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Steady State in Two-Dimensional Diffusion-Controlled Reactions

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We investigate the conditions under which a steady state can be reached in a two-dimensional diffusion-controlled trapping reaction. If there is no interaction between trap and diffusing particles, the reaction rate decreases monotonically to zero. Here we show that a logarithmic attractive potential between trap and diffusing particles leads to a finite steady-state reaction rate. A steady state can also be reached if the diffusing particles move under the action of a uniform external field. More unexpectedly, a steady-state rate can be obtained in the absence of any "assisting field" if the trap grows due to the absorption of the diffusing particles. The reaction rates are calculated in all cases.

KEY WORDS: Trapping; droplet; diffusion-controlled reactions; steady state; biased diffusion; two dimensions.

I. INTRODUCTION

Diffusion-controlled reactions (DCRs) occur in many areas of physics, chemistry and biology.[1,2] In practice, the corresponding diffusive processes are often effectively confined to a two-dimensional space.[3,4] Although two-dimensional diffusion is extensively discussed in textbooks,[5,6] no attention seems to have been paid to the interesting question of the existence and nature of a steady state (SS) in two-dimensional DCRs. The purpose of this paper is to examine the conditions under which such a SS may arise. Since the most interesting quantity in practical problems is the reaction rate, to avoid ambiguities we will call steady state to any state such that the reaction rate is independent of time.

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It is well-known that, if we start with a uniform density of noninteracting, mobile reactants, the flux into a fixed trap (i.e., the reaction rate) in two dimensions decreases asymptotically as $1/\ln(t)$.[6,7] The physical reason for the absence of steady state is the slow replenishment of the depletion region that surrounds the trap, which grows continuously. In higher-dimensional systems, on the other hand, there are more diffusion paths and a SS is eventually reached.[8,9] Because of the slow divergence of the logarithm, we expect the two-dimensional problem to be marginal: any modification of the model that favours a faster replenishment of the trap neighbourhood should lead to a steady state.

Following and slightly generalizing the conventional ideas in DCRs,[1,10,11] we assume that there is an infinite domain containing an initially uniform distribution of noninteracting diffusing particles, which may react with a fixed finite trap of characteristic size a. It is convenient to use the dimensionless space and time variables $\vec{\rho}=\vec{r}/a$. and $\tau=Dt/a^2$, where D is the diffusion coefficient. The evolution of the concentration $C(\vec{\rho}, \tau)$ is controlled by the diffusion equation

$$\frac{\partial C}{\partial \tau}=\nabla^2 C, \tag{1}$$

subject to the initial condition $C(\vec{\rho}, 0)=C_0$. The boundary conditions are $C(\infty, \tau)=C_0$ and, at the trap surface,

$$\frac{\partial C}{\partial \zeta}=\Gamma C. \tag{2}$$

Here Γ is the dimensionless trapping rate and ζ is an (outwardly directed) coordinate normal to the trap surface. Equation (2) is usually termed the radiation boundary condition;[6] if $\Gamma=\infty$ the trap is "perfect," otherwise the trap is "imperfect".

A SS solution of Eq. (1) in cylindrical coordinates (ρ, θ) must have the form,

$$C_{SS}(\rho, \theta)=[A+B\ln(\rho)]\, f(\theta). \tag{3}$$

Since the boundary condition at infinity demands that $B=0$, it is impossible to obtain a SS for any finite trap (except, obviously, for the perfect reflector case $\Gamma=0$). The remainder of this paper will explore three different conditions under which a SS may arise.

II. STEADY STATE I: A CENTRAL FIELD

The most obvious way of inducing a faster replenishment of the depletion region around the trap is to add a central, attractive potential $V(\rho)$. In this case, Eqs. (1) and (2) must be generalized, respectively, to

$$\frac{\partial C}{\partial \tau} = \nabla^2 C + D^{-1} \nabla \cdot (C \nabla V), \tag{4}$$

and

$$\frac{\partial C}{\partial \zeta} = \left[\Gamma - \frac{1}{D} \frac{\partial V}{\partial \zeta} \right] C, \tag{5}$$

