Nonequilibrium Distribution Function Theory of Many-Particle Effects in the Reversible Reactions of the Type $A+B \leftrightarrow C+B$

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We study the relaxation kinetics of reversible reactions of the type $A + B \rightleftharpoons C + B$ by applying the many-particle kernel theory, which we have developed to investigate many-particle effects on general diffusion-influenced reactions. It is shown that for the target model, where A and C molecules are immobile and their interconversion is induced by the encounter with the B molecules that are present in much excess, the many-particle kernel theory gives a result that coincides with the known exact result.

Key Words : Reversible diffusion-influenced reaction, Many-particle effects, Nonequilibrium distribution function theory

Introduction

For the last two decades, a great deal of effort has been directed to investigate the many-particle effects on the kinetics of reversible diffusion-influenced reactions.[1-18] In reversible reactions, reactant molecules that were extinguished by the forward reaction are regenerated by the backward reaction. In general, the regenerated reactant would see a non-equilibrium distribution of reactant partners that depends on its previous reaction history. Accordingly, the regenerated reactant would have a time-dependent probability of encountering reaction partners. This fact makes it difficult to develop a rigorous theory for the kinetics of reversible reactions.

By now, there are several theoretical frameworks dealing with the kinetics of reversible reactions. Among these, reduced distribution function (RDF) approach has been one of the most popular one,[1-4,9-12,17] which starts from a hierarchical set of evolution equations for the RDFs of the reactant molecules. Explicit solution to the set of kinetic equations is then obtained by introducing a truncation approximation called the dynamic superposition approximation (SA).[1,2,9-12,17] Due to its simplicity and flexibility, the SA-based RDF approach has been applied to many types of reactions,[1,2,9-12,17,19,20] one of which is reversible association-dissociation reaction, $A + B \rightleftharpoons C$.[1,2,9-12] For this type of reactions, the prediction of the SA-based RDF theory agrees well with that of Brownian dynamics (BD) simulation,[18] in the asymptotic time region as well as at short times.[21]

However, it was revealed by Yang, Lee, and Shin (YLS) that for other simple reversible reactions of the type $A + B \rightleftharpoons C + B$, the SA-based RDF theory shows large discrepancy from the exact results.[6] In addition, Gopich and Burshtein reported that the quantum yield for the latter type of reactions calculated by the SA-based RDF theory differs much from the exact one.[15] Instead of the SA-based RDF theory, YLS presented another theoretical framework in which memory equation for the one-particle reactant density

field is obtained by applying Mori projection operator technique[22] to formal master kinetic equation describing complete many-particle reaction dynamics. Then the memory function appearing in the resulting memory equation was analyzed by fully renormalized kinetic theory developed by Mazenko.[23] The result of their theory was in better agreement with the exact results than that of the SA-based RDF theory, for the reactions of the type $A + B \rightleftharpoons C + B$. Also for the reversible reaction of the type $A + B \rightleftharpoons C$, the YLS theory was shown to provide a better qualitative explanation on the BD simulation[18] results than the SA-based RDF theory did, except at long times;[7] the YLS theory predicts an incorrect amplitude of the asymptotic decay curve. More recently, Gopich, Kipriyanov, and Doktorov applied the modified integral encounter theory (MET) to the reversible reaction of the type $A + B \rightleftharpoons C + B$.[14] In MET, a formal solution to the master kinetic equation is manipulated with the density expansion of the propagator and sophisticated diagrammatic technique. In the work, it was shown that the MET and the YLS theory have the comparable accuracy.

However, unfortunately, even the MET and the YLS theory become inaccurate as the reactant density increases, because low reactant density approximations are addressed in both theories: the result of the former predicts a slower relaxation and that of the latter predicts a faster relaxation than the exact result. And neither of them reduces correctly to the exact Smoluchowski result[24] in the irreversible limit. Therefore, there was acute need for developing more rigorous theory for the reversible reaction kinetics.

