Long-Time Tails in the Kinetics of Reversible Bimolecular Reactions

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A new approach is developed to study the relaxation of concentrations to equilibrium in reversible bimolecular reactions. For $A + B \rightleftharpoons C$, a general analytic expression is derived for the amplitude of the power law ($t^{-d/2}$) asymptotics for arbitrary diffusion coefficients and concentrations of the reactants. Our formalism is based on the analysis of the time correlation functions describing the equilibrium fluctuations of the concentrations. This powerful and simple procedure can be readily used to study other bimolecular reactions such as $A + B \rightleftharpoons C + D$.

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To determine the kinetics of diffusion-influenced reversible reactions, such as $A + B \rightleftharpoons C$, over the entire time range, one must solve a many body problem. This problem simplifies considerably (but not sufficiently to yield an exact solution) when the B's are in great excess and when two of the species are static. When A and C are static, based on an approximate microscopic theory and on the results of simulations, it has been conjectured [1] that the normalized deviations of the concentrations from their equilibrium values decay asymptotically as $K_e/(1 + K_eB_e)^2(4\pi D_Bt)^{-d/2}$, where d is the dimension, K_e is the equilibrium constant, and D_B and B_e are the diffusion constant and the concentration of the species in excess. This result has recently been rigorously proved for $d = 1, 3$ by using a sophisticated many body perturbation technique [2]. This technique was previously used to treat the case $D_B = D_C = 0$, where it was found that the concentrations relax as $K_e/(1 + K_eB_e)^{1/2}(4\pi D_At)^{-3/2}$ in three dimensions [3]. The structure of these results suggests that, at least for pseudo-first-order reactions, a general simple result for the amplitude of the power law relaxation might exist.

The fact that, in bimolecular reversible reactions, the concentrations approach equilibrium not exponentially but rather as $t^{-d/2}$ was first discovered by using simple physical arguments involving spatial concentration fluctuations [4]. The basic idea is that, since the initial and equilibrium spatial fluctuations are different, a redistribution of particles through diffusion must occur before equilibrium can be reached. Since the relaxation due to reaction proceeds exponentially, the final approach to equilibrium is determined by the diffusion of the particles. The power law decay was subsequently obtained in various ways [5,6]. However, it was only recently that fluctuation theory yielded rigorous expressions for the amplitude of the relaxation in a few special cases [7]. Unfortunately, this approach, based on field theory techniques, does not appear to be applicable to static A or B particles [7]. Thus at present there is no overlap between results obtained by microscopic and what may be called hydrodynamic approaches.

The purpose of this paper is to present the complete solution of the asymptotics of $A + B \rightleftharpoons C$ for uniform random initial concentrations. Our starting point is a set of reaction-diffusion equations that describes concentration fluctuations at equilibrium. These are obtained by adding diffusive terms and random forces to the conventional nonlinear rate equations of chemical kinetics [8]. We then calculate equilibrium time correlation functions of the concentrations in Fourier space. To get the relaxation of the concentrations for the system removed from equilibrium, we exploit the Onsager regression hypothesis that equilibrium concentration fluctuations and small deviations of the bulk concentrations from equilibrium have the same relaxation law. In the standard theory of light scattering by chemically reacting systems, one linearizes the reaction-diffusion equations about equilibrium [8–10]. That is, one neglects the term that is quadratic in the deviations of the concentrations from their equilibrium values. Here we treat this quadratic nonlinearity as a small perturbation in the simplest possible way.

This nonlinearity gives rise to the $t^{-d/2}$ relaxation of the concentrations to equilibrium just like it is the nonlinearity in the Navier-Stokes equation that is responsible for the long-time tail of the velocity autocorrelation function [11]. However, these problems are different and, in fact, the problem considered below is a much simpler example of how a nonlinearity can alter the long-time dynamics of a stochastic system.

