Microscopic theory for the diffusive evolution of an isoconcentration surface

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We determine the schedule for the diffusive evolution of isoconcentration "surfaces" into a semi-infinite region, initially empty of diffusant, for a particular time-invariant boundary condition corresponding to constant diffusant concentration. This result is obtained by exploiting the correspondence between solutions of the Fokker-Planck equation for this boundary-value problem and the known fundamental solution in an unbounded space. We find that the initial evolution is linear, as predicted by us in earlier work, while the long-time behavior is as $t^{1/2}$, which is the solution predicted from the diffusion equation over the entire time domain. The transition between these limiting regions is described by a more complicated functional dependence.

I. INTRODUCTION

Moving boundary problems involving diffusion processes appear in a wide variety of situations[1,2] of topical interest. Mathematically similar problems are also encountered in the context of the heat equation and both types of problems are often referred to as Stefan problems.[3] The only exact solutions for these problems that we are aware of are of the similarity type that exploit the occurrence of a similarity variable $\bar{x}=\alpha x t^{-1/2}$. Since these only apply in relatively few cases, many approximate analytical and numerical procedures have been devised for more general situations.[1,2] The macroscopic level of description is utilized in all these treatments, with the diffusion and heat equations providing the dynamical description. We restrict our attention here to the former, which as is well known,[4] is inaccurate in both temporal and spatial boundary layers where microscopic scale effects can play an important role.

Previously, we considered several situations where a moving boundary evolves as the result of a diffusion process in the context of a low-level approximation to the Fokker-Planck equation (FPE).[5,6] In each instance we have shown that the universal boundary growth $x^*=at^{1/2}$ predicted by the diffusion equation (DE) is only correct at long times and that the initial layer characterizing prediffusive ballistic motion is described by a linear growth law $x^*=a't$. We have been unable to obtain, however, the general growth law which has these two limits at short and long times. Our purpose here is to examine a very simple moving boundary problem which has similar features, i.e., a universal growth law $x^*=at^{1/2}$ predicted by the DE, for which we are also able to obtain an *exact* closed solution for the FPE. Even for the case of fixed boundary value problems we are unaware of *any* similar results for the FPE except for that of a reflecting boundary[7] that follows, by the method of images, from the fundamental solution in an unbounded region.[8] Like the latter, the solution we obtain is also derived from the unbounded region fundamental solution, but as will be discussed later, our result is less general.

The physical problem we consider is quite simple: the evolution of a surface of constant concentration in a semi-infinite space $0 \le x \le \infty$, initially at zero density of diffusant, when the boundary $x=0$ is maintained at constant concentration. Our interest is motivated by the total lack of any supplementary conditions such as are usually required at the evolving interface, e.g., flux matching. Despite its relative simplicity, this problem also results in the universal $t^{1/2}$ growth law found in more complicated situations in the context of the DE, and it is likely that the growth law found at the FPE level of description is also characteristic of such situations. Although our primary interest in this problem here is thus to gain insight into more interesting situations, we do note, without elaboration, later (Sec. IV) one particular limited application of the result obtained.

The rest of the paper proceeds as follows. Section II describes the DE solution, including the correspondence relationship that allows us to apply the solution for an unbounded domain to the boundary value problem described earlier. In Sec. III we consider the FPE solution and also note an interesting related result which is implicit in some earlier work[9] utilizing a different approach and does not seem to be widely known. The concluding section (Sec. IV) contains a discussion of the results obtained, including a description of one limited direct application.

II. DIFFUSION EQUATION SOLUTION

Consider the situation where initially the concentration of diffusant $c(x,t)$ in $0<x<\infty$ is identically zero and for $t>0$ $c(0,t)=c_0$. If $c(x,t)$ satisfies the DE, $c_t=Dc_{xx}$, then the unique solution that satisfies the above conditions is

$$c(x,t)=c_0\left[1-\operatorname{erf}\frac{x}{(4Dt)^{1/2}}\right] . \tag{1}$$

Therefore the constant concentration "surface" $c=c^*<c_0$ is specified by $x^*(t)$, which is given by Eq. (1) as

$$x^*(t)=a(4Dt)^{1/2} , \tag{2}$$

where

$$1-\frac{c^*}{c_0}=\text{erf}(a) , \tag{3}$$

i.e., $xt^{-1/2}$ is a similarity variable.