Recently, we reported an advanced RDF theory that does not rely on the dynamic SA.[3,4] In the work, it was shown that the RDF formalism gives a formally exact non-Markovian rate equation and exact expressions for the time-dependent reactant number densities. The rate kernels appearing in the rate equation and the reactant number density expressions involve a many-particle kernel (MPK) that carries the information on the mean-field dynamical influence of surrounding reactant molecules on the reaction between a pair of

reactant molecules. The expressions for the many-particle kernels were determined in a systematic manner by considering the evolution equations for the three-particle RDFs. This new solution procedure in the RDF formalism has been widely cited as the MPK theory in ensuing literature.[25,26] When it was applied to the reversible association reaction, $A + B \rightleftharpoons C$,[3] the results of the MPK theory were better than any previously reported theory and showed almost perfect agreement with the BD simulation[18] for the whole time range and for any sets of reaction parameters.

In the present work, we study the relaxation kinetics of reversible reactions of the type $A + B \rightleftharpoons C + B$ by applying the MPK theory. It is shown that the striking success of the MPK theory is not limited only to the reactions of the type $A + B \rightleftharpoons C$: the MPK theory turns out to give the known *exact results*, when it is applied to the reactions of the type $A + B \rightleftharpoons C + B$.

Theory

The observable quantities are time-dependent number densities of A and C molecules denoted by $a(t)$ and $c(t)$, respectively. On the other hand, the number density of B molecules assumed to be present in great excess of A and C molecules would remain effectively constant and is denoted by C_B. For the sake of simplicity, we consider the reaction system where the spherical A and C molecules with radius σ are immobile while the B molecules are mobile point particles and mutually independent. The chemical reaction between A (or C) and B molecules is assumed to occur when B molecules come into contact with A (or C) molecule. Only for the just mentioned simple reaction model, the exact analytic result is available.

According to reaction scheme, we can write down the kinetic equations for the time-dependent reactant number density as[1]

$$\frac{d}{dt}a(t) = -\frac{d}{dt}c(t) = -\kappa_f C_{AB}(\sigma, t) + \kappa_r C_{CB}(\sigma, t) \quad (1)$$

Here, κ_f and κ_r represent the inherent rate parameters for the forward and the reverse bimolecular reaction. The first and the second terms describe the changes in the time-evolutions of the number densities due to the forward and the reverse bimolecular reactions, respectively. The two-particle RDF $C_{AB}(r,t)$ in the first term represents the averaged product of the number densities of A and B molecules at the two locations separated by r, and the other two-particle RDF $C_{CB}(r,t)$ in the second term has the similar meaning. The evolution equations for these functions are, in turn, given by

$$\frac{d}{dt}C_{AB}(r, t) = L(r)C_{AB}(r, t)$$
$$+ \frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}}[-\kappa_f C_{AB}(r, t) + \kappa_r C_{CB}(r, t)] \quad (2)$$
$$-\kappa_f C_{ABB}(r, \sigma, t) + \kappa_r C_{CBB}(r, \sigma, t).$$

$$\frac{d}{dt}C_{CB}(r, t) = L(r)C_{CB}(r, t)$$
$$+ \frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}}[\kappa_f C_{AB}(r, t) - \kappa_r C_{CB}(r, t)] \quad (3)$$
$$+ \kappa_f C_{ABB}(r, \sigma, t) - \kappa_r C_{CBB}(r, \sigma, t).$$

$L(r)$ in Eqs. (2) and (3) denotes the operators describing the thermal motion of B molecules. In d spatial dimension, its explicit expression is given as $L(r)f(r) = D_B r^{1-d}(d/dr)r^{d-1} e^{-U}(d/dr)e^{U}f(r)$, where D_B is the diffusion constant of B molecules and $U(r)$ is the potential of mean force (in units of thermal energy) between A (or C) and B molecules. The second terms on the right sides of Eqs. (2) and (3) take account of the changes in the two-particle RDFs due to the forward and the backward bimolecular reactions $A + B \rightleftharpoons C + B$. γ_d is the metric factor that depends on the dimensionality, d, of the reaction system; it equals for 4π, for $d = 3$, 2π for $d = 2$, and 2 for $d = 1$. For the simpler one-dimensional system where B molecules reside at one side of an A or C molecule, $\gamma_d = 1$. The third and the fourth terms describe the changes due to the competitive reactions of a third B molecule with the A and C molecules whose pair dynamics with the B molecule at a distance r is of primary concern. These terms contain the three-particle RDFs, $C_{ABB}(r,r',t)$ and $C_{CBB}(r,r',t)$; $C_{ABB}(r,r',t)$ denotes the averaged product of the number density of A molecules and the number densities of B molecules at the two locations separated from the A by r and r', and $C_{CBB}(r,r',t)$ has the similar physical meaning. In turn, the evolution equations for these three-particle RDFs are given by

