Depletion region for diffusion-controlled reactions in a field

C. A. Condat
Department of Physics, University of Puerto Rico, Mayagüez, Puerto Rico 00681

G. Sibona and C. E. Budde
Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

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The effects of a uniform field on the distribution of mobile particles in the presence of a fixed trap are analyzed. Even small fields are shown to have a drastic effect on magnitudes, such as the reaction rate and the mean distance $\langle L \rangle$ from the trap to its nearest neighbor. If the field points *towards* the trap, a steady state is reached exponentially fast. In this steady state there is a depletion hole next to the trap, whose size depends on the ratio between the drift velocity V and the diffusion coefficient D. If c is the initial concentration of mobile particles, the long-time reaction rate is simply $c|V|$. If the field points *away* from the trap, the maximum of the probability distribution function for the distance to a nearest neighbor moves away from the trap with constant speed (if $V=0$, $\langle L \rangle \sim t^{1/4}$) and the reaction rate decays as $t^{-3/2}\exp(-V^2t/4D)$, where t is time.

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I. INTRODUCTION

In the analysis of diffusion-controlled reactions it is usually assumed [1,2], following the pioneering work of Smoluchowski [3,4], that there is a concentration gradient of the other species in the neighborhood of a reactant molecule. The molecular motion in this gradient is described by a diffusion equation with a suitable boundary condition. The detailed study of the nearest-neighbor distances in diffusion-controlled reactions is much more recent, having been started by Weiss, Kopelman, and Havlin in 1989 [5]. These authors consider a randomly distributed ensemble of random walkers (A) diffusing in the presence of a fixed trap (B). The reaction $A+B \rightarrow B$ occurs when one of the walkers reaches the trap. Due to this reaction, the density of the reacting mobile particles becomes nonuniform. To investigate this phenomenon, Weiss, Kopelman, and Havlin calculated the probability density function (PDF) $f(L,t)$ for the nearest-neighbor distance L at time t. Using this function, they showed that the average distance from the trap to its nearest neighbor increases asymptotically as $\langle L \rangle \sim t^{1/4}$. Because of the depletion of A particles around the trap, the trapping rate decreases as $t^{-1/2}$. Taitelbaum *et al.* later generalized the calculation of Ref. [5] to include the case of imperfect traps [6]. This was done, following Collins and Kimball [1], by introducing a radiation boundary condition at the location of the trap.

In this paper we analyze the effects of a uniform field on the distribution of nearest-neighbor distances. The field does not affect the stationary traps, but introduces a preferred direction of motion for the mobile reactants. This asymmetry will result in substantial modifications of such quantities as $\langle L \rangle$ and the trapping rate. Of particular interest is the competition between absorption and field-induced replenishment of the region around the trap when the field points *towards* the trap. Could a steady-state situation arise where the field-induced replenishment exactly compensates for the absorption? If the field points *away* from the trap, on the other hand, we expect that the depletion region will grow much faster than for the field-free case. What is the law for this growth? In this paper we give an answer to these questions by calculating the probability distribution function for the nearest-neighbor distances, the mean distance to the nearest neighbor, and the trapping rate.

II. MODEL

Consider an infinite one-dimensional system containing a random distribution of noninteracting mobile particles with a specified initial concentration c. These particles may fall into a fixed, impenetrable trap located at the origin. This trap is characterized by the conditional rate γ that trapping (i.e., the reaction) will occur given that the particle has reached the trap. The probability density $p(x,t;x_0)$ for finding a particle that departed from site x_0 at the time $t=0$ at the location x at a later time t can be obtained by solving the diffusion equation with a bias,

$$\frac{\partial p}{\partial t}=D\frac{\partial^2 p}{\partial x^2}-V\frac{\partial p}{\partial x} , \tag{1}$$

where D is the diffusion coefficient for the mobile particles and V their drift velocity, which is a direct measure of the field strength. Since the current now contains a convective term, the radiation boundary condition must be modified to read

$$\left[\frac{\partial p}{\partial x}\right]_{x=0}=\left[\gamma+\frac{V}{D}\right]p(x,t;x_0) . \tag{2}$$

