Statistics of Particle Diffusion in Spherical Geometry*

B. T. McClure
Minneapolis-Honeywell Research Center, Hopkins, Minnesota
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The diffusion of particles from the center of a sphere of radius R is considered theoretically. An expression is obtained for the probability that a particle will be collected at a small probe within the sphere rather than at the surface. This result forms the basis for an experiment to determine the momentum transfer cross section Q_m for electrons in a gas. The only parameter which must be known in order to obtain absolute cross sections by the technique proposed is the acceptance coefficient for electrons at the probe. The probability A_c that a particle will have exactly c collisions characterized by a constant cross section Q before striking the surface of the sphere for the first time is evaluated. It is assumed that these collisions are not correlated with the diffusion process. In contrast with previous work the present method takes into account the variation of total diffusion time as well as the probability of a particular number of collisions during a given time. The probabilities A_0, A_1, and A_2 are given in terms of elementary functions and a recursion relationship is given for the other A's. The expression $A_0=y \operatorname{csch} y$ (where $y=RN(3QQ_m)^{1/2}$ and N is the gas density) is useful in an experiment to determine the cross section for inelastic collisions between electrons and gases. The probability of more than any given number of collisions, the average number of collisions, and the mean-square deviation from this average are also evaluated.

I. INTRODUCTION

THE principal objective of this work is to develop the theoretical basis for a diffusion experiment to determine the cross section for inelastic collisions between electrons and gases. The relevant experimental technique is essentially the same as that of Maier-Leibnitz[1] who used the theory of Harries and Hertz.[2] We develop results in spherical geometry rather than in the cylindrical geometry employed by Maier-Leibnitz. This geometry has several advantages which will not be discussed in detail.

The first situation to be considered is a steady state in which a constant particle current flows to a partially reflective surface. We obtain a relationship between gas density and the current collected by a suitable probe within the sphere. The result suggests a simple technique for determining the momentum transfer cross section which is fundamental in the interpretation of any diffusion experiment.

Before discussing the statistics of the collisions suffered by particles as they diffuse from the center to the surface of a sphere we evaluate the probability that a particle which is at the center of a sphere at $t=0$ will reach the surface during $(t, t+dt)$. This is done in detail only for the case of a completely absorbing surface. We then integrate the Poisson distribution of the number of collisions during a given interval over the distribution of arrival times at the surface. This approach differs from that of Hertz *et al.* in that the Poisson distribution is invoked before rather than after averaging over various times.

Although this work is motivated by our interest in the diffusion of electrons in a gas the conclusions which we reach are, with suitable modification, applicable to the diffusion of any sort of particles in spherical geometry so long as the cross sections remain constant. For example, one might consider the diffusion of atoms excited to a metastable state or the diffusion of neutrons. In these cases it would be more difficult to realize experimental conditions which conform closely to the model we discuss than it would be for the case of electrons in a gas.

II. STEADY-STATE SOLUTION

When first-order transport theory applies, the net particle current density due to diffusion is[3–7]

$$\mathbf{\Gamma}=-\nabla(DF), \tag{1}$$

where F denotes the density of diffusing particles. We shall consider the diffusion of particles which all have the same speed v. In this case the f_0^0 of Allis[8] Eq. (30.5) is an appropriately normalized delta function and

$$D=v/3NQ_m. \tag{2}$$

The density of particles with which the diffusing particles collide is N and the momentum transfer cross section which characterizes the collisions is Q_m. Let $\sigma(\theta)$ denote the cross section for scattering by an angle θ

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[1] H. Maier-Leibnitz, Z. Physik **95**, 499 (1935).

[2] W. Harries and G. Hertz, Z. Physik **46**, 177 (1927).

[3] W. P. Allis, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 383. Alternative expressions for D in terms of ν, l, or Q are discussed in this reference as well as in the subsequent references 4–6.

[4] David J. Rose and Melville Clark, Jr., *Plasmas and Controlled Fusion* (Tech. Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1961), pp. 14, 63 ff.

[5] Sanborn C. Brown, *Basic Data of Plasma Physics* (Tech. Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1959), pp. 24 and 47.