$$\frac{\partial}{\partial t}C_{ABB}(r, r', t) = [L(r) + L(r')]C_{ABB}(r, r', t)$$
$$+ \frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}}[-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{CBB}(r, r', t)]$$
$$+ \frac{\delta(r' - \sigma)}{\gamma_d \sigma^{d-1}}[-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{CBB}(r, r', t)] \quad (4)$$
$$-\kappa_f C_{ABBB}(r, r', \sigma, t) + \kappa_r C_{CBBB}(r, r', \sigma, t).$$

$$\frac{\partial}{\partial t}C_{CBB}(r, r', t) = [L(r) + L(r')]C_{CBB}(r, r', t)$$
$$- \frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}}[-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{CBB}(r, r', t)]$$
$$- \frac{\delta(r' - \sigma)}{\gamma_d \sigma^{d-1}}[-\kappa_f C_{ABB}(r, r', t) + \kappa_r C_{CBB}(r, r', t)] \quad (5)$$
$$+ \kappa_f C_{ABBB}(r, r', \sigma, t) - \kappa_r C_{CBBB}(r, r', \sigma, t).$$

Each term in the right sides of Eqs. (4) and (5) has a similar physical meaning with the corresponding term in Eqs. (2) and (3). In analogous manner, we can write down the evolution equations for the higher-order RDFs up to N-th order, where N is the number of B molecules in reaction

system. For treating the macroscopic system where N is order of Avogadro number, we introduce a truncation approximation, instead of solving the whole set of hierarchical equations.

Before doing this, let us look for the formally exact solutions. The method of solution can be delineated more clearly in the Laplace domain. Denoting the Laplace transform of a function $f(t)$ by $\hat{f}(s)[\equiv \int_0^\infty dt e^{-st} f(t)]$, we can rewrite Eq. (1) as

$$s\hat{a}(s) - a_0 = -[s\hat{c}(s) - c_0]$$
$$= -\kappa_f \hat{C}_{AB}(\sigma, s) + \kappa_r \hat{C}_{CB}(\sigma, s) \equiv \hat{\alpha}(s) \qquad (6)$$

where we have defined an auxiliary function $\hat{\alpha}(s)$. a_0 and c_0 denote the initial value of $a(t)$ and $c(t)$. Next by defining a *many-particle kernel* according to the equation

$$\hat{\alpha}(s)C_B[\hat{\xi}(r,s) + g(r)]$$
$$= -\kappa_f \hat{C}_{ABB}(r, \sigma, s) + \kappa_r \hat{C}_{CBB}(r, \sigma, s), \qquad (7)$$

we can obtain the formally exact formula for the two-particle RDFs as

$$\Delta\hat{C}_{AB}(r,s) = \frac{\hat{\alpha}(s)}{s - L(r)}\left[\frac{\delta(r-\sigma)}{\gamma_d \sigma^{d-1}} + C_B\hat{\xi}(r,s)\right] \qquad (8)$$

$$\Delta\hat{C}_{CB}(r,s) = -\frac{\hat{\alpha}(s)}{s - L(r)}\left[\frac{\delta(r-\sigma)}{\gamma_d \sigma^{d-1}} + C_B\hat{\xi}(r,s)\right] \qquad (9)$$

from Eqs. (2) and (3) respectively. In Eqs. (8) and (9), $\Delta\hat{C}_{AB}(r,s) = \hat{C}_{AB}(r,s) - a(s)C_B g(r)$ and $\Delta\hat{C}_{CB}(r,s) = \hat{C}_{CB}(r,s) - \hat{c}(s)C_B g(r)$, where $g(r)$ denotes the equilibrium pair correlation function obeying $L(r)g(r)=0$. The initial pair correlation of A-B or C-B pair are assumed to be given by $g(r)$ so that $C_{AB}(r,0) = a_0 C_B g(r)$ and $C_{CB}(r,0) = c_0 C_B g(r)$. Then, by substituting Eqs. (8) and (9) into Eq. (6), we get a rate equation as