III. ONE-PARTICLE SOLUTION

The one-particle probability density $p(x,t;x_0)$ can be obtained with the help of the transformation [4]

$$p(x,t;x_0)=e^{Vx/2D-V^2t/4D}r(x,t;x_0)\ . \tag{3}$$

Equations (1) and (2) are now transformed into

$$\frac{\partial r}{\partial t}=D\frac{\partial^2 r}{\partial x^2} \tag{4}$$

and

$$\left[\frac{\partial r}{\partial x}\right]_{x=0}=\left[\gamma+\frac{V}{2D}\right]r(x,t;x_0)\ , \tag{5}$$

respectively. The initial condition for r is

$$r(x,0;x_0)=e^{-Vx_0/2D}\delta(x-x_0)\ . \tag{6}$$

The solution to Eq. (4) with these initial and boundary conditions can be obtained from Ref. [7]. We find

$$p(x,t;x_0)=e^{V(x-x_0)/2D-V^2t/4D}\times\left[p_a-\left[\gamma+\frac{V}{2D}\right]p_b\right]\ , \tag{7}$$

with

$$p_a=\frac{1}{2(\pi Dt)^{1/2}}[e^{-(x-x_0)^2/4Dt}+e^{-(x+x_0)^2/4Dt}] \tag{8}$$

and

$$p_b=e^{D(\gamma+V/2D)^2t+(\gamma+V/2D)(x+x_0)}\times\operatorname{erfc}\left[\frac{x+x_0}{2(Dt)^{1/2}}+\left[\gamma+\frac{V}{2D}\right](Dt)^{1/2}\right]\ , \tag{9}$$

where erfc is the complementary error function [10]. Since the mobile particles do not interact, Eq. (7) contains all the information we need.

IV. MANY-PARTICLE SOLUTION

We start by writing a general formula for the probability $\Phi_L(\gamma,t)$ that there are no particles in the interval $[0,L]$ at time t, given that N mobile, noninteracting particles departed from an M-site lattice at time $t=0$ and that a trap of strength γ is located at the origin [8,9]

$$\Phi_L(\gamma,t)=\sum_{s_1=1}^{M}\cdots\sum_{s_N=1}^{M}\prod_{i=1}^{N}P_L(i,t)u(s_1,s_2,\ldots,s_N)\ . \tag{10}$$

This formula is valid for an arbitrary initial distribution $u(s_1,s_2,\ldots,s_N)$ of N mobile particles. $P_L(i,t)$ is the probability that the ith particle is beyond L at time t. By assuming that the initial distribution is random, $u=M^{-N}$, and taking the $M,N\to\infty$ limit (with $c=N/M$), we obtain

$$\Phi_L(\gamma,t)=e^{-cQ_L(\gamma,t)}\ , \tag{11}$$

with

$$Q_L(\gamma,t)=\sum_{i=1}^{\infty}[1-P_L(i,t)]\ , \tag{12}$$

or, in the continuum limit,

$$Q_L(\gamma,t)=\int_0^L dx\int_0^\infty dx_0\,p(x,t;x_0)\ . \tag{13}$$

With some patience, the integrals in Eq. (13) can be evaluated in terms of error functions. Long-time forms may be obtained using the asymptotic expansion [10]

$$\sqrt{\pi}z\,\operatorname{erfc}(z)=e^{-z^2}\left[1-\frac{1}{2z^2}+\frac{3}{4z^4}-\ldots\right]\ . \tag{14}$$

Our result (11) is valid for a one-sided problem with an impenetrable trap. If there were no field, and we were to let the particles reach the trap from both sides, an extra factor of 2 would appear in the exponent of Eq. (11) [5]. Because of the loss of symmetry caused by the introduction of the field, the presentation of the results is slightly simpler if we consider the one-sided case.

