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Theory of Diffusion-Controlled Intrachain Reactions of Polymers. II.

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ABSTRACT: As a continuation of a previous paper, an analysis is made of the diffusion-controlled ring closure reaction of a harmonic spring model of polymers for the case of finite k (k being an intrinsic second-order reaction rate constant). The upper bound and the lower bound for an apparent first-order reaction rate constant k_1 are calculated by the variational principle of Rayleigh—Ritz and that of Doi respectively. These bounds are found to have very close values, and with the use of them, the error produced by the closure approximation is estimated for all values of k.

KEY WORDS Ring Closure Reaction / Diffusion-Controlled / Harmonic Spring Model / Reaction Rates / Variational Principles / Upper and Lower Bounds / Radiation Boundary Condition /

In a previous paper[1] (to be referred to as I), we have discussed an intramolecular reaction of a harmonic spring model of polymers for the purpose of examining the validity of the closure approximation of Wilemski and Fixman.[2,3] We have calculated an apparent first—order reaction rate k_1 exactly by an integral equation method and compared this with the result of the closure approximation. However, rigorous solutions were obtained only for the case of the diffusion-controlled limit, *i.e.*, the case where an intrinsic second-order reaction rate k is infinite. For the general case of finite k, we have no rigorous solutions to be compared with the closure approximation; however, certain bounds for k_1 can be obtained by variational principles.

In the present paper, we calculate the upper and the lower bounds for k_1 and compare these results with those of the closure approximation. As was shown by Doi,[4] k_1 is related to the smallest eigenvalue of a certain Hermitian operator. Then the upper bound is easily obtained by the conventional method of Rayleigh-Ritz.[5] The lower bound for k_1 is calculated by the method proposed recently by Doi.[4]

These bounds are found to have very close values and may be regarded as almost the exact values. From these values, the deviation produced by the closure approximation is discussed for all values of k.

BASIC EQUATIONS

We consider a pair of active sites bound by a harmonic spring with mean square length L^2. The active sites are assumed to react on each other with the intrinsic second-order reaction rate constant k if their separation is within a distance R. Then the distribution function $P(\boldsymbol{r}, t)$ of the unreacted site pair obeys the diffusion equation:[2,3]

$$\left\{\frac{\partial}{\partial t}+\mathscr{L}(\boldsymbol{r})+kS(\boldsymbol{r})\right\}P(\boldsymbol{r}, t)=0 \qquad (1)$$

$$\mathscr{L}(\boldsymbol{r})=-D\frac{\partial}{\partial \boldsymbol{r}}\left(\frac{1}{k_{\mathrm{B}}T}\frac{\partial U}{\partial \boldsymbol{r}}+\frac{\partial}{\partial \boldsymbol{r}}\right) \qquad (2)$$

$$U(\boldsymbol{r})=\frac{3k_{\mathrm{B}}T}{2L^2}|\boldsymbol{r}|^2 \quad \text{(potential energy of the spring)} \qquad (3)$$

$$S(\boldsymbol{r})=\left(\frac{4\pi R^3}{3}\right)^{-1}H(R-|\boldsymbol{r}|) =\begin{cases}\left(\dfrac{4\pi R^3}{3}\right)^{-1} & (|\boldsymbol{r}|\leq R)\\ 0 & (|\boldsymbol{r}|>R)\end{cases} \qquad (4)$$

where D is a relative diffusion constant of the pair and $k_{\mathrm{B}}T$ the Boltzman constant multiplied by temperature.

The unreacted fraction of the active pair $\chi(t)$ at time t is obtained from $P(\boldsymbol{r}, t)$ as

$$\chi(t)=\int \mathrm{d}^3 r P(\boldsymbol{r}, t) \tag{5}$$

Usually, $\chi(t)$ decreases in a simple exponential law:[1]

$$\chi(t) \simeq \exp(-k_1 t) \tag{6}$$

The rate constant k_1 is the apparent first-order reaction rate constant and the quantity of most importance.