Equation (1) results from the solution of an explicit boundary-value problem. In the case of the FPE, explicit boundary-value problems pose a formidable challenge and we are unaware of any closed-form solutions that have been obtained, except for the case of a reflecting boundary[7] where the solution is obtained from the method of images from the known fundamental solution for an unbounded region.[8] With this latter result in mind, we now consider the solution for the DE in an unbounded region for the situation where $c(x,0)=2c_0H(-x)$ with $H(x)$ the standard Heaviside function, i.e., initially the negative half-space has a uniform concentration $2c_0$ while the positive half-space is at concentration zero. The solution for this initial value problem is identical to Eq. (1). Regarding that result now in the context of the initial value problem, we can directly infer the solution to the boundary-value problem by noting that the concentration $c(0,t)$ remains fixed at c_0. Thus we are encouraged to look for a similar correspondence between solutions of the FPE in which the solution for the semi-infinite boundary value problem follows from the solution of an initial value problem in an unbounded space. The latter can, in principle, then be found directly from the known fundamental solution[8] by standard methods. We now show that this program can be implemented explicitly in the context of the problem we are considering.

III. FOKKER-PLANCK EQUATION SOLUTION

The FPE describes the distribution function $F(x,v,t;x_0,v_0)$ in the extended position-velocity (x-v) space[4] and provides a description at the microscopic level in contradistinction to the DE which is limited to the macroscopic level of description.[10] Here the subscripts denote initial values. The connection with the macroscopic description is through relationships between moments of F and the macroscopic variables, e.g.,[11]

$$\hat{c}(x,t)=\int dx_0dv_0F(x_0,v_0)\int dv\, F(x,v,t;x_0,v_0) , \tag{4}$$

where $F(x_0,v_0)$ is the initial state distribution function. For the situation

$$F(x_0,v_0)=f^0(v)2c_0H(-x_0) , \tag{5}$$

where f^0 is the Maxwell-Boltzmann equilibrium velocity distribution function, we can integrate the known fundamental unbounded solution F_∞ as indicated in Eq. (4), and we obtain

$$\hat{c}(x,t)=c_0\left[1-\text{erf}\frac{x\xi}{(4kT)^{1/2}(t\xi-1+\theta)^{1/2}}\right] , \tag{6}$$

where $\xi=kT/D$ is the friction coefficient and $\theta=\exp-\xi t$.

Since $\hat{c}(0,t)=c_0$, we again have a correspondence between the solution of a boundary value problem and an initial value problem in an unbounded space. However, as noted earlier, this result is less general than in the corresponding DE case. Here we have the solution for a particular boundary condition that corresponds to Eq. (5), and not for the general case. Specifically, the boundary condition is given from

$$F(x,v,t)=\int dx_0dv_0f^0(v)2c_0H(-x)F_\infty(x,v,t;x_0,v_0) \tag{7a}$$

$$=f^0(v)c_0[1-\text{erf}A(x,v,t)] , \tag{7b}$$

where

$$A(x,v,t)=\frac{x\xi+(1-\theta)v}{(2kT)^{1/2}(2t\xi-3+4\theta-\theta^2)^{1/2}} , \tag{8}$$

and at the boundary, $x=0$.

The physical requirement that $\hat{c}(0,t)=c_0$ can be satisfied by an infinite number of choices for $F(0,v,t)$. In principle, the initial condition $F(x_0,v_0)$ corresponding to a specific boundary condition can be found by solving the integral equation

$$F(0,v,t)=\int dx_0dv_0F(x_0,v_0)F_\infty(0,v,t;x_0,v_0) , \tag{9}$$

but in general this will be a formidable task. In any event, the question of an appropriate boundary condition to use in a microscopic description is problematic.[12] This issue has not received a great deal of attention, beyond elaborations of Maxwell's original treatment for scattering at a wall,[12] because of the overwhelming emphasis on approximate solutions with the distribution function represented in terms of a few of its moments, which requires boundary conditions only for the latter.