Let $A(\boldsymbol{r}, t)$, $B(\boldsymbol{r}, t)$, and $C(\boldsymbol{r}, t)$ be the local random concentrations of A, B, and C particles. When the particles are weakly interacting (i.e., an ideal solution) the concentration fluctuations due to diffusion in the presence of chemical reaction are described by the following system of equations:

$$\frac{\partial}{\partial t} A(\boldsymbol{r}, t) = D_A \nabla^2 A - k_a AB + k_d C + f_A(\boldsymbol{r}, t), \quad \text{(1a)}$$

$$\frac{\partial}{\partial t} B(\boldsymbol{r},t) = D_B \nabla^2 B - k_a AB + k_d C + f_B(\boldsymbol{r},t)\,, \tag{1b}$$

$$\frac{\partial}{\partial t} C(\boldsymbol{r},t) = D_C \nabla^2 C + k_a AB - k_d C + f_C(\boldsymbol{r},t)\,. \tag{1c}$$

The first terms on the right-hand side of Eqs. (1a)–(1c) describe the diffusion of A, B, and C particles with diffusion coefficients D_A, D_B, and D_C. The next two terms describe the chemical reaction with the association k_a and dissociation k_d rate constants. Finally, the last terms represent noise in the system. For the present purposes, we need only to assume that they have zero mean and are statistically uncorrelated with the initial concentrations. The initial concentrations are the equilibrium ones and when the system is infinite the distribution of particles is Poissonian [12] with mean concentrations A_e, B_e, and C_e. They obey the mass action law $K_e A_e B_e = C_e$, where $K_e = k_a/k_d$ is the equilibrium constant.

Let the Fourier transform of the concentration deviations from equilibrium, $\boldsymbol{c}(\boldsymbol{q},t)$, be a vector with the components $c_1(\boldsymbol{q},t) = \int d\boldsymbol{r}\, \exp(i\boldsymbol{q}\boldsymbol{r})[A(\boldsymbol{r},t) - A_e]$, etc. Equations (1a)–(1c) can then be rewritten as

$$\frac{\partial}{\partial t}\boldsymbol{c}(\boldsymbol{q},t) = -\boldsymbol{K}(\boldsymbol{q})\boldsymbol{c} - k_a \boldsymbol{v} \int \frac{d\boldsymbol{q}'}{(2\pi)^d} \times c_1(\boldsymbol{q}-\boldsymbol{q}',t)c_2(\boldsymbol{q}',t) + \boldsymbol{f}(\boldsymbol{q},t)\,. \tag{2}$$

Here $\boldsymbol{v}$ is a column vector with components $(1,1,-1)$, and $\boldsymbol{f}(\boldsymbol{q},t)$ is a vector with the random forces f_A, f_B, and f_C in $\boldsymbol{q}$ space as components. Matrix $\boldsymbol{K}(\boldsymbol{q})$ contains both diffusion and reaction terms:

$$\boldsymbol{K}(\boldsymbol{q}) = \begin{pmatrix} k_a B_e & k_a A_e & -k_d \\ k_a B_e & k_a A_e & -k_d \\ -k_a B_e & -k_a A_e & k_d \end{pmatrix} + q^2 \begin{pmatrix} D_A & 0 & 0 \\ 0 & D_B & 0 \\ 0 & 0 & D_C \end{pmatrix}. \tag{3}$$

We begin by calculating the 3×3 matrix of concentration correlation functions with elements $\langle c_j(\boldsymbol{q},t)c_l^*(\boldsymbol{q}',0)\rangle$, where $\langle\cdots\rangle$ denotes the ensemble averaging over the noise and equilibrium (Poissonian) initial conditions. It is convenient to define the relaxation matrix $\boldsymbol{R}(\boldsymbol{q},t)$ as

$$\langle \boldsymbol{c}(\boldsymbol{q},t)\boldsymbol{c}^\dagger(\boldsymbol{q}',0)\rangle = \boldsymbol{R}(\boldsymbol{q},t)\langle \boldsymbol{c}(\boldsymbol{q},0)\boldsymbol{c}^\dagger(\boldsymbol{q}',0)\rangle\,. \tag{4}$$