[6] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), Chap. I.

[7] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943). The transition from the random walk viewpoint to the diffusion viewpoint is discussed in Chap. I.

[8] Reference 3, p. 412.

into a solid angle $d\Omega$, then[3–6]

$$Q_m = \int \sigma(\theta)(1-\cos\theta)d\Omega.$$

Consider Eq. (1) for the steady state in which a constant particle current, I, flows isotropically from a source at the center of a sphere and D is independent of position. Conservation of particles requires that the current be independent of the distance r from the source. Thus

$$I = 4\pi r^2 \Gamma_r = -4\pi r^2 D dF/dr, \tag{3}$$

except at $r=0$. Let $J(r)=F(r)v/4$ denote the random particle current density. The boundary condition which conserves particles at the surface $r=R$ having an acceptance coefficient B_w is

$$\Gamma_R = -D\frac{dF}{dr}\bigg|_R = B_w J(R) = \frac{F(R)vB_w}{4}. \tag{4}$$

The solution of Eq. (3) which satisfies Eq. (4) is

$$F(r) = \frac{I}{4\pi D}\left(\frac{1}{r}-\frac{1}{R}\right)+\frac{I}{\pi R^2 v B_w}. \tag{5}$$

This equation gives the steady-state density of particles everywhere except within about one mean free path of $r=0$ or $r=R$.

We now consider the particle current collected by a probe situated within the sphere. In order that Eq. (5) describe the spatial distribution of *charged* particles there must be no electric field within the sphere. It is especially important that the probe itself introduce no field because such a field would preferentially disturb the distribution near the probe and thus influence the current collected. In order that the probe not disturb the distribution given by Eq. (5), it is also necessary that the probe be small enough so that the current i which it collects is a negligible fraction of I. The total current collected by a probe satisfying these conditions is

$$i = \int BJ(r)dS = \frac{Bv}{4}\int F(r)dS, \tag{6}$$

where the integration extends over the area S of the probe and B is the acceptance coefficient of the probe surface.

Let $H=i/I$ denote the proportion of the total current which is collected by the probe. When the expression for $F(r)$ given by Eq. (5) and the value of D given by Eq. (2) are put into Eq. (6), we obtain

$$H = \frac{B}{16\pi}\left[\frac{4S}{R^2 B_w}+3NQ_m\int\left(\frac{1}{r}-\frac{1}{R}\right)dS\right]. \tag{7}$$

If we let $B=B_w=1$, the value of H given by Eq. (7) is the probability that a particle diffusing from the center of a sphere will *collide with* the probe before it reaches the surface of the sphere. With general values of B and B_w, H is the probability that the particle will be *collected* by the probe rather than by the surface of the sphere.

Equation (7) predicts that when first-order transport theory applies and the probe satisfies the conditions specified preceding Eq. (6), H is a linear function of N for a given electron energy. This result suggests the following procedure to determine Q_m as a function of electron energy: plot measured values of H as a function of N for various energies. The results should be straight lines with nonzero intercepts which depend upon the acceptance coefficient of the sphere. The slope of one of these lines is a measure of Q_m at the energy in question. We see from Eq. (7) that

$$Q_m = (16\pi dH/dN)\Big/ 3B\int(1/r-1/R)dS. \tag{8}$$

This expression involves only the acceptance coefficient of the probe surface and the geometric factor which is incorporated in the integral. In case all of the probe surface is located at $r=R/2$ the geometric factor is simply S/R so that Eq. (8) becomes $Q_m=16\pi R(dH/dN)/3BS$. Since Eq. (5) is not valid near $r=0$ or $r=R$, the probe used for an experimental determination of dH/dN in Eq. (8) must not collect a significant current from either of these regions.

The technique we have suggested is worthwhile because it gives a direct determination of the cross section for momentum transfer collisions. It incorporates the factor $(1-\cos\theta)$ without requiring auxiliary scattering experiments or calculation. In a sense, an apparatus fulfilling the conditions of this theory would be an analog computer for evaluating Q_m.