$$\hat{\alpha}(s) \equiv -\kappa_f \hat{C}_{AB}(\sigma, s) + \kappa_r \hat{C}_{CB}(\sigma, s)$$
$$= -\hat{k}_f(s)\hat{a}(s)C_B + \hat{k}_r(s)\hat{c}(s)C_B \qquad (10)$$

where

$$\frac{\hat{k}_f(s)}{k_f^{eq}} = \frac{\hat{k}_r(s)}{k_r^{eq}} = \frac{1}{\hat{F}(s)}; \qquad (11)$$

$$F(s) = 1 + \frac{\kappa_f + \kappa_r}{s - L(r)}\left[\frac{\partial(r-\sigma)}{\gamma_d \sigma^{d-1}} + C_B\hat{\xi}(r,s)\right]\Bigg|_{r=\sigma} \qquad (12)$$

Here, k_f^{eq} and k_r^{eq} denote equilibrium forward and backward reaction rate constants given by $\kappa_f g(\sigma)$ and $\kappa_r g(\sigma)$, respectively. Note that the forward and the backward rate kernels $\hat{k}_f(s)$ and $\hat{k}_r(s)$ defined in Eq. (11) satisfy the detailed balance condition $\hat{k}_f(s)/\hat{k}_r(s) = k_f^{eq}/k_r^{eq} \equiv K_{eq}$ exactly, irrespective of the specific form of evolution operator $L(r)$ and the many-particle kernel $\hat{\xi}(r,s)$. In terms of the rate kernels, we can obtain the following expressions

for $\hat{a}(s)$ and $\hat{c}(s)$ from Eqs. (6) and (10):

$$\hat{a}(s) = \hat{Y}_A(s|A)a_0 + \hat{Y}_A(s|C)c_0 \qquad (15)$$

$$\hat{c}(s) = \hat{Y}_C(s|A)a_0 + \hat{Y}_C(s|C)c_0 \qquad (16)$$

where

$$\hat{Y}_A(s|A) = [s + \hat{k}_r(s)C_B]/Q \qquad (17)$$

$$\hat{Y}_A(s|C) = \hat{k}_r(s)C_B/Q \qquad (18)$$

$$\hat{Y}_C(s|A) = \hat{k}_f(s)C_B/Q \qquad (19)$$

$$\hat{Y}_C(s|C) = [s + \hat{k}_f(s)C_B]/Q \qquad (20)$$

with $Q = s^2 + s[\hat{k}_f(s)C_B + \hat{k}_r(s)C_B]$. Here, $Y_A(t|A)$ is the probability that an A molecule at time 0 is found still as A molecule at a later time t, while $Y_C(t|A)$ is the probability that an A molecule at time 0 is found to be C molecule at a later time t. $Y_C(t|C)$ and $Y_C(t|A)$ have the similar meanings. An *exact reciprocal relation* holds between $Y_A(t|C)$ and $Y_C(t|A)$. By comparing Eqs. (18) and (19), we get

$$\frac{\hat{Y}_C(s|A)}{\hat{Y}_A(s|C)} = \frac{\hat{k}_f(s)}{\hat{k}_r(s)} = K_{eq}. \qquad (21)$$

In addition, we can also get the *exact generalized mass action law, i.e.*

$$Y_A(t|A) + Y_A(t|C)K_{eq} = 1 \qquad (22)$$

$$Y_C(t|A)K_{eq}^{-1} + Y_C(t|C) = 1 \qquad (23)$$

Note that we have not yet made any approximation and the results obtained up to now are exact. However, as in Eqs. (12) and (13), the complicated many-particle effects are incorporated into the rate kernels $\hat{k}_f(s)$ and $\hat{k}_r(s)$ through the many-particle kernel $\hat{\xi}(r,s)$ that is not yet determined.

