Homogenization of boundary conditions for surfaces with regular arrays of traps

Alexander M. Berezhkovskii[a)]
Center for Information Technology, National Institutes of Health, 10401 Fernwood Road, Bethesda, Maryland 20817

Michael I. Monine
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540; Lewis-Sigler Institute for Integrative Genomics, Carl Icahn Laboratory, Princeton University, Princeton, New Jersey 08544; Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695

Cyrill B. Muratov
Department of Mathematical Sciences, New Jersey Institute of Technology, University Heights, Newark, New Jersey 07102-1982

Stanislav Y. Shvartsman[b)]
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540 and Lewis-Sigler Institute for Integrative Genomics, Carl Icahn Laboratory, Princeton University, Princeton, New Jersey 08544

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The problem of trapping of diffusing particles by nonoverlapping absorbing patches randomly or regularly located on a surface arises in numerous settings. Examples include diffusion current to ensembles of microelectrodes, ligand binding to cells, mass transfer to heterogeneous surfaces, ligand accumulation in cell culture assays, etc. (see Refs. 1–15 and references therein). The problem is extremely complicated because the boundary conditions on the surface are nonuniform: absorbing on the patches and reflecting otherwise. There is, however, an approximation that greatly simplifies the analysis when the layer of medium above the surface is sufficiently thick. The approximation is based on the fact that, far from the surface, fluxes and concentrations become uniform in the lateral direction and, therefore, indistinguishable from those in the case of uniformly absorbing surface. Keeping this in mind, one can replace the nonuniform boundary conditions on the surface by a uniform radiation-type boundary condition with a properly chosen trapping rate κ (see e.g., Ref. 16 and references therein). We have demonstrated how this procedure works in the case of randomly distributed traps in Refs. 17 and 18. Here we consider the problem with traps regularly distributed over the surface.

Our aim is to predict the dependence of κ on the trap concentration and parameters of the traps and diffusing particles over the entire concentration range. At low concentrations κ is equal to the product of the concentration and the trapping rate constant of an isolated trap.[4] It turns out that the low-concentration linear dependence of κ on the trap concentration fails very early, and κ grows with the concentration much faster even when only a small fraction of the surface is covered by the traps.[17] This happens because "interaction" between traps decays very slowly, as $1/L$, where L is the intertrap distance.[19] As a consequence, collective effects due to this interaction, which lead to the enhancement of the trapping rate, manifest themselves already at low concentrations. In Ref. 17 we reported a boundary homogenization approach for surfaces randomly covered by nonoverlapping circular traps. To describe the enhancement of the trapping rate compared to the linear regime, we introduced the function $F(\sigma)$ of the trap surface fraction σ and suggested an approximate formula for this function. In Ref. 18 we found that the enhancement due to the collective effects was insensitive to whether the traps were identical or polydisperse and their radii are allowed to fluctuate. This suggests that the enhancement depends only on σ and is weakly sensitive to the details of the trap arrangement on the surface. To check this hypothesis here we study homogenization of boundaries with regular arrangements of identical traps. Our results support this hypothesis. We find that the values of κ for the three different arrangements and for random distribution of traps are close to each other (the difference is within 20%).

In addition, here we study homogenization of periodic nonuniform boundaries formed by alternating absorbing and reflecting stripes. Such boundaries are special because the conventional ideology (based on the existence of a trivial limiting behavior of κ when $\sigma \to 0$) fails in this case since a stationary flux to an isolated absorbing strip does not exist.[20] Nevertheless, we are able to overcome this difficulty and find the effective trapping rate for such a boundary. In our analysis we use the computer-assisted boundary homogenization approach suggested in Ref. 17: First, based on the limiting behavior and dimensional arguments we express κ in terms of an unknown dimensionless function of the dimensionless trap surface fraction $\sigma, F(\sigma)$. We then determine this function using the dependence $\kappa(\sigma)$, which is found by Brownian dynamics simulations as described in Ref. 17 or by solving numerically the corresponding diffusion equation with non-uniform boundary conditions on the patchy surface.