evaluated at the trap surface. Arguably the most interesting potential in this class is the two-dimensional Coulomb potential $V = q \ln \rho$.[12, 13] It is easy to see that this potential leads to a SS for an arbitrary finite trap. The reason is that the radial flux $j(\rho)$ far from the trap (where the concentration varies slowly) is proportional to $1/\rho$. Therefore, the total inward current across a circumference of radius ρ, $J(\rho) = 2\pi\rho j(\rho)$, tends to a finite value when $\rho \to \infty$. An analytical solution is possible if we consider a circular trap. Defining $q' = q/D$, we see that the SS concentration solves the radial equation,

$$\frac{\partial^2 C}{\partial \rho^2} + \frac{(1+q')}{\rho} \frac{\partial C}{\partial \rho} = 0, \tag{6}$$

with the boundary condition that the radial derivative at the trap surface $\rho = 1$ must be equal to $(\Gamma - q')\, C(\rho = 1)$. We obtain,

$$C(\rho) = C_0 \left\{ 1 - \left(1 - \frac{q'}{\Gamma} \right) \rho^{-q'} \right\}. \tag{7}$$

It is interesting that the "charge" appears in the exponent. The concentration is plotted in Fig. 1 for $\Gamma = 1$ and several values of q'. While for weak absorption ($q'/\Gamma > 1$), the concentration grows monotonically as we approach the trap, for strong absorption ($q'/\Gamma < 1$), it decreases monotonically. The concentration is everywhere constant if $\Gamma = q'$. On the other hand, the concentration at the trap edge, $C(1) = q' C_0/\Gamma$, grows with decreasing Γ in such a way that it ensures that the reaction rate, $|J(1)| = q' C_0$ is Γ-independent.

In a recent paper,[14] Koplik and co-workers studied a different aspect of the logarithmic potential problem. Supposing that the diffusing particle

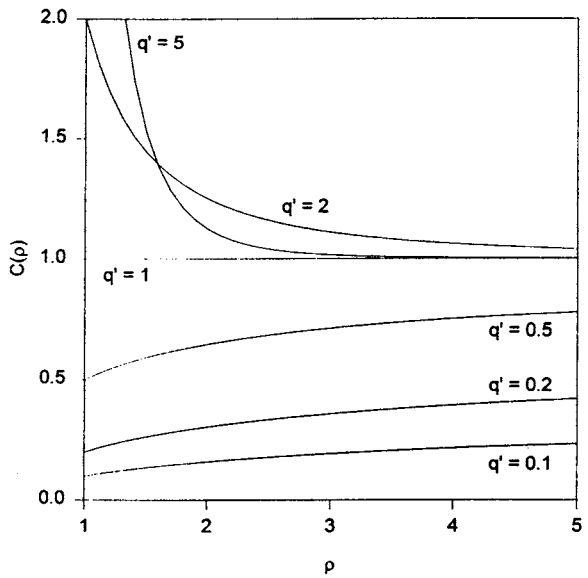

Fig. 1. Steady-state concentration as a function of the dimensionless radius for a circular trap and a central logarithmic potential. Here $\Gamma = 1$ and the values of $q' = q/D$ are detailed in the figure.

is confined to an annulus whose inner wall is a perfectly absorbing trap and whose outer wall is a perfect reflector, they calculated the transit-time probabilities for the cases of inward and outward flows. They also analyzed the case when the outer wall is the trap. Taken together their calculation and ours offer a detailed picture of diffusion in a two-dimensional radial flow of the form $j(\rho) \sim A/\rho$ and of the strong ("non-universal") dependence of the results on the magnitude of the amplitude A.