To determine the many-particle kernel $\hat{\xi}(r,s)$ as defined in Eq. (7), we should evaluate $\hat{C}_{ABB}(r, \hat{r}, s)$ and $\hat{C}_{CBB}(r, \hat{r}, s)$. From Eqs (4) and (5), we can derive

$$\hat{C}_{ABB}(r,r,s) = \hat{a}(s)C_B^2 g(r)g(r')$$
$$+ \frac{\hat{\alpha}(s)C_B}{s - L(r) - L(r')}\frac{\delta(r-\sigma)}{\gamma_d \sigma^{d-1}}[g(r') + \hat{\xi}(r',s)]$$
$$+ \frac{\hat{\alpha}(s)C_B}{s - L(r) - L(r')}\frac{\delta(r'-\sigma)}{\gamma_d \sigma^{d-1}}[g(r) + \hat{\xi}(r,s)]$$
$$+ \frac{\hat{\alpha}(s)C_B^2}{s - L(r) - L(r')}[g(r)\hat{\xi}(r',s) + g(r')\hat{\xi}(r,s)$$
$$+ \hat{\xi}(r,s)\hat{\xi}(r',s)] \qquad (24)$$

$$\hat{C}_{CBB}(r,r,s) = \hat{c}(s)C_B^2 g(r)g(r')$$
$$- \frac{\hat{\alpha}(s)C_B}{s - L(r) - L(r')}\frac{\delta(r-\sigma)}{\gamma_d \sigma^{d-1}}[g(r') + \hat{\xi}(r',s)]$$

$$- \frac{\hat{\alpha}(s)C_B}{s - L(r) - L(r')}\frac{\delta(r' - \sigma)}{\gamma_d \sigma^{d-1}}[g(r) + \hat{\xi}(r, s)]$$

$$- \frac{\hat{\alpha}(s)C_B^2}{s - L(r) - L(r')}[g(r)\hat{\xi}(r', s) + g(r')\hat{\xi}(r, s)$$

$$+ \hat{\xi}(r, s)\hat{\xi}(r', s)] \tag{25}$$

with the use of the following approximation to truncate the hierarchy at the level of three-particle reaction dynamics:

$$- \kappa_f \hat{C}_{ABBB}(r, r', \sigma, s) + \kappa_r \hat{C}_{CBBBB}(r, r', \sigma, s)$$

$$\cong C_B[g(r) + \hat{\xi}(r, s)][-\kappa_f \hat{C}_{ABB}(r', \sigma, s)$$
$$+ \kappa_r \hat{C}_{CBBB}(r', \sigma, s)] \tag{26}$$

$$= \alpha(s)C_B^2[g(r) + \hat{\xi}(r, s)][g(r') + \hat{\xi}(r', s)]$$

Then by substituting Eqs. (6), (8), (9), (24) and (25) into Eq. (7), we can obtain the following integral equation for $\hat{\xi}(r, s)$:

$$\hat{\xi}(r, s) = \frac{k_f^{eq} + k_r^{eq}}{s - L(r)}\left[\frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}} + \hat{\xi}(r, s)C_B\right]$$

$$- \frac{\kappa_f + \kappa_r}{s - L(r) - L(r')}[\frac{\delta(r - \sigma)}{\gamma_d \sigma^{d-1}}\hat{\xi}(r', s) \tag{27}$$

$$+ \frac{\delta(r' - \sigma)}{\gamma_d \sigma^{d-1}}\hat{\xi}(r, s) + \hat{\xi}(r', s)\hat{\xi}(r, s)C_B]$$

Then, according to the appendix of Ref. 4, $\hat{F}(s)$ defined in Eq. (13) in terms of many-particle kernel satisfying Eq. (27) can be approximately given by

$$\hat{F}(s) \cong \frac{(k_f^{eq} + k_r^{eq})C_B\hat{Y}_A^{ir, eff}(s)}{1 - s\hat{Y}_A^{ir, eff}(s)} \tag{28}$$