To utilize the variational principle, let us rewrite the problem in an Hermitian form. We introduce an operator $\mathscr{D}(\boldsymbol{r})$ defined by

$$P_{\mathrm{eq}}(\boldsymbol{r})\mathscr{D}(\boldsymbol{r})(\varphi(\boldsymbol{r})/P_{\mathrm{eq}}(\boldsymbol{r}))=\mathscr{L}(\boldsymbol{r})\varphi(\boldsymbol{r}) \tag{7}$$

with

$$P_{\mathrm{eq}}(\boldsymbol{r})=\left(\frac{3}{2\pi L^2}\right)^{3/2}\exp\left(-\frac{3}{2L^2}|\boldsymbol{r}|^2\right)$$

(equilibrium distribution function) (8)

that is,

$$\mathscr{D}(\boldsymbol{r})=-D\frac{\partial^2}{\partial \boldsymbol{r}^2}+\frac{D}{k_{\mathrm{B}}T}\frac{\partial U}{\partial \boldsymbol{r}}\frac{\partial}{\partial \boldsymbol{r}} \tag{9}$$

The operator $\mathscr{D}$ becomes Hermitian if the scalar product between any two functions φ and φ' is defined as the average of the product $\varphi\varphi'$ over the equilibrium state, *i.e.*,

$$\langle\varphi|\mathscr{D}\varphi'\rangle=\langle\mathscr{D}\varphi|\varphi'\rangle \tag{10}$$

where

$$\langle\varphi|\varphi'\rangle \equiv \int \mathrm{d}^3 r P_{\mathrm{eq}}(r)\varphi\varphi' \equiv \langle\varphi\varphi'\rangle \tag{11}$$

Let $\varphi_n{}^*$ be eigenfunctions of the operator $\mathscr{D}+kS$:

$$\{\mathscr{D}(\boldsymbol{r})+kS(\boldsymbol{r})\}\varphi_n{}^*(\boldsymbol{r})=\varepsilon_n{}^*\varphi_n{}^*(\boldsymbol{r})$$

($\varepsilon_n{}^*$: eigenvalues) (12)

Then $P(\boldsymbol{r}, t)$ can be solved as

$$P(\boldsymbol{r}, t)=\sum_n \varphi_n{}^*\langle\varphi_n{}^*\rangle P_{\mathrm{eq}}\exp(-\varepsilon_n{}^* t) \tag{13}$$

Here the system is assumed to be in equilibrium at $t=0$. From eq 5, 11, and 13, we have

$$\chi(t)=\sum_n \langle\varphi_n{}^*\rangle^2\exp(-\varepsilon_n{}^* t) \tag{14}$$

Equation 14 indicates that the asymptotic decaying rate k_1 is equal to the smallest eigenvalue $\varepsilon_0{}^*$ (see eq 6). Thus our problem is reduced to calculating the smallest eigenvalue of the operator $\mathscr{D}+kS$.

UPPER BOUND

First, we apply the variational principle of Rayleigh—Ritz[5] to eq 1. If $\varphi(\boldsymbol{r})$ is an arbitrary function, the variational principle reads

$$k_1 \leq I_{\mathrm{R}}[\varphi]=\frac{\langle\varphi(\mathscr{D}+kS)\varphi\rangle}{\langle\varphi^2\rangle} \tag{15}$$

This inequality gives the upper bound for k_1.