It is easy to see that a SS can *only* occur for potentials whose asymptotic behaviour is logarithmic. If $V(\rho)$ grows faster than $\ln(\rho)$ as $\rho \to \infty$, the inward current diverges asymptotically and no SS is possible. A more interesting situation arises if the field is everywhere inwardly directed, but the potential tends asymptotically to a constant. Suppose for example that $V(\rho) = \alpha\rho^{-n}$, $n > 0$, $\alpha < 0$. Since the attractive field is strong near the trap, many particles fall into it at short times and the depletion zone evolves fast. However, the field is asymptotically very weak and the convective current vanishes in the limit $\rho \to \infty$. Therefore, the depletion region will grow continuously and a SS will never be reached. Of course, a SS is attained if we restrict the diffusion space to an annulus whose

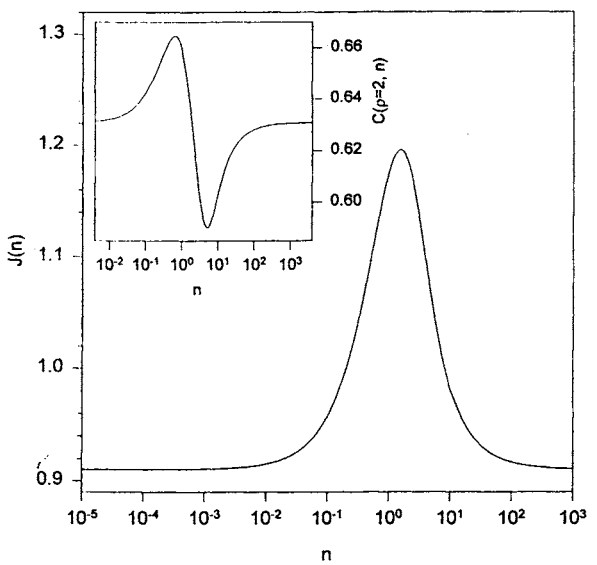

Fig. 2. Steady-state reaction rate as a function of potential shape if the diffusion space is an annulus whose outer radius is $\delta = 3$. Trap and diffusing particles interact through the central potential $V(\rho) = \alpha\rho^{-n}$ (here $\alpha = -1$ and $C_0 = 1$). Inset: the steady-state concentration at $\rho = 2$ as a function of n.

(dimensionless) outer radius is δ and assume $C(\delta) = C_0$. In this case, the result for a perfect trap is,

$$C(\rho) = C_0 e^{\alpha'(\delta^{-n} - \rho^{-n})} \left[\frac{Ei(\alpha') - Ei(\alpha'\rho^{-n})}{Ei(\alpha') - Ei(\alpha'\delta^{-n})} \right], \tag{8}$$

where $\alpha' = \alpha/D$ and $Ei(x)$ is the exponential integral. Note that $C(\rho) \to 0$ everywhere if $\delta \to \infty$. Starting from Eq. (8) it is straightforward to calculate the reaction rate. The variation of this rate with the exponent n is displayed in Fig. 2. Note that the rate is minimized if there is *no* field (the opposite is true for a repulsive power-law interaction, $\alpha > 0$, for which Eq. (8) is still valid). The complicate dependence of the rate and concentration (detailed in the inset,) on n is due to the complex interplay of the variations of the radial force with ρ and n (but $n = 0$ and $n = \infty$ must yield the same result!).

III. STEADY STATE II: A UNIFORM FIELD

A somewhat less evident procedure to replenish the depletion region is to introduce a uniform field, which we will characterize through the drift

velocity v. A moment's thought reveals that the effective number of particles brought into the trap neighbourhood by the resulting biasing field will be higher than the number effectively removed by the field. As a consequence, a SS may be established. In this case, it is convenient to use the dimensionless drift velocity $W = va/2D$ and to rewrite Eq. (4) in terms of the dimensionless Cartesian pair (χ, ξ):

$$\frac{\partial^2 C}{\partial \chi^2} + \frac{\partial^2 C}{\partial \xi^2} + 2W \frac{\partial C}{\partial \xi} = 0. \tag{9}$$

Defining $\Delta = \sqrt{W^2 - b^2}$, where b is a separation constant, it is clear that we can write the solution to Eq. (9) as $C(\chi, \xi) = C_0 + C_1(\chi, \xi)$, where C_1 is a superposition of solutions of the form $\exp(-b\,|\chi|)\exp[-(W \pm \Delta)\,\xi]$. If $W = 0$ the solutions are oscillatory and the boundary condition at infinity cannot be fulfilled. Any nonzero drift W, on the other hand, introduces a converging factor which ensures the fulfillment of the boundary condition and the existence of a steady state.