Here, $\hat{Y}_A^{ir, eff}(s)$ is the survival probability of A molecules undergoing the irreversible reaction $A+B \to B$ with the effective equilibrium forward rate constant given by $k_f^{eq} + k_r^{eq}$. The exact expression for $\hat{Y}_A^{ir, eff}(s)$ is given by

$$Y_A^{ir, eff}(t) = \exp[-C_B\int_0^\infty d\tau k^{SM}(\tau)] \tag{29}$$

where $k^{SM}(t)$ is the time-dependent rate coefficients that can be derived from the Smoluchowski approach for the irreversible reaction. The expression for $k^{SM}(t)$ are given by

$$\frac{k^{SM}(t)}{k_f^{eq} + k_r^{eq}} = \Omega(k\sqrt{t/t_D}) \qquad (d=1) \tag{30}$$

$$\frac{k^{SM}(t)}{k_f^{eq} + k_r^{eq}} =$$

$$k\left(\frac{2}{\pi}\right)^2 \int_0^\infty \frac{dx}{x} \frac{\exp(-x^2 t/t_D)}{[xJ_1(x) + kJ_0(x)]^2 + [xY_1(x) + kY_0(x)]^2}$$
$$(d=2) \tag{31}$$

$$\frac{k^{SM}(t)}{k_f^{eq} + k_r^{eq}} = \frac{1}{1 + k}\{1 + k\Omega[(1 + k)\sqrt{t/t_D}]\} \quad (d=3) \tag{32}$$

where $k = (k_f^{eq} + k_r^{eq})/\gamma_d\sigma_D^{d-2}D_B$, $t_D = \sigma_D^2/D_B$, $\Omega(x) = (x^2)\mathrm{erfc}(x)$, and J_n, and Y_n are the nth order Bessel functions of the first and the second kind, respectively.[27] The effective contact distance σ_D are defined by

$$\sigma_D = \left\{\int_\sigma^\infty dr \exp[U(r)]r^{-2}\right\}^{-1} \tag{33}$$

When the effect of potential of mean force is negligible, $U(r) \cong 0$, the expressions for k^{SM} given by Eqs. (30)-(32) becomes exact. We now have the expressions for the time-dependence of the reactant number densities in the Laplace domain, given by Eqs. (15)-(20) with the rate kernels in Eqs. (11) and (28). These Laplace domain results can be converted numerically to the time domain with the use of a numerical inverse-Laplace transform routine.[28]

Results and Discussion

As can be verified from Eqs. (15)-(20), the equilibrium value of $a(t)$ and $c(t)$ are $k_r^{eq}(a_0 + c_0)/(k_f^{eq} + k_r^{eq})$ $[\equiv a_{eq}]$ and $k_f^{eq}(a_0 + c_0)/(k_f^{eq} + k_r^{eq})$ $[\equiv c_{eq}]$, respectively, and the reactant number densities relax to the equilibrium values according to the following relaxation law

$$\frac{\Delta\hat{a}(s)}{\Delta a(0)} = \frac{\Delta\hat{c}(s)}{\Delta c(0)} = \frac{1}{s + [k_f(s) + k_r(s)]C_B} \tag{34}$$

where $\Delta a(t) = a(t) - a_{eq}$ and $\Delta c(t) = c(t) - c_{eq}$. When the expressions of the rate kernels given by Eqs. (11) and (28) are substituted into Eq. (34), the result can be put down in the time domain as

$$\frac{\Delta a(t)}{\Delta a(0)} = \frac{\Delta c(t)}{\Delta c(0)} = Y_A^{ir, eff}(t). \tag{35}$$

In fact, for the simple reversible reactions of the type $A + B \rightleftarrows C + B$, there exist an easy way to prove the relaxation predicted by Eqs. (29) and (35) is exact one.[15] However, none of general purpose many-particle theories for reversible reactions succeeded in recover the exact result for this type of reactions.

In the present theory, the error in the truncation approximation, Eq. (26) that was introduced to derive the equation for $\hat{\xi}(r, s)$ in a closed form is exactly cancelled by that in Eq. (28) which relates the diffusion effect function $\hat{F}(s)$ to the irreversible survival probability. Fortunately, this type of error cancellation also occurs in parallel when MPK theory is applied to other type of reactions.[3,4]

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