Here the difficulty is how to choose the trial function $\varphi(\boldsymbol{r})$. Trial functions expressed in a linear combination of the eigenfunctions of $\mathscr{D}$ are not appropriate because such trial functions yield $I_{\mathrm{R}}[\varphi]\rightarrow\infty$ as $k\rightarrow\infty$. An appropriate trial function can be obtained as follows: we decompose $\mathscr{D}+kS$ as

$$\left.\begin{aligned} &\mathscr{D}+kS=\mathscr{D}_0+\mathscr{D}_1 \\ &\mathscr{D}_0(\boldsymbol{r})\equiv -D\frac{\partial^2}{\partial \boldsymbol{r}^2}+kS(\boldsymbol{r}) \\ &\mathscr{D}_1(\boldsymbol{r})\equiv\frac{D}{k_{\mathrm{B}}T}\frac{\partial U}{\partial \boldsymbol{r}}\cdot\frac{\partial}{\partial \boldsymbol{r}}=\frac{3D}{L^2}\boldsymbol{r}\cdot\frac{\partial}{\partial \boldsymbol{r}} \end{aligned}\right\} \tag{16}$$

Note that $\mathscr{D}_0$ is the diffusion operator for the free particle system under reaction. For this system, there exists a steady state which satisfies

$$\mathscr{D}_0\varphi=0 \tag{17}$$

Solution of this equation is[4]

$$\varphi(r)=\begin{cases} \dfrac{\sinh \kappa r}{\kappa r \cosh \kappa R} & (r \leq R) \\ 1-\dfrac{R\alpha}{r} & (r>R) \end{cases} \tag{18}$$

with

$$\alpha=\left(1-\frac{\tanh \kappa R}{\kappa R}\right), \qquad \kappa=\frac{\sqrt{6B}}{L},$$

$$B=k\frac{L^2}{6D}\left(\frac{4\pi R^3}{3}\right)^{-1} \tag{19}$$

We employ eq 18 as the trial function of eq 15.

By use of eq 17, eq 15 is reduced to

$$k_1 \leq \frac{\langle\varphi\mathscr{D}_1\varphi\rangle}{\langle\varphi^2\rangle}=\frac{\langle\varphi(3D/L^2)r(\mathrm{d}/\mathrm{d}r)\varphi\rangle}{\langle\varphi^2\rangle} \tag{20}$$

As in I, we use the dimensionless variable $\gamma=\sqrt{3/2}\,R/L$, assuming it to be small. Then the r.h.s. of eq 20 can be expressed in a power series of γ. For example,

$$\begin{aligned}\langle\varphi^2\rangle &= \int_{r\le R} \mathrm{d}^3r\, P_{\mathrm{eq}}(r)\left(\frac{\sinh \kappa r}{\kappa r \cosh \kappa R}\right)^2 + \int_{r>R} \mathrm{d}^3r\, P_{\mathrm{eq}}(r)\left(1-\frac{R\alpha}{r}\right)^2 \\ &= \int \mathrm{d}^3r\, P_{\mathrm{eq}}(r)\left(1-\frac{R\alpha}{r}\right)^2 + \mathrm{O}(\gamma^3) \\ &= \langle 1\rangle - 2\alpha\left\langle\frac{R}{r}\right\rangle + \alpha^2\left\langle\frac{R^2}{r^2}\right\rangle + \mathrm{O}(\gamma^3) \\ &= 1-\frac{4}{\sqrt{\pi}}\alpha\gamma + 2\alpha^2\gamma^2 + \mathrm{O}(\gamma^3)\end{aligned} \tag{21}$$

Similarly, we have

$$\langle\varphi\mathscr{D}_1\varphi\rangle = \frac{6D}{L^2}\left[\frac{1}{\sqrt{\pi}}\alpha\gamma - \alpha^2\gamma^2 + \left(-\frac{1}{\sqrt{\pi}}\alpha + \frac{2}{\sqrt{\pi}}\alpha^2 + \frac{3}{2\sqrt{\pi}}\beta\right)\gamma^3 + \mathrm{O}(\gamma^4)\right] \tag{22}$$

with

$$\beta = \frac{1}{(\kappa R)^2} - \frac{\tanh \kappa R}{(\kappa R)^3} - \frac{\tanh^2 \kappa R}{3(\kappa R)^2} \tag{23}$$

