Rates of Diffusion-Limited Reaction in Periodic Systems

David C. Torney[1] and Byron Goldstein[1]

The pseudopotential and perturbation theory are used to derive the first three terms in the expansion of the smallest eigenvalue of the Helmholtz equation both for infinite two-dimensional systems with an array of perfectly absorbing circles centered on (1) a square lattice and (2) a triangular lattice, and also for infinite three-dimensional systems both with arrays of perfectly absorbing interspersed cylinders and with an array of perfectly absorbing spheres centered on (1), a simple cubic lattice, (2) a body-centered cubic lattice, and (3) a face-centered cubic lattice. In all cases, the perturbation parameter involves the ratio of the radius of the absorber to the lattice spacing. These eigenvalues and the corresponding eigenfunctions are used to compute the first three terms of expansions of the first passage time of a diffusing point particle randomly placed outside the absorbers. Expressing the perturbation parameter as a function of the area or volume fraction occupied by the absorbers reveals a remarkable similarity among the rates of diffusion-limited reaction for arrays of absorbers and the corresponding radially symmetric system containing one central absorber.

KEY WORDS: Pseudopotential; perturbation theory; boundary-value problem; nonseparable; Helmholtz equation; Lambert series; first passage time; circles; cylinders; spheres; two dimensions; square lattice; triangular lattice; three dimensions; simple cubic; body-centered cubic; face-centered cubic; Sinai's billiard.

1. INTRODUCTION

Given the complete set of eigenfunctions $\Psi_m^{(0)}(\mathbf{x})$ and eigenvalues $k_m^{2(0)}$ for the Helmholtz equation,

$$(\nabla^2 + k_m^{2(0)})\, \Psi_m^{(0)}(\mathbf{x}) = 0 \tag{1}$$

---

[1] Theoretical Biology and Biophysics, Theoretical Division, Group T-10, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

725

satisfying homogeneous boundary conditions on a boundary B, the pseudopotential has been used to introduce a boundary perturbation in the form of an additional small spherical boundary on which the eigenfunctions vanish.[1] The pseudopotential $\xi U(\mathbf{x}; \xi)$ is a linear operator; including it on the right in Eq. (1),

$$(\nabla^2 + k_m^2)\,\Psi_m = \xi U(\mathbf{x}; \xi)\,\Psi_m(\mathbf{x}) \tag{2}$$

establishes the additional spherical boundary. Provided that the perturbation parameter ξ is much less than 1, Eq. (2) is solved using Rayleigh–Schrödinger perturbation theory.[2] ξ can be taken to be the order of the ratio of the radius ε of the sphere to the smallest distance between the sphere's center and the boundary B. One can add many small spherical boundaries; then ξ is the order of the ratio of ε to the smallest distance between spheres or between any sphere and B.

The pseudopotential employes singular solutions for the Helmholtz operator centered in the sphere. The amplitudes of these singular solutions enforce the vanishing boundary condition on the sphere's surface. The pseudopotential has been used to generate the correct perturbation expansion of the eigenvalues and eigenfunctions for two three-dimensional problems with the foregoing characteristics.[1]

Although one can imagine several generalizations of the pseudopotential, one of the purposes of this paper is to give a derivation and application of the pseudopotential for a two-dimensional region bounded by B in which one or more circles are introduced on which $\Psi_m(\mathbf{x})$ vanishes. As an application, we determine the expansion of the smallest eigenvalue and its eigenfunction for Eq. (1) with an infinite array of perfectly absorbing circles centered on the points of a square lattice with lattice spacing L. The "unit cell" for this problem is taken to be a square of side L with the normal derivative of $\Psi_m(\mathbf{x})$ vanishing on its perimeter B, a *reflecting* boundary condition, and with a centered circular boundary of radius ε on which $\Psi_m(\mathbf{x})$ vanishes, an *absorbing* boundary condition. The expansion parameter ξ is taken to be $[\log(L/\varepsilon)]^{-1}$. The first three terms in the expansion of the smallest eigenvalue and its eigenfunction determine the first three terms in the expansion of the first passage time (the first moment of the probability of survival until time t) of a diffusing object placed at random outside the absorbing circle. We also obtain the analogous solution of Eq. (1), for an infinite triangular array of absorbing circles. We take the "unit cell" to contain two circles, and we impose periodicity for a rectangle bounded by B rather than a boundary condition. The expansion of the exact smallest eigenvalue and eigenfunction are obtained by the application of the two-dimensional pseudopotential to a separable problem, with the boundaries being an absorbing circle centered

in a reflecting circle. To further demonstrate the utility of the "two-dimensional" pseudopotential, we find expansions of the smallest eigenvalue for periodic arrays of absorbing nonintersecting cylinders.

We also use the three-dimensional pseudopotential[1] to find the corresponding solutions of problems in which arrays of perfectly absorbing spheres are centered on the points of simple cubic (sc), body-centered cubic (bcc) and face-centered cubic (fcc) lattices.

In the last section these results are used to give the first two terms in expansions of the rates of diffusion-limited reaction. We obtain rates for the aforementioned arrays of circles. We obtain the same results for the diffusion-limited reaction rates in the three-dimensional arrays of spheres that were previously obtained from time-independent formulations.[3,4] Beyond the new feature of tackling the time-dependent problems with the same boundaries, one can appreciate that the systematic pseudopotential method allows one to solve a variety of particular problems within the same framework of perturbation theory.

2. PSEUDOPOTENTIAL FOR TWO DIMENSIONS

The derivation of the pseudopotential follows closely that given for three dimensions, with some minor modifications. The pseudopotential $\xi U(\mathbf{x}; \xi)$ is derived by first separating the eigenfunctions of Eq. (1) into radial and angular parts about the center of the circle of radius ε:

$$\Psi_{\mathbf{m}}(\mathbf{x}) = \sum_{n=0}^{\infty} A_{\mathbf{m}n} \cos(n\theta)[J_n(k_{\mathbf{m}}r) - T_n(k_{\mathbf{m}}\varepsilon) \, Y_n(k_{\mathbf{m}}r)]$$

$$T_n(\zeta) \equiv J_n(\zeta)/Y_n(\zeta) \tag{3}$$

$$\Psi_{\mathbf{m}n}(r) \equiv A_{\mathbf{m}n}[J_n(k_{\mathbf{m}}r) - T_n(k_{\mathbf{m}}\varepsilon) \, Y_n(k_{\mathbf{m}}r)]$$

For the purposes of pedagogy, cosine angular dependence is assumed; the derivation is the same for terms containing $\sin(n\theta)$.

Although Eq. (3) exactly satisfies the vanishing boundary condition on the circle, it does so by using in addition to the Bessel functions of the first kind of order n, $J_n(\zeta)$, bounded for real ζ, Bessel functions of the second kind, the Weber functions of order n, $Y_n(\zeta)$, singular as ζ goes to zero. This singular behavior can be evoked by a term as on the right of Eq. (2), because the operator of Eq. (1) acting on $\Psi_{\mathbf{m}}(\mathbf{x})$ as given in Eq. (3) results in the following equation for all n:

$$(\nabla^2 + k_{\mathbf{m}}^2 - n^2/r^2) \, \Psi_{\mathbf{m}n}(r)$$

$$= -A_{\mathbf{m}n} T_n(k_{\mathbf{m}}\varepsilon)(\nabla^2 + k_{\mathbf{m}}^2 - n^2/r^2) \, Y_n(k_{\mathbf{m}}r)$$

$$= -A_{\mathbf{m}n}(1 + \delta_n) \, 2^{n+1}n! \, T_n(k_{\mathbf{m}}\varepsilon) \, \delta(\mathbf{x})/(k_{\mathbf{m}}r)^n \tag{4}$$

The symbol δ_n equals 1 if n equals 0; otherwise δ_n equals 0. With the two coordinates x_1 and x_2, the symbol $\delta(\mathbf{x})$ is equivalent to $\delta(x_1)\,\delta(x_2)$, the latter being the Dirac delta function. To derive the right-hand side of Eq. (4), one notes first that everywhere but the origin it must vanish because $J_n(\zeta)$ and $Y_n(\zeta)$ are the eigenfunctions for the operator on the left-hand side. One needs to use the leading term in the expansion of $Y_n(\zeta)$ as ζ goes to zero[5] and to use Green's first theorem,[6]

$$\int_R dA\, f(\mathbf{x})\,\nabla^2 g(\mathbf{x}) = \oint ds\, f(\mathbf{x})\hat{\mathbf{n}} \cdot \nabla g(\mathbf{x}) - \int_R dA\,\nabla f(\mathbf{x})\cdot\nabla g(\mathbf{x})$$

In our case R is a circular region of radius δ, the line integral follows the circumference in the positive direction, $\hat{\mathbf{n}}$ is the unit vector in the outward normal direction, and $\cdot$ is the vector dot product. When one integrates the right-hand side of Eq. (4) over R after multiplying by r^n, one gets an integral of this form; the line integral is constant as δ goes to zero, manifesting the delta function, and the integrand of the new surface integral exactly cancels the integrand on the left proportional to n^2/r^2. In the limit that δ goes to zero, all other terms vanish. Thus we see that using the singular solutions of the Helmholtz equation to create the vanishing boundary condition on a circle entails a new term at only one point [see Eq. (2)].

