Journal of Statistical Physics, Vol. 30, No. 2, 1983

Diffusion-Controlled Reactions among Stationary Sinks

Robert I. Cukier[1]

We summarize results of some of our calculations in diffusion-controlled reaction theory. We derive the transport equation describing a diffusing species which can react with a set of randomly distributed spherical sinks. Both the form of the transport equation and the dependence on sink volume fraction of the reaction rate and the effective diffusion coefficient are discussed.

KEY WORDS: Diffusion-controlled reactions; sphere suspensions.

1. INTRODUCTION

The theory of diffusion-controlled reactions was developed by Smoluchowski.(1) He showed that the flux into a molecule A in a fluid with a diffusing species which reacted on contact with the surface of A is given by $k_D = 4\pi D_0 a$. Here D_0 is the diffusion coefficient in the fluid and a is the A radius. For sufficiently low A concentration $c = M/\Omega$ (M A's in volume Ω) $k_f = ck_D$. As c increases, the reactive fluid density field about a given A is influenced by the other A's; thus the rate $k_f \neq ck_D$. Furthermore, the presence of the A's modifies the diffusion coefficient.

In this article we summarize some of our efforts toward extending Smoluchowski's work to the higher concentration regime. Thus, consider a simple model consisting of fluid, particles, and spherical sinks. The sinks are much larger than the particles and distributed as dilute hard spheres, uniformly, but without overlap. The fluid carries the reactive particles by Fickian diffusion and the particles are instantaneously absorbed on contact with the stationary sinks. We anticipate the transport equation

$$(\partial/\partial t)N(\mathbf{r},t) = D\,\nabla^2 N(\mathbf{r},t) - k_f N(\mathbf{r},t) \tag{1}$$

Presented at the Symposium on Random Walks, Gaithersburg, MD, June 1982.

Supported in part by the National Science Foundation under Grant No. CHE-78-07849.

[1] Department of Chemistry, Michigan State University, E. Lansing, Michigan 48824-1322.

in terms of the sphere configuration averaged particle density $N(\mathbf{r},t)$, effective diffusion coefficient D, and rate coefficient k_f. For spherical sinks both D and k_f are functions of the sink volume fraction $\phi = 4\pi a^3 c/3$.

The issue of calculating the ϕ dependence of k_f and D has been addressed by several authors.(2–5) However, more fundamental issues also arise.(6) To introduce them we formally express the reaction–diffusion system by a Langevin-like equation (after Laplace time transformation):

$$(z - D_0\nabla^2)n(\mathbf{r},z) = -\int d\mathbf{r}'\,\Sigma(\mathbf{r},\mathbf{r}',z)n(\mathbf{r}',z) + R(\mathbf{r},z) + N_0(\mathbf{r}) \qquad (2)$$

Here $n(\mathbf{r},z)$ is the sphere configuration-dependent coarse-grained particle density

$$n(\mathbf{r},z) = (2\pi)^{-3}\int_{k<1/b} d\mathbf{k}\,n(\mathbf{k},z) \qquad (3)$$

with $b \gg a$ and $N_0(\mathbf{r})$ the (configuration-independent) initial condition. The memory function $\Sigma(\mathbf{r},\mathbf{r}',z)$ and random "force" $R(\mathbf{r},z)$ are given by multiple scattering expansions in terms of the sphere-free fluid propagator $G_0 = \exp(-\alpha r)/4\pi D_0 r$ with $\alpha = (z/D_0)^{1/2}$ and sphere scattering functions T_i $(i = 1,2,\ldots,M)$. The $\{T_i\}$ incorporate the exact scattering power of each sink for arbitrary sink geometry, though they can be explicitly evaluated only for simple geometries.(3) R satisfies $\langle R\rangle = 0$ where the bracket denotes the sphere configuration average. (Σ and R are related in a different fashion than by the conventional fluctuation–dissipation theorem of the second kind since here the fluctuations are generated by the random sink distribution.) Now separate the particle density according to $n(\mathbf{r},t) = N(\mathbf{r},t) + \delta n(\mathbf{r},t)$, $[N(\mathbf{r},t) = \langle n\rangle(\mathbf{r},t)]$, with N the deterministic motion and δn the fluctuating motion. Then N (δn) satisfies Eq. (2) without (with) the random "force" term.

The following questions arise in the attempted passage from Eq. (2) to Eq. (1).