Before considering the above result, Eq. (6) for $\hat{c}(x,t)$ in Sec. IV, we digress briefly to consider some of the details related to how this result was obtained. A related result was obtained much earlier by Mazo,[9] who explicitly found

$$F(x,t;x_0,v_0)=\int dv\, F_\infty(x,v,t;x_0,v_0) . \tag{10}$$

Although he did not then determine $\hat{c}(x,t)$, he did explicitly obtain the generalized diffusion equation (GDE) that describes that quantity and, implicitly, a generalized Fick's law. By proceeding more directly we have elided the need to solve a GDE: however, that information, as well as the explicit generalized Fick's law, emerges as we proceed from Eq. (4) to Eq. (6), e.g., we found that the necessary integration could be carried out most simply by evaluating $\hat{c}_x(x,t)$ (and integrating the result) rather than determining $\hat{c}(x,t)$ directly, and in this process the following relationship between the flux $j(x,t)$ and $\hat{c}(x,t)$ becomes clear:

$$j(x,t)=\int dv\, vF(x,v,t) \tag{11a}$$

$$=-\int dv\, vf^0(v)c_0[1-\text{erf}A(x,v,t)] \tag{11b}$$

$$=-(1-\theta)D\hat{c}_x(x,t) . \tag{11c}$$

This is Fick's law with a time-dependent diffusion coefficient $(1-\theta)D$ (which reduces to D for $t\xi\gg 1$).

IV. RESULTS AND DISCUSSION

The schedule for the constant concentration surface is found by inspection from Eq. (6),

$$\hat{x}^*(t)=(4D)^{1/2}a[t+\xi^{-1}(\theta-1)]^{1/2} . \quad (12)$$

The initial layer is seen to develop linearly as described by us earlier[5,6] with a transition to the characteristic diffusive $t^{1/2}$ behavior, which prevails for times $\xi t \gg 1$. A transitional growth, combining both algebraic and exponential behavior, connects the asymptotic regions. It is clear from Eq. (12) that the ratio of the DE result Eq. (2) to the FPE result Eq. (12) depends on the value of ξt only (see Fig. 1),

$$E(\xi t)\equiv\frac{x^*(t)}{\hat{x}^*(t)}=[1+(\xi t)^{-1}(\theta-1)]^{-1/2} , \quad (13)$$

and that the initial and transient growth determined from the latter result will be slower than that predicted by the DE, i.e., $E(\xi t)\geq 1$ with equality reached (approximately) for $\xi t \sim 0(10^1)$. Some typical values of ξ^{-1} range from 10^5 in aerosol systems, for particles of unit density and radius 2×10^{-6} cm at 23 °C, to 10^{15} for aluminum atoms in silicon at 1300 °C, and smaller and larger values also occur.

The particular value of the foregoing is that we have been able to demonstrate an explicit result for a simple moving boundary problem in the context of the FPE. The particular boundary value, given by Eqs. (7) and (8) with $x=0$, is imposed by the method of solution and in this respect our result is not completely general. However, we expect that this result offers insight into more complicated situations and a wider class of boundary conditions. As a final point, we mention that the situation we have described can be used, in a well-defined approximation, to describe the motion of the impurity ionization interface in a semiconductor.[13]

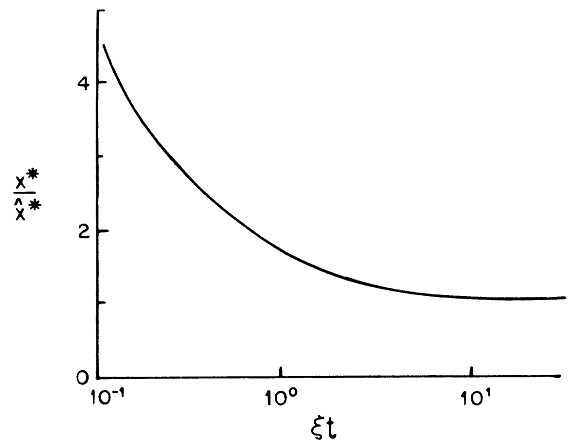

FIG. 1. $x^*/\hat{x}^*$ as a function of ξt.

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