The amplitude of the singular part of $\Psi_{mn}(r)$ is equal to $-A_{mn}T_n(k_m\varepsilon)$, from Eq. (4). Therefore, once A_{mn} is replaced by a linear operation at the origin on $\Psi_{mn}(r)$ which gives the amplitude of the non-singular part of $\Psi_{mn}(r)$, Eq. (4) self-consistently determines the $\Psi_{mn}(r)$ satisfying the new vanishing boundary condition on the circle. Multiplying the right-hand side by $\cos(n\theta)$ and summing over n gives the two-dimensional pseudopotential. A convenient operation meeting these requirements is the following. To educe the amplitude of $J_n(k_m r)$, one must multiply $\Psi_{mn}(r)$ by r^n and take $2n$ derivatives with respect to r near the origin. The resulting leading order term arises from $Y_n(k_m r)$ and is proportional to $\log(k_m r/2)$, and the constant term that follows contains the amplitude of $J_n(k_m r)$. Thus, if one now divides by $\log(k_m r/2)$, takes the derivative with respect to r, multiplies by $r\log^2(k_m r/2)$, and takes the limit $r \to 0$, one will have isolated a constant proportional to the amplitude of $J_n(k_m r)$. Thus, obtaining A_{mn} in the following way meets the requirements of the pseudopotential:

$$A_{mn} = \frac{-r\log^2(k_m r/2)}{(2n-1)!!\, k_m^n\, C_n}\frac{\partial}{\partial r}\frac{1}{\log(k_m r/2)}\frac{\partial^{2n}}{\partial r^{2n}}\left[r^n\Psi_{mn}(r)\right]\Bigg|_{r=0} \qquad (5)$$

with

$$(-1)!! \equiv 1, \qquad (2n+1)!! \equiv (2n+1)(2n-1)!!; \qquad n \geqslant 0$$

$$C_0 \equiv 1 - \frac{2\gamma}{\pi} T_0(k_m \varepsilon)$$

$$C_n \equiv 1 - \frac{2T_n(k_m \varepsilon)}{\pi} \left(\sum_{j=1}^{2n} j^{-1} - \frac{1}{2} \sum_{j=1}^{n} j^{-1} + \gamma \right); \qquad n > 0$$

$$\gamma \equiv 0.577216...$$

The substitution of Eq. (5) for A_{mn} into the last line of Eq. (4) results in the two-dimensional pseudopotential:

$$(\nabla^2 + k_m^2) \, \Psi_m(\mathbf{x})$$

$$= \sum_{n=0}^{\infty} \frac{\cos(n\theta) \, 2^{n+1}(1 + \delta_n)n! \, T_n(k_m \varepsilon) \, r^{1-n} \log^2(k_m r/2) \, \delta(\mathbf{x})}{(2n-1)!! \, k_m^{2n} C_n}$$

$$\times \left\{ \frac{d}{dr} \frac{1}{\log(k_m r/2)} \frac{d^{2n}}{dr^{2n}} \, [r^n \Psi_{mn}(r)] \right\} \qquad (6)$$

To make Eq. (6) complete, one must include an analogous sum on n from 1 to infinity of terms with $\sin(n\theta)$ and a $\sin(n\theta)$-averaged $\Psi_{mn}(r)$. Expanding $T_n(k_m \varepsilon)$ for small values of the argument gives

$$(\nabla^2 + k_m^2) \, \Psi_m(\mathbf{x}) = \frac{2\pi r \log^2(k_m r/2) \, \delta(\mathbf{x})}{\log(k_m \varepsilon/2)} \frac{d}{dr} \frac{\Psi_{m0}(r)}{\log(k_m r/2)}$$

$$+ O\left[\left(\frac{\varepsilon}{L} \right)^2 \left(\log \frac{L}{\varepsilon} \right)^{-1} \right] \qquad (7)$$

Note that this simplification holds only for those eigenvalues for which $k_m \varepsilon$ is much less than unity.

Thus, the angle-independent part of the mth eigenfunction can generate the leading terms of a perturbation expansion with ξ the reciprocal of a logarithm. Further, for eigenfunctions having these leading terms, one can replace $2/k_m$ on the right side of Eqs. (6) and (7) with L, a length representative of the distance between the boundary B and the center of the circle. The error introduced by this substitution is of one higher order in $[\log(L/\varepsilon)]^{-1}$ and will be exactly corrected in the following perturbation step. The resulting formula,

$$(\nabla^2 + k_m^2) \, \Psi_m(\mathbf{x}) = \frac{2\pi r \log^2(L/r) \, \delta(\mathbf{x})}{\log(L/\varepsilon)} \frac{d}{dr} \frac{\Psi_{m0}(r)}{\log(L/r)}$$

$$+ O\left[\left(\frac{\varepsilon}{L} \right)^2 \left(\log \frac{L}{\varepsilon} \right)^{-1} \right] \qquad (8)$$

can now be used with a perturbation method because the eigenvalue appears only on the left.

Neglecting terms of order $(\varepsilon/L)^2 [\log(L/\varepsilon)]^{-1}$, we obtain the pseudopotential as

$$\xi U(\mathbf{x}; \xi) \sim \xi U(\mathbf{x}) \equiv \xi 2\pi r \log^2 \left(\frac{L}{r}\right) \delta(\mathbf{x}) \frac{d}{dr} \frac{(1/2\pi) \int_0^{2\pi} d\theta}{\log(L/r)} \qquad (9)$$

$$\xi = [\log(L/\varepsilon)]^{-1}$$

A merit of this pseudopotential is that, to leading order, one has only the multiplicative factor ξ. This pseudopotential rejects any logarithmic singularity of its operand and thereby educes the constant part b of its operand at the origin. For example, if

$$\lim_{r \to 0} \Psi_{m0}(r) = a \log(L/r) + b + o(1)$$

then

$$\xi U(\mathbf{x}) \Psi_m(\mathbf{x}) = [\log(L/\varepsilon)]^{-1} 2\pi b \, \delta(\mathbf{x})$$

In conjunction with the perturbation method, the pseudopotential generates a correction

$$-b \frac{\log(L/r)}{\log(L/\varepsilon)}$$

to the eigenfunction at each step, thereby lowering by one power of ξ the value of the eigenfunction on the circle. After n perturbation steps, one will have n corrections to the eigenvalue k_m^2 and the eigenfunction $\Psi_m(\mathbf{x})$:

$$k_m^2 \sim k_m^{2(0)} + \xi k_m^{2(1)} + \cdots + \xi^n k_m^{2(n)}$$
$$\Psi_m(\mathbf{x}) \sim \Psi_m^{(0)}(\mathbf{x}) + \xi \Psi_m^{(1)}(\mathbf{x}) + \cdots + \xi^n \Psi_m^{(n)}(\mathbf{x}) \qquad (10)$$

When one substitutes these approximations into Eq. (2) with $\xi U(\mathbf{x})$ given by Eq. (9), the error is $O(\xi)^{n+1}$. Furthermore, one will have satisfied the boundary condition on B exactly and the boundary condition on the circle to $O(\xi)^{n-1}$. One can further apprehend the correctness of Eqs. (2) and (9) by the examination of the smallest eigenvalue and eigenfunction of the problems discussed in the following sections.

3. CIRCLE IN A SQUARE

The two-dimensional pseudopotential (9) is used to determine the first three terms in the expansion in powers of $[\log(L/\varepsilon)]^{-1}$ of the smallest eigenvalue and its eigenfunction in the boundary value problem

$$(\nabla^2 + k^2) \Psi(\mathbf{x}) = 0$$

with the following boundary condition and periodicity condition:

$$\Psi(x_1, x_2) = 0 \qquad \text{if} \quad x_1^2 + x_2^2 = \varepsilon^2$$

$$\Psi(x_1, x_2) = \Psi(x_1 + mL, x_2 + nL), \qquad m, n \in Z$$

The eigenvalues and eigenfunctions of the Helmholtz equation for this array of absorbing circles are involved in the quantum mechanical formulation of Sinai's billiard.[7]

To begin, the orthogonal eigenvalues and eigenfunctions for the problem without the perturbing centered circular boundary having the symmetry of the perturbed problem are as follows:

$$k_{i_1 i_2}^{2(0)} = \left(\frac{2\pi}{L}\right)^2 (i_1^2 + i_2^2)$$

$$\Psi_{i_1 i_2}^{(0)}(\mathbf{x}) = \frac{2 \cos(2\pi i_1 x_1/L) \cos(2\pi i_2 x_2/L)}{L(1 + \delta_{i_1})^{1/2} (1 + \delta_{i_2})^{1/2}}$$