We have considered the diffusion of particles which all have the same speed and cross section. A value of Q_m given by Eq. (8) represents an average over the actual energy distribution. Thus, the technique is most useful when the energy distribution of the electrons is narrow compared to the average. The theory does not take into account any asymmetry of the source. In an experiment involving electrons in a gas one should, therefore, strive for an isotropic source which supplies as nearly monoenergetic electrons as possible. In the absence of inelastic collisions, gas density can be chosen large enough so that diffusion theory applies but small enough so that the electron energy changes very little during diffusion. When inelastic collisions occur, some loss of resolution results. The extent of this loss depends upon the cross sections in the particular gas being studied.

III. DISTRIBUTION OF ARRIVAL TIMES

In order to evaluate the probability $K(t)dt$ that a particle which is at the center of a sphere at $t=0$ will arrive at $r=R$ during $(t, t+dt)$, we consider the probability current associated with the diffusion of a single particle. Let $W(r,t)dV$ be the conditional probability of finding a particle known to be at the origin at $t=0$ in dV at time t. Chandrasekhar[7] and others have shown that after a time long enough for many collisions $W(r,t)$ satisfies a diffusion equation with appropriate boundary conditions. In the case we are considering, the diffusion coefficient is given by Eq. (2) and is independent of r. The appropriate equation is

$$\partial W/\partial t = D\nabla^2 W.$$

For a spherically symmetric problem, this becomes

$$\frac{\partial W}{\partial t}=\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial W}{\partial r}\right). \tag{9}$$

In contrast with the discussion of Sec. II, we neglect reflection at the surface of the sphere. We shall obtain at the end of Sec. IV certain approximate results which apply when the surface is reflective. The appropriate initial and boundary conditions in the present case are

$$4\pi r^2 W(r,0)=\delta(r), \tag{10a}$$

$$W(R,t)=0, \tag{10b}$$

where $\delta(r)$ is zero except at $r=0$ and $\int\delta(r)dr=1$ whenever the range of integration includes $r=0$. Upon making the substitution $G(r,t)=rW(r,t)$, Eqs. (9) and (10) become

$$\partial G/\partial t = D\partial^2 G/\partial r^2, \tag{11a}$$

$$4\pi r G(r,0)=\delta(r), \tag{11b}$$

$$G(R,t)=0. \tag{11c}$$

An uncritical application of the recipe for determining Fourier coefficients leads to the following "solution" of Eq. (11a) subject to Eqs. (11b) and (11c):

$$G(r,t)=\frac{1}{2R^2}\sum_{s=1}^{\infty} s\sin\frac{sr}{\Lambda}\exp(-s^2t/T), \tag{12}$$

where $\Lambda\equiv R/\pi$ and $T\equiv\Lambda^2/D$. In the text we ignore the fact that this series does not converge for $t=0$ and proceed heuristically. A somewhat more satisfactory discussion leading to the same conclusions is contained in the Appendix.

The net probability current at $r=R$ is

$$\begin{aligned} K(t)&=[-4\pi r^2 D\nabla W]_R \\ &=-4\pi R^2 D\left[\frac{r\partial G/\partial r - G}{r^2}\right]_R \\ &=-4\pi RD(\partial G/\partial r)_R. \end{aligned} \tag{13}$$

We substitute the expression for G given by Eq. (12) into the last line of Eq. (13) and interchange the order of summation and differentiation. This is justified when the resulting series converges. Thus,

$$K(t)=\frac{2}{T}\sum_{s=1}^{\infty}(-)^{s+1}s^2\exp(-s^2t/T), \tag{14}$$

except at $t=0$ when $K(t)$ is known to be zero. This equation gives the distribution of arrival times at the surface $r=R$ for particles which are at the center of the sphere at $t=0$.