If the field points *away* from the trap ($V>0$), the mobile particles drift away from the trap and the size of the depletion region grows rapidly. The asymptotic form of Q_L is given by

$$Q_L(\gamma,t\to\infty)=\frac{4\sqrt{D}\,(D\gamma+V)e^{-V^2t/4D}}{\sqrt{\pi}V)^4(\gamma+V/2D)^2t^{3/2}}\times\left[\left[LV\gamma+\frac{LV^2}{2D}-2D\gamma\right]e^{LV/2D}+2D\gamma\right]. \tag{15}$$

If the field points *towards* the trap ($V<0$), a balance is reached between drift and absorption and a steady-state flow is obtained. The long-time form for the probability that the nearest neighbor to the trap is not in $[0,L]$ is given by

$$\Phi_L(\gamma,\infty)=e^{-cQ_L(\gamma,\infty)}\ , \tag{16}$$

where

$$Q_L(\gamma,\infty)=L+\left[\frac{1}{\gamma}-\frac{1}{W}\right](1-e^{-WL}) \tag{17}$$

depends on D and V only through the ratio $W=|V|/D$. If $V<0$ there is therefore a steady-state depletion hole, whose characteristic size L^* can be defined through

$$\Phi_{L^*}(\gamma,\infty)=e^{-1}\ . \tag{18}$$

The characteristic hole size is depicted in Fig. 1 for $c=0.25$ and several values of γ. In the high-field limit, L^* vanishes as

$$L^*(W\to\infty)\sim-\frac{1}{W}\ln\left[1-\frac{\gamma}{c}\right]\ , \tag{19}$$

for small absorption ($\gamma<c$), while for $\gamma>c$, the hole tends to a finite size

$$L^*(W\to\infty)\to\frac{1}{c}-\frac{1}{\gamma}\ . \tag{20}$$

For perfect absorption ($\gamma=\infty$) we recover the initial Poisson distribution: the field instantaneously replenishes the absorbed particles. For imperfect traps, an excess of mobile particles accumulates in the neighborhood of the trap. If the absorption is low enough ($\gamma<c$), this excess

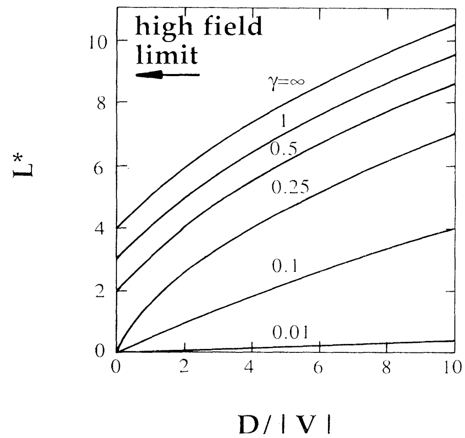

FIG. 1. Steady-state hole size as a function of $1/W=D/|V|$ for $c=0.25$ and the values of γ indicated next to the curves. Note the disappearance of the depletion region in the high-field limit for low absorption ($\gamma<c$).

is so large that the depletion region disappears altogether.

A steady state is not possible in the absence of a field. Indeed, if $W\to 0$, L^* diverges as a square root, $L^*\sim(2/cW)^{1/2}$.

The steady-state form (17) is approached in different ways, depending on the field strength. Writing $Q_L(\gamma,t)=Q_L(\gamma,\infty)+\Delta Q$, we find that, for $t\to\infty$,

$$\Delta Q\sim\begin{cases} t^{-3/2}e^{-V^2t/4D} & (-2D\gamma<V<0)\,, \quad (21)\\ t^{-1/2}e^{-V^2t/4D} & (V=-2D\gamma)\,, \quad (22)\\ e^{-(|V|-D\gamma)\gamma t} & (V<-2D\gamma)\,. \quad (23)\end{cases}$$

The steady state is always reached exponentially fast, but the exponent depends on the absorption constant only for high fields. For low fields the coefficient of the leading term diverges when $V\to 0-$ and when $V\to-(2D\gamma)+$. This suggests that the power of t must be higher for these special values, which effectively occurs (it jumps to $t^{-1/2}$). The $V=0$ limit was studied in detail in Refs. [5,6]. The slower convergence for the $V=-2D\gamma$ case is due to the vanishing of the slope of the transformed one-particle probability density $r(x)$ at $x=0$.

The existence of a threshold separating weak from strong fields is well known in the case of the trapping model, in which a single mobile particle is released into a line containing a random distribution of fixed traps [11]. There are three length scales in this model: The diffusion length $l_D=(2Dt)^{1/2}$, the drift length $l_V=Vt$, and the mean distance l_T between traps. The threshold occurs when the relation $l_T l_V=l_D^2$ is satisfied [12]. A similar relation is found for our problem if the field points towards the trap (this is the case for which a comparison is relevant). Defining the absorption length $l_A=1/\gamma$, we find from Eqs. (21)–(23) that the threshold occurs for $l_A l_V=l_D^2$.

