}\mathbf{r}_x\cdot\mathbf{r}_x & \mathbf{r}_x\cdot\mathbf{r}_y\\ \mathbf{r}_x\cdot\mathbf{r}_y & \mathbf{r}_y\cdot\mathbf{r}_y\end{bmatrix}=\begin{bmatrix}1+f_x^2 & f_xf_y\\ f_xf_y & 1+f_y^2\end{bmatrix} \tag{9}$$

and calculate the determinant δ^2. The contravariant metric tensor is constructed as the inverse matrix of Eq. (9). $\mathbf{M}^{-1}$ is equal to $\mathbf{K}$ defined by Eq. (6).

It follows from Eq. (8) that the Laplace equation can be written as follows:

$$\frac{1}{\delta}\nabla_{xy}\cdot(\delta\mathbf{K}\nabla_{xy}\phi)=0, \tag{10}$$

or, in an expanded form,

$$\left(1-\frac{f_x^2}{\delta^2}\right)\phi_{xx}+\left(1-\frac{f_y^2}{\delta^2}\right)\phi_{yy}-\frac{2f_xf_y}{\delta^2}\phi_{xy}-\frac{1}{\delta^4}\times[(1+f_y^2)f_{xx}-2f_xf_yf_{xy}+(1+f_x^2)f_{yy}]\times(f_x\phi_x+f_y\phi_y)=0. \tag{11}$$

III. 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 $\{(x,y)\in\mathbf{R}^2:|x|<\lambda_1/2,|y|<\lambda_2/2\}$ 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) on the surface $\mathcal{S}$ must verify the following periodicity conditions:

$$\begin{aligned} c(x+\lambda_1,y,z)-c(x,y,z)&=\lambda_1, \quad & \nabla_{\mathcal{S}}c(x+\lambda_1,y,z)&=\nabla_{\mathcal{S}}c(x,y,z),\\ c(x,y+\lambda_2,z)&=c(x,y,z), & \nabla_{\mathcal{S}}c(x,y+\lambda_2,z)&=\nabla_{\mathcal{S}}c(x,y,z).\end{aligned} \tag{12}$$

Conditions (12) must be fulfilled at the edges of the surface located on the planes $x=\pm\lambda_1/2$, $y=\pm\lambda_2/2$. Then Eqs. (1) and (12) are considered as a conjugation problem on $\mathcal{S}$.

It follows from Sec. II 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

$$\phi\left(\frac{\lambda_1}{2},y\right)-\phi\left(-\frac{\lambda_1}{2},y\right)=\lambda_1,\quad \frac{\partial\phi}{\partial x}\left(\frac{\lambda_1}{2},y\right)=\frac{\partial\phi}{\partial x}\left(-\frac{\lambda_1}{2},y\right),$$
$$\phi\left(x,\frac{\lambda_2}{2}\right)=\phi\left(x,-\frac{\lambda_2}{2}\right),\qquad \frac{\partial\phi}{\partial y}\left(x,\frac{\lambda_2}{2}\right)=\frac{\partial\phi}{\partial y}\left(x,-\frac{\lambda_2}{2}\right). \tag{13}$$

Problem (11) [or (13)] are standard jump problems on the torus represented by the rectangle Q with identified opposite sides for the elliptic equation (11). There are various methods to solve such problems. The most popular ones are the method of integral equations [27] and the method of finite elements [20]. 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 problems (11) and (13) 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 with the amplitude A of the oscillation of the surface. A is supposed to be of order 1; hence, the ratio A/λ_1 is characterized by the small parameter $\varepsilon = 2\pi/\lambda_1$. We also assume that λ_1 and λ_2 have the same scale, i.e., the parameter $\omega = \lambda_1/\lambda_2$ is of order $O(\varepsilon^0)$. Let us make a change of variables in the function $f(x,y)$ from Eq. (2) and equate it to $h(\xi,\eta)$, where the function $h(\xi,\eta)$ is defined for $|\xi| \leq \pi$, $|\eta| \leq \pi/\omega$, 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., $h(\xi+2\pi,\eta)=h(\xi,\eta)=h[\xi,\eta+(2\pi/\omega)]$ 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, $h_{\xi\xi}$, $h_{\xi\eta}$, and $h_{\eta\eta}$ are of smaller order than λ_1 and λ_2 since

$$f_x=\varepsilon h_\xi,\qquad f_y=\varepsilon h_\eta,$$
$$f_{xx}=\varepsilon^2 h_{\xi\xi},\quad f_{xy}=\varepsilon^2 h_{\xi\eta},\quad f_{yy}=\varepsilon^2 h_{\eta\eta}. \tag{14}$$

Theorem 2. Problem (11) [or (13)] have a unique solution up to an arbitrary additive constant. This solution is represented in the form

$$\phi(x,y)=x+\varepsilon\Phi(\xi,\eta)+O(\varepsilon^2), \tag{15}$$

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

$$\Phi_{\xi\xi}+\Phi_{\eta\eta}=h_\xi(h_{\xi\xi}+h_{\eta\eta}). \tag{16}$$

The proof of the theorem is standard and it is based on the asymptotic analysis applied to problem (11) [or (13)].