The relaxation of the bulk concentrations $A(t)$, $B(t)$, and $C(t)$ from a uniform (random) initial condition that is close to equilibrium is then obtained as follows. Assuming that decay of the bulk concentrations to equilibrium is the same as the decay of equilibrium concentration fluctuations, we have

$$\boldsymbol{C}(t) = \boldsymbol{R}(\boldsymbol{q}=0,t)\boldsymbol{C}(0)\,, \tag{5}$$

where $\boldsymbol{C}(t)$ is a vector with the components $C_1(t) = A(t) - A_e$, $C_2(t) = B(t) - B_e$, and $C_3(t) = C(t) - C_e$. Since the total number of particles is conserved during the reaction, $C_1(t) = C_2(t) = -C_3(t)$ and hence $\boldsymbol{C}(t)$ equals $\boldsymbol{v}$ times some function of time. Consequently, the concentration relaxation function defined as $\mathcal{R}(t) = C_i(t)/C_i(0)$ is the same for all i and is the eigenvalue of the relaxation matrix $\boldsymbol{R}$ at $\boldsymbol{q} = 0$ corresponding to eigenvector $\boldsymbol{v}$:

$$\boldsymbol{R}(0,t)\boldsymbol{v} = \mathcal{R}(t)\boldsymbol{v}\,. \tag{6}$$

In the standard theory of light scattering [8–10] the nonlinear term in Eq. (2) is neglected because it is quadratic in the deviations of the concentrations from their equilibrium values. $\boldsymbol{R}(\boldsymbol{q},t)$ is then obtained by first solving for $\boldsymbol{c}(\boldsymbol{q},t)$, multiplying the result on the left by $\boldsymbol{c}^\dagger(\boldsymbol{q}',0)$, and finally taking the equilibrium average by using the fact that the noise and the initial concentration fluctuations are uncorrelated. In this way, one finds that $\boldsymbol{R}(\boldsymbol{q},t) = \exp[-\boldsymbol{K}(\boldsymbol{q})t]$. Since $\boldsymbol{K}(0)\boldsymbol{v} = k_0\boldsymbol{v}$ where $k_0 = k_d + k_a(A_e + B_e)$, it follows from Eq. (6) that $\mathcal{R}(t) = \exp(-k_0 t)$ which is the standard result of ordinary chemical kinetics.

To go beyond this theory, we treat the nonlinearity as a small perturbation and solve Eq. (2) iteratively in lowest order. Specifically, we first formally solve this equation for $\boldsymbol{c}(\boldsymbol{q},t)$, approximating c_1 and c_2 in the nonlinear term by the solution of the linearized problem. We then multiply the result by $\boldsymbol{c}^\dagger(\boldsymbol{q}',0)$ and take the equilibrium average. By using the statistical independence of the noise and the initial conditions, we obtain

$$\langle \boldsymbol{c}(\boldsymbol{q},t)\boldsymbol{c}^\dagger(\boldsymbol{q}',0)\rangle = e^{-\boldsymbol{K}(\boldsymbol{q})t}\langle \boldsymbol{c}(\boldsymbol{q},0)\boldsymbol{c}^\dagger(\boldsymbol{q}',0)\rangle - e^{-\boldsymbol{K}(\boldsymbol{q})t} * k_a \boldsymbol{v} \int \frac{d\boldsymbol{q}''}{(2\pi)^d} \langle [e^{-\boldsymbol{K}(\boldsymbol{q}-\boldsymbol{q}'')t}\boldsymbol{c}(\boldsymbol{q}-\boldsymbol{q}'',0)]_1 [e^{-\boldsymbol{K}(\boldsymbol{q}'')t}\boldsymbol{c}(\boldsymbol{q}'',0)]_2 \boldsymbol{c}^\dagger(\boldsymbol{q}',0)\rangle\,, \tag{7}$$

