

Exact Asymptotic Relaxation of Pseudo-First-Order Reversible Reactions

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The relaxation kinetics of the diffusion-influenced reversible reaction $A + B \rightleftharpoons C$ is studied in the pseudo-first-order limit ($[B] \gg [A]$) when A and C are static and the B 's move independently with diffusion coefficient D . For the initial condition $[A(0)] = 1$, $[C(0)] = 0$, it is shown that the asymptotics of $[A(t)]$ for $t \rightarrow \infty$ is given in d dimensions by $(1 + K_{\text{eq}}[B])^{-1} + K_{\text{eq}}^2[B]/(1 + K_{\text{eq}}[B])^3 f_d(t)$ with $f_1(t) = (\pi Dt)^{-1/2}$, $f_2(t) = (4\pi Dt)^{-1}$, and $f_3(t) = (4\pi Dt)^{-3/2}$, and where K_{eq} is the equilibrium constant. By comparing with accurate simulations, this result is found to be exact for $d = 1$, and we predict that it is exact for higher dimensions. [S0031-9007(97)04276-2]

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Arguably the simplest irreversible diffusion-influenced reaction is $A + B \rightarrow 0$ in the limit that $[B] \gg [A]$. When A is static and the B 's diffuse independently, the concentration of A is exactly described by the Smoluchowski result: $[A(t)] = \exp[-[B] \int_0^t k_{\text{irr}}(\tau) d\tau]$, where $k_{\text{irr}}(t)$ is the familiar time-dependent rate coefficient. The reversible analog ($A + B \rightleftharpoons C$) has not been solved exactly but has been attacked by a variety of analytic approaches [1–8]. In one dimension, computer simulations of the kinetics of this reaction were first performed independently by Agmon, Schnörer, and Blumen [9], and Szabo and Zwanzig [10]. Both of these papers suggested that the concentration of A approaches its equilibrium value as $t^{-1/2}$. In particular, by performing a long simulation involving a large number of particles for a single set of parameters, Szabo and Zwanzig [10] presented rather convincing evidence that this asymptotic behavior is exact in the thermodynamic limit. These authors also compared the predictions of several theories with the simulations. They found excellent agreement at short times. Small but significant deviations were seen at longer times, especially as the reaction approached the irreversible limit.

The most successful theory was the “superposition approximation” (SA) approach [4,10] based on the work of Lee and Karplus [1]. This theory involves only the reactive pair distribution function between A and B and can be regarded [4] as the natural generalization of the Smoluchowski theory of irreversible reactions. By linearizing this theory near equilibrium, Szabo [4] was able to express analytically the Laplace transform of the concentration deviation in terms of the transform of k_{irr} . In this way, it was found that the SA predicted that equilibrium is approached as $t^{-d/2}$ in d dimensions [4,10]. Thus while the SA was not exact at long times, it did predict the $t^{-1/2}$ dependence found in the simulations.

The validity of the $t^{-d/2}$ asymptotics was questioned by the experimental study of Huppert *et al.* [11] who

monitored the kinetics of reversible proton transfer after photoexcitation of a dye. Based on an analysis of their data, it appeared that equilibrium was approached as $t^{-\alpha}$ where α , while close to $3/2$, depended on the proton concentration. This apparent deviation from the theoretical asymptotics motivated Agmon and Edelstein [12] to reinvestigate the kinetics of this reaction in one dimension at extremely long times for a wide range of parameters. To do this they had to develop a new and powerful Brownian dynamics algorithm to handle reversible reactions. Their work showed unambiguously [12–15] that for all concentrations equilibrium was approached as $t^{-1/2}$. Moreover, they found, in agreement with earlier work [10], that the SA approach, while it does predict $t^{-1/2}$ asymptotics, does not predict the correct amplitude and deteriorates as the product of the equilibrium constant and the B concentration increases.

This state of affairs led Naumann [16] to extend the SA by explicitly considering not only the A – B pair correlation function (g_{AB}), but also the pair correlation function between C and B (g_{CB}). Starting with the exact hierarchy satisfied by the many-particle reduced distribution functions, he truncated this hierarchy by invoking superposition approximations for both AB and CB distribution functions, and obtained a coupled set of nonlinear partial differential equations involving the concentrations g_{AB} and g_{CB} .

In this paper we consider this extended approach (ESA) in d dimensions and compare its predictions in one dimension with essentially exact results obtained via Brownian dynamic simulations. By linearizing the ESA about equilibrium, we obtain an analytic expression for the Laplace transform of the deviation of the concentration from its equilibrium value, in terms of the transform of the time-dependent rate coefficient of irreversible reactions. Using this, we obtain an analytic expression for the concentration as $t \rightarrow \infty$, which turns out to be exact in one dimension.