Remark 1. An explicit form of the function Φ will be given in Section VI.

Remark 2. The asymptotic analysis applied to the problems (11) and (13) can be extended to higher terms $O(\varepsilon^m)$, where $m \geq 3$. We shall do it in Sec. VI for the case $\lambda_1 = \lambda_2$.

Remark 3. The general unit cells of doubly periodic functions in the plane are parallelograms [28]. In order to solve the Poisson equation in each step of the cascade in such cells, it is possible to apply the same asymptotic expansions using Green's functions [27]. However, application of Green's functions implies too long computations. In Sec. VI, we could construct a fast solver for the Poisson equation in rectangular unit cells only. The case of parallelograms requires a separate investigation and is not considered in the present paper.

IV. DIFFUSION TENSOR. 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

$$\mathbf{D}\cdot\overline{\nabla c}=\frac{1}{\lambda_1\lambda_2}\int\int_{\mathcal{S}}\mathbf{q}\,d\sigma_{\mathcal{S}}=\frac{1}{\lambda_1\lambda_2}\int\int_Q \mathbf{q}\,\delta\,dx\,dy, \tag{17}$$

where the imposed gradient is equal to the vector $\overline{\nabla c}$. The opposite $\mathbf{q}$ of the local flux is defined by Eq. (7), 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 [29]. Note that definition (17) is consistent with the definition of the surface capacity [19].

The Laplace equation (10) 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 Eq. (17) 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

$$\boldsymbol{\Lambda}=\frac{1}{\delta}\begin{bmatrix} 1+f_y^2 & -f_x f_y \\ -f_x f_y & 1+f_x^2 \end{bmatrix}. \tag{18}$$

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

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

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

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

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

For the rest of this section, we assume that Q is a square cell. Following Matheron [21], 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 $\boldsymbol{\Lambda}^*$ corresponding to the resistivity tensor $\mathbf{R}^*$ in the principal axes becomes

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

The effective conductivity tensor $\boldsymbol{\Lambda}_e^*$ has the same form as $\boldsymbol{\Lambda}_e$, 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 $\boldsymbol{\Lambda}_e$ (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 from Sec. I):

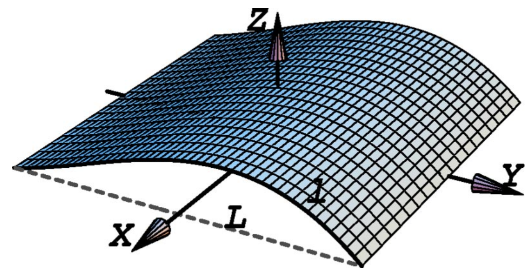

FIG. 1. Cylindrical surface.

$$\det \mathbf{D} = D_{xx} D_{yy} - D_{xy}^2 = 1. \tag{19}$$

There is a surprising consequence of Eq. (19) 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 Sec. I).

Consider an example which illustrates the physical essence of theorem 1. Let the surface be cylindrical and its generator parallel to the x axis (see Fig. 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 $\overline{\partial c/\partial x}$ is parallel to the x axis. Then, the total flux of solute is equal to $-lD(\overline{\partial c/\partial x})$. Second, the imposed gradient is along the y-axis; the corresponding flux is given by $-(D/l)(\overline{\partial c/\partial y})$.

Hence, these relations can be summarized by $D_{xx} = lD$ and $D_{yy} = D/l$; therefore we get $D_{xx} D_{yy} = D^2$. In other 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.

V. DIFFUSION TENSOR FOR A GENERAL CELL AT LOW ORDER

In Sec. IV, we obtained an exact result for diffusion on isotropic surfaces. For general surfaces represented by a square cell, formula (19) has been deduced. We now proceed to discuss general surfaces represented by a rectangular cell. In order to determine $\mathbf{D}$ from Eq. (17), 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

$$(D_{xx}, D_{xy})^{\mathsf{T}} = \frac{1}{\lambda_1 \lambda_2} \int\int_{S} \mathbf{q}\, d\sigma_S = \frac{1}{\lambda_1 \lambda_2} \int\int_{Q} \mathbf{q}\, \delta\, dx\, dy, \tag{20}$$

where the vector $\mathbf{q}$ is defined by Eq. (7). Substituting Eqs. (6) and (7) into Eq. (20), we obtain

$$D_{xx} = \frac{1}{\lambda_1 \lambda_2} \int\int_{Q} \frac{1}{\sqrt{f_x^2 + f_y^2 + 1}} \times \left((f_y^2 + 1) \frac{\partial \phi}{\partial x} - f_x f_y \frac{\partial \phi}{\partial y} \right) dx\, dy. \tag{21}$$