V. PDF FOR THE NEAREST-NEIGHBOR DISTANCES

Once $Q_L(\gamma,t)$ is known, the PDF of the distance from the trap to the nearest mobile particle can be calculated by taking the derivative

$$f_L(\gamma,t)=-\frac{\partial\Phi_L}{\partial L}\,. \quad (24)$$

This function was evaluated numerically and the resulting graphics exhibit some interesting features. In Figs. 2(a) and 2(b) we plot f_L as a function of L for several values of the time and the field pointing *away* from the trap. We choose $\gamma=\frac{1}{9}$, $c=0.25$, $D=10$, and $V=1$. At short times, the maximum remains at the location of the trap. At $t\approx 75$, a well-defined peak clearly emerges at a nonzero value of L; due to the action of the field, the nearest particle is often far from the trap. At long times, the peak is seen to move with the drift velocity while it is subject to diffusive widening [its width increases as $(Dt)^{1/2}$]. The effects of diffusion are more marked behind the advancing peak, where a small tail appears. These features are also seen in Fig. 3, where we plot f_L as a function of L for $t=10$ and several values of the diffusion coefficient. The other parameters are the same as in Fig. 2. If D is large enough, the trailing feature grows until the $L\neq 0$ peak disappears; since the diffusion is high, it is likely that we will find upstream-moving particles in the

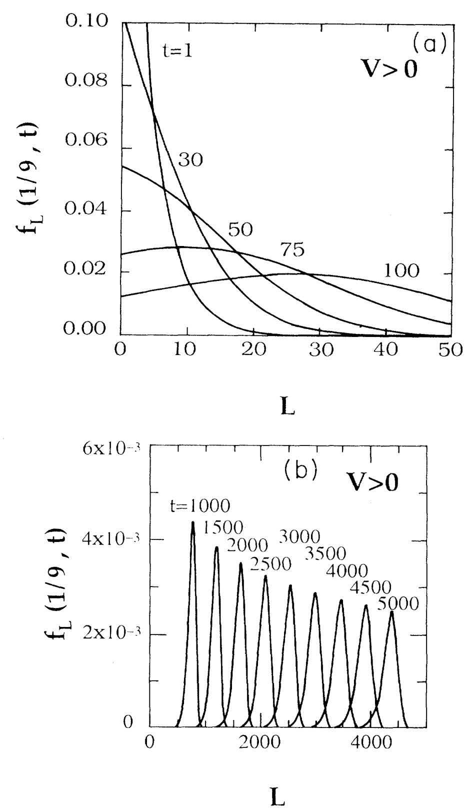

FIG. 2. PDF of the distance from the trap to the nearest mobile particle for drift *away* from the trap and the times indicated next to the curves. Here $\gamma=\frac{1}{9}$, $D=10$, $c=0.25$, and $V=1$. (a) Short times. (b) Long times.

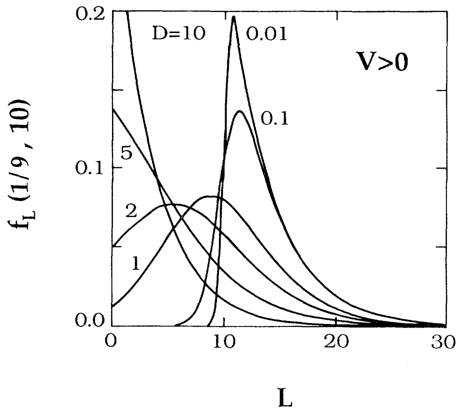

FIG. 3. PDF of the distance from the trap to the nearest mobile particle for $t=10$ and several values of the diffusion coefficient. The other parameters are as in Fig. 2.

neighborhood of the trap. In Fig. 4 we plot f_L as a function of L for various values of the drift velocity, the rest of the parameters being as in Fig. 2. Obviously the moving peak forms faster for higher fields.