Defining

$$U_{i_1 i_2; \, j_1 j_2}^{(k); \, (l)} = \int_{-L/2}^{L/2} dx_1 \, dx_2 \, \Psi_{i_1 i_2}^{(k)}(\mathbf{x}) \, U(\mathbf{x}) \, \Psi_{j_1 j_2}^{(l)}(\mathbf{x})$$

with $U(\mathbf{x})$ the pseudopotential operator given in Eq. (9), and using the Rayleigh–Schrödinger perturbation theory[2] for a two-dimensional problem gives

$$k_{00}^{2(1)} \equiv U_{00; \, 00}^{(0); \, (0)} = 2\pi/L^2 \tag{11}$$

Furthermore,

$$\Psi_{00}^{(1)}(\mathbf{x}) = - \sum_{i_1, i_2 = 0}^{\infty}{}' \frac{\Psi_{i_1 i_2}^{(0)}(\mathbf{x}) \, U_{i_1 i_2; \, 00}^{(0); \, (0)}}{k_{i_1 i_2}^{2(0)}}$$

In this paper, a primed summation indicates that the term with all indices equal to zero is omitted. Substituting the value of $U_{i_1 i_2; \, 00}^{(0); \, (0)}$ and the other quantities given above, we obtain

$$\Psi_{00}^{(1)}(\mathbf{x}) = -\frac{2}{\pi L} \sum_{i_1, i_2 = 0}^{\infty}{}' \frac{\cos(2\pi i_1 x_1/L) \cos(2\pi i_2 x_2/L)}{(1 + \delta_{i_1})(1 + \delta_{i_2})(i_1^2 + i_2^2)} \tag{12}$$

It is interesting to note

$$\nabla^2 \Psi_{00}^{(1)}(\mathbf{x}) = \frac{-2\pi}{L} \left[\frac{1}{L^2} - \sum_{i_1, i_2 = -\infty}^{\infty} \delta(x_1 - i_1 L) \, \delta(x_2 - i_2 L) \right]$$

Therefore $\Psi_{00}^{(1)}(\mathbf{x})$ is a periodic Green's function for the Laplace operator plus a constant. This is perhaps the easiest way to see that as ρ goes to zero,

$$\Psi_{00}^{(1)}(\mathbf{x}) \sim \frac{\log \rho}{L} + \frac{\alpha_s}{L} - \frac{\pi\rho^2}{2L} + \cdots \qquad \rho^2 = \frac{x_1^2 + x_2^2}{L^2} \tag{12'}$$

In terms of the constant α_s, the second-order correction to the eigenvalue is

$$k_{00}^{2(2)} \equiv U_{00}^{(0)};_{00}^{(1)} = 2\pi\alpha_s/L^2 \tag{13}$$

After reducing the double sum in Eq. (12) to a single sum,[8] one finds the constant α_s to be

$$\alpha_s = \log(2\pi) - \pi/6 - 2l(2\pi) = 1.3105329... \tag{14}$$

with $l(x)$ the Lambert series,

$$l(x) = \sum_{k=1}^{\infty} k^{-1} \exp(-kx)/[1 - \exp(-kx)]$$

$$= -\log \left\{ \prod_{k=1}^{\infty} [1 - \exp(-kx)] \right\} \tag{15}$$

$$= \tfrac{1}{3} \log\{2q^{1/4}/[\vartheta_2(0)\,\vartheta_3(0)\,\vartheta_4(0)]\}; \qquad q = \exp(-x/2)$$

$$l(2\pi) = \tfrac{1}{2} \log[\pi \exp(-\pi/6)/\mathbf{K}(2^{-1/2})] = 1.872682450... \times 10^{-3}$$

Only the first three terms of the rapidly convergent Lambert series are necessary to establish the numerical value appearing in Eq. (14). The "closed form" involving theta functions follows from the infinite-product representation of $\vartheta_1'(0)$; and the relationship between the three theta functions and the complete elliptic integral $\mathbf{K}(k)$ could be used in the evaluation of $l(2\pi)$. The constant α_s has been evaluated previously in a related context.[9] All of the numerical values for the constants appearing in this paper are expected to be accurate to the number of places given and have been rounded up if necessary. A contour plot of $\Psi_{00}^{(1)}(\mathbf{x})$ with $L = 1$ is shown in Fig. 1, illustrating in particular the logarithmic singularity.

The second-order eigenfunction is found from the formula

$$\Psi_{00}^{(2)}(\mathbf{x}) = - \sum_{i_1,i_2 = 0}^{\infty}{}' \frac{\Psi_{i_1 i_2}^{(0)}(\mathbf{x})}{k_{i_1 i_2}^{2(0)}} \left[U_{i_1 i_2}^{(0)};_{00}^{(1)} + \frac{k_{00}^{2(1)}}{k_{i_1 i_2}^{2(0)}} U_{i_1 i_2}^{(0)};_{00}^{(0)} \right]$$

$$= -\frac{1}{L} \sum_{i_1,i_2 = 0}^{\infty}{}' \frac{\cos(2\pi i_1 x_1/L)\, \cos(2\pi i_2 x_2/L)}{(1 + \delta_{i_1})(1 + \delta_{i_2})(i_1^2 + i_2^2)}$$

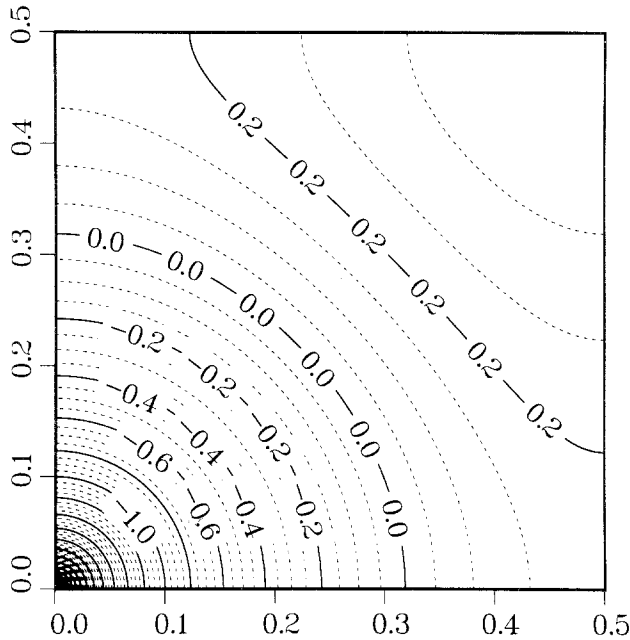$$\times \left[\frac{2\alpha_s}{\pi} + \frac{1}{\pi^2(i_1^2 + i_2^2)} \right] \tag{16}$$

Fig. 1. A contour plot of $\Psi_{00}^{(1)}(\mathbf{x})$ [Eq. (12)] with $L = 1.0$. Both the x and y axes extend between 0 and 0.5. Because of the symmetry of the problem, only the first quadrant is shown, and the maximum value of the function, 0.3466..., is at the upper right corner. Every fourth contour is labeled with the value of the function and thickened. The dashed contours are equally spaced at intervals of 0.05. The value of the function on a radius equal to 0.1 varies less than 0.02%.

A contour plot of $\Psi_{00}^{(2)}(\mathbf{x})$ is similar in appearance to that of $\Psi_{00}^{(1)}(\mathbf{x})$, but $\Psi_{00}^{(2)}(\mathbf{x})$ has larger gradients. The method used to find $k_{00}^{2(2)}$ gives

$$k_{00}^{2(3)} \equiv U_{00;00}^{(0);(2)} = \frac{2\pi}{L^2}\left(\alpha_s^2 - \frac{\beta_s}{\pi^2}\right) \tag{17}$$

$$\beta_s = \sum_{i_1,i_2=0}^{\infty}{}' \frac{1}{(1+\delta_{i_1})(1+\delta_{i_2})(i_1^2+i_2^2)^2} = 1.506703010... \tag{18}$$

Again, a related formula[8] is used to reduce the double sum to a single sum, and β_s is decomposed into a few numbers, including the zeta function $\zeta(3)$ and two rapidly convergent series analogous to Lambert series (see Appendix A). These are all the results we need to find three terms in the perturbation expansion of a first passage time problem, as will be seen below.

Higher order terms in the expansions of the eigenfunctions and eigenvalues for this problem and others solved using the pseudopotential can be

obtained from standard perturbation formulas. It is to be expected that the higher the order, the more manipulations required. Because of the logarithm in the perturbation parameter, one may need more than three terms for accuracy in a particular application.