The component D_{xy} is calculated as follows:

$$D_{xy}=\frac{1}{\lambda_1\lambda_2}\int\int_Q\frac{1}{\sqrt{f_x^2+f_y^2+1}}\times\left(-f_xf_y\frac{\partial\phi}{\partial x}+(f_x^2+1)\frac{\partial\phi}{\partial y}\right)dx\,dy. \tag{22}$$

The function $\phi(x,y)$ from Eqs. (21) and (22) is solution of the problems (11) and (13).

Let us apply the formulas (21) and (22) to the first order approximation. Substitution of Eq. (15) into Eqs. (21) and (22) yields

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

We apply the Green formula

$$\int\int_G(\Phi)_\xi d\xi d\omega=\int_{\partial G}\Phi d\omega, \tag{23}$$

and use the periodicity of Φ to obtain

$$D_{xx}=1-\varepsilon^2\frac{\omega}{8\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}(h_\xi^2-h_\eta^2)d\xi d\eta+O(\varepsilon^4). \tag{24}$$

Similar arguments yield the formulas

$$D_{xy}=\varepsilon^2\frac{\omega}{\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}h_\xi h_\eta d\xi d\eta+O(\varepsilon^4), \tag{25}$$

$$D_{yy}=1+\varepsilon^2\frac{\omega}{8\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}(h_\xi^2-h_\eta^2)d\xi d\eta+O(\varepsilon^4). \tag{26}$$

In terms of f, Eqs. (24)–(26) take the form

$$\mathbf{D}=\begin{bmatrix}1-\frac{1}{2\lambda_1\lambda_2}\int\int_Q(f_x^2-f_y^2)dx\,dy & -\frac{1}{\lambda_1\lambda_2}\int\int_Q f_xf_ydx\,dy\\ -\frac{1}{\lambda_1\lambda_2}\int\int_Q f_xf_ydx\,dy & 1+\frac{1}{2\lambda_1\lambda_2}\int\int_Q(f_x^2-f_y^2)dx\,dy\end{bmatrix}+O(\lambda_1^{-m}\lambda_2^{-n}), \tag{27}$$

where $m+n=4$.

Formulas (24)–(27) have the following interpretation in the space $\mathcal{L}_2$ endowed by the scalar product and the norm:

$$\langle F,G\rangle=\frac{\omega}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}F(\xi,\eta)G(\xi,\eta)d\xi d\eta,$$
$$\|F\|^2=\langle F,F\rangle. \tag{28}$$

For instance, Eqs. (24)–(26) can be written as

$$\mathbf{D}=\mathbf{I}-\varepsilon^2\begin{bmatrix}-\frac{1}{2}(\|h_\xi\|^2-\|h_\eta\|^2) & \langle h_\xi,h_\eta\rangle\\ \langle h_\xi,h_\eta\rangle & \frac{1}{2}(\|h_\xi\|^2-\|h_\eta\|^2)\end{bmatrix}+O(\varepsilon^4). \tag{29}$$

Formula (29) 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 2. For the definiteness, consider the component D_{xx}. Equation (15) can be further expanded as

$$\phi(x,y)=x+\varepsilon\Phi(\xi,\eta)+\varepsilon^2\phi_2(\xi,\eta)+\varepsilon^3\phi_3(\xi,\eta)+O(\varepsilon^4), \tag{30}$$

where ϕ_2 and ϕ_3 are unknown functions. Substitution of Eq. (30) into Eq. (21) yields

$$D_{xx}=\frac{\omega}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}\Bigg[1-\varepsilon^2\left(\frac{1}{2}(h_\xi^2-h_\eta^2)-\Phi_\xi\right)+\varepsilon^3(\phi_2)_\xi+\varepsilon^4\left((\phi_3)_\xi-\frac{1}{2}(h_\xi^2-h_\eta^2)\right)\Phi_\xi-h_\xi h_\eta\Phi_\eta+\frac{1}{2}(h_\xi^2+h_\eta^2)\times\left(\frac{3}{4}-h_\eta^2\right)\Bigg]d\xi d\eta+O(\varepsilon^5). \tag{31}$$

