Rigorous Derivation of the Long-Time Asymptotics for Reversible Binding

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Using an iterative solution in Laplace-Fourier space, we supply a rigorous mathematical proof for the long-time asymptotics of reversible binding in one dimension. The asymptotic power law and its concentration dependent prefactor result from diffusional and many-body effects which, unlike for the corresponding irreversible reaction and in classical chemical kinetics, play a dominant role in shaping the approach to equilibrium.

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Are many-body and mobility effects important for bimolecular reactions in condensed phases? The simplest irreversible diffusion influenced reaction, $A + B \to C$, has been studied by von Smoluchowski [1] in the pseudounimolecular limit where $c \equiv [B]$ far exceeds $[A]$, the concentration of A. It has since been demonstrated several times [2–4] that for the "target problem" [5] of a static A molecule, the von Smoluchowski theory is equivalent to an exact solution of a pair problem. Even when A is mobile the deviations from this theory are small [5,6], so that truly many-body effects are hardly observable. Mobility effects introduce short-time deviations from exponentiality which are hard to detect experimentally. The conclusion from this celebrated problem might be that the theory of diffusion influenced reactions [7] deals with negligible corrections to classical chemical kinetics.

The situation changes dramatically for reversible reactions

$$A + B \underset{k_d}{\overset{k_a}{\rightleftarrows}} C\,,$$

in which every dissociation event renews the competition of B particles over binding to A. In the pseudounimolecular case, chemical kinetics predicts an approach to equilibrium as $\exp[-(k_d + ck_a)t]$. In contrast, experiment [8], simulations [9–11], and most theoretical approaches [12–25] agree that the ultimate approach to equilibrium is a power law, $t^{-d/2}$ in d dimensions, but there is no rigorous proof for this result. In addition, there is no agreement on the concentration dependence of the prefactor, which changes with the level of the (approximate) many-body theory employed.

Fluctuation analysis of bimolecular chemical reactions [12] first suggested that the asymptotic approach to equilibrium is a power law rather than exponential, but precise expressions were not provided. The simple "superposition approximation" (SA) for the reversible target problem [13] suggested that the survival probability of an initially unbound A to remain so by time t, denoted $P_A(t)$, obeys the following asymptotic law in d dimensions [16,17]:

$$P_A(t) \sim \frac{1}{1 + cK_{\mathrm{eq}}} + \frac{cK_{\mathrm{eq}}^2}{(1 + cK_{\mathrm{eq}})^{\alpha}} \frac{1}{(4\pi Dt)^{d/2}}\,, \quad (1)$$

where $\alpha = 2$. D is the diffusion coefficient of the B particles. The (association) equilibrium coefficient, in the absence of long-range interactions between A and B, is given by $K_{\mathrm{eq}} = k_a/k_d$. Comparison with one-dimensional Brownian simulations [9–11] showed that the correct prefactor differs from the simple SA prediction. A linearized version of an enhanced SA developed later gave $\alpha = 3$ [22,23], and that already agreed with the simulations. Consequently Naumann, Shokhirev, and Szabo [22] conjectured that Eq. (1) with $\alpha = 3$ is the exact asymptotic behavior. Interestingly, this also follows from an earlier analysis of bimolecular reaction-diffusion equations (provided that some misprints in Eq. (12) of Ref. [18] are corrected) and [26] from the "bimolecular boundary condition" of Ref. [15]. Most recently, the conjecture has been contested [24]. The challenge remains to find a rigorous proof starting from the exact equations of motion. This challenge is met below.

Our proof is based on the diagrammatic technique of Gopich and Doktorov [21], which was previously applied to the problem of static reversible traps (mobile A which binds reversibly to randomly distributed static B's). In the present approach, the exact many-particle diffusion equations are first transformed to Fourier-Laplace space, then converted to an integral equation which is solved iteratively. We show that only two iterations are required for obtaining the asymptotic behavior. Diffusion-limited reactions are most anomalous in one dimension, which provides the most stringent test for such theories [27]. While the structure of our proof is independent of dimensionality, more specialized, "radial" Fourier transforms are required in dimensions $d > 1$ [28]. Thus it is best appreciated in the simplest case of one-dimensional diffusion, without sink terms or potentials. The additional technical detail required to generalize it to $d = 3$ is available in Ref. [28].