4. A TRIANGULAR ARRAY OF CIRCLES

The related problem of determining the perturbation expansion of the smallest eigenvalue and the corresponding eigenfunction for the Helmholtz equation with a vanishing boundary condition in the exterior of a regular triangular array of circles separated by the distance L involves two minor accretions to the analysis of the problem with the square array solved in the preceding section. First, it is convenient to generate the infinite triangular array by periodically repeating a rectangular "unit cell" with horizontal length L and vertical length $3^{1/2}L$ centered on the origin, containing two circles of radius ε centered on the points $(L/4, 3^{1/2}L/4)$ and $(-L/4, -3^{1/2}L/4)$. And the zeroth-order eigenfunctions are all four combinations of the sine functions and cosine functions. The smallest unperturbed eigenvalue (zero) has a unique (constant) eigenfunction, so one can use the procedure given above with the sum over eigenfunctions including, for each pair of indices, all combinations of sine and cosine. If one were to compute the expansion of any other eigenvalue of this system, one would need to use perturbation theory for degenerate eigenfunctions.[10] The expansion parameter ξ is taken to be $[\log(L/\varepsilon)]^{-1}$, as above. Following the procedures of the previous section, we have

$$k_{00}^{2(0)} = 0, \qquad k_{00}^{2(1)} = \frac{4\pi}{3^{1/2}L^2}$$

$$k_{00}^{2(2)} = \frac{4\pi\alpha_t}{3^{1/2}L^2}, \qquad k_{00}^{2(3)} = \frac{4\pi}{3^{1/2}L^2}\left(\alpha_t^2 - \frac{4\beta_t}{3\pi^2}\right)$$

$$\Psi_{00}^{(0)}(\mathbf{x}) = \frac{1}{3^{1/4}L}$$

$$\Psi_{00}^{(1)}(\mathbf{x}) = \frac{-4}{3^{3/4}L}\sum_{i_1 i_2 = 0}^{\infty}{}' \frac{1}{(1+\delta_{i_1})(1+\delta_{i_2})(i_1^2 + i_2^2/3)}$$

$$\times \left[\cos\frac{2\pi i_1 x_1}{L}\cos\frac{\pi i_1}{2}\cos\frac{2\pi i_2 x_2}{3^{1/2}L}\cos\frac{\pi i_2}{2} \right.$$

$$\left. + \sin\frac{2\pi i_1 x_1}{L}\sin\frac{\pi i_1}{2}\sin\frac{2\pi i_2 x_2}{3^{1/2}L}\sin\frac{\pi i_2}{2} \right]$$

(19)

with

$$\alpha_t = \log(2\pi) - 2l(2\pi3^{1/2}) - 2m(\pi3^{1/2}) - \frac{\pi3^{1/2}}{12}$$

$$= 1.39303795...\tag{20}$$

with $l(x)$ given in Eq. (15) and with

$$m(x) = \sum_{k=1}^{\infty} (-)^k k^{-1} \exp(-kx)/[1 - \exp(-2kx)]$$

$$= -\tfrac{1}{2}\{l(2x) + \log[\vartheta_3(0)]\}, \qquad q = \exp(-x)$$

$$= -\tfrac{1}{6}\log\{2q^{1/4}[\vartheta_3(0)]^2/[\vartheta_2(0)\,\vartheta_4(0)]\}$$

$$l(2\pi3^{1/2}) = \tfrac{1}{2}\log[\pi2^{1/3}\exp(-\pi3^{1/2}/6)/\mathbf{K}(\sin(\pi/12))]$$

$$= 1.8779062... \times 10^{-5}$$

$$m(\pi3^{1/2}) = -\tfrac{1}{6}\log[4\exp(-\pi3^{1/2}/4)] = -4.32413966... \times 10^{-3}$$

and the constant appearing in $k_{00}^{2(3)}$

$$\beta_t = \sum_{i_1 i_2}' \frac{1}{(1 + \delta_{i_1})(1 + \delta_{i_2})[i_1^2 + (i_2^2/3)]^2}$$

$$= 3.4519622...\tag{21}$$

this last summation being restricted to nonnegative i_1, i_2; either i_1 and i_2 are both even or both odd and the prime indicates that both equal zero is excluded. Equation (21) is numerically evaluated in the same way as Eq. (18). As expected, $\Psi_{00}^{(1)}(\mathbf{x})$ has two singularities in the unit cell, one at the center of each circle.

5. RADIAL SYMMETRY

We now repeat the steps used above for a separable problem having an exact solution. Solving Eq. (1) between two concentric circles of radii ε and R with $\partial\Psi_m(r)/\partial r|_R$ and $\Psi_m(\varepsilon)$ equal zero leads to eigenfunctions of r alone, and therefore the terms in the exact two-dimensional pseudopotential (6) with n greater than zero vanish. One begins with the orthonormal eigenfunctions for the problem with the inner circle removed

$$\Psi_m^{(0)}(r) = \frac{J_0(k_m r)}{\pi^{1/2} R J_0(k_m R)}$$

with k_m the mth nonnegative root of $J_1(kR) = 0$. Using the pseudopotential given in Eq. (9) with $\xi = [\log(R/\varepsilon)]^{-1}$ gives

$$k_0^{2(0)} = 0, \qquad \Psi_0^{(0)}(r) = \frac{1}{\pi^{1/2}R}$$

$$k_0^{2(1)} = \frac{2}{R^2}, \qquad \Psi_0^{(1)}(r) = \frac{-1}{\pi^{1/2}R}\left[\log\left(\frac{R}{r}\right) - \frac{3}{4} + \frac{1}{2}\left(\frac{r}{R}\right)^2\right]$$

$$k_0^{2(2)} = \frac{3}{2R^2}, \qquad \Psi_0^{(2)}(r) = \frac{1}{\pi^{1/2}R}\left\{-\frac{3}{4}\log\left(\frac{R}{r}\right) + \frac{5}{12}\right. \tag{22}$$

$$\left. + \left[\frac{1}{2}\log\left(\frac{R}{r}\right) - \frac{1}{4}\right]\left(\frac{r}{R}\right)^2 + \frac{1}{16}\left(\frac{r}{R}\right)^4\right\}$$

$$k_0^{2(3)} = \frac{5}{6R^2}$$

Fourier–Bessel expansions of the functions appearing in the eigenfunctions have been used to reduce the sums resulting from the application of the perturbation theory. The approximations to the eigenvalue are those found by expanding the exact eigenvalue. The Rayleigh–Schrödinger perturbation theory takes the coefficient of the zeroth-order eigenfunction to be one,[2] and thus generates orthogonal but not orthonormal eigenfunctions—the explanation for the small difference between the second-order eigenfunction given above and the corresponding term in the expansion of the exact orthonormal eigenfunction in powers of ξ. Obtaining the correct solution to this problem further corroborates the two-dimensional pseudopotential [Eq. (9)] and its application.

6. ARRAYS OF ORTHOGONAL CYLINDERS

The purpose of this section is to apply the pseudopotential derived for two dimensions to problems with periodic arrays of nonintersecting perfectly absorbing cylinders. For these problems, the pseudopotential extends along the axes of the cylinders. We consider the smallest eigenvalue and eigenfunction for two orthogonal arrays. One could use the pseudopotential also for periodic arrays of nonorthogonally placed cylinders; the restriction is that they neither intersect nor come close to intersection. The expansion parameter ξ is taken to be $[\log(L/\varepsilon)]^{-1}$, with L the side of the centered cubic unit cell and ε the cylinder radius.

The first array has two cylinders in the unit cell. One cylinder's axis is the line formed by the intersection of the planes $x_1 = 0$ and $x_3 = -L/4$. The

other cylinder's axis is the line formed by the intersection of the planes $x_2 = 0$ and $x_3 = L/4$. Periodicity generates an infinitely tall stack of orthogonally alternating equivalent parallel layers of parallel cylinders. The pseudopotential (9) becomes

$$U(\mathbf{x}) = 2\pi \left[r_1 \log^2 \left(\frac{L}{r_1} \right) \delta(x_1) \, \delta \left(x_3 + \frac{L}{4} \right) \frac{\partial}{\partial r_1} \frac{1}{\log(L/r_1)} \right.$$

$$\left. + r_2 \log^2 \left(\frac{L}{r_2} \right) \delta(x_2) \, \delta \left(x_3 - \frac{L}{4} \right) \frac{\partial}{\partial r_2} \frac{1}{\log(L/r_2)} \right]$$

with $r_1^2 = x_1^2 + (x_3 + L/4)^2$ and $r_2^2 = x_2^2 + (x_3 - L/4)^2$.

In practice, the angular integral appearing in Eq. (9) is not required for these problems. Using this pseudopotential with the perturbation formulas given above gives the analogous results.

The expansion for the smallest eigenvalue is

$$k_{000}^{2(1)} = \frac{4\pi}{L^2}$$

$$k_{000}^{2(2)} = \frac{4\pi}{L^2} \left(\alpha_s + \frac{\pi}{12} \right)$$

$$k_{000}^{2(3)} = \frac{4\pi}{L^2} \left[\left(\alpha_s + \frac{\pi}{12} \right)^2 + \frac{7\pi^2}{720} - \frac{2\beta_s}{\pi^2} + \frac{2\beta(1)}{\pi^2} \right]$$

with

$$\beta(x) = \sum_{i_1, i_2 = 0}^{\infty} \sum_{i_3 = 1}^{\infty} \frac{(-)^{i_1 + i_2}}{(1 + \delta_{i_1})(1 + \delta_{i_2})(i_1^2 + xi_3^2)(i_2^2 + xi_3^2)}$$

$$= \frac{\pi^2}{x} \sum_{j=1}^{\infty} \frac{\exp - (2\pi j x^{1/2})}{j^2 [1 - \exp - (2\pi j x^{1/2})]^2}$$

and

$$\beta(1) = 1.850856357... \times 10^{-2}$$

The constants α_s and β_s are given in Eqs. (14) and (18).