Then eq 20 becomes

$$k_1\tau_0 \leqq \frac{1}{\sqrt{\pi}}\alpha\gamma + \left(\frac{4}{\pi}-1\right)\alpha^2\gamma^2 + \left\{-\frac{1}{\sqrt{\pi}}\alpha + \frac{2}{\sqrt{\pi}}\alpha^2 + \left(\frac{16}{\pi\sqrt{\pi}} - \frac{1}{\sqrt{\pi}}\right)\alpha^3 + \frac{3}{2\sqrt{\pi}}\beta\right\}\gamma^3 + \mathrm{O}(\gamma^4) \tag{24}$$

with

$$\tau_0 = \frac{L^2}{6D} \tag{25}$$

The numerical results for $k_1\tau_0$ are listed in Table I.

Table I. The reaction rate: $k_1\cdot(L^2/6D)$

B	Rayleigh—Ritz	Doi	Closure approximation	Radiation boundary condition
$\gamma=0.05$				
1	0.0000935	0.0000935	0.0000935	0.0000933
10^3	0.0196	0.0195	0.0190	0.0220
10^5	0.0280	0.0278	0.0238	0.0286
∞	0.0289	0.0287	0.0239	0.0287
$\gamma=0.2$				
1	0.00556	0.00555	0.00555	0.00534
10^3	0.114	0.111	0.0977	0.118
10^5	0.123	0.120	0.0993	0.121
∞	0.124	0.121	0.0993	0.121

Equation 24 has the following asymptotic forms: For the diffusion-controlled limit, *i.e.*, $k\to\infty$:

$$k_1\tau_0 = \frac{\gamma}{\sqrt{\pi}} + \mathrm{O}(\gamma^2) \tag{26}$$

which coincides with the asymptotic form of the exact results obtained in I. On the other hand, for $k\to 0$, we have

$$k_1\tau_0 = \frac{4\gamma^3}{3\sqrt{\pi}}B + \mathrm{O}(\gamma^5) \tag{27}$$

which is equal to the equilibrium reaction rate given by

$$k_{1\mathrm{eq}} = kP_{\mathrm{eq}}(R) \simeq k\left(\frac{3}{2\pi L^3}\right)^{3/2} = \frac{4\gamma^3}{3\sqrt{\pi}}B\frac{1}{\tau_0}\quad(\gamma\ll 1) \tag{28}$$

LOWER BOUND

Next we apply the variational principle of Doi[4] to eq 1. His variational principle is stated as follows: Let $\varphi(r)$ be an arbitrary function and $I_{\mathrm{D}}[\varphi]$ be defined as the smallest solution of the equation

$$\left\langle\varphi\left(S + kS\frac{1}{\mathscr{D} - I_{\mathrm{D}}[\varphi]}S\right)\varphi\right\rangle = 0 \tag{29}$$

Then it is proved that

$$k_1 \geqq I_{\mathrm{D}}[\varphi] \tag{30}$$

provided that k_1 is smaller than the second smallest eigenvalue of $\mathscr{D}$. As was shown by Doi,[4] the closure approximation of Wilemski and Fixman[2,3] is equivalent to the choice of the trial function as $\varphi(r)=1$.

Equation 29 may be rewritten in terms of the eigenfunctions of $\mathscr{D}(\mathscr{D}\varphi_p = \varepsilon_p\varphi_p)$ as

$$\langle S\varphi^2\rangle + k\sum_p \frac{\langle S\varphi_p\varphi\rangle^2}{\varepsilon_p - I_{\mathrm{D}}[\varphi]} = 0 \tag{31}$$

where $\sum_p$ means the sum over all eigenstates. Since the trial function $\varphi(\boldsymbol{r})$ can be chosen as spherically symmetric, only the spherically symmetric eigenfunctions are included in eq 31. These are[1]

$$\varphi_n(r)=\sqrt{\frac{\sqrt{\pi}\ n!}{2\Gamma(3/2+n)}}L_n^{1/2}(3r^2/2L^2)$$

$(L_n^{1/2}$: the Laguerre polynomials) (32)

$$\varepsilon_n=n/\tau_0 \qquad (n=0, 1, 2, \ldots)$$

Thus we have

$$\langle S\varphi^2\rangle+k\sum_{n=0}^{\infty}\frac{\langle S\varphi_n\varphi\rangle^2}{\left(\dfrac{n}{\tau_0}\right)-I_{\rm D}[\varphi]}=0 \qquad (33)$$

We choose the trial function as $\varphi(r)=r^m$ and determine the exponent m so as to maximize the functional $I_{\rm D}[r^m]$.