1. Is there a spatial gradient expansion of Σ which allows the space local representation of Eq. (1)?
2. Is there a time scale expansion of Σ which leads to the time local form of Eq. (1)?
3. With regard to the fluctuations, what are the statistical properties of R and what do they imply about δn? Are they small, and Gaussian? If so, then the N equation represents the macroscopic behavior but if not, how do the fluctuations modify the description of the transport?
4. How can the ϕ dependence of k_f and D be systematically calculated for moderate values of ϕ and reasonably approximated for large values of ϕ (ϕ approaching random close packed)? Note that k_f and D are potentially measurable independently of the transport equation so that

these are physical parameters even if Eq. (1) does not fully characterize the transport.

In Section 2 we discuss a rigorous method that can address the issues just raised. It is a perturbative method and as such is not a practical technique for calculating k_f and D at high sphere concentration. Thus, in Section 3 we turn to approximate nonperturbative methods which are directed to the higher concentration regime.

2. SCALING EXPANSIONS

We have recently[(6)] adapted a scaling expansion method advanced by Mori[(7)] to this reaction–diffusion problem. The philosophy is as follows. Three kinds of expansions are conventionally used to obtain macroscopic transport equations from microscopic equations: expansions in density (here sink concentration c), in spatial gradients ∇, and in "slowness" parameter $z(\partial/\partial t)$. Mori points out that they are related and that the expansion must be carried out consistently. This is accomplished by a scaling expansion method in which asymptotic limits of the macroscopic parameters are taken to effect a space-time coarse graining and by so doing to extract the macroscopic description from the microscopic details.

The basic scaling for the reaction–diffusion system is obtained from the low-concentration (independent sphere) deterministic equation

$$\partial N/\partial t = D_0\nabla^2 N - k_D c N \tag{4}$$

Since $k_D = 4\pi D_0 a$, the length l and time τ scales are $\kappa^{-1} = l = 1/(4\pi a c)^{1/2}$ and $\tau = l^2/D_0$. Since $l \gg b \gg a$ we introduce a scaling $l \to Sl$, $a \to a$ with $S \gg 1$ and all molecular quantities such as D_0 are kept fixed. The notation introduced above lets us indicate how lengths, time, etc. become large. The space-time coarse graining is then produced by the scaling $\mathbf{r} \to S\mathbf{r}$, $t \to S^{\theta}t$($z \to S^{-\theta}z$) for distances $|r| \geqslant b$ where θ is a positive exponent to be determined. Then, this scaling leads to $(\kappa a) \to S^{-1}(\kappa a)$, $\phi \to S^{-2}\phi$, $M \to S^{d-2}M$, $\Omega \to S^d\Omega$ where d (dimensionality) = 3 here. The three kinds of expansions are then expressed by the scaling $c \to S^{-2}c$, $\nabla \to S^{-1}\nabla$, $z \to S^{-2}z$. Thus, the expansion in S^{-1} enables us to carry out the space-time coarse graining, which leads to the macroscopic equation, in a manner consistent with the sphere concentration expansion! This is in contrast to a conventional small parameter expansion.

The spatial coarse graining divides the system volume Ω into cells of volume b^d and eliminates intracellular degrees of freedom. The concentration c goes to zero as S increases but the number of sinks in a cell, cb^d, is proportional to $S^{(d-2)}$. Thus for $d = 3$ each cell has many sinks and we expect that the fluctuations δn will be small and Gaussian. Clearly, the dimensionality plays a crucial role and we shall discuss this important aspect of the formalism shortly.

Define scaling exponents α and β by $N(\mathbf{r},z)\rightarrow N^S(S\mathbf{r},S^{-\theta}z) = S^{-\alpha}N(\mathbf{r},z)$ and $\delta n(\mathbf{r},z)\rightarrow \delta n^S(S\mathbf{r},S^{-\theta}z) = S^{-\beta}\delta n(\mathbf{r},z)$ and *scale invariants* $\tilde{N}$ and $\delta\tilde{n}$ by $N(\mathbf{r},z) = b^{-\alpha}\tilde{N}(\mathbf{r}/b,b^{\theta}z,\kappa b)$ and $\delta n(\mathbf{r},z) = b^{-\beta}\delta n(\mathbf{r}/b,b^{\theta}z,\kappa b)$. The former statements indicate how the deterministic and fluctuating quantities depend on S; the latter note that the macroscopic equations must be invariant under the given scaling. Introduction of the exponents α and β enable us to precisely specify the relative sizes of N and δn.