The second array we consider has three cylinders in the unit cell. The axes of the three cylinders are the lines formed by the intersection of the planes $x_1 = L/4$ and $x_2 = -L/4$, the planes $x_2 = L/4$ and $x_3 = -L/4$, and the planes $x_3 = L/4$ and $x_1 = -L/4$. The array has full cubic symmetry, with three equivalent interspersed orthogonal stacks of parallel layers composed of parallel cylinders. It could be constructed by putting cylinders

on the centers of the square holes that one would see if one looked perpendicular to the layers of the first array. The expansion of the smallest eigenvalue is

$$k_{000}^{2(1)} = \frac{6\pi}{L^2}$$

$$k_{000}^{2(2)} = \frac{6\pi}{L^2}\left(\alpha_s + \frac{\pi}{6}\right)$$

$$k_{000}^{2(3)} = \frac{6\pi}{L^2}\left[\left(\alpha_s + \frac{\pi}{6}\right)^2 + \frac{7\pi^2}{240} - \frac{3\beta_s}{\pi^2} + \frac{8\beta(4)}{\pi^2}\right]$$

with the formula for $\beta(4)$ given in the previous case, and

$$\beta(4) = 8.604739884... \times 10^{-6}$$

It is interesting to note that, whereas $k_{000}^{2(1)}$ reflects only the number of cylinders, the orientation of the cylinders is first manifested in $k_{000}^{2(2)}$.

Furthermore, unlike the two-dimensional problems discussed, more than two summations are required (in general) for the representations of the higher order terms in the expansion of the eigenvalues and eigenfunctions.

7. ARRAYS OF SPHERES

These calculations follow closely those for the arrays of circles, and we omit many of the details. Expansions in the perturbation parameter of the average rate of trapping of diffusing point particles randomly placed (in the exterior) in the presence of arrays of perfectly absorbing spheres have been given.[3,4] Using the three-dimensional pseudopotential,[1] we compute expansions for the expected lifetime of such a particle with perfectly absorbing spheres centered on the simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) lattices. As above, to get the first three terms in the expansion of the first passage time, one needs only the first three terms in the expansion of the smallest eigenvalue and the first two corrections to the corresponding eigenfunction. For our purposes, the three-dimensional pseudopotential is $4\pi\delta(\mathbf{x})(\partial/\partial r)r$, and ξ is taken equal to ε/L, with ε the sphere radius and L the length of the side of the cubic "unit cell."[1]

The case of absorbing spheres centered on the simple cubic lattice results in the "unit cell" being a cube with a central sphere. Due to the symmetry of the problem, there will be a vanishing normal derivative of the eigenfunctions on the surface of the cube. There is complete analogy with the two-dimensional problem of a centered absorbing circle within a reflecting square treated above, and the results follow:

$$k_{000}^{2(1)} = \frac{4\pi}{L^2}$$

$$k_{000}^{2(2)} = \frac{4\pi\alpha_{sc}}{L^2}$$

$$k_{000}^{2(3)} = \frac{4\pi}{L^2}\left(\alpha_{sc}^2 - \frac{8}{\pi^2}\beta_{sc}\right)$$

(23)

$$\Psi_{000}^{(1)}(\mathbf{x}) = \frac{-8}{\pi L^{3/2}} \sum_{i_1,i_2,i_3=0}^{\infty\prime} \frac{\cos(2\pi i_1 x_1/L)\cos(2\pi i_2 x_2/L)\cos(2\pi i_3 x_3/L)}{(1+\delta_{i_1})(1+\delta_{i_2})(1+\delta_{i_3})(i_1^2 + i_2^2 + i_3^2)}$$

$$\alpha_{sc} = 2.837297479...$$

(24)

$$\beta_{sc} = \sum_{i_1,i_2,i_3=0}^{\infty\prime} \frac{1}{(1+\delta_{i_1})(1+\delta_{i_2})(1+\delta_{i_3})(i_1^2 + i_2^2 + i_3^2)^2}$$

$$= 2.0665395...$$

(25)

The numerical constant α_{sc} has been evaluated.[9,11-13,20] We evaluate it in a new way in Appendix B. The primed summation in Eqs. (23) and (25) is over all nonnegative i_1, i_2, and i_3, excluding $(0, 0, 0)$. Techniques similar to those described above are used to evaluate β_{sc} (see Appendix A).

The remaining two problems, with the spheres centered on the bcc lattice or on the fcc lattice require that the "unit cell," a cube of side L centered on the origin, contains more than one absorbing sphere. There is much in common with the problem having the triangular array of circles. Using periodicity with length L to establish the bcc array, it is sufficient to place two spheres in the "unit cell" centered at $(L/4, L/4, L/4)$ and $(-L/4, -L/4, -L/4)$, and to establish the fcc array it is sufficient to place four spheres centered at $(L/4, L/4, L/4)$, $(-L/4, -L/4, L/4)$, $(-L/4, L/4, -L/4)$, and $(L/4, -L/4, -L/4)$. Because of the symmetry imposed by these arrays, one must now use the eight combinations of either using a sine or a cosine function for each of the three variables. The results for the bcc case are

$$k_{000}^{2(1)} = \frac{8\pi}{L^2}$$

$$k_{000}^{2(2)} = \frac{8\pi}{L^2}\alpha_{bc}$$

$$k_{000}^{2(3)} = \frac{8\pi}{L^2}\left(\alpha_{bc}^2 - \frac{32}{\pi^2}\beta_{bc}\right)$$

$$\Psi_{000}^{(1)}(\mathbf{x}) = \frac{-16}{\pi L^{3/2}} \sum_{i_1,i_2,i_3=0}^{\infty}{}' \frac{1}{(1+\delta_{i_1})(1+\delta_{i_2})(1+\delta_{i_3})(i_1^2+i_2^2+i_3^2)}$$

$$\times \left(\cos\frac{2\pi i_1 x_1}{L}\cos\frac{\pi i_1}{2}\cos\frac{2\pi i_2 x_2}{L}\cos\frac{\pi i_2}{2} \right.$$

$$\times \cos\frac{2\pi i_3 x_3}{L}\cos\frac{\pi i_3}{2}$$

$$+ \sin\frac{2\pi i_1 x_1}{L}\sin\frac{\pi i_1}{2}\sin\frac{2\pi i_2 x_2}{L}\sin\frac{\pi i_2}{2}$$

$$\times \cos\frac{2\pi i_3 x_3}{L}\cos\frac{\pi i_3}{2}$$

$$+ \sin\frac{2\pi i_1 x_1}{L}\sin\frac{\pi i_1}{2}\cos\frac{2\pi i_2 x_2}{L}\cos\frac{\pi i_2}{2}$$

$$\times \sin\frac{2\pi i_3 x_3}{L}\sin\frac{\pi i_3}{2}$$

$$+ \cos\frac{2\pi i_1 x_1}{L}\cos\frac{\pi i_1}{2}\sin\frac{2\pi i_2 x_2}{L}\sin\frac{\pi i_2}{2}$$

$$\left. \times \sin\frac{2\pi i_3 x_3}{L}\sin\frac{\pi i_3}{2}\right) \tag{26}$$

$$\alpha_{bc} = 3.639240... \tag{27}$$

$$\beta_{bc} = \sum_{i_1,i_2,i_3=0}^{1} \frac{1}{(1+\delta_{i_1})(1+\delta_{i_2})(1+\delta_{i_3})(i_1^2+i_2^2+i_3^2)^2}$$

$$= 0.79182201... \tag{28}$$

The primed summation in Eq. (26) has the same meaning as in Eq. (23). The value of α_{bc} is given in Ref. 13. The sum leading to β_{bc}, $\sum_{i_1 i_2 i_3}^{1}$ is over nonnegative indices, and furthermore the sum $i_1 + i_2 + i_3$ is even, and

$(0, 0, 0)$ is excluded. Techniques similar to those described above are used to evaluate β_{bc}.