We begin with a vacant static reversible trap, A, at the origin ($x = 0$) and N noninteracting, diffusing B particles (of identical diffusion coefficient D) randomly distributed on $[-L/2, L/2]$. Their concentration is thus $c = N/L$. When a B particle reaches the origin, it may bind with a rate coefficient k_a provided that the trap is still vacant. C may in turn release a B particle, with a dissociation coefficient k_d. We wish to obtain the survival probability,

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$P_A(t)$, for A to be vacant at time t after the initiation of the process in the "thermodynamic limit" (Tlim) in which $L \to \infty$ and $N \to \infty$, while maintaining $c = N/L$ constant.

The state of the (finite) system is defined by $N + 1$ "state vectors." In the "A state" (vacant site) the vector $\vec{x} = (x_1, \ldots, x_N)$ denotes the location of particles $B_1, \ldots, B_N$. In the "C_i state" (bound B_i), the vector $\vec{x}_{\neq i} = (x_1, \ldots, x_i = 0, \ldots, x_N)$ depicts the location of the remaining $N - 1$ particles. We denote the probability density functions (F) in the two states by $F_A(\vec{x}, t)$ and $F_{C_i}(\vec{x}_{\neq i}, t)$, respectively. These obey the $N + 1$ coupled diffusion equations [20]

$$\frac{\partial F_A(\vec{x}, t)}{\partial t} = \sum_{i=1}^{N} \left[D \frac{\partial^2 F_A}{\partial x_i^2} - k_a \delta(x_i) F_A + k_d \delta(x_i) F_{C_i} \right], \tag{2a}$$

$$\frac{\partial F_{C_i}(\vec{x}_{\neq i}, t)}{\partial t} = \sum_{j \neq i = 1}^{N} D \frac{\partial^2 F_{C_i}}{\partial x_j^2} + k_a \int_{-\infty}^{\infty} dx_i \, \delta(x_i) F_A - k_d F_{C_i}, \tag{2b}$$

($i = 1, \ldots, N$) subject to the initial distribution

$$F_A(\vec{x}, 0) \equiv F_A^0(\vec{x}) = L^{-N}, \qquad F_{C_i}(\vec{x}_{\neq i}, 0) = 0, \tag{3}$$

namely, all the B particles are equivalent and randomly distributed around the vacant trap. Unlike other theoretical approaches (e.g., the SA), which start from approximate equations, we begin from the exact microscopic description of the N-particle problem in Eq. (2). The first term on its right-hand side (rhs) describes the free motion of each unbound B particle, whereas the localized sink terms (*not* boundary conditions) depict the probability of each particle to bind and unbind per unit time.

In the Tlim we have an infinite number of coupled partial differential equations and their solution, even asymptotically, seems formidable. These become simpler, algebraic equations in Laplace-Fourier space. Laplace transform over time and Fourier transform (FT) over space are defined by

$$\tilde{F}(\vec{x}, s) \equiv \int_0^{\infty} dt \exp(-st) F(\vec{x}, t),$$

$$\hat{F}(\vec{\lambda}, t) \equiv \int_{-\infty}^{\infty} dx_1 \ldots \int_{-\infty}^{\infty} dx_N \exp(\iota \vec{\lambda} \cdot \vec{x}) F(\vec{x}, t),$$

where $\vec{\lambda} \cdot \vec{x} = \sum_{i=1}^{N} \lambda_i x_i$ is the usual scalar product and $\iota \equiv \sqrt{-1}$. Using the Fourier representation of the delta function, $2\pi\delta(x) = \int_{-\infty}^{\infty} d\lambda \exp(-\iota\lambda x)$, and applying both transforms to Eqs. (2) gives

$$(s + \Lambda^2) \hat{\tilde{F}}_A(\vec{\lambda}, s) = \hat{F}_A^0(\vec{\lambda}) - k_a \sum_{i=1}^{N} \mathcal{I}_i \hat{\tilde{F}}_A + k_d \sum_{i=1}^{N} \hat{\tilde{F}}_{C_i}, \tag{4a}$$

$$(s + \Lambda_{\neq i}^2 + k_d) \hat{\tilde{F}}_{C_i}(\vec{\lambda}_{\neq i}, s) = k_a \mathcal{I}_i \hat{\tilde{F}}_A, \tag{4b}$$

where $\Lambda^2 = D\vec{\lambda} \cdot \vec{\lambda}$ and $\Lambda_{\neq i}^2 = D\vec{\lambda}_{\neq i} \cdot \vec{\lambda}_{\neq i}$. The integration operator over the ith Fourier component is $\mathcal{I}_i \equiv \int_{-\infty}^{\infty} d\lambda_i / 2\pi$. Note that the FT of the initial distribution for a finite interval,

$$\hat{F}_A^0(\vec{\lambda}) = \prod_{i=1}^{N} \frac{2}{L\lambda_i} \sin\left(\frac{L\lambda_i}{2}\right), \tag{5}$$

obeys $\hat{F}_A^0(\vec{0}) = 1$, but if we let $L \to \infty$ then $\hat{F}_A^0(\vec{\lambda}) \to (2\pi/L)^N \prod_{i=1}^{N} \delta(\lambda_i)$.