where "*" denotes time convolution $f(t) * g(t) = \int_0^t f(t-t')g(t')\,dt'$. Note that the random forces do not contribute to this order and thus the same result would be obtained if these forces were averaged out right from the beginning. The properties of the correlation functions for a uniform (Poisson) equilibrium distribution are

$$\langle c_i(\boldsymbol{q}_1,0)c_j^*(\boldsymbol{q}_2,0)\rangle = \delta_{ij}(2\pi)^d\delta(\boldsymbol{q}_1 - \boldsymbol{q}_2)C_i^e\,, \tag{8a}$$

$$\langle c_i(\boldsymbol{q}_1,0)c_j(\boldsymbol{q}_2,0)c_l^*(\boldsymbol{q}_3,0)\rangle = \delta_{ij}\delta_{il}(2\pi)^d\delta(\boldsymbol{q}_1 + \boldsymbol{q}_2 - \boldsymbol{q}_3)C_i^e\,, \tag{8b}$$

where $C_1^e = A_e$, $C_2^e = B_e$, and $C_3^e = C_e$. Using these in Eq. (7), we find [see Eq. (4)]

$$\boldsymbol{R}(\boldsymbol{q},t) = e^{-\boldsymbol{K}(\boldsymbol{q},t)} - k_a e^{-\boldsymbol{K}(\boldsymbol{q},t)}\boldsymbol{v} * \boldsymbol{u}^\top(\boldsymbol{q},t)\,, \tag{9}$$

where row vector $\boldsymbol{u}^\top(\boldsymbol{q},t)$ has the components

$$u_j(\boldsymbol{q},t) = \int \frac{d\boldsymbol{q}'}{(2\pi)^d}[e^{-\boldsymbol{K}(\boldsymbol{q}-\boldsymbol{q}')t}]_{1j}[e^{-\boldsymbol{K}(\boldsymbol{q}')t}]_{2j}\,. \tag{10}$$

The Fourier transform of $\boldsymbol{R}(\boldsymbol{q},t)$ in the time domain determines the light scattering spectrum [8].

The concentration relaxation function, which is the eigenvalue of $\boldsymbol{R}(0,t)$ corresponding to the eigenvector $\boldsymbol{v}$, is

$$\mathcal{R}(t) = e^{-k_0 t} - k_a \int_0^t d\tau\, e^{-k_0(t-\tau)} \sum_{j=1}^{3} v_j \int \frac{d\boldsymbol{q}'}{(2\pi)^d} [e^{-\boldsymbol{K}(\boldsymbol{q}')\tau}]_{1j} [e^{-\boldsymbol{K}(\boldsymbol{q}')\tau}]_{2j} . \tag{11}$$

To find its asymptotic behavior, it is convenient to represent the exponentials in Eq. (11) as a sum over eigenvalues $\lambda_i(\boldsymbol{q})$ of matrix $\boldsymbol{K}(\boldsymbol{q})$: $\exp[-\boldsymbol{K}(\boldsymbol{q})t] = \sum_{i=1}^{3} \boldsymbol{X}_i \exp[-\lambda_i(\boldsymbol{q})t]$, where $\boldsymbol{X}_i$ are built from the appropriate eigenvectors. Such a decomposition can be used to define the "normal modes" of the linearized reaction-diffusion system [8,10]. Two of three modes live infinitely long as $\boldsymbol{q} \to 0$ (hydrodynamic modes) while the third one has a finite lifetime. In the $\boldsymbol{q} \to 0$ limit, the eigenvalues of $\boldsymbol{K}(\boldsymbol{q})$ are $\lambda_{1,2} = q^2 \mathcal{D}_{1,2}$ and $\lambda_3 = k_0 + q^2 \mathcal{D}_3$, where $\mathcal{D}_i$ are given by