Our microscopic many-particle model can be described as follows. A single static A is surrounded by B 's at concentration $[B]$ which do not interact with each other and move with diffusion coefficient D . The interaction of B with A and C is described by the same spherically symmetric potential of mean force $U(r)$. The reaction between A and B occurs at contact (i.e., when the interparticle separation is R) with the intrinsic rate constant κ_a . The intrinsic dissociation constant of C to form a contact pair is κ_d . The equilibrium constant K_{eq} is $\kappa_a e^{-\beta U(R)}/\kappa_d$ [with $\beta = (k_B T)^{-1}$]. We choose concentration units so that $[A(t)] + [C(t)] = 1$. The equilibrium concentration of A is $[A(\infty)] = (1 + K_{\text{eq}}[B])^{-1}$. Below, we explicitly consider the initial condition $[A(0)] = 1$ and thus $[A(t)]$ denotes the concentration at time t for this initial condition. The simulations were performed with initial condi-

tion $[A(0)] = 0$. We denote the concentrations at time t for this initial condition by $[A(t)]_0$. These two quantities are related by $[A(t)] + K_{\text{eq}}[B][A(t)]_0 = 1$, which is exact for the above many-particle model [10].

The ESA equations obtained by Naumann for $d = 1$ [16] can be readily generalized to d dimensions. In this approach, the concentrations satisfy

$$\frac{d[A]}{dt} = -k_{\text{ESA}}(t)[A(t)][B] + \kappa_d[C(t)], \quad (1)$$

where $k_{\text{ESA}}(t)$ is related to the AB pair correlation function at contact by

$$k_{\text{ESA}}(t) = \kappa_a g_{\text{AB}}(R, t). \quad (2)$$

The pair correlation functions $g_{\text{AB}}(r, t)$ and $g_{\text{CB}}(r, t)$ satisfy

$$\partial_t g_{\text{AB}} = D \nabla e^{-\beta U(r)} \nabla e^{\beta U(r)} g_{\text{AB}} - \kappa_d \frac{[C(t)]}{[A(t)]} (g_{\text{AB}} - g_{\text{CB}}), \quad (3)$$

$$\partial_t g_{\text{CB}} = D \nabla e^{-\beta U(r)} \nabla e^{\beta U(r)} g_{\text{CB}} + k_{\text{ESA}}(t) \frac{[A(t)][B]}{[C(t)]} (g_{\text{AB}} - g_{\text{CB}}), \quad (4)$$

subject to the initial conditions $g_{\text{AB}}(r, 0) = g_{\text{CB}}(r, 0) = e^{-\beta U(r)}$ and the boundary conditions

$$(\mathbf{J}g_{\text{AB}})_{r=R} = \kappa_a g_{\text{AB}}(R, t) - \kappa_d \frac{[C(t)]}{[A(t)][B]}, \quad (5)$$

$$(\mathbf{J}g_{\text{CB}})_{r=R} = 0, \quad (6)$$

where \mathbf{J} is the flux operator [$\mathbf{J} = D e^{-\beta U(x)} (\partial/\partial x) e^{\beta U(x)}$ for $d = 1$, $2\pi r D e^{-\beta U(r)} (\partial/\partial r) e^{\beta U(r)}$ for $d = 2$, and $4\pi r^2 D e^{-\beta U(r)} (\partial/\partial r) e^{\beta U(r)}$ for $d = 3$]. Equation (6) means that C cannot react with B . When $g_{\text{CB}}(r, t)$ is approximated by $g_{\text{AB}}(r, t)$, the above equations reduce to the SA equations [4].

One can linearize the above equations near equilibrium. By setting

$$[A(t)] = (1 + K_{\text{eq}}[B])^{-1} + \Delta(t), \quad (7)$$

$$[C(t)] = K_{\text{eq}}[B](1 + K_{\text{eq}}[B])^{-1} - \Delta(t) \quad (8)$$

in the above equations and retaining only terms linear in $\Delta(t)$, one can show that for a spherically symmetric potential $U(r)$, the Laplace transform of $\Delta(t)$ [$\hat{f}(s) = \int_0^\infty e^{-st} f(t) dt$] is given by

$$\frac{\hat{\Delta}(s)}{\Delta(0)} = \{s + (\kappa_a e^{-\beta U(R)}[B] + \kappa_d) s \hat{k}_{\text{sg}}(s)/k_{\text{sg}}(0)\}^{-1}, \quad (9)$$

where

$$\frac{1}{s \hat{k}_{\text{sg}}(s)} = \frac{1}{s \hat{k}_{\text{irr}}(s)} + \frac{K_{\text{eq}}[B]}{(s + \kappa_a e^{-\beta U(R)}[B] + \kappa_d) \hat{k}_{\text{irr}}(s + \kappa_a e^{-\beta U(R)}[B] + \kappa_d)}. \quad (10)$$