We proceed by rewriting Eqs. (4) as

$$\hat{\tilde{F}}_A(\vec{\lambda}, s) = \hat{\tilde{G}}_0 \left(\hat{F}_A^0 - k_a \sum_{i=1}^{N} W(\Lambda_{\neq i}) \mathcal{I}_i \hat{\tilde{F}}_A \right), \tag{6}$$

where the effective A-B reactivity term is

$$W(z) = \frac{s + z^2}{s + k_d + z^2}. \tag{7}$$

It describes an "encounter," which is the convoluted effect of recombination with one B particle, diffusion of the remaining $N - 1$ particles, and subsequent dissociation of the bound B.

$$\hat{\tilde{G}}_0(\vec{\lambda}, s) = (s + \Lambda^2)^{-1}$$

is the Laplace-Fourier transform (LFT) of the free diffusion Green function, $G_0(\vec{x}, t) = \prod_{i=1}^{N} \exp(-x_i^2/4Dt)/\sqrt{4\pi Dt}$.

It is possible to iterate over Eq. (6), and this procedure clearly produces a good short-time approximation. However, to improve the convergence properties at long times, we first replace G_0 by an effective Green function, $G_{\text{eff}}(\vec{x}, t)$, whose LFT is defined by

$$\hat{\tilde{G}}_{\text{eff}}(\vec{\lambda}, s) = [s + \Lambda^2 + ck_a W(\Lambda)]^{-1}. \tag{8}$$

This function has two useful limiting forms. If all the Fourier variables vanish, one obtains the effective Green function integrated over all spatial coordinates

$$\hat{\tilde{G}}_{\text{eff}}(\vec{0}, s) = \frac{s + k_d}{s(s + k_d + ck_a)} = \frac{1}{1 + cK_{\text{eq}}} \left(\frac{1}{s} + \frac{cK_{\text{eq}}}{s + k_d + ck_a} \right). \tag{9}$$

This describes a simplified evolution of A, which is correct at both $t = 0$ and $t = \infty$. Otherwise, when both $\vec{\lambda}_{\neq i}$ and x_i vanish, we obtain, by back FT, an effective pair Green function

$$\tilde{g}_{\text{eff}}(s) \equiv \mathcal{I}_i \hat{\tilde{G}}_{\text{eff}}(\vec{\lambda}_{\neq i} = \vec{0}, s) = \frac{1}{1 + cK_{\text{eq}}} \left(\frac{1}{\sqrt{4Ds}} + \frac{cK_{\text{eq}}}{\sqrt{4D(s + k_d + ck_a)}} \right), \tag{10a}$$

$$g_{\text{eff}}(t) = \frac{1}{1 + cK_{\text{eq}}} \frac{1}{\sqrt{4\pi Dt}} (1 + cK_{\text{eq}} e^{-(k_d + ck_a)t}), \tag{10b}$$

representing an AB_i pair at zero separation.

By inserting Eq. (8) into Eq. (6) we obtain

$$\hat{\tilde{F}}_A(\vec{\lambda},s) = \hat{\tilde{G}}_{\rm eff}\Bigg[\hat{F}_A^0 - k_a\Bigg(\sum_{i=1}^{N} W(\Lambda_{\neq i})\mathcal{I}_i - cW(\Lambda)\Bigg)\hat{\tilde{F}}_A\Bigg]. \quad (11)$$

It is seen how the use of $G_{\rm eff}$ results in renormalization of the integral operator, which will facilitate the derivation of the asymptotic behavior. Note that Eq. (11) is still exact, and that solving it for the survival probability,

$$P_A(t) \equiv \mathrm{Tlim}\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_N\, F_A(\vec{x},t)\,, \quad (12a)$$

$$\tilde{P}_A(s) = \mathrm{Tlim}\,\hat{\tilde{F}}_A(\vec{0},s)\,, \quad (12b)$$

in the Tlim requires taking the limits of $N \to \infty$ and $\vec{\lambda} \to \vec{0}$.