First, we note that application of the Green formula (23) cancels the unknown functions ϕ_2 and ϕ_3. Hence Eq. (31) becomes

$$D_{xx}=\frac{\omega}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi/\omega}^{\pi/\omega}\left(1-\frac{\varepsilon^2}{2}(h_\xi^2-h_\eta^2)+\varepsilon^4\left(-\frac{1}{2}(h_\xi^2-h_\eta^2)\times\Phi_\xi-h_\xi h_\eta\Phi_\eta+\frac{1}{8}(3h_\xi^4+2h_\xi^2h_\eta^2-h_\eta^4)\right)\right)d\xi d\eta+O(\varepsilon^6). \tag{32}$$

Here, $O(\varepsilon^5)$ was changed into $O(\varepsilon^6)$, because it can be shown that $\mathbf{D}$ is an even function of ε. Formula (32) can be written as follows:

$$D_{xx}=1+\frac{\varepsilon^2}{2}(\|h_\xi\|^2-\|h_\eta\|^2)+\varepsilon^4\Bigg[\frac{1}{8}(3\|h_\xi^2\|^2+2\langle h_\xi^2,h_\eta^2\rangle-\|h_\eta^2\|^2)-\frac{1}{2}\langle h_\xi^2-h_\eta^2,\Phi_\xi\rangle-\langle h_\xi h_\eta,\Phi_\eta\rangle\Bigg]+O(\varepsilon^6). \tag{33}$$

Recall that $|\nabla h|^2=h_\xi^2+h_\eta^2$. Equation (33) shows that calculation of D_{xx} up to $O(\varepsilon^6)$ requires only the knowledge of function $\Phi(\xi,\eta)$ from Theorem 2. The same is true for the tensor $\mathbf{D}$.

Let us consider an elementary example of the surface:

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

Then,

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

where ω is recalled to be equal to λ_1/λ_2. The Poisson equation (16) becomes

$$\Phi_{\xi\xi}+\Phi_{\eta\eta}=-(1+\omega^2)\cos\xi\sin\xi\sin^2\omega\eta. \tag{34}$$

It is easily seen that the function

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

is doubly periodic and satisfies Eq. (34). D_{xx} is deduced from Eq. (33) 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

$$D_{xy}=0,$$

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

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

Remark 4. 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.

VI. DIFFUSION TENSOR FOR SQUARE CELLS AT HIGHER ORDERS

A. 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 formulas for the tensor $\mathbf{D}$ of higher order in $\varepsilon=2\pi/\lambda$. According to the general scheme given in Sec. III, we solve the surface Laplace equation on the surface with the following boundary conditions:

$$\phi\left(\frac{\lambda}{2},y\right)-\phi\left(-\frac{\lambda}{2},y\right)=\lambda,\quad \frac{\partial\phi}{\partial x}\left(\frac{\lambda}{2},y\right)=\frac{\partial\phi}{\partial x}\left(-\frac{\lambda}{2},y\right),$$
$$\phi\left(x,\frac{\lambda}{2}\right)=\phi\left(x,-\frac{\lambda}{2}\right),\qquad \frac{\partial\phi}{\partial y}\left(x,\frac{\lambda}{2}\right)=\frac{\partial\phi}{\partial y}\left(x,-\frac{\lambda}{2}\right), \tag{35}$$

by using the fast variables $\xi=\varepsilon x$, $\eta=\varepsilon y$, where $\varepsilon=2\pi/\lambda$. Hence, ω is equal to 1. 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 2 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,

$$\phi(x,y)=\sum_{k=-1}^{\infty}\varepsilon^k\phi_k(\xi,\eta), \tag{36}$$

where $\phi_{-1}(\xi,\eta)=\xi$, $\phi_0(\xi,\eta)=0$; the unknown functions ϕ_k $(k=1,2,...)$ 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 Eq. (10) as an expansion in ε in terms of the fast variables. First, we introduce the matrices

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

In order to calculate Eqs. (20) and (22), we rewrite the vector $\mathbf{q}$ in terms of the fast variables

$$\mathbf{q}=\delta\mathbf{K}\nabla_{xy}\phi=\frac{1}{\delta}(\mathbf{I}+\varepsilon^2\mathbf{P})\nabla_{xy}\phi. \tag{37}$$