The results for the fcc case are

$$k_{000}^{2(1)} = \frac{16\pi}{L^2}$$

$$k_{000}^{2(2)} = \frac{16\pi\alpha_{fc}}{L^2}$$

$$k_{000}^{2(3)} = \frac{16\pi}{L^2}\left(\alpha_{fc}^2 - \frac{128}{\pi^2}\beta_{fc}\right)$$

$$\Psi_{000}^{(1)}(\mathbf{x}) = \frac{-32}{\pi L^{3/2}} \sum_{i_1, i_2, i_3 = 0}^{\infty}{}' \frac{1}{(1 + \delta_{i_1})(1 + \delta_{i_2})(1 + \delta_{i_3})(i_1^2 + i_2^2 + i_3^2)}$$

$$\times \left(\cos\frac{2\pi i_1 x_1}{L} \cos\frac{\pi i_1}{2} \cos\frac{2\pi i_2 x_2}{L} \cos\frac{\pi i_2}{2} \right.$$

$$\times \cos\frac{2\pi i_3 x_3}{L} \cos\frac{\pi i_3}{2}$$

$$+ \sin\frac{2\pi i_1 x_1}{L} \sin\frac{\pi i_1}{2} \sin\frac{2\pi i_2 x_2}{L} \sin\frac{\pi i_2}{2}$$

$$\left. \times \sin\frac{2\pi i_3 x_3}{L} \sin\frac{\pi i_3}{2} \right) \tag{29}$$

$$\alpha_{fc} = 4.5848756... \tag{30}$$

$$\beta_{fc} = \sum_{i_1, i_2, i_3 = 0}^{2} \frac{1}{(1 + \delta_{i_1})(1 + \delta_{i_2})(1 + \delta_{i_3})(i_1^2 + i_2^2 + i_3^2)^2}$$

$$= 0.31442669... \tag{31}$$

The primed summation in Eq. (29) has the same meaning as in Eq. (23). The value of α_{fc} is given in Ref. 13. The sum leading to β_{bc}, $\sum_{i_1 i_2 i_3}^{2}$, is over nonnegative indices, and furthermore i_1, i_2, and i_3 are either all even or all odd, and $(0, 0, 0)$ is excluded. Techniques similar to those described above are used to evaluate β_{fc}.

The three-dimensional pseudopotential also gives the correct first three terms in the expansion of the exact smallest eigenvalue and eigenfunction for a separable problem with an absorbing sphere centered in a reflecting sphere, analogous to the radially symmetric two-dimensional problem discussed above.

8. FIRST PASSAGE TIMES

One can expand an arbitrary initial probability density $P_0(\mathbf{x})$ in the eigenfunctions $\Psi_{\mathbf{m}}(\mathbf{x})$ of the Helmholtz equation to obtain the time-dependent solution of the diffusion equation,

$$D\,\nabla^2 P = \partial P/\partial t \tag{32}$$

By separating the time variable, one gets the solution in the form

$$P(\mathbf{x}, t) = \sum_{\mathbf{m}} a_{\mathbf{m}}\,\Psi_{\mathbf{m}}(\mathbf{x})\exp(-k_{\mathbf{m}}^2\,Dt) \tag{33}$$

with $\Psi_{\mathbf{m}}(\mathbf{x})$ satisfying Eq. (1), and

$$a_{\mathbf{m}} = \int_\varepsilon d\mathbf{x}\,P_0(\mathbf{x})\,\Psi_{\mathbf{m}}(\mathbf{x})\bigg/\int_\varepsilon d\mathbf{x}\,[\Psi_{\mathbf{m}}(\mathbf{x})]^2$$

The integral sign $\int_\varepsilon$ indicates integration over all space between the circle of radius ε and the boundary B. The first passage time $\bar{t}$ is defined to be

$$\bar{t} \equiv \int_\varepsilon d\mathbf{x} \int_0^\infty dt\,P(\mathbf{x}, t)$$

In what follows, subscripts are attached to $\bar{t}$ to distinguish particular problems. If we choose $P_0(\mathbf{x})$ equal to a constant P_0, then

$$\bar{t} = (P_0/D)\sum_{\mathbf{m}}\left[\int_\varepsilon d\mathbf{x}\,\Psi_{\mathbf{m}}(\mathbf{x})\right]^2\bigg/k_{\mathbf{m}}^2\int_\varepsilon d\mathbf{x}\,[\Psi_{\mathbf{m}}(\mathbf{x})]^2 \tag{34}$$

For the two-dimensional problem of the circle centered in the square, $P_0 = (L^2 - \pi\varepsilon^2)^{-1}$; for all $\mathbf{m} = (i_1, i_2)$ except $(0, 0)$, $\int_\varepsilon d\mathbf{x}\,\Psi_{\mathbf{m}}^{(0)}(\mathbf{x})$ is proportional to $\varepsilon(i_1^2 + i_2^2)^{-1/2}\,J_1(2\pi\varepsilon(i_1^2 + i_2^2)^{1/2}/L)$, and $\int_\varepsilon d\mathbf{x}\,\Psi_{\mathbf{m}}^{(0)}(\mathbf{x})$ is proportional to $(\varepsilon^2/L)\log(\varepsilon/L)$. The latter results, along with the existence of the sums leading to higher order corrections, are sufficient to show that the term $\mathbf{m} = (0, 0)$ in the sum (34) is solely responsible for the expansion of $\bar{t}_s$ in powers of ξ, equal to $[\log(L/\varepsilon)]^{-1}$, from ξ^{-1} through ξ^1.

Substituting the expansion of the eigenvalue and eigenfunction of $\mathbf{m} = (0, 0)$ into Eq. (34) gives

$$\bar{t}_s \sim L^2\left\{1 - \frac{\xi k_{00}^{2(2)}}{k_{00}^{2(1)}} + \xi^2\left(\left[\frac{k_{00}^{2(2)}}{k_{00}^{2(1)}}\right]^2 - \frac{k_{00}^{2(3)}}{k_{00}^{2(1)}} - \int_\varepsilon d\mathbf{x}\,[\Psi_{00}^{(1)}(\mathbf{x})]^2\right)\right\}$$

$$\times\,[(L^2 - \pi\varepsilon^2)\,D\xi\,k_{00}^{2(1)}]^{-1} \tag{35}$$

$$\xi = [\log(L/\varepsilon)]^{-1}$$

Performing the integral in Eq. (35) reveals that to order 1 the term in parentheses multiplying ξ^2 equals 0 [see Eqs. (11)–(18)]. Including the numerical value of the constant α_s [Eq. (14)] gives

$$\bar{t}_s = (L^2/2\pi D)\{\log(L/\varepsilon) - 1.3105329... + O[\log(L/\varepsilon)]^{-2}\} \qquad (36)$$

A formula analogous to Eq. (35) holds for the triangular array. Including the numerical value of the constant α_t [Eq. (19)] gives

$$\bar{t}_t = (3^{1/2}L^2/4\pi D)\{\log(L/\varepsilon) - 1.39303795... + O[\log(L/\varepsilon)]^{-2}\} \qquad (37)$$

The same procedure applied to the problem of the absorbing circle within the reflecting circle, for which the expansion of the eigenfunction and eigenvalue were given in a previous section, gives the correct first three terms in the expansion of $\bar{t}$ previously obtained.[14] In this case, all terms of $O[\log(L/\varepsilon)]^{-n}$ vanish for $n \geq 1$. We do not know if this is also true in Eqs. (36) and (37).

Finally, Eqs. (32)–(35) and results from the last section are carried over to the problem of the mean first passage time in three-dimensional problems. Analogous results are used to prove that only the eigenvalue $\mathbf{m} = (0, 0, 0)$ contributes the first three terms in the expansion of $\bar{t}$ in powers of ξ. Namely, for all $\mathbf{m}$ except $(0, 0, 0)$, only the eigenfunctions that are the product of three cosine functions have a nonvanishing integral $\int_\varepsilon d\mathbf{x} \, \Psi_{\mathbf{m}}^{(0)}(\mathbf{x})$, proportional to

$$\varepsilon^2 (i_1^2 + i_2^2 + i_3^2)^{-1/2} j_1(2\pi\varepsilon(i_1^2 + i_2^2 + i_3^2)^{1/2}/L)$$

with $j_1(\xi)$ the spherical Bessel function of the first kind.[5] Also, $\int_\varepsilon d\mathbf{x} \, \Psi_{\mathbf{m}}^{(1)}(\mathbf{x})$ is proportional to ε^2. For the three-dimensional problems, $P_0 = (L^3 - n\frac{4}{3}\pi\varepsilon^3)^{-1}$, with $n = 1$ in the simple cubic case, 2 in the body-centered cubic case, and 4 in the face-centered cubic case.

For the simple cubic case (the centered absorbing sphere within a reflecting cube), Eq. (35) becomes

$$\bar{t}_{sc} = L^3 \left\{ 1 - \frac{\xi k_{000}^{2(2)}}{k_{000}^{2(1)}} + \xi^2 \left(\left[\frac{k_{000}^{2(2)}}{k_{000}^{2(1)}} \right]^2 - \frac{k_{000}^{2(3)}}{k_{000}^{2(1)}} - \int_\varepsilon d\mathbf{x} \, [\Psi_{000}^{(1)}(\mathbf{x})]^2 \right) \right\}$$

$$\times \, [(L^3 - \tfrac{4}{3}\pi\varepsilon^3) \, D\xi \, k_{000}^{2(1)}]^{-1} \qquad (38)$$

$$\xi = \varepsilon/L$$

Here the integral $\int_\varepsilon$ is performed over the space between the surface of the sphere and the cube. It is found that the quantity in the parentheses multiplying ξ^2 in Eq. (38) is zero, to order 1.