IV. PROBABILITY OF A PARTICULAR NUMBER OF COLLISIONS

We wish to determine the probability A_c that a particle which diffuses from the center of a sphere will have had exactly c collisions characterized by a cross section Q before it reaches the surface $r=R$. First, we determine the probability P_c that such a particle will have exactly c collisions during a time t. Let the average collision rate of the particle be $\nu=NQv$. Divide the interval of duration t into k equal intervals. If the probability q of a Q-type collision in each of these intervals is independent of what occurs in the other intervals, P_c is given by the binomial distribution $[k!/c!(k-c)!]q^c(1-q)^{k-c}$, where $q=\nu t/k$. In the limit of large k this approaches the Poisson distribution so that

$$P_c(\nu t)=\frac{(\nu t)^c\exp(-\nu t)}{c!}. \tag{15}$$

Insofar as the diffusion process is independent of the Q-type collisions, $P_c(\nu t)$ and $K(t)$ are uncorrelated and the probability A_c is given by the integral

$$A_c=\int_0^{\infty}P_c(\nu t)K(t)dt. \tag{16}$$

The assumptions we have made are less restrictive than those of Maier-Leibnitz, Hertz, *et al.* For comparison their argument is paraphrased in italics. *The average number of collisions $\bar{c}$ which a particle has while diffusing to a surface is equal to the integral of the total collision rate per unit volume weighted by the probability that a particle from an element of volume will reach the surface in question divided by the total rate at which particles reach the surface.* In our geometry all particles reach the surface so that $\bar{c}$ is equal to (ν/I) multiplied by the total number of diffusing particles in the space, i.e., $\bar{c}=(\nu/I)\int FdV$. When $\bar{c}$ is evaluated in this way using the expression for F given by Eq. (5) *without* the term involving reflection, we find $\bar{c}=y^2/6$ where

$$y^2\equiv\nu R^2/D=\pi^2\nu T=3(NR)^2QQ_m. \tag{17}$$

If the average number of collisions experienced by a particle before it reaches a surface is $\bar{c}$ the probability that it will have had no collisions is $exp(-\bar{c})$. This conclusion would follow if all particles, in fact, required the same time to reach the surface, for then A_c would be given directly by the Poisson distribution. The difference between this work and that of Hertz is that we treat t in Eq. (15) as a variable and not as an average time. We shall see that this approach gives different expressions for A_c than would be obtained by following Hertz's reasoning. However, when the average over all A_c's is evaluated, one still obtains $\bar{c}=y^2/6$.

The application of diffusion theory places no restrictions on the magnitude of y itself. However, there must be an adequate number of momentum transfer collisions. This is assured when $3(NRQ_m)^2$ is not too small.

When Eqs. (14) and (15) are substituted into Eq. (16) and the order of summation and integration is reversed, we obtain

$$A_c=\frac{2\nu^c}{Tc!}\sum_{s=1}^{\infty}(-)^{s+1}s^2L_c, \tag{18}$$

where $L_c\equiv\int_0^\infty t^c\exp(-\nu t)\exp(-s^2t/T)dt$. In order to simplify the integrals of Eq. (18), let $x=t(\nu+s^2/T)$. Then

$$L_c=\int_0^\infty x^ce^{-x}dx\Big/(\nu+s^2/T)^{c+1}. \tag{19}$$

Note that the numerator of this expression is equal to $c!$. When Eqs. (17) and (19) are substituted in Eq. (18), we obtain

$$A_c(y)=\frac{2\pi^2}{y^2}\sum_{s=1}^{\infty}\frac{(-)^{s+1}s^2}{[1+(\pi s/y)^2]^{c+1}}. \tag{20}$$

For finite y, these series are summable for $c=0$ and convergent for all other c. As indicated by the notation adopted at this point, A_c depends only upon the variable y.

We have obtained an expression for $A_c(y)$ assuming that Q and Q_m are constant. If inelastic collisions occur, Eq. (20) is not valid for particles whose energy is changed enough so that Q or Q_m is altered. We must also recall that the result applies to the collisions suffered before a particle reaches the surface $r=R$. In case the surface reflects some of the particles, the result we have obtained is valid only as the particles reach the surface for the first time.