Here, in agreement with Eq. (36),

$$\nabla_{xy}\phi=\sum_{k=0}^{\infty}\varepsilon^k\nabla\phi_{k-1}, \tag{38}$$

since $\nabla_{xy}=\varepsilon\nabla$, where $\nabla=(\partial/\partial\xi,\partial/\partial\eta)^{\mathsf T}$ is the gradient in the fast variables. Using Eqs. (37) and (38), we obtain

$$\mathbf{q}=\frac{1}{\delta}(\mathbf{I}+\varepsilon^2\mathbf{P})(\varepsilon\nabla\phi)=\nabla\phi_{-1}+\sum_{n=1}^{\infty}\varepsilon^{2n}\Bigg(\nabla\phi_{2n-1}+\sum_{m=1}^{n}A_mH^{m-1}((2m-1)H\mathbf{I}-2m\mathbf{P})\nabla\phi_{2n-2m-1}\Bigg)+\sum_{n=1}^{\infty}\varepsilon^{2n+1}\Bigg(\nabla\phi_{2n}+\sum_{m=1}^{n}A_mH^{m-1}\times((2m-1)H\mathbf{I}-2m\mathbf{P})\nabla\phi_{2n-2m}\Bigg), \tag{39}$$

where

$$A_m=\frac{(-1)^m(2m-3)!!}{(2m)!!} \quad \text{and} \quad H:=|\nabla h|^2=h_\xi^2+h_\eta^2. \tag{40}$$

We put $n!!=1$ for all $n\leqslant 0$. Applying the operator $\boldsymbol{\nabla}_{xy}$ to (39), we obtain the Laplace operator on $\mathcal{S}$ as a series in the powers of ε,

$$\begin{aligned}\delta\Delta_{\mathcal{S}}\phi&=\boldsymbol{\nabla}_{xy}\cdot(\delta\mathbf{K}\boldsymbol{\nabla}_{xy}\phi)\\&=\varepsilon^2\boldsymbol{\nabla}\cdot\left(\frac{1}{\delta}(\mathbf{I}+\varepsilon P)\boldsymbol{\nabla}\phi\right)\\&=\sum_{n=1}^{\infty}\varepsilon^{2n+1}\left(\Delta\phi_{2n-1}+\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m-1})\right)\\&\quad+\sum_{n=1}^{\infty}\varepsilon^{2n+2}\left(\Delta\phi_{2n}+\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m})\right),\end{aligned} \tag{41}$$

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

$$\begin{aligned}\mathcal{L}_m(\phi)&=(2m-1)H^m\Delta\phi+mH^{m-1}\\&\quad\times[(2m-1)\boldsymbol{\nabla}H\cdot\boldsymbol{\nabla}\phi-2\boldsymbol{\nabla}\cdot(\mathbf{P}\boldsymbol{\nabla}\phi)]\\&\quad-2m(m-1)H^{m-2}\boldsymbol{\nabla}H\cdot(\mathbf{P}\boldsymbol{\nabla}\phi),\end{aligned} \tag{42}$$

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

$$\Delta\phi_{2n-1}=-\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m-1}), \tag{43}$$

$$\Delta\phi_{2n}=-\sum_{m=1}^{n}A_m\mathcal{L}_m(\phi_{2n-2m}), \tag{44}$$

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

One can see that Eq. (44) becomes

$$\Delta\phi_{2n}=0,\quad n=1,2,\ldots, \tag{45}$$

since the initial term ϕ_0 is equal to zero. It follows from Liouville's theorem for the class of doubly periodic functions [28] that $\phi_{2n}=\text{constant}$ for $n=1,2,\ldots$.

Let us write the first two equations of Eq. (43):

$$\Delta\phi_1=h_\xi(h_{\xi\xi}+h_{\eta\eta}),$$

$$\begin{aligned}\Delta\phi_3&=\frac{1}{2}(h_\xi^2-h_\eta^2)[(\phi_1)_{\xi\xi}-(\phi_1)_{\eta\eta}]+2h_\xi h_\eta(\phi_1)_{\xi\eta}+(h_{\xi\xi}\\&\quad+h_{\eta\eta})[h_\xi(\phi_1)_\xi+h_\eta(\phi_1)_\eta]-\frac{1}{2}h_\xi[h_\xi^2(3h_{\xi\xi}+h_{\eta\eta})\\&\quad+h_\eta^2(h_{\xi\xi}+3h_{\eta\eta})+4h_\xi h_\eta h_{\xi\eta}].\end{aligned} \tag{46}$$

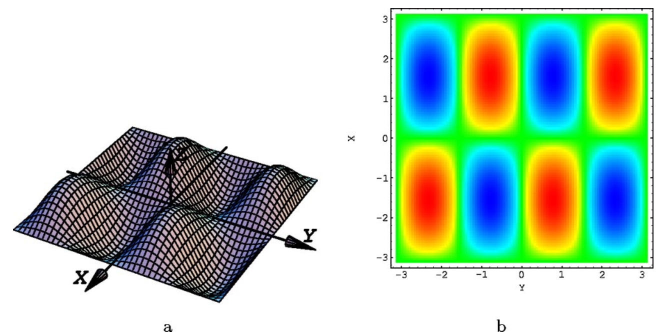

FIG. 2. Example 1. The surface $\mathcal{S}$ defined by Eq. (53).