$$\mathcal{D}_{1,2} = \left[\sum k_\alpha (D_\beta + D_\gamma) \pm \sqrt{\sum [k_\alpha^2 (D_\beta - D_\gamma)^2 + 2 k_\alpha k_\beta (D_\gamma - D_\alpha)(D_\gamma - D_\beta)]} \right] \bigg/ 2k_0 , \tag{12a}$$

$$\mathcal{D}_3 = \sum_{\alpha=1}^{3} k_\alpha D_\alpha / k_0 . \tag{12b}$$

Here k_α and D_α are defined by the diagonal elements of $\boldsymbol{K}(\boldsymbol{q})$ in Eq. (3) as $K_{\alpha\alpha}(\boldsymbol{q}) = k_\alpha + D_\alpha q^2$. The sums in Eq. (12a) are taken over permutations.

At long times only small values of $\boldsymbol{q}$ contribute to the integral in Eq. (11). Using the spectral representation of $\exp[-\boldsymbol{K}(\boldsymbol{q})t]$ and evaluating the integrals, we find that, as $t \to \infty$,

$$\mathcal{R}(t) \sim \frac{K_e}{1 + K_e(A_e + B_e)} \left\{ \frac{f(2,2) + g^2(1)}{(8\pi \mathcal{D}_1 t)^{d/2}} + \frac{f(1,1) + g^2(2)}{(8\pi \mathcal{D}_2 t)^{d/2}} - \frac{f(1,2) + f(2,1) + 2g(1)g(2)}{[4\pi(\mathcal{D}_1 + \mathcal{D}_2)t]^{d/2}} \right\}, \tag{13}$$

where $f(i,j)(\mathcal{D}_1 - \mathcal{D}_2)^2 = [\beta(\mathcal{D}_i + \mathcal{D}_3 - 2D_A) + D_A - \mathcal{D}_i][\alpha(\mathcal{D}_j + \mathcal{D}_3 - 2D_B) + D_B - \mathcal{D}_j]$, $g(i)(\mathcal{D}_1 - \mathcal{D}_2) = \sqrt{\alpha\beta}\,(\mathcal{D}_i - D_C)$, and $\alpha = K_e A_e [1 + K_e(A_e + B_e)]^{-1}$, $\beta = \alpha B_e / A_e$. Note that the coefficients are determined solely by the diffusion constants, the equilibrium constant, and the equilibrium (or, equivalently, the initial) concentrations. The asymptotics consist of three terms that correspond to the two hydrodynamic modes and their cross term. Let us consider some special cases where this result simplifies.

(a) Pseudo-first-order reaction.—As $A_e \to 0$, the first two terms in Eq. (13) vanish, so the relaxation function becomes

$$\mathcal{R}(t) \sim \frac{K_e}{(1 + K_e B_e)^2} [4\pi(D_B + \mathcal{D})t]^{-d/2}, \tag{14}$$

where $\mathcal{D} = (D_A + K_e B_e D_C)/(1 + K_e B_e)$. This result is surprisingly simple: $D_B + \mathcal{D}$ is just the average of the relative diffusion coefficients, $D_A + D_B$ and $D_C + D_B$, weighted by the fraction of the time the system is in the A [i.e., $(1 + K_e B_e)^{-1}$] and C [i.e., $K_e B_e (1 + K_e B_e)^{-1}$] states. This relaxation function reduces to the known exact results for the reversible target problem ($D_A = D_C = 0$) [1,2] and to the reversible trapping problem ($D_B = D_C = 0$) [3].

(b) Two equal diffusion coefficients: $D_B = D_C$.—The relaxation function now contains two nonzero terms:

$$\mathcal{R}(t) \sim \frac{2K_e^3 A_e B_e}{[1 + K_e(A_e + B_e)]^3} (8\pi \mathcal{D} t)^{-d/2} + \frac{K_e}{[1 + K_e(A_e + B_e)]^2} [4\pi(D_B + \mathcal{D})t]^{-d/2}, \tag{15}$$

where now the effective diffusion coefficient is $\mathcal{D} = [(1 + K_e A_e)D_A + K_e B_e D_C]/[1 + K_e(A_e + B_e)]$. The last term in Eq. (15) is the generalization of the previous case, reducing to it in the limit $A_e \to 0$ or $B_e \to 0$. The first term, however, does not appear in the pseudo-first-order case since it vanishes as $A_e \to 0$. When $D_A = D_B = D_C$, Eq. (15) reduces to the result first obtained by Rey and Cardy [7].