We can also look at the position $L_{\max}$ of the maximum of the PDF $f_L(\gamma,t)$. A numerical evaluation shows that at long times $L_{\max}\to Vt$, in agreement with the results presented in Figs. 2(b) and 4.

If $V<0$ (field pointing *towards* the trap), we have a completely different picture. When W is large the peak is centered at the origin, becoming sharper if the magnitude of the drift is increased or if the diffusion coefficient is decreased. This can be seen in Fig. 5(a), where we present $f_L(\frac{1}{9},\infty)$ for several moderately large values of W. In Fig. 5(b), for which we selected smaller values of W, the field is too weak to replenish the trap neighborhood and the peak moves towards higher values of L. This occurs if $W<\gamma^2/(\gamma+c)$, the location of the peak maximum being given by

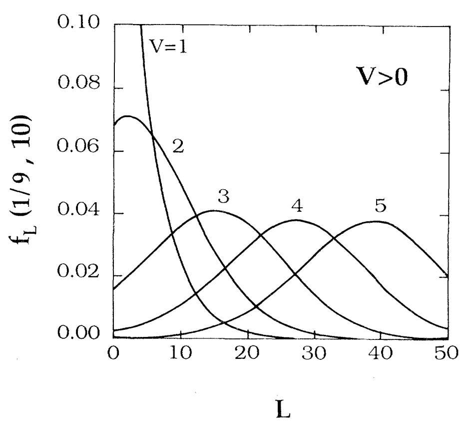

FIG. 4. Similar to Fig. 3, but fixing $D=10$ and varying the (positive) drift velocity V.

$$L_{\max}=\frac{1}{W}\ln\left[\frac{1-\frac{W}{\gamma}}{1+\frac{W}{2c}-\frac{W}{2c}\left[1+\frac{4c}{W}\right]^{1/2}}\right]. \tag{25}$$

VI. MEAN DISTANCE TO THE NEAREST NEIGHBOR

Another magnitude whose relevance to this problem was pointed out by Weiss, Kopelman, and Havlin [5] is the mean distance to the nearest neighbor,

$$\langle L\rangle=\int_0^\infty Lf_L(\gamma,t)dL=\int_0^\infty \Phi_L(\gamma,t)dL\ . \tag{26}$$

In the absence of a field, $\langle L(t\to\infty)\rangle\to(Dt)^{1/4}/c^{1/2}$, independently of the value of the absorption constant [6]. When a field is added, the behavior of $\langle L\rangle$ changes drastically. If $V<0$, it tends to a finite value,