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 $\boldsymbol{\nabla}\phi_1$ and so on. Therefore, the cascade (43) 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 formulas the flux, i.e., the derivatives of $\phi_k(\xi,\eta)$, it is useless to determine this arbitrary constant at each step of cascade (43).

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

$$(D_{xx},D_{xy})^{\mathsf{T}}=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\delta\mathbf{q}\,d\xi\,d\eta, \tag{47}$$

where $\mathbf{q}$ has the form of Eq. (39). Hence, Eq. (47) becomes

$$\begin{aligned}(D_{xx},D_{xy})^{\mathsf{T}}&=(1,0)^{\mathsf{T}}+\sum_{n=1}^{\infty}\varepsilon^{2n}\\&\quad\times\sum_{m=1}^{n}A_m[(2m-1)\mathbf{b}_{n,m}-2m\mathbf{c}_{n,m}],\end{aligned} \tag{48}$$

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

$$\mathbf{b}_{n,m}=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}H^m\boldsymbol{\nabla}\phi_{2n-2m-1}d\xi\,d\eta,$$

$$\mathbf{c}_{n,m}=\frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}H^{m-1}\mathbf{P}\boldsymbol{\nabla}\phi_{2n-2m-1}d\xi\,d\eta, \tag{49}$$

and A_m and H are given by Eq. (40).

Let us represent the function h as a Fourier series:

$$h(\xi,\eta)=\sum_{s,t}[a_{st}\cos(s\xi+t\eta)+b_{st}\sin(s\xi+t\eta)]. \tag{50}$$

We can assume in representation (50) that s varies from 0 to $+\infty$, and that t varies from $-\infty$ to $+\infty$, because

$$\begin{aligned}&a_{s,t}\cos(s\xi+t\eta)+b_{s,t}\sin(s\xi+t\eta)\\&\quad=a_{s,t}\cos(-s\xi-t\eta)-b_{s,t}\sin(-s\xi-t\eta).\end{aligned}$$

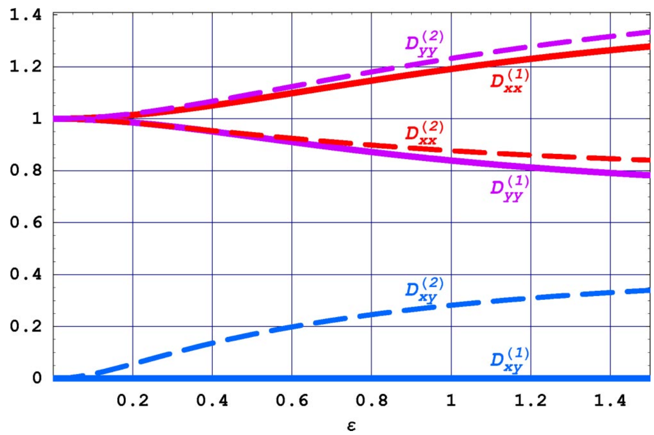

FIG. 3. Dependence of the tensor **D** components on ε for the surfaces defined by Eq. (53) (solid lines) and by Eq. (55) (broken lines).

We can also take $b_{0,t}=0$ for $t\leqslant 0$, 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 (50), we have to solve in each step of cascade (46) a Poisson equation with a right hand side of the general form

$$\gamma(\xi,\eta)=\alpha\cos(s\xi+t\eta)+\beta\sin(s\xi+t\eta), \tag{51}$$

where α and β are constants. Terms (51) appear because of the following operations at each step of cascade (43): (i) all partial derivatives of Eq. (51) have the form (51), (ii) the result of the multiplication of terms (51) 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

$$\phi(\xi,\eta)=-\frac{\gamma(\xi,\eta)}{s^2+t^2}. \tag{52}$$

Hence, this solution is of the same form as Eq. (51).

It is necessary to note that at each step of cascade (43), the constant term with $s=t=0$ never appears because the right hand side of Eq. (43) is a sum of derivatives of trigonometric functions. Hence, the denominator of Eq. (52) is never zero.

In order to calculate the integrals in Eq. (47), we represent the integrands as Fourier series. Then, $1/4\pi^2\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}p(\xi,\eta)d\xi d\eta$ 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.

Basically, the same methodology can be applied to the derivation of the second order terms starting from Eq. (47). This is detailed in Appendix A of Ref. [25].