We proceed to solve Eq. (11) iteratively. The iteration parameter, $k_a W(\Lambda)$, behaves as $K_{\rm eq}(s + \Lambda^2)$ for small s and Λ^2. Hence the expansion for $P_A(t)$ is convergent for long times. The zeroth iteration on Eq. (11) gives

$$\hat{\tilde{F}}_A^{(0)}(\vec{\lambda},s) = \hat{\tilde{G}}_{\rm eff}\hat{F}_A^0\,. \quad (13)$$

Setting $\vec{\lambda} = \vec{0}$, $\hat{F}_A^0(\vec{0}) = 1$, and applying Eq. (9) gives, for small s,

$$\tilde{P}_A^{(0)}(s) \sim \frac{1}{s(1 + cK_{\rm eq})}\,, \quad (14)$$

whose Laplace inverse is the equilibrium limit of Eq. (1).

The first iteration substitutes $\hat{\tilde{F}}_A^{(0)}$ for $\hat{\tilde{F}}_A$ in the rhs of Eq. (11), yielding

$$\hat{\tilde{F}}_A^{(1)} - \hat{\tilde{F}}_A^{(0)} = -k_a\hat{\tilde{G}}_{\rm eff}\Bigg(\sum_{i=1}^{N} W(\Lambda_{\neq i})\mathcal{I}_i - cW(\Lambda)\Bigg) \times \hat{\tilde{G}}_{\rm eff}\hat{F}_A^0\,. \quad (15)$$

Because $\mathcal{I}_i\hat{\tilde{G}}_{\rm eff}(\vec{\lambda},s)\hat{F}_A^0(\vec{\lambda}) = L^{-1}\hat{\tilde{G}}_{\rm eff}(\vec{\lambda}_{\neq i},s)\hat{F}_A^0(\vec{\lambda}_{\neq i})$ and all particles are equivalent, Eq. (15) vanishes in the Tlim for $\vec{\lambda} = \vec{0}$.

The leading nonconstant term in Eq. (1), the main objective of our derivation, arises from the second iteration

$$\hat{\tilde{F}}_A^{(2)} - \hat{\tilde{F}}_A^{(1)} = k_a^2\hat{\tilde{G}}_{\rm eff}\Bigg(\sum_{i=1}^{N} W(\Lambda_{\neq i})\mathcal{I}_i - cW(\Lambda)\Bigg) \times \hat{\tilde{G}}_{\rm eff}\Bigg(\sum_{j=1}^{N} W(\Lambda_{\neq j})\mathcal{I}_j - cW(\Lambda)\Bigg)\hat{\tilde{G}}_{\rm eff}\hat{F}_A^0\,. \quad (16)$$

In the desired limit, we may cancel $cW(\Lambda)$ from the first bracket and $\sum_{j\neq i=1}^{N} W(\Lambda_{\neq j})\mathcal{I}_j - cW(\Lambda)$ from the second, obtaining

$$\Delta\tilde{P}_A^{(2)}(s) \equiv \tilde{P}_A^{(2)} - \tilde{P}_A^{(1)} = \mathrm{Tlim}\lim_{\vec{\lambda}\to\vec{0}}\sum_{i=1}^{N}[k_a\hat{\tilde{G}}_{\rm eff}W(\Lambda_{\neq i})\mathcal{I}_i]^2\hat{\tilde{G}}_{\rm eff}\hat{F}_A^0\,. \quad (17)$$

The first integration eliminates λ_i, and the second was already performed explicitly for $\vec{\lambda}_{\neq i} = \vec{0}$ in Eq. (10a). Hence we obtain

$$\Delta\tilde{P}_A^{(2)}(s) = c[k_a W(0)\,\hat{\tilde{G}}_{\rm eff}(\vec{0},s)]^2\tilde{g}_{\rm eff}(s)\,. \quad (18)$$

Using Eqs. (7), (9), and (10) we find, in the limit of small s, that

$$\Delta\tilde{P}_A^{(2)}(s) \sim \frac{cK_{\rm eq}^2}{(1 + cK_{\rm eq})^3}\,\frac{1}{\sqrt{4Ds}}\,. \quad (19)$$

Its Laplace inverse gives the leading nonconstant term in Eq. (1) for $d = 1$ with $\alpha = 3$, as conjectured by Naumann *et al.* [22].