Equation (9) is the generalization of a result obtained within the framework of the SA [4], reducing to it when k_{sg} is replaced by k_{irr} . Since $k_{\text{irr}}(0) = \kappa_a e^{-\beta U(R)}$ but $k_{\text{sg}}(0) = k_{\text{irr}}(0)/(1 + K_{\text{eq}}[B])$, the ESA yields (see below) the identical power law asymptotics as the SA, but with an amplitude that is smaller by a factor $(1 + K_{\text{eq}}[B])$. The subscript "sg" was chosen because it turns out that k_{sg} is the generalization of k_{irr} to the *stochastically gated* irreversible reaction in which the system fluctuates between an "open" or reactive state (i.e., A) and a "closed" or inert state (i.e., C) with rate coefficients



[see Eqs. (2.8) in Ref. [17]].

In order to construct a linearized ESA approximation (LESA) that is applicable to all times, we choose $\Delta(0)$ so that Eq. (7) is exact at $t = 0$. This gives

$$[A(t)] = (1 + K_{\text{eq}}[B])^{-1} + \frac{K_{\text{eq}}[B]}{1 + K_{\text{eq}}[B]} \frac{\Delta(t)}{\Delta(0)}, \quad (12)$$

where $\Delta(t)/\Delta(0)$ is given by Eq. (9). To implement the LESA one needs $\hat{k}_{\text{irr}}(s)$. Neglecting interaction forces [$U(r) = 0$], for $d = 1, 2, 3$ these are given by (see, for example, Ref. [18])

$$\hat{k}_{\text{irr}}(s) = \frac{\kappa_a(D/S)^{1/2}}{\kappa_a + (DS)^{1/2}}, \quad d = 1 \quad (13)$$

$$= \frac{\kappa_a 2\pi D (sR^2/D)^{1/2} K_1((sR^2/D)^{1/2})}{s\{\kappa_a K_0((sR^2/D)^{1/2}) + 2\pi D (sR^2/D)^{1/2} K_1((sR^2/D)^{1/2})\}}, \quad d = 2 \quad (14)$$

$$= \frac{\kappa_a 4\pi DR [1 + (sR^2/D)^{1/2}]}{s\{\kappa_a + 4\pi DR [1 + (sR^2/D)^{1/2}]\}}, \quad d = 3, \quad (15)$$

where the K_n are modified Bessel functions of the second kind.

For $U(r) \neq 0$ and $d = 3$ the following asymptotic approximation for k_{irr} is exact when $s \rightarrow 0$ or $s \rightarrow \infty$

$$\hat{k}_{\text{irr}}(s) \asymp \frac{\kappa_a e^{-\beta U(R)} 4\pi DR_e [1 + (sR_e^2/D)^{1/2}]}{s\{\kappa_a e^{-\beta U(R)} + 4\pi DR_e [1 + (sR_e^2/D)^{1/2}]\}}, \quad (16)$$

where

$$R_e^{-1} = \int_R^\infty r^{-2} e^{\beta U(r)} dr \quad (17)$$

(see Ref. [18]). To find the long-time limit behavior of $[A(t)]$ within the LESA, we take the $s \rightarrow 0$ limit of the Laplace transform of Eq. (12) with $\hat{\Delta}(s)/\Delta(0)$ given by Eqs. (9) and (10). In this way we find for the initial condition $[A(0)] = 1$ [and by assuming for $d = 1$ and $d = 2$ quite analogous asymptotic $\hat{k}_{\text{irr}}(s)$ approximations for $U \neq 0$ as Eq. (16) for $d = 3$]

$$[A(t)] = (1 + K_{\text{eq}}[B])^{-1} + \frac{K_{\text{eq}}^2[B]}{(1 + K_{\text{eq}}[B])^3} \begin{cases} (\pi Dt)^{-1/2}, & d = 1, \\ (4\pi Dt)^{-1}, & d = 2, \\ (4\pi Dt)^{-3/2}, & d = 3. \end{cases} \quad (18)$$

For future reference we shall also need the corresponding result for the initial condition $[A(0)] = 0$. This is readily found by using the exact relation $[A(t)] + K_{\text{eq}}[B][A(t)]_0 = 1$ to be

$$[A(t)]_0 = (1 + K_{\text{eq}}[B])^{-1} - \frac{K_{\text{eq}}}{(1 + K_{\text{eq}}[B])^3} \begin{cases} (\pi Dt)^{-1/2}, & d = 1, \\ (4\pi Dt)^{-1}, & d = 2, \\ (4\pi Dt)^{-3/2}, & d = 3. \end{cases} \quad (19)$$