This problem is discussed in detail in ref. 8. After Laplace transforming the time-dependent differential equation, we separate variables using polar coordinates (ρ, θ) and write the solution as an eigenfunction expansion. The expansion coefficients α_j can be obtained by applying the boundary conditions. This leads to an equation of the form $\mathcal{M}\vec{\alpha} = \vec{\beta}$, where $\vec{\alpha}$ is the vector formed by the α_j's. The elements of the tri-diagonal matrix $\mathcal{M}$ and the vector $\vec{\beta}$ depend on Γ, W, and the Laplace variable. The SS concentration $C(\rho, \theta)$ is obtained by solving the matrix equation numerically. This method allows a careful discussion of the properties of the SS solution. The contour plots show that an enhanced concentration region usually arises upstream an imperfect trap, while a depletion zone appears downstream. Once the concentration is known, we can calculate the particle flux into the trap and, upon an angular integration, we obtain the SS reaction rate, which is observed to increase monotonically with Γ and W.

Since there is no steady state in the absence of a field, it is of particular interest to analyze the properties of the SS concentration and reaction rate in the limit $W \to 0$. By approximating the relevant entries in $\mathcal{M}$ and $\vec{\beta}$, we can solve the matrix equation analytically. For the concentration we find,

$$C(\rho) = C_0 \left(1 - \frac{E + \ln(W\rho/2)}{E + \ln(W/2) - 1/\Gamma}\right), \tag{10}$$

with $E = 0.5772...$ being the Euler constant.[15] This solution is valid for a circular trap in the region $\rho \ll W^{-1}$, which becomes arbitrarily large as

$W \to 0$. Note that the problem is isotropic in this approximation. The SS reaction rate is

$$J = -\frac{2\pi}{\ln(W/2) + E - 1/\Gamma}. \tag{11}$$

The ubiquitous presence of the logarithms indicates the marginality of the two-dimensional problem.

In the opposite limit of strong fields, the current at the trap is completely convection-controlled and has the form

$$J(t \to \infty, v \to \infty) = 2avG(\Gamma)\, C_0, \tag{12}$$

where $2a$ is the trap cross section and G is a monotonically increasing function of Γ that satisfies $G(0) = 0$ (perfect reflector) and $G(\infty) = 1$ (perfect trap).

IV. STEADY STATE III: A GROWING TRAP

The nature of the SS to be discussed in this Section is completely different. Instead of introducing a field that helps to replenish the depletion region, we will let the trap grow into it, while preserving its shape. If the trap is an effectively two-dimensional (pancake-shaped) droplet that grows due to the absorption of the trapped particles at its surface, the reaction rate tends to a constant.

The number $n(t)$ of particles contained in the droplet can be expressed as $n(t) = \pi a^2(t)\, C_i$, where C_i is the particle density inside the droplet. If C_i is constant we can calculate the droplet growth rate in terms of the reaction rate $J[a(t)]$ using the relation

$$a(t) = \left\{ a_0^2 + \frac{1}{\pi C_i} \int_{t_0}^{t} J[a(t')]\, dt' \right\}^{1/2}, \tag{13}$$

where $a_0 = a(t_0)$ is the droplet radius at the initial time t_0. This is actually an integral equation for the droplet radius. The problem can be simplified by the use of the following adiabatic approximation:[9] If the droplet growth is slow enough, we can consider the distribution of the mobile particles to be that corresponding to a fixed-radius trap whose radius is equal to the true instantaneous trap radius. In this case, we can use the known expressions for the particle flux to a trap of fixed radius.[6,7] This approximation is suitable if the length a particle diffuses is much longer than the increment in the radius in the same time interval. In practice, this

will imply that we must demand that $C_0 \ll C_i$, a condition that should be generally met. For simplicity we consider here only the case in which the droplet is modelled by a perfect trap. In this case, the current into a *fixed-radius* trap of radius a is

$$J(t) = \frac{8C_0D}{\pi}\int_0^\infty \frac{dx}{x}\frac{e^{-(Dt/a^2)x^2}}{[J_0(x)]^2+[Y_0(x)]^2} \equiv C_0F(a^2/t), \tag{14}$$

where J_0 and Y_0 are Bessel functions. This suggests setting $a(t) = At^{1/2}$. Eq. (14) may then be written as,

$$At^{1/2} = \left[a_0^2 + \frac{C_0}{\pi C_i}\int_{t_0}^{t} F(A^2)\,dt'\right]^{1/2}, \tag{15}$$