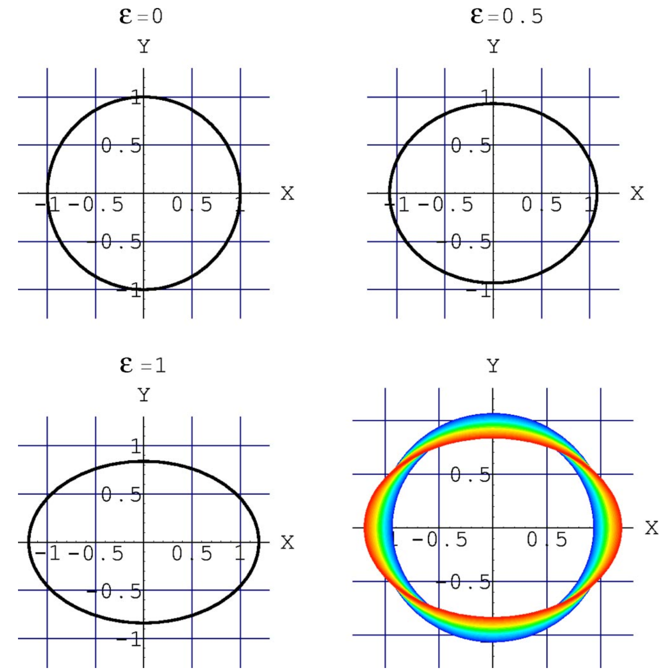

FIG. 4. Example 1. Dependence of the tensor **D** on ε for the surface defined by Eq. (53): $\varepsilon=0$, 0.5, and 1 in the first three pictures and for all ε $(0\leqslant\varepsilon\leqslant 1)$ in the last picture.

B. Numerical examples

The general algorithm is given in Appendix B of Ref. [25].

1. Example 1

Let us consider an example where the surface $\mathcal{S}$ is given by the function (see Fig. 2)

$$h(\xi,\eta)=\sin\xi\sin 2\eta=\frac{1}{2}[\cos(\xi-2\eta)-\cos(\xi+2\eta)]. \tag{53}$$

Then, application of the algorithm yields the following formulas for **D**

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

$$D_{xy}=0,\quad D_{yy}=D_{xx}^{-1}. \tag{54}$$

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 Sec. VI A. The last two equalities from (54) are obtained by straightforward computations up to $O(\varepsilon^{22})$ and they numerically confirm theorem 1. The components of the tensor **D** (54) for $0 \leqslant \varepsilon \leqslant 1$ are presented as function on ε in Fig. 3. The tensor ellipse of **D** [30] is presented in Fig. 4.

2. Example 2

Consider another example when the surface $\mathcal{S}$ is given by the function (see Fig. 5)

$$h(\xi,\eta)=\cos(3\xi-\eta)-\frac{3}{4}\cos(\xi-3\eta)+\frac{1}{2}\cos(\xi+3\eta)-\frac{1}{4}\cos(3\xi+\eta). \tag{55}$$

In this case, we obtain

$$D_{xx}=\frac{1+65.0538\varepsilon^2+1442.10\varepsilon^4+12868.4\varepsilon^6+40773.5\varepsilon^8+25197.8\varepsilon^{10}}{1+65.5538\varepsilon^2+1471.43\varepsilon^4+13418.5\varepsilon^6+44493.4\varepsilon^8+32159.0\varepsilon^{10}}, \tag{56}$$

$$D_{xy}=\frac{1.875\varepsilon^2+104.697\varepsilon^4+1881.82\varepsilon^6+11724.5\varepsilon_8+15838.8\varepsilon^{10}}{1+65.5259\varepsilon^2+1509.92\varepsilon^4+14484.6\varepsilon^6+51634.2\varepsilon^8+37182.9\varepsilon^{10}}, \tag{57}$$

$$D_{yy}=\frac{1+75.2283\varepsilon^2+1968.17\varepsilon^4+20570.5\varepsilon^6+70022.0\varepsilon^8+46386.5\varepsilon^{10}}{1+74.7283\varepsilon^2+1930.49\varepsilon^4+19610.8\varepsilon^6+61118.0\varepsilon^8+30072.0\varepsilon^{10}}. \tag{58}$$

We apply here the Padé approximation (10, 10). The components of the tensor **D** [Eq. (56)] are presented in Fig. 3. The tensor ellipse of **D** is presented in Fig. 6.

VII. APPLICATIONS TO PLANE SURFACES WITH VARIABLE DIFFUSION COEFFICIENTS

In this section we shall provide two examples of variable diffusion coefficients on the atomic scale as often investigated in the references cited in Sec. I. In the first case, the previous formalism can be readily applied while in the second case, the whole methodology could be applied again, but some portions of the symbolic algorithm should be modified.

First, suppose that the local diffusion is a spatially periodic tensor $\mathbf{D}_l$ which is of the form

$$\mathbf{D}_l=\delta\mathbf{K}, \tag{59}$$

where **K** is given by Eq. (6).