Substituting the results from the last section, Eqs. (23)–(25), leads to

$$\bar{t}_{\rm sc} = (L^2/4\pi D)[(L/\varepsilon) - \alpha_{\rm sc} + O(\varepsilon/L)^2] \tag{39}$$

Similarly, for the cases with the spheres centered on the bcc lattice or the fcc lattice, using Eqs. (26)–(31) gives

$$\bar{t}_{\rm bc} = (L^2/8\pi D)[(L/\varepsilon) - \alpha_{\rm bc} + O(\varepsilon/L)^2] \tag{40}$$

$$\bar{t}_{\rm fc} = (L^2/16\pi D)[(L/\varepsilon) - \alpha_{\rm fc} + O(\varepsilon/L)^2] \tag{41}$$

The relevance of Eqs. (36), (37), and (39)–(41) to the steady-state rate of trapping by arrays of perfectly absorbing circles and spheres is discussed in the next section.

9. DIFFUSION-LIMITED REACTION RATES

We have used the pseudopotential to obtain the expansion of the smallest eigenfunction and eigenvalue for the Helmholtz equation, these being sufficient to find the first terms in the expansion of the first passage time problem.

If one defines

$$Q(\mathbf{x}) = \int_0^\infty dt\, P(\mathbf{x}, t) \tag{42}$$

where $P(\mathbf{x}, t)$ is a solution of Eq. (33) with an initial density $P_0(\mathbf{x})$, then $Q(\mathbf{x})$ satisfies Poisson's equation

$$D\,\nabla^2 Q(\mathbf{x}) + P_0(\mathbf{x}) = 0 \tag{43}$$

and the first passage time for the time-dependent problem is obtained from this time-independent formulation:

$$\bar{t} = \int_\varepsilon d\mathbf{x}\, Q(\mathbf{x}) \tag{44}$$

It was not $\bar{t}$, but k, the rate constant of steady-state diffusive flux, that was determined in a time-independent setting.[3,4] The product of k, a (the number of absorbers per unit volume), and the integral over the "unit cell" of the steady-state density equals the steady-state diffusive flux from a "unit cell." Therefore, k is defined by

$$ka \int_\varepsilon d\mathbf{x}\, Q(\mathbf{x}) = ka\bar{t} = -D \int_{\delta\varepsilon} d\mathbf{s}\, \hat{\mathbf{n}} \cdot \nabla Q(\mathbf{s}) = 1 \tag{45}$$

with the second integral over the surface of the absorbers in the "unit cell," and $\hat{n}$ the outward unit normal vector. In what follows, we use the reciprocal relation between $\bar{t}$ and k given in Eq. (45).

One can derive a pseudopotential for the solution of Eq. (43). One then employs singular solutions satisfying the boundary condition on B exactly. The resulting perturbation expansion is more implicit than in the methods described herein. This runs largely parallel to the methods of Refs. 3 and 4, and although it has its advantages, largely due to systematizing the procedures, the issues one would need in order to carry the perturbation to infinite order and thereby obtain an exact solution to the problem are the same, regardless of the perturbation method used. The nature of these issues is revealed in this as well as in a related problem of electrical conductivity of a composite medium.[15,16]

For the two-dimensional problems, to facilitate comparison, we employ a common expansion parameter $\log(\phi)^{-1}$, with ϕ the fraction of the area occupied by the absorbing circles. First, for the radially symmetric case, the expansion of the smallest eigenvalue is given in Eq. (22), and with $\phi = (\varepsilon/R)^2$ and $a = 1/\pi R^2$,

$$k_{2r} = \frac{-4\pi D}{\log \phi} \left[1 - \frac{1.5}{\log \phi} + \frac{(1.5)^2}{\log(\phi)^2} + O(\log \phi)^{-3} \right] \tag{46}$$

Second, for the square array of absorbing circles, with reference to Eqs. (11), (13), and (14), and with $\phi = \pi(\varepsilon/L)^2$ and $a = L^{-2}$,

$$k_s = \frac{-4\pi D}{\log \phi} \left[1 - \frac{1.4763366...}{\log \phi} + \frac{(1.4763366...)^2}{\log(\phi)^2} + O(\log \phi)^{-3} \right] \tag{47}$$

And third, for the triangular array of absorbing circles, with reference to Eqs. (19) and (20), and with $\phi = (2\pi/3^{1/2})(\varepsilon/L)^2$ and $a = 2/3^{1/2}L^2$,

$$k_t = \frac{-4\pi D}{\log \phi} \left[1 - \frac{1.4975050...}{\log \phi} + \frac{(1.4975050...)^2}{\log(\phi)^2} + O(\log \phi)^{-3} \right] \tag{48}$$

The remarkable fact is that k_{2r}, k_s, and k_t, which are the steady state rates of absorption per circle, are nearly identical for the same value of ϕ, so long as $\log(1/\phi)$ is substantially larger than unity.

For the three-dimensional problems, to facilitate comparison, the expansion parameter ξ is changed to the volume fraction ϕ occupied by the spheres. For the radially symmetric problem in three dimensions[14] $\phi = (\varepsilon/R)^3$ and $a = 3/4\pi R^3$,

$$k_{3r} = 4\pi D\varepsilon[1 + 1.8\phi^{1/3} + (1.8)^2 \phi^{2/3} + O(\phi)] \tag{49}$$

For the array of spheres on the simple cubic lattice, $\phi = 4\pi\varepsilon^3/3L^3$ and $a = L^{-3}$,

$$k_{sc} = 4\pi D\varepsilon[1 + 1.760119...\phi^{1/3} + (1.760119...)^2 \phi^{2/3} + O(\phi)] \qquad (50)$$

For the body-centered cubic array, $\phi = 8\pi\varepsilon^3/3L^3$ and $a = 2L^{-3}$,

$$k_{bc} = 4\pi D\varepsilon[1 + 1.791862...\phi^{1/3} + (1.791862...)^2 \phi^{2/3} + O(\phi)] \qquad (51)$$

For the face-centered cubic array, $\phi = 16\pi\varepsilon^3/3L^3$ and $a = 4L^{-3}$,

$$k_{fc} = 4\pi D\varepsilon[1 + 1.791753...\phi^{1/3} + (1.791753...)^2 \phi^{2/3} + O(\phi)] \qquad (52)$$

These results agree with those given previously.[3,4] Reference 4 gives an explicit form for the ϕ dependence from which more terms in the expansion can be calculated. As in two dimensions, the agreement between these formulas is striking for ϕ substantially less than unity. A caveat is that for arrays of infinitely extended objects, such as the arrays of cylinders previously discussed, the perturbation parameter is different. Furthermore, based on the differences in the second terms in the expansions of the smallest eigenvalue for different spatial arrangements, we do not expect such close agreement in the second term of the expansions of the corresponding rates.

10. CONCLUSION

The pseudopotential is useful for obtaining perturbation expansions of the eigenfunctions for boundary value problems of the type considered here. We have illustrated its use for the Helmholtz equation in two and three dimensions, but it can serve the same function for other PDEs in any number of dimensions greater than one. It can be generalized to problems on which the perturbing boundaries are any surface of a coordinate system in which the PDE separates[2] and to problems with more general boundary conditions on the perturbing boundaries. Although we focus on the smallest eigenvalue, when one uses perturbation theory, the pseudopotential generates a large number of the perturbed eigenvalues and eigenfunctions of the Helmholtz equation satisfying the boundary conditions to a given order. It is noteworthy that the perturbation begins with a state in which the perturbing boundary does not exist.

We have used the perturbation expansions of these eigenvalues and eigenfunctions to determine the expansions of the first passage time of a diffusing point particle placed in regular arrays of perfectly absorbing n-spheres in two and three dimensions with the volume fraction of spheres

much less than one. For these arrays, there is a remarkable independence of the diffusion-limited reaction rate on the geometry of the array, so long as the fraction ϕ is small. Furthermore, the agreement with the easily solvable radially symmetric problems gives one confidence to use mean-field arguments and simplified geometries for calculating the rates of diffusion-limited reaction in both two and three dimensions under some circumstances.

APPENDIX A

In this Appendix we give some details of the numerical evaluation of summations required for the evaluation of the constants β_s, β_t, β_{sc}, β_{bc}, and β_{fc}.