In Figs. 1 and 2 we compare Brownian dynamics curves of Edelman and Agmon (see Figs. 6 and 9 in Ref. [19]) for $d = 1$ with ESA relaxation curves based on Eqs. (1)–(6) and with the LESA asymptotics predicted for $[A(t)]_0$ in

Eq. (19). The ESA curves were calculated using an implicit finite-difference scheme for time, applied previously by one of us in Refs. [20–23]. Figure 1 corresponds to the “concentration series” studied in Ref. [19] ($\kappa_a = D = 1$, $\kappa_d = 0.1$, $[B] = 0.002, 0.02, 0.2, 0.4$), whereas Fig. 2 corresponds to the parameter sets of the “reactivity series” ($\kappa_a = D = 1$, $[B] = 0.4$, $\kappa_d = 0.001, 0.01, 0.1, 1$).

The figures demonstrate that the ESA approach, which is the best one can do by truncating the reduced distribution function hierarchy at the pair level using superposition, correctly predicts both the amplitude and power exponent of the relaxation to equilibrium in one dimension. When $K_{\text{eq}}[B] \ll 1$, it predicts the time course of the concentrations with high accuracy. However, when $K_{\text{eq}}[B] > 1$, it fails to describe the kinetics in the preasymptotic region. This is somewhat disappointing and a reflection of the complexity of what appears at first sight to be a simple problem. It is well known that one dimension, although of limited experimental interest, does

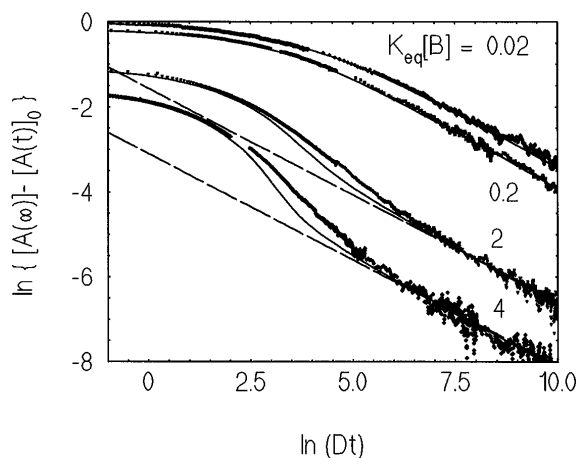


FIG. 1. Comparison of the ESA predictions for $[A(\infty)] - [A(t)]_0$ (full lines) with Brownian dynamics simulation data (data marks) and with the asymptotic LESA prediction (19) in $d = 1$ (broken lines) for the “concentration series” in Ref. [19] ($\kappa_a = D = 1$, $\kappa_d = 0.1$, varying $[B]$).

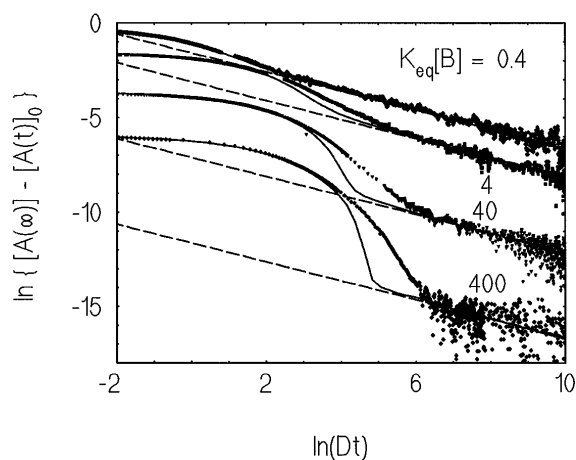


FIG. 2. Comparison of the ESA predictions for $[A(\infty)] - [A(t)]_0$ (full lines) with Brownian dynamics simulation data (data marks) and with the asymptotic LESAs prediction (19) in $d = 1$ (broken lines) for the “reactivity series” in Ref. [19] ($\kappa_a = D = 1$, $[B] = 0.4$, varying κ_d).

provide the most demanding test for theories of diffusion-influenced reactions. Therefore, it is expected that the ESA and LESAs will be more satisfactory in three dimensions. Since our derivation of the amplitude and exponent of the relaxation to equilibrium treats all dimensions on equal footing, we fully expect that our result will turn out to be exact in $d = 2, 3$. The availability of an exact analytic expression for both the time course and amplitude of the relaxation to equilibrium of this many-body model, should serve as a stimulus to finding an exact solution valid for all times or at least a rigorous proof of our asymptotic result.

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