It would be quite cumbersome to evaluate A_c considering the possibility of reflection at the surface $r=R$ because the boundary condition given by Eq. (10b) would be replaced by the more complicated Eq. (4). However, we can obtain an approximation which takes into account reflection at the surface if we ignore the distribution of arrival times. When the complete Eq. (5) is used for $F(r)$, the average number of collisions is

$$\bar{h}=(\nu/I)\int F(r)dV=\frac{y}{6}\left[y+\frac{8}{B_w}\left(\frac{Q}{3Q_m}\right)^{1/2}\right].$$

In the approximation that all particles reach the surface at $\bar{t}=\bar{h}/\nu$ the A_c's are given by $A_c=\bar{h}^c(1/c!)\exp(-\bar{h})$.

V. EVALUATION OF $A_c(y)$

In working with the probabilities $A_c(y)$ it is convenient to define the series

$$U_c(y)=2\sum_{s=1}^{\infty}\frac{(-)^{s+1}}{[1+(s\pi/y)^2]^c}. \tag{21}$$

Like the A_c's these series are summable for $c=0$ and convergent for other c's. The series $U_0(y)$ sums to 1. According to Whittaker and Watson,[9]

$$\text{csch}y=1/y-2y\sum_{s=1}^{\infty}(-)^{s+1}/(y^2+s^2\pi^2).$$

From this result we see that $U_1=1-y\,\text{csch}y$.

Consider the difference between successive $U_c(y)$'s.

$$\begin{aligned}U_c-U_{c+1}&=2\sum_{s=1}^{\infty}(-)^{s+1}\left(\frac{1}{[1+(s\pi/y)^2]^c}-\frac{1}{[1+(s\pi/y)^2]^{c+1}}\right) \\ &=2\sum_{s=1}^{\infty}(-)^{s+1}\left(\frac{(s\pi/y)^2}{[1+(s\pi/y)^2]^{c+1}}\right) \\ &=A_c(y).\end{aligned} \tag{22}$$

The rearrangement of the terms of the U series which is done in the first line of Eq. (22) is justified by the absolute convergence of the series except for $c=0$. From Eqs. (20) and (21) it can be shown directly that A_0 sums to (U_0-U_1). Using the particular values of U_0 and U_1 given following Eq. (21), we see that the probability that a particle will reach the surface $r=R$ without having a Q-type collision is $A_0=y\,\text{csch}y$. This result is to be compared with $\exp(-y^2/6)$ obtained following Eq. (17) by extending the reasoning of Hertz to spherical geometry. For small y both $\exp(-y^2/6)$ and $A_0\approx1-y^2/6$. The difference between A_0 and $\exp(-y^2/6)$ is quite important for large y, however; for then $A_0\approx2y\exp(-y)$. This shows that the contribution to A_0 of arrival times earlier than the average changes the $\exp(-y^2/6)$ dependence into one which decreases less rapidly than $\exp(-y)$.

Consider the derivative of $U_c(y)$

$$\begin{aligned}\frac{dU_c(y)}{dy}&=2\sum_{s=1}^{\infty}\frac{(-c)(-)^{s+1}(-2s^2\pi^2/y^3)}{[1+(s\pi/y)^2]^{c+1}} \\ &=\frac{2c}{y}A_c(y).\end{aligned} \tag{23}$$

The series which result from the interchange of the

[9] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1952), 4th ed., p. 136.

order of differentiation and summation in Eq. (23) converge except for $c=0$ so the resulting expression is valid except for $c=0$. From Eqs. (22) and (23) we obtain a recursion relationship between successive U_c's: $U_{c+1}=U_c-(y/2c)(dU_c/dy)$. With this result it is possible to obtain any U_c in terms of $U_1=1-y\,\text{csch}y$.