The summation

$$
\sum_{i,j=1}^{\infty} (i^2 + j^2)^{-2} = -\frac{\pi^4}{180} + \frac{\pi\zeta(3)}{4}
$$
$$
+ \frac{\pi}{2} \sum_{j=1}^{\infty} \frac{\exp(-2j\pi)}{j^2[1-\exp(-2j\pi)]}\left[j^{-1} + \frac{2\pi}{1-\exp(-2j\pi)}\right]
$$
$$
= 0.424379776... \tag{A1}
$$

is evaluated by using formula (17.3.16) of Ref. 8 to perform one of the summations. The value of $\zeta(3)$ is given on p. 811 of Ref. 5. Only a few terms of the rapidly convergent series on the right are needed to establish the numerical value. Two other summations are similarly evaluated:

$$
\sum_{i,j=1}^{\infty} [(2i-1)^2 + (2j-1)^2]^{-2} = 0.282506814... \tag{A2}
$$

$$
\sum_{i,j=1}^{\infty} (i^2 + j^2/3)^{-2} = 0.746153867... \tag{A3}
$$

When one evaluates analogous three-indexed summations appearing in the evaluation of the constants for the three-dimensional problems, the following summation appears:

$$
\sum_{i,j=1}^{\infty} (i^2 + j^2)^{-3/2} = \pi^2/6 - \zeta(3)/2 + 4\pi \sum_{m,n=1}^{\infty} mK_1(2mn\pi)/n
$$
$$
= 1.05634852... \tag{A4}
$$

The transformation to the form on the right can be wrought by using the identity[17,18]

$$
(i^2 + j^2)^{-3/2} = \frac{2}{\pi i}\int_0^{\infty} d\xi\, \xi \sin(i\xi)\, K_0(j\xi)
$$

with $K_0(\zeta)$ the modified Bessel function of the second kind of order zero.[5] The modified Bessel function of the second kind of order one appearing in the summation is exponentially small for large values of the argument and only the nine terms with $3 > m, n \geqslant 1$ are necessary to establish the numerical value given above. Similarly,

$$\sum_{i,j=1}^{\infty} [(2i-1)^2 + (2j-1)^2]^{-3/2} = 0.51616622... \qquad (A5)$$

The summations (A4) and (A5) are used in the evaluation of

$$\sum_{i,j,k=1}^{\infty} (i^2 + j^2 + k^2)^{-2} = 0.61822741... \qquad (A6)$$

$$\sum_{i,j,k=1}^{\infty} [(2i-1)^2 + (2j-1)^2 + (2k-1)^2]^{-2} = 0.18526797... \qquad (A7)$$

$$\sum_{i,j,k=1}^{\infty} [(2i-1)^2 + (2j-1)^2 + (2k)^2]^{-2} = 0.079634357... \qquad (A8)$$

APPENDIX B

Here we give details of the numerical evaluation of the constant α_{sc} [Eq. (24)]. First, using the symmetry of $\Psi_{000}^{(1)}(\mathbf{x})$, we look at the point $(\delta, 0, 0)$. From Eq. (23)

$$\Psi_{000}^{(1)}(\delta, 0, 0) = -\frac{8}{\pi L^{3/2}} \sum_{i_1, i_2, i_3 = 0}^{\infty}{}' \frac{\cos(2\pi i_1 \delta/L)}{(1 + \delta_{i_1})(1 + \delta_{i_2})(1 + \delta_{i_3})(i_1^2 + i_2^2 + i_3^2)}$$

$$\sim \frac{1}{\delta L^{1/2}} + \frac{\alpha_{sc}}{L^{3/2}} + o(1) \qquad (B1)$$

Terms that are $o(1)$ as δ goes to zero will be omitted. One evaluates separately those elements of the sum with zero i_1, i_2, or i_3. A triple sum remains; performing the summation on i_1,

$$\sigma = \sum_{i_1, i_2, i_3 = 1}^{\infty} \frac{\cos(2\pi i_1 \delta/L)}{i_1^2 + i_2^2 + i_3^2} = \frac{\pi}{2}\sigma_1 + \pi\sigma_2 - \frac{1}{2}\sum_{i_1 i_2 = 1}^{\infty} (i_1^2 + i_2^2)^{-1} \qquad (B2)$$

with

$$\sigma_1 \equiv \sum_{i_1, i_2 = 1}^{\infty} \frac{\exp - [2\pi(i_1^2 + i_2^2)^{1/2} \delta/L]}{(i_1^2 + i_2^2)^{1/2}} \qquad (B3)$$

$$\sigma_2 \equiv \sum_{i_1, i_2 = 1}^{\infty} \frac{\exp - [2\pi(i_1^2 + i_2^2)^{1/2}]}{(i_1^2 + i_2^2)^{1/2}\{1 - \exp - [2\pi(i_1^2 + i_2^2)^{1/2}]\}} \qquad (B4)$$

The summation on the right of Eq. (B2), whose value is infinite, in the appropriate limiting operation, cancels exactly the double summation occurring from those terms in Eq. (B1) with $i_1 = 0$. Using

$$\frac{\pi}{2} \frac{e^{-\alpha a}}{a} = \int_0^\infty dx \frac{\cos \alpha x}{a^2 + x^2}$$

and performing the summation over the index i_2, one transforms Eq. (B3) to

$$\sigma_1 = \frac{\pi}{2} \sum_{i_1 = 1}^\infty \int_0^\infty dx \frac{\cos(2\pi\delta x/L)}{(i_1^2 + x^2)^{1/2}} + \frac{\pi}{4} \log \left(1 - \exp -\frac{2\pi\delta}{L} \right) + \pi\sigma_3 \quad (B5)$$

$$\sigma_3 \equiv \sum_{i_1 = 1}^\infty \int_0^\infty dx \frac{\exp -[2\pi(i_1^2 + x^2)^{1/2}]}{(i_1^2 + x^2)^{1/2} \{1 - \exp -[2\pi(i_1^2 + x^2)^{1/2}]\}} \quad (B6)$$

The summation in Eq. (B5) is performed by noting that the integral is the Bessel function of the second kind of index 0, $K_0(2\pi i_1 \delta/L)$; the summation over these Bessel functions can be performed[19]:

$$\sum_{i_1 = 1}^\infty K_0 \left(\frac{2\pi i_1 \delta}{L} \right) \sim \frac{L}{4\delta} + \frac{1}{2} \left(\gamma + \log \frac{L}{2\delta} \right) + o(1) \quad (B7)$$

$$\gamma = 0.577216...$$

Collecting these results and performing similar reductions on the terms with zero i_1, i_2, or i_3 gives

$$\alpha_{\text{sc}} = -8 \left[\frac{\pi}{24} - \frac{1}{2} \log 2 + \frac{1}{4} (\gamma - \log \pi) + l(2\pi) + \sigma_2 + \sigma_3 \right]$$

$$= 2.837297479... \quad (B8)$$

where $l(2\pi)$ is the Lambert series defined in Eq. (15). The sums σ_2 and σ_3 have the same rapid convergence; they are evaluated numerically with only those 16 terms with $4 \geqslant i_1, i_2 \geqslant 1$ for σ_2 and those four terms with $4 \geqslant i \geqslant 1$ for σ_3 and $l(2\pi)$ required to obtain the numerical value given, accurate to ten places. This value is in agreement with the only value for α_{sc}, given to ten places.[20]

This direct method of obtaining the constant α_{sc} has its advantages in the context of numerical analysis over the Ewald method. One could pursue in this fashion further terms in the expansion of $\Psi_{000}^{(1)}(\delta, 0, 0)$ in powers of δ.

ACKNOWLEDGMENTS

REFERENCES

1. Kerson Huang and C. N. Yang, *Phys. Rev.* **105**:767–775 (1957).
2. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, Vol. 2 (McGraw-Hill, New York, 1953), p. 1001.
3. J. R. Lebenhaft and R. Kapral, *J. Stat. Phys.* **20**:25–56 (1979).
4. B. U. Felderhof, *Physica* **130A**:34–56 (1985).
5. M. Abramowitz and I. Stegun, eds., *Handbook of Mathematical Functions* (U. S. Government Printing Office, Washington, D. C., 1964), p. 360.
6. R. Courant, *Differential and Integral Calculus*, Vol. 2 (Blackie, London, 1936), p. 367.
7. M. V. Berry, *Ann. Phys. (N.Y.)* **131**:163–216 (1981).
8. Eldon R. Hansen, *A Table of Series and Products* (Prentice-Hall, Englewood Cliffs, New Jersey, 1975), p. 243.
9. H. Hasimoto, *J. Fluid Mech.* **5**:317–328.
10. Linus Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935), p. 165.
11. Otto Emersleben, *Phys. Z.* **24**:73–80 (1923).
12. Otto Emersleben, *Phys. Z.* **24**:97–104 (1923).
13. Rosemary A. Coldwell-Horsfall and Alexei A. Maraudin, *J. Math. Phys.* **1**:395–404 (1960).
14. Howard C. Berg and Edward M. Purcell, *Biophys. J.* **20**:193–219 (1977).
15. Lord Rayleigh, *Phil. Mag.* **34**:481–502 (1892).
16. Harold Levine, *J. Inst. Math. Appl.* **2**:12–28 (1966).
17. Dikeos Soumpasis, *J. Chem. Phys.* **69**:3190–3196 (1978).
18. G. N. Watson, *A Treatise on the Theory of Bessel Functions*, 2nd ed. (University Press, Cambridge, 1966), p. 388.
19. I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic Press, New York, 1980), p. 978.
20. W. L. Slattery, G. D. Doolen, and H. E. DeWitt, *Phys. Rev. A* **21**:2087–2095 (1980).