(c) Two equal diffusion coefficients: $D_A = D_B$.—All three terms of the asymptotics are manifested in this case:

$$\mathcal{R}(t) \sim \frac{2K_e A_e B_e}{(A_e + B_e)^2 [1 + K_e(A_e + B_e)]} (8\pi D_B t)^{-d/2} + \frac{2K_e A_e B_e}{(A_e + B_e)^2 [1 + K_e(A_e + B_e)]^3} (8\pi \mathcal{D} t)^{-d/2}$$
$$+ \frac{K_e (A_e - B_e)^2}{(A_e + B_e)^2 [1 + K_e(A_e + B_e)]^2} [4\pi(D_B + \mathcal{D})t]^{-d/2} \tag{16}$$

with $\mathcal{D} = [D_A + K_e(A_e + B_e)D_C]/[1 + K_e(A_e + B_e)]$. This result coincides with the asymptotics obtained in Ref. [7] only if we specialize to the case that $A_e = B_e$.

We have presented a simple unified derivation of the long-time asymptotics of the reversible reaction $A + B \rightleftharpoons C$ in the framework of fluctuation theory. The fact that our general expression [Eq. (13)] reduces to few previously known exact results is of course only a necessary condition for it to be exact in general. However, because these exact results span different regions of parameter space and were obtained by completely different and nonoverlaping methods, we fully expect that our result is exact for uniform random initial conditions in ideal (i.e., the particles are not strongly interacting) solutions. Our procedure can be readily used to treat more complex bimolecular reactions. (Needless to say, this procedure works for simpler reactions such as $A + A \rightleftharpoons A_2$, where we obtain the result given in Ref. [7].) The asymptotics will be a power law for any reversible chemical reaction for which (i) the rate equations are nonlinear and (ii) at least one linear combination of the concentrations does not change with time. This latter requirement means that the reaction matrix $\boldsymbol{K}(0)$ must have at least one zero eigenvalue. This is necessary for the occurrence of a slow hydrodynamic mode (i.e., an eigenvalue that vanishes as $\boldsymbol{q}^2$ as $\boldsymbol{q} \to 0$) which, when coupled by the nonlinearity, gives rise to the long-time tail.

We conclude by presenting a few results for $A + B \rightleftharpoons C + D$. In this case, there are three long-lived modes and, in general, the asymptotics consist of six terms. In the pseudo-first-order limit ($A_e \to 0$, $C_e \to 0$), one can show that

$$\mathcal{R}(t) \sim \frac{K_e B_e}{(K_e B_e + D_e)^2}[4\pi(D_D + \mathcal{D})t]^{-d/2} + \frac{K_e D_e}{(K_e B_e + D_e)^2}[4\pi(D_B + \mathcal{D})t]^{-d/2} \tag{17}$$

with $\mathcal{D} = (D_e D_A + K_e B_e D_C)/(K_e B_e + D_e)$ and $K_e = C_e D_e/(A_e B_e)$. When all of the diffusion coefficients are the same,

$$\mathcal{R}(t) \sim \left[\frac{K_e(A_e + B_e + C_e + D_e)}{[K_e(A_e + B_e) + C_e + D_e]^2} + \frac{2(K_e - 1)^2 K_e A_e B_e}{[K_e(A_e + B_e) + C_e + D_e]^3}\right](8\pi D t)^{-d/2}. \tag{18}$$

The general result is too complex to be presented here, but no new ideas or techniques are involved in its derivation.

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