We begin with triangular (tr), square (sq), and hexagonal (hex) lattices of perfectly absorbing circular disks of radius a. When the surface concentration of the disks, n, is low enough, the traps act independently of each other, and the flux to a single trap is given by the Hill formula[20] for the flux to an isolated disk on a reflecting wall, $4Dac$, where D is the particle diffusion constant and c is the particle concentration at infinity. In this regime, the steady-state flux per unit surface area is given by $J=4Danc$. This flux can be written in terms of the effective trapping rate κ as $J=\kappa c$, which leads to the following expression for κ:

$$\kappa = 4Dan = \frac{4D}{\pi a}\sigma, \quad \sigma \to 0, \tag{1}$$

where $\sigma=\pi a^2 n$ is the fraction of the surface area occupied by traps. This is equivalent to the boundary homogenization suggested by Shoup and Szabo[4] in their intuitively appealing derivation of the Berg-Purcell result for the stationary flux of diffusing particles to a sphere randomly covered by small absorbing disks.[3] We can generalize Eq. (1) to the case of arbitrary σ by writing κ in the form

$$\kappa(\sigma) = \frac{4D}{\pi a}F(\sigma). \tag{2}$$

While the function $F(\sigma)$ depends on the lattice type, its limiting behavior at small σ is universal: $F(\sigma)=\sigma$, when $\sigma \ll 1$.

We determine approximate formulas for $F(\sigma)$ that covers the entire range of $\sigma<\sigma_{\max}$, where $\sigma_{\max}=\pi/(2\sqrt{3})$, $\pi/4$, and $\pi/(3\sqrt{3})$ for the triangle, square, and hexagonal lattices, respectively, by fitting the dependences $\kappa(\sigma)$ obtained numerically. We find that

$$F(\sigma) = \frac{\sigma(1 + A\sqrt{\sigma} - B\sigma^2)}{(1-\sigma)^2} \tag{3}$$

when substituted into Eq. (2) with $A=1.62$, 1.75, 1.37 and $B=1.36$, 2.02, 2.59 for the triangle, square, and hexagonal lattices fits the numerical data for the three lattices with relative errors less than 7%, 9%, and 3%, respectively. The form of $F(\sigma)$ in Eq. (3) is chosen so as to predict the asymptotic behavior of this function in the two limiting cases: $\sigma\to 0$ and $\sigma\to 1$, in agreement with numerical results. In a careful numerical study we found that $F(s)/s-1 \sim s^{1/2}$ for $s\ll 1$ and $F(s)\sim 1/(1-s)^2$ for $1-s\ll 1$, in all three cases. The exponent 2 in the last term of the numerator is also chosen to minimize the relative error of $F(s)$ given by Eq. (3) for the entire range of s, as compared with numerical results. We note that these fitting functions are robust in the sense that the accuracy of our approximations is not very sensitive to the choice of coefficients A and B. We also point out that the data for randomly arranged traps[17] can be fitted by Eq. (3) with $A=0.34$ and $B=-0.58$ with the relative error less than 5%. Importantly, the values for κ for all of these lattices are quite close to each other (the difference is within 20%), indicating that the homogenized boundary condition is not too sensitive to the microstructure of the surface.

Next we compare the dependence $F_{\mathrm{tr}}(\sigma)$ with an approximate expression that can be derived using the results obtained by Keller and Stein (KS) in Ref. 1. The theory developed by Keller and Stein is based on two approximations: (i) approximation of the hexagonal cylinder associated with each disk by a circular cylinder and (ii) the constant flux assumption which neglects variation of the steady-state flux through the disk with the distance from the disk center. Denoting the function $F_{\mathrm{tr}}(\sigma)$ obtained from the KS solution by $F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)$ one can obtain

$$F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma) = \frac{\pi(\sigma/\sigma_{\max}^{\mathrm{tr}})^{3/2}}{16\sum_{n=1}^{\infty} J_1^2(j_{1,n}\sqrt{\sigma/\sigma_{\max}^{\mathrm{tr}}})/j_{1,n}^3 J_0^2(j_{1,n})}, \tag{4}$$

where $\sigma_{\max}^{\mathrm{tr}}=\pi/(2\sqrt{3})$ and $j_{1,n}$ are zeros of the Bessel function $J_1(z)$, i.e., positive roots of the equation $J_1(j_{1,n})=0$.[21] The functions $F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)$ and $F_{\mathrm{tr}}(\sigma)$ are very close at $\sigma<0.5$: as $\sigma\to 0$ $F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)\to(3\sqrt{3}\pi/16)\sigma\approx 1.02\sigma$, while exact asymptotic behavior predicted by Eq. (3) is $F_{\mathrm{tr}}(\sigma)=\sigma$. The difference between the two functions becomes pronounced for $\sigma>0.5$. When σ approaches its maximum value, $\sigma_{\max}^{\mathrm{tr}}$, the function $F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)$ diverges as $1/(\sigma_{\max}^{\mathrm{tr}}-\sigma)^2$, whereas $F_{\mathrm{tr}}(\sigma)$ given by Eq. (3) remains finite.