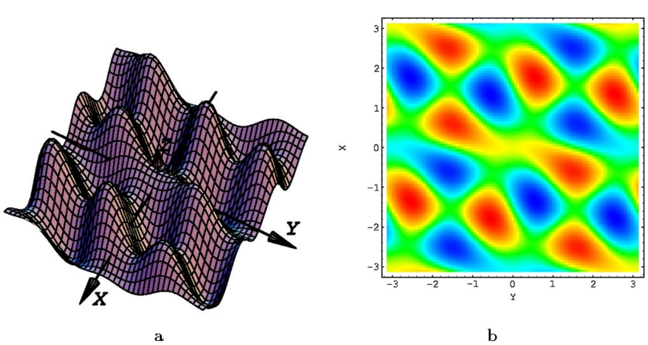

FIG. 5. Example 2. The surface $\mathcal{S}$ defined by Eq. (55).

Then, it is obvious that the previous methodology applies. The following example would correspond to the simplest possible anisotropic case and would be induced by an imaginary surface of the form

$$z=z_o+\epsilon\sin x. \tag{60}$$

The resulting local diffusion tensor would be

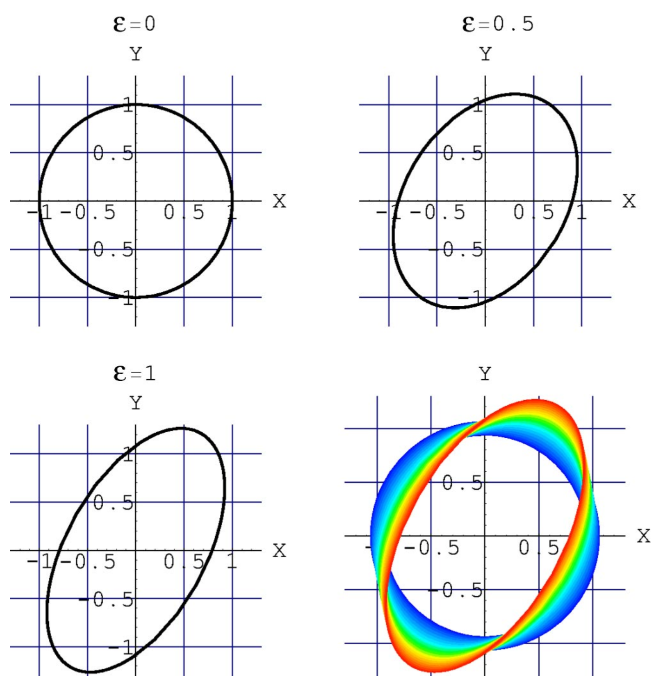

FIG. 6. Example 2. Dependence of the tensor **D** on ε for the surface defined by Eq. (55).

$$\mathbf{D}_l = \frac{1}{(1+\epsilon^2\cos^2 x)^{1/2}}\begin{bmatrix} 1 & 0 \\ 0 & 1+\epsilon^2\cos^2 x \end{bmatrix}. \tag{61}$$

Then, the whole machinery developed in the previous sections would apply.

Conversely, if $\mathbf{D}_l$ is a known spatially periodic tensor, it is possible in some cases to derive a function $f(x,y)$ such that it verifies Eq. (59).

When this is not the case, one has to solve directly the equation

$$\nabla_{xy}\cdot(\mathbf{D}_l\cdot\nabla_{xy}c)=0. \tag{62}$$

The same method can be easily applied to Eq. (62), since we do not use constraints on **K** in the algorithm described in Sec. IV. For instance, suppose that we have a local diffusion coefficient equal to

$$D_l = D_o(1+\epsilon\sin x\sin y) \tag{63}$$

Then, the macroscopic diffusion can be expressed as

$$D = D_o\left(1-\frac{\epsilon^2}{8}-\frac{\epsilon^4}{64}-\frac{\epsilon^6}{5120}\right)+O(\varepsilon^8). \tag{64}$$

VIII. CONCLUSION

The main purpose of this paper was to obtain analytical formulas for the macroscopic diffusion tensor of surfaces. We derived a boundary value problem for the Laplace operator (11). We applied an asymptotic analysis to study the boundary problem and deduced approximate analytical formulas. We proved theorem 2, where the local field is determined up to $O(\varepsilon^2)$ in terms of the function $\Phi(\xi,\eta)$ satisfying a Poisson equation. The results of the calculation of the local field were applied to the determination of the macroscopic diffusion tensor **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 formulas for **D** were deduced. The tensor **D** was computed up to $O(\varepsilon^{22})$ for two particular surfaces. Technical details are supplied in Ref. [25].

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