If $C_0F(A^2)(t-t_0) \gg \pi C_i a_0^2$, this reduces to,

$$C_iA^2 = C_0F(A^2) \tag{16}$$

We have solved Eq. (15) numerically, inserting $J(t)$ from Eq. (14) and choosing $t_0 = 0$ and $a_0 = 1$. Some of our results are presented in Fig. 3, where we show the time dependence of the droplet radius for several values

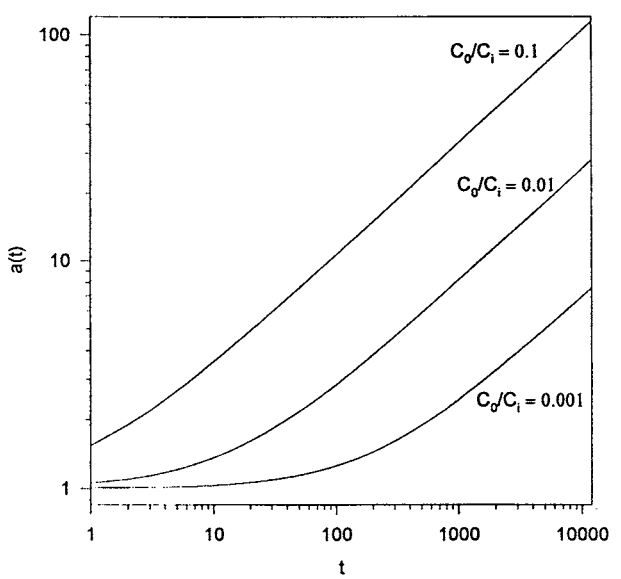

Fig. 3. Time dependence of the droplet radius for the values of the ratio between the inner and outer concentrations detailed in the figure. All drops start with unit radius at $t = 0$.

of the parameter C_0/C_i. The long-time $t^{1/2}$ dependence is evident. The reaction rate $F(A^2)$ becomes t-independent and the system reaches a steady state (with a growing trap).

Remark. In the case of a droplet growing in a medium where the particles are also subject to a strong drift v, the droplet radius will grow as $a(t) \sim [(C_0/C_i)\, vt]^{1/2}$.

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REFERENCES

1. S. A. Rice, *Diffusion-Limited Reactions* (Comprehensive Chemical Kinetics, Vol. 25), Elsevier, Amsterdam, 1985.
2. Volume with papers presented at the conference on Models of Non-Classical Reaction Rates (National Institutes of Health, Bethesda, Maryland, March 1991), and references therein. *J. Stat. Phys.* **65:** Nos. 5/6.
3. Ch. S. Owen, *J. Chem. Phys.* **62:**3204 (1975).
4. J. R. Philip, J. H. Knight, and R. T. Waechter, *Water Resour. Res.* **25:**16 (1989).
5. J. Crank, *The Mathematics of Diffusion*, 2nd. Ed. (Oxford University Press, Oxford, 1975).
6. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd. Ed. (Oxford University Press, Oxford, 1959).
7. H. Taitelbaum, *Phys. Rev. A* **43:**6592 (1991).
8. G. Sibona, C. E. Budde, and C. A. Condat, *Phys. Rev. E* **54:**6232 (1996).
9. G. Sibona, C. E. Budde, and C. A. Condat, *Physica A* **231:**317 (1996).
10. M. von Smoluchowski, *Z. Phys. Chem.* **92:**129 (1917).
11. F. C. Collins, and G. E. Kimball, *J. Colloid Sci.* **4:**425 (1949).
12. J. M. Kosterlitz and D. J. Thouless, *J. Phys. C: Solid St. Phys.* **6:**1181 (1973).
13. B. Jancovici, *Phys. Rev. Lett.* **46:**386 (1981).
14. J. Koplik, S. Redner, and E. J. Hinch, *Phys. Rev. E.* **50:**4650 (1994).
15. *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover, New York 1965).