Substituting $F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)$ with $\sigma_{\max}^{\mathrm{tr}}=1$ into Eq. (2) one obtains an estimate for the uniform trapping rate of homogenized boundary at the bottom of a long cylinder containing an absorbing disk of radius a at the center of its bottom. This estimate was compared with the trapping rate obtained numerically. We found that the latter is higher than the rate predicted using $F_{\mathrm{cyl}}^{\mathrm{KS}}(\sigma)=F_{\mathrm{tr}}^{\mathrm{KS}}(\sigma)|_{\sigma_{\max}^{\mathrm{tr}}=1}$. Numerical results are well described by the function $F_{\mathrm{cyl}}(\sigma)$,

$$F_{\mathrm{cyl}}(\sigma) = \frac{\sigma(1 + 1.37\sqrt{\sigma} - 0.37\sigma^2)}{(1-\sigma)^2}, \tag{5}$$

which has the same form as $F_{(\sigma)}$ in Eq. (3). The relative error of the predicted rate was less than 1% over the range of $\sigma<0.9$.

Boundary homogenization of planar surfaces covered by periodic arrays of parallel stripes, which are ideal traps for diffusing particles, has a specific feature. The point is that the limiting behavior of κ at small σ [similar to that in Eq. (1) for disk-shaped traps] is singular.[16] The reason is that the flux to an isolated strip located on an otherwise reflecting plane does not have a stationary solution[22] analogous to Hill's solution for disk-shaped traps. In this case we use dimensional arguments (κ has dimensions of velocity) to write $\kappa(\sigma)$ in the form similar to that in Eq. (2),

$$\kappa(\sigma) = \frac{D}{l}F_{\mathrm{str}}(\sigma), \tag{6}$$

where l is the width of a single absorbing strip. One can derive an approximate solution for $F_{\mathrm{str}}(\sigma)$ using the constant flux approximation (cfa), which neglects variation of the flux across the strip. The result is

$$F_{str}^{cfa}(\sigma) = \frac{\pi^3\sigma^3}{\sum_{n=1}^{\infty} (1/n^3)[\sin(\pi n\sigma)]^2}. \quad (7)$$

As $\sigma \to 0$ the function $F_{str}^{cfa}(\sigma)$ approaches zero as $\pi\sigma/\ln(1/\sigma)$, in agreement with the exact asymptotic behavior.[16] The function $F_{str}^{cfa}(\sigma)$ diverges as $\sigma \to 1$. Its asymptotic behavior in this limiting case is given by $\pi/\{(1-\sigma)^2 \ln[1/(1-\sigma)]\}$. This asymptotic behavior agrees up to a logarithmic factor with the exact asymptotic behavior given by $F_{str}(\sigma) \propto 1/(1-\sigma)^2$.[23] Once again, keeping the two exact asymptotic behaviors in mind, we can write an expression for $F_{str}(\sigma)$, which approximates the values of $F_{str}(\sigma)$ found numerically, in the form

$$F_{str}(\sigma) = \frac{\pi\sigma}{(1-\sigma)^2 \ln(2.6 + 0.7/\sigma)}. \quad (8)$$

Substituting this function into Eq. (6) one can predict $\kappa(\sigma)$ over the entire range of σ with the relative error less than 5%. We note that the function $\kappa(\sigma)$ in Eq. (6), with $F_{str}(\sigma)$ given by Eq. (8), also provides an effective trapping rate for a nonuniform boundary in the two-dimensional problem of diffusion in a semi-infinite plane. Here the boundary constraining the plane is a straight line formed by alternating identical absorbing and reflecting intervals of lengths l and $(\sigma^{-1}-1)l$, respectively, where σ is the fraction of the boundary covered by absorbing intervals. The nonanalytic behavior of $F(\sigma)$ near $\sigma = 0$ is due to the fact that two traps on the plane "feel" each other even when they are separated by extremely large distances.

In summary, the main results of this note are given in Eqs. (2), (3), and (6)–(8). These expressions show how the trapping rate κ that enters into the homogenized boundary condition depends on the surface fraction σ occupied by traps. Equations (2) and (6) also show that the boundary becomes perfectly absorbing at any fixed value of σ when the characteristic size of the traps, a or l, tends to zero. One can generalize our expressions for κ to the case of partially absorbing traps and/or noncircular traps using the relations from Refs. 8, 17, and 18.

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[a]Permanent address: Karpov Institute of Physical Chemistry, Moscow, Russia.
[b]Author to whom correspondence should be addressed. FAX: 609-258-0211. Electronic mail: stas@princeton.edu

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