Scaling the Langevin equation and analyzing the scaled forms of Σ and R, expressed in their multiple scattering representations, leads to the following observations.

1. *All* terms in the diagrammatic expansion of Σ can be systematically ordered in S^{-1}. In this screened problem there are terms which are divergent to varying degrees and conventionally one sums the integrands of the most divergent diagrams to all orders in c to obtain a convergent result. Scaling assigns the same order to every most divergent diagram and thus provides an objective ordering of these, as well as all less divergent and nondivergent, diagrams.

2. The memory function Σ, and this is a crucial result, is exactly decomposable as $\Sigma = \Sigma_L(r/a,zl^2) + \Sigma_N(r/l,zl^2)$. Since $N = N(r/l,zl^2)$, Σ_L can be expanded in gradients to yield $k_f(\nabla^2)^0$, $D(\nabla^2)^1$ and Burnett $(\nabla^2)^2$ etc. coefficients. But Σ_N cannot be expanded. Its space variation is on the same scale as that of N—the macroscopic process is space nonlocal.

3. Summing diagrams can only be carried out to low order (in S^{-1}): we have summed to order S^{-2} and find that the resulting space-nonlocal macroscopic equation is local in time to this order. The screening, which arises from the reaction, dominates the frequency dependence of the renormalized propagator (see 4).

4. Diagrammatic resummations were carried out to rigorously introduce the renormalized propagator $G(\mathbf{r},z) = \exp[-(\kappa^2 + z/D_0)^{1/2}r]/4\pi D_0 r$. This propagator eliminates the zero-frequency divergences occurring in the bare propagator expansion.

5. The diagrammatic analysis of Σ shows that there are three (to the order of the calculation, S^{-2}) classes of interactions: (a) long-range (ring and various iterated rings) which sum to a renormalized propagator expansion and are local in their effect—depend on r/a; (b) short-range interactions not expressible in terms of renormalized propagators which are space local. Their value is determined by the hard-sphere cutoff—thus sphere impenetrability is important to enforce properly in this problem; (c) long-range interactions expressible in terms of the renormalized propagator which are nonlocal in space.

6. Calculation of the random force correlation function $\langle RR \rangle$ (to lowest order in S^{-1}) shows that the fluctuations are indeed small compared with the deterministic motion. They are described by a linear Langevin equation with Gaussian, but nonwhite, noise. Analyzing the fluctuations for arbitrary space dimension d shows that $\beta - \alpha = (d - d_c)/2$ where $d_c = 2$. For $d > 2$ fluctuations are small relative to the deterministic motion, for $d \leqslant 2$ the fluctuations are as important as the deterministic motion and are an indication that, for this dimensionality, the chosen scaling is questionable.

The transport equation is found to be

$$(\partial/\partial t)N(\mathbf{r},t) = D_0(1+2\phi)\nabla^2 N - ck_D\left[1 + (3\phi)^{1/2} + (\phi/2)(5 + 3\ln 3)\right]N + \left(ck_D^2\right)^2 \int G^3(\mathbf{r}-\mathbf{r}')N(\mathbf{r}',t)d\mathbf{r}' \tag{5}$$

correct to order S^{-2}, where $G(r) = \exp[-\kappa r]/4\pi D_0 r$. The space nonlocality of the transport equation disappears if we consider the density $N(\mathbf{r},t)$ on a longer spatial scale l_F than l, since then $\Sigma_N(r/l)$ can be expanded in gradients in powers of $(l/l_F)^2$. The new rate coefficient so obtained is the old rate plus $(ck_D^2)^2\int d\mathbf{r}\, G(\mathbf{r})$. Neglecting space gradients ($l_F \to \infty$) yields a pure absorption transport equation $\partial N/\partial t = -k_f N$. (This regime can be obtained either by further coarse-graining the reaction-diffusion macroscopic equation or by starting from the Langevin equation and considering a scaling with $b \gg l$ with l fixed now.) Experiments which only measure rates should be compared to this result. For example, fluorescence quenching measures just an intensity which corresponds to the pure absorption regime.