Equation (22) enables us to express the probability that the number of collisions will be between α and β inclusive as the difference between two U's:

$$\sum_{n=\alpha}^{\beta} A_n=U_\alpha-U_{\beta+1}.$$

The case $\alpha=0$, $\beta=c-1$ is particularly useful:

$$\sum_{n=0}^{c-1} A_n=1-U_c. \tag{24}$$

When Eq. (24) is substituted into the expression for $A_c(y)$ obtained from Eq. (23) we find

$$A_c(y)=\frac{-y}{2c}\frac{d}{dy}\Big[\sum_{n=0}^{c-1} A_n(y)\Big].$$

Thus, we can obtain any A_c except A_0 in terms of the A_c's of smaller index. This is a practical way to obtain the first few A_c's. For example

$$A_1(y)=-(y/2)dA_0/dy=(y/2)\,\text{csch}y(y\,\text{coth}y-1)$$

and

$$A_2(y)=-(y/4)d(A_0+A_1)/dy$$
$$=(y/8)\,\text{csch}y[(y^2-1)+2y^2\,\text{csch}^2y-y\,\text{coth}y].$$

The result given by Eq. (24) also yields an interesting physical interpretation of U_c. The probability of some number $(0,1,2,\cdots)$ of collisions is unity. Thus, since the probability of $c-1$ or fewer collisions is $(1-U_c)$, U_c is the probability of c or more collisions.

VI. MEAN COLLISION NUMBERS AND rms DEVIATION FROM THE MEAN

The mean number of collisions can be evaluated using Eqs. (21) and (22).

$$\bar{c}=\sum_{n=1}^{\infty} nA_n(y)$$
$$=(U_1-U_2)+2(U_2-U_3)+\cdots+n(U_n-U_{n+1})+\cdots$$
$$=\sum_{n=1}^{\infty} U_n(y)-\lim_{n\to\infty}[nU_{n+1}(y)]$$
$$=2\sum_{n=1}^{\infty}\sum_{s=1}^{\infty}\frac{(-)^{s+1}}{[1+(s\pi/y)^2]^n}.$$

The fourth line follows from the third because the limit term is zero for preassigned, finite y. Because each of the U series converges absolutely, the order of the summations may be interchanged. When this is done and we note that

$$\sum_{n=1}^{\infty}[1+(s\pi/y)^2]^{-n}=(s\pi/y)^{-2},$$

we find that

$$\bar{c}=2(y/\pi)^2\sum_{s=1}^{\infty}\frac{(-)^{s+1}}{s^2}$$
$$=y^2/6, \tag{25}$$

in agreement with the result obtained in the discussion following Eq. (17). The rms deviation of the collision numbers from $\bar{c}$ may be evaluated by considerations similar to those preceding Eq. (25). The result turns out to be

$$\langle(c-\bar{c})^2\rangle_{\text{av}}^{1/2}=[\bar{c}(1+2\bar{c}/5)]^{1/2}.$$

When the variation of the path length during diffusion is ignored the rms deviation from the mean is just $(\bar{c})^{1/2}$.

VII. SUMMARY

We have shown that the relationship between the momentum transfer cross section Q_m and the current collected by a suitable probe is given by Eq. (8). This result is the basis for a direct experiment to determine Q_m.

We have determined the probability that a particle will have any given number of collisions characterized by a cross section Q as it diffuses from the center to the surface of a sphere. In particular the probability that it will have no Q-type collisions is $y\,\text{csch}y$, where y is defined by Eq. (17). This result differs considerably from that which would be obtained by applying the method of Hertz *et al.* in spherical geometry because we have considered the variation of the paths which particles take during diffusion. This consideration alters the interpretation of experiments to determine inelastic cross sections with diffusion techniques by virtue of introducing a different relationship between the cross sections and the measured probability of reaching a surface without having had a collision.

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APPENDIX. ALTERNATIVE TREATMENT OF THE TRANSIENT PROBLEM

In order to avoid the complications associated with the series on the right side of Eq. (12) it is helpful to substitute a well-behaved function for $\delta(r)$ in Eq. (11b). A derivation analogous to that contained in the text then proceeds straightforwardly. A single interchange of the order of a limiting process and a summation is required in the final step to evaluate the probabilities A_c.