Continuing in a similar fashion, we find for the nth order term in the thermodynamic limit that

$$\Delta\tilde{P}_A^{(n)}(s) = (-k_a)^n \lim_{\vec{\lambda}\to\vec{0}}\sum(2\pi c)^p \prod_{j=1}^{n}[\hat{\tilde{G}}_{\rm eff}W(\Lambda_{\neq i_j})\mathcal{I}_{i_j}] \times \hat{\tilde{G}}_{\rm eff}\prod_{k=1}^{p}\delta(\lambda_k)\,. \quad (20)$$

The operator product involves n terms for p distinct B particles. Each particle, B_{i_j} $(1 \le i_j \le p)$, encounters A at least twice, hence $n \ge 2p$. In each encounter this particle binds, and the remaining $N - 1$ particles diffuse freely until it unbinds. The sum in Eq. (20) is performed over all possible p $(1 \le p \le [n/2])$ and over distinct permutations of identical particles.

To show that higher order terms do not contribute to the coefficient of $t^{-1/2}$, we use a dimensional argument. Introducing a dimensionless integration variable, $\lambda_j = \lambda_j'\sqrt{s/D}$, we find that $\mathcal{I}_j \propto \sqrt{s}$ and $\delta(\lambda_j) \propto \delta(\lambda_j')/\sqrt{s}$. In addition, for small s, the dominant s dependence of the other relevant functions is $\hat{\tilde{G}}_{\rm eff} \propto s^{-1}$ and $W \propto s$. Thus a term involving p distinct particles in $\Delta\tilde{P}_A^{(n)}(s)$ is proportional to $s^{-1+(n-p)/2}$. As $n \ge 2p$, the $1/\sqrt{s}$ term comes solely from the second order term $(n = 2)$ with one particle involved $(p = 1)$. We have checked this argument by going to third and fourth order. For $n = 3$ we also have only $p = 1$, so that

$$-\Delta\tilde{P}_A^{(3)}(s) = c[k_a W(0)]^3[\hat{\tilde{G}}_{\rm eff}(\vec{0},s)\;\tilde{g}_{\rm eff}(s)]^2 \sim \frac{cK_{\rm eq}^3}{(1 + cK_{\rm eq})^4}\Bigg(\frac{1}{4D} + \frac{cK_{\rm eq}}{2D}\sqrt{\frac{s}{k_d + ck_a}}\Bigg). \quad (21)$$

This contributes a $t^{-3/2}$ term.

The next term in the asymptotic expansion comes from the $n = 4$ term with $p = 2$. It goes like $1/t$, so that we extend Eq. (1) for $d = 1$ by writing

$$P_A(t) \sim \frac{1}{1 + cK_{\rm eq}} + \frac{cK_{\rm eq}^2}{(1 + cK_{\rm eq})^3}\,\frac{1}{(4\pi Dt)^{1/2}} + \frac{2c^2K_{\rm eq}^4}{(1 + cK_{\rm eq})^5}\,\frac{1}{4\pi Dt}\,. \quad (22)$$

The leading $t^{-1/2}$ term represents a modified pair problem, and reflects the return probability of a given B particle to the origin, corrected by the mean-field influence of all other B's. Indeed, it arises solely from the second order term in the expansion and involves in its evaluation only the coordinates of a single B ($p = 1$). This means that asymptotically a given B particle may encounter A at most twice. To understand the origin of the $\alpha = 3$ behavior (as opposed to the incorrect $\alpha = 2$ predicted by the simple SA) we have performed the expansion starting from Eq. (6). It shows that $\alpha = 2$ corresponds to ignoring single encounters with other B particles, which might occur in between two encounters with a given B. The more complex many-body effects ($p \geq 2$) occur at intermediate times, and cannot be described by any kind of modified pair dynamics.

The proof in three dimensions follows the same principles, though it is technically more involved [28]. Again, we find that Eq. (1) holds, with $\alpha = 3$ and $d = 3$. A less trivial dimensional dependence occurs in the *second* term of the expansion, which in three dimensions goes as $t^{-5/2}$ instead of the t^{-1} behavior predicted in one dimension.

In the natural sciences, very few many-body problems may be solved exactly, even asymptotically. The problem of obtaining a rigorous derivation for the long-time approach to equilibrium for reversible binding has remained open for over a decade. Fortunately, it has now been possible to solve this problem, and the solution might hopefully inspire new approaches to other many-body problems. Our derivation provides a unique proof that both diffusional and many-body effects exert non-negligible influence on bimolecular reactivity in the reversible case. Since reversibility is the rule rather than the exception, advances in the field of reversible diffusion influenced reactions should eventually lead to reassessment of the classical description of chemical kinetics.

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