3. EFFECTIVE MEDIUM THEORY

The scaling expansion approach just described is rigorous, but difficult to carry out beyond low order in S^{-1}. If we agree to focus on length scales longer than the screening scale l where the nonlocal behavior is absent and just consider the steady-state situation we can proceed in a more conventional (but approximate) fashion. Then a calculation of $\Sigma(k)$ can be expanded in k^2 to give by definition $k_f = \Sigma(0)$ and $D = D_0 + \delta D$ with $\delta D = [d^2\Sigma(k)/dk^2]_{k=0}$. Rather than express $\Sigma(k)$ in terms of the bare propagator G_0 and sphere scattering operators $\{T_i\}$, it is evident that an expansion in terms of a renormalized propagator such as $G(k) = [D_0(k^2 + \kappa^2)]^{-1}$ should be carried out if a higher concentration theory is desired. One way of introducing this feature is via an effective medium calculation.$^{(4,5)}$ In this approach an approximate memory function W (with corresponding propagator G_W) is added to both sides of the microscopic transport equation and the result is written schematically as $\Sigma - W = f(W)$. Given some

$W = W(G_W)$ we can solve for Σ. If the choice $W = \Sigma$ is made then a self-consistent equation $f(\Sigma) = 0$ is obtained. Following this scheme we generated the *exact* result

$$0 = \langle L(1 - GL)^{-1}\rangle\langle(1 - GL)^{-1}\rangle^{-1} \tag{6}$$

where $L = \Sigma - \sum_{i=1}^{M} T_i$ and T_i is the sphere scattering operator for the ith sphere in the true medium, i.e., $T_i = T_i(\Sigma)$. Truncation of Eq. (6) is required: the simplest is $\langle L\rangle = 0$, thus

$$\Sigma(k) = \sum_{i=1}^{M} \langle T_i\rangle(k) \tag{7}$$

This expression must be solved self-consistently for Σ (since the right-hand side depends on Σ). We have done so by numerical iteration about the low-concentration result $\Sigma^{(0)}(k) = \sum_{l=0}^{\infty}(2l + 1)^2 j_l^2(ka)$ where the $\{j_l\}$ are spherical Bessel functions. This generates all of $\Sigma(k)$ from which k_f and D are obtained by k^2 expansion. Another approach is to expand Eq. (7) directly to obtain two equations in k_f and D which are solved self-consistently. As the volume fraction increases the all-wave-vector and the hydrodynamic approaches differ increasingly but are qualitatively the same. For $\phi \leqslant 0.1$ the effective medium calculation is in good agreement with the scaling expansion method.

The calculations presented here can be extended to more sophisticated truncations of the effective medium identity of Eq. (6). In particular, it would be useful to include all scatterings among pairs of spheres in the effective medium. In this way, the pair distribution function of the spheres would enter the calculation explicitly.

Other aspects of this reaction–diffusion system are under active investigation. In particular we have used the radiation boundary condition in an effective medium calculation to explore the weakening of the diffusion control case all the way to the limit of no reaction.(8) Also, it is evident that the calculations sketched here can be used for different physical problems such as the viscosity of sphere suspensions(9) and thermal conductivity of two phase materials.

REFERENCES

1. M. V. Smoluchowski, *Phys. Z.* **17**:(1916).
2. R. A. Reck and S. Prager, *J. Chem. Phys.* **42**:3027 (1965); B. U. Felderhof and J. M. Deutch, *J. Chem. Phys.* **64**:4551 (1976); B. U. Felderhof, *Ibid.* **66**:4385 (1977); B. U. Felderhof, J. M. Deutch, and U. M. Titulaer, *Ibid* **76**:4178 (1982); J. R. Lebenhaft and R. Kapral, *J. Stat. Phys.* **20**:25 (1979); M. Bixon and R. Zwanzig, *J. Chem. Phys.* **75**:2354 (1982); T. R. Kirkpatrick, *J. Chem. Phys.* **76**:4255 (1982).

3. M. Muthukumar and R. I. Cukier, *J. Stat. Phys.* **26**:453 (1981).
4. M. Muthukumar, *J. Chem. Phys.* **76**:2667 (1982).
5. R. I. Cukier and K. Freed, *J. Chem. Phys.* Vol. 78 (1983), to appear.
6. M. Tokuyama and R. I. Cukier, *J. Chem. Phys.* **76**:6206 (1982).
7. H. Mori, *Prog. Theor. Phys.* **53**:1817 (1975); H. Mori and K. J. McNeil, *Ibid.* **57**, 770 (1977); M. Tokuyama and H. Mori, *Ibid.* **56**:1073 (1976); **58**:92 (1977).
8. R. I. Cukier, *J. Phys. Chem.* Vol. 87 (1983), to appear.
9. M. Tokuyama and R. I. Cukier, *Phys. Rev. Lett.* **48**:1604 (1982).