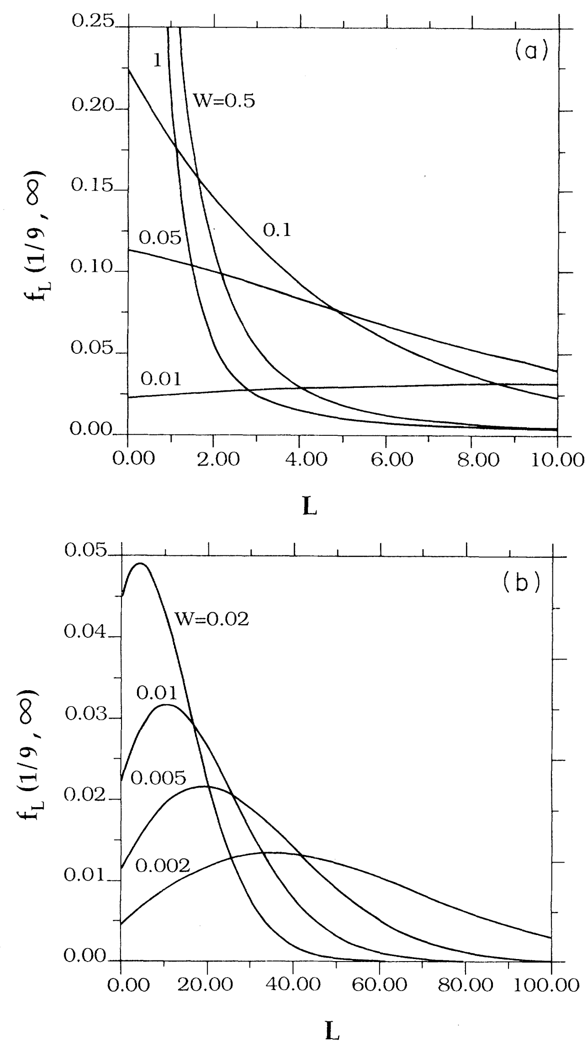

FIG. 5. Steady-state PDF for $\gamma=\frac{1}{9}$, $c=0.25$, and several values of $V<0$. The chosen values of $W=|V|/D$ are indicated next to each curve. Here the $L\neq 0$ peak appears for $W<0.034\,19$. (a) Large drifts. (b) Small drifts.

$$\langle L(t\to\infty)\rangle = \frac{e^{cA}}{W(cA)^{c/W}}\bar{\gamma}\left[\frac{c}{W},cA\right], \tag{27}$$

where $\bar{\gamma}(a,x)$ is the incomplete gamma function [10] and $A=1/W-1/\gamma$. The diffusion coefficient and the drift velocity appear again only through W. For weak fields, $\langle L\rangle\to(\pi/2cW)^{1/2}$, in agreement with our result for L^*.

If $V>0$, $\langle L\rangle$ diverges at long times and a complicated expression obtains. It is easier to look at the evolution of the location of the maximum $L_{\max}$ of $f_L(\gamma,t)$ (see Sec. V).

VII. TRAPPING RATE

The trapping (or reaction) rate can be calculated directly from the flux $J(t)$ at the trap [5] which contains both diffusive and convective contributions,

$$J(t)=-c\int_0^\infty\left[D\left[\frac{\partial p}{\partial x}\right]_{x=0} - Vp(x=0,t;x_0)\right]dx_0 . \tag{28}$$

This can be computed using Eq. (7). We give only the long-time results. If $V<0$, a convection-dominated steady state is reached. We obtain $J(t\to\infty)=-c|V|$. If $V>0$, $J(t)$ decreases exponentially due to the convection,

$$J(t\to\infty)\sim-\frac{2c\gamma\sqrt{D}\,(D\gamma+V)}{\sqrt{\pi}V^2(\gamma+V/2D)^2t^{3/2}}e^{-V^2t/4D} . \tag{29}$$

This may be compared with the zero-field result [6] $J(t\to\infty)\sim-2c[D/(\pi t)]^{1/2}$, which is independent of the trap strength. For $V>0$, the asymptotic result depends on the nature of the trap.

VIII. CONCLUSION

We have investigated in detail the effects of the addition of a field on the statistical properties of the nearest-neighbor distances to a fixed, imperfect trap. We found that, for fields pointing towards the trap, a steady-state depletion hole is formed whose size depends on the ratio between drift velocity and diffusion coefficient. This steady state is reached exponentially fast. The long-time limit of the reaction rate is convection dominated. For fields pointing away from the trap, the peak of the probability distribution function of the distance between the trap and the nearest mobile particle moves away from the trap with the drift velocity, while the reaction rate decays exponentially due to convection away from the trap.

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[1] F. C. Collins and G. E. Kimball, J. Colloid Sci. **4**, 425 (1949).
[2] S. A.Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
[3] M. von Smoluchowski, Ann. Phys. (Leipzig) **48**, 1103 (1915).
[4] M. von Smoluchowski, Z. Phys. Chem. (Leipzig) **92**, 129 (1917).
[5] G. H. Weiss, R. Kopelman, and S. Havlin, Phys. Rev. A **39**, 466 (1989).
[6] H. Taitelbaum, R. Kopelman, G. H. Weiss, and S. Havlin, Phys. Rev. A **41**, 3116 (1990).
[7] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids,* 2nd ed. (Oxford University Press, Oxford, 1986), p. 358.
[8] M. Tachiya, Radiat. Phys. Chem. **17**, 447 (1981).
[9] C. A. Condat, Phys. Rev. A **39**, 2112 (1989).
[10] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. Stegun (Dover, New York, 1965).
[11] B. Movaghar, B. Pohlmann, and D. Würtz, Phys. Rev. A **29**, 1568 (1984).
[12] C. A. Condat and D. P. Prato, Phys. Lett. A **180**, 388 (1993).