Instead of the initial condition given by Eq. (11b) of the text consider the following:

$$G_\epsilon(r,0)=0 \quad \text{for} \quad r>\epsilon, \qquad (A1)$$
$$=3r/4\pi\epsilon^3 \quad \text{for} \quad r\leq\epsilon,$$

where ϵ is any radius satisfying $0<\epsilon<R$. Note that $G_\epsilon(r,0)$ defined in this way is normalized so that

$$\int_0^R W(r,0)dV=\int_0^R (1/r)G_\epsilon(r,0)dV=1.$$

For small ϵ, the initial density is concentrated near $r=0$. Each term of the expression

$$G_\epsilon(r,t)=\frac{3\Lambda}{2\pi^2\epsilon^3}\sum_{s=1}^{\infty}\frac{a_s(\epsilon)}{s^2}\sin\left(\frac{rs}{\Lambda}\right)\exp(-s^2t/T) \qquad (A2)$$

satisfies Eqs. (11a) and (11c) when s is an integer, $\Lambda\equiv R/\pi$ and $T\equiv\Lambda^2/D$. The coefficients $a_s(\epsilon)$ can be chosen so that $G_\epsilon(r,0)$ satisfies Eq. (A1):

$$a_s(\epsilon)=\frac{2\pi^2\epsilon^3s^2}{3\Lambda}\left[\int_0^R G_\epsilon(r,0)\sin(rs/\Lambda)dr\right]\bigg/\int_0^R \sin^2(rs/\Lambda)dr$$
$$=\sin(\epsilon s/\Lambda)-(\epsilon s/\Lambda)\cos(\epsilon s/\Lambda).$$

The function $G_\epsilon(r,0)$ satisfies the hypotheses of Fourier's theorem[10] for any $\epsilon>0$. This assures us that, since the coefficients $a_s(\epsilon)$ have been determined by the prescribed method, the series on the right side of Eq. (A2) evaluated for $t=0$ converges to $G_\epsilon(r,0)$ except for $r=\epsilon$. We substitute the expression given by Eq. (A2) into $K(t,\epsilon)=-4\pi RD[\partial G_\epsilon(r,t)/\partial r]_R$. The result,

$$K(t,\epsilon)=\frac{6RD}{\pi\epsilon^3}\sum_{s=1}^{\infty}\frac{(-)^{s+1}a_s(\epsilon)}{s}\exp(-s^2t/T), \qquad (A3)$$

is valid whenever ϵ and t are positive. When $K(t,\epsilon)$ given by Eq. (A3) replaces $K(t)$ in Eq. (16) we find an expression analogous to Eq. (18) which is well behaved for nonzero ϵ:

$$A_c(y,\epsilon)=\frac{6}{\pi y^2}\left(\frac{R}{\epsilon}\right)^3\sum_{s=1}^{\infty}\frac{(-)^{s+1}a_s(\epsilon)}{s[1+(s\pi/y)^2]^{c+1}}. \qquad (A4)$$

The physical situation with which we are concerned corresponds to the limit of small ϵ. Equation (20) of the text follows from Eq. (A4) if we take this $\lim_{\epsilon\to0}A_c(y,\epsilon)$ by interchanging the order of differentiations with respect to ϵ and summation of the series.

If we define a function $U_c(y,\epsilon)$ analogous to $U_c(y)$ in Eq. (21) as follows:

$$U_c(y,\epsilon)=6\left(\frac{\Lambda}{\epsilon}\right)^3\sum_{s=1}^{\infty}\frac{(-)^{s+1}a_s(\epsilon)}{s^3[1+(s\pi/y)^2]^c}. \qquad (A5)$$

We find that

$$A_c(y,\epsilon)=U_c(y,\epsilon)-U_{c+1}(y,\epsilon). \qquad (A6)$$

The series $U_0(y,\epsilon)$ obtained by taking $c=0$ in Eq. (A5) converges to 1 for any ϵ satisfying $0<\epsilon<R$. As ϵ approaches 0, $U_1(y,\epsilon)$ approaches

$$2y^2\sum_{s=1}^{\infty}(-)^{s+1}/[y^2+(s\pi)^2],$$

which is a series representation of $1-y\,\text{csch}y$. These results together with Eq. (A6) yield the following result: $\lim_{\epsilon\to0}A_c(y,\epsilon)=y\,\text{csch}y$. The reasoning used here is easier to justify than the heuristic line followed in the text.

[10] Reference 9, p. 175.