Since $I_{\rm D}[r^m]$ is supposed to be very small compared to $1/\tau_0^1$, we expand eq 33 in a power series of $I_{\rm D}$:

$$\langle S\varphi^2\rangle-k\frac{D_0}{I_{\rm D}}+k\sum_{l=1}^{\infty}C_l\tau_0^l I_{\rm D}^{l-1}=0 \qquad (34)$$

where

$$D_n=\langle S\varphi_n r^m\rangle^2 \qquad (35)$$

$$C_l=\sum_{n=1}^{\infty}\frac{D_n}{n^l} \qquad (36)$$

The maximum $I_{\rm D}$ can be obtained by solving eq 33 (or 34) and $\partial I_{\rm D}[r^m]/\partial m=0$ simultaneously. Since this procedure is cumbersome and the results do not strongly depend on m, as will be shown below, we solved eq 34 by employing an approximate value of m determined by the following procedure: In the case of $\gamma \ll 1$, we can obtain an analytic expression for $I_{\rm D}$ as

$$I_{\rm D}[r^m]\tau_0 =\frac{4B\gamma^3(2m+3)(2m+5)}{\sqrt{\pi}\,(m+3)^2(2m+5)+8\sqrt{\pi}\,B\gamma^2(m+3)(2m+3)} \qquad (\gamma \ll 1) \quad (37)$$

whose derivation is described in Appendix I. Equation 37 takes a maximum at the value of m satisfying

$$8B\gamma^2=\frac{2m(m+3)(2m+5)^2}{(2m+3)^2} \qquad (38)$$

As an example, $I_{\rm D}$ solved from eq 34 by retaining up to the term $l=5$ in the summation is shown in Figure 1 for the case of $\gamma=0.2$ and $B=5000$. It is observed that the variation of $I_{\rm D}$ near its maximum is rather small and that the maximum $I_{\rm D}$ is well predicted by the value

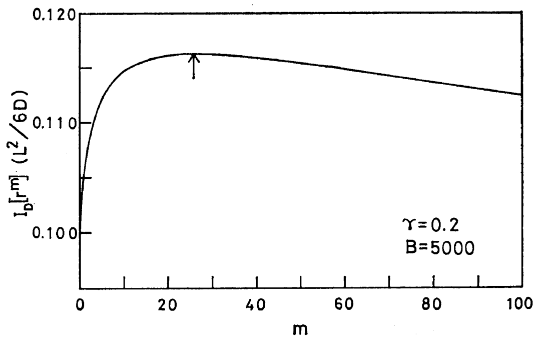

Figure 1. Solution of eq 34 as a function of m (maximum $I_{\rm D}$ predicted by eq 38 corresponds to $m=25.8$).

m determined by eq 38 (the arrow shows the solution of eq 38). Thus the value m given by eq 38 may be used even when γ is not very small. Utilizing this approximate m, we calculated the maximum $I_{\rm D}$ as a function of B for several values of γ. Calculations were also performed for the case of the closure approximation ($m=0$ in eq 34). The results are also included in Table I.

In the case of small γ, we can show that eq 37 with eq 38 yields the exact asymptotic values of k_1: In the limit of $B\rightarrow\infty$, eq 37 takes the maximum value of

$$I_{\rm D}\tau_0=\frac{\gamma}{\sqrt{\pi}} \qquad (\gamma \ll 1, B \gg 1) \quad (39)$$

at $m=\infty$. This coincides with the asymptotic expression of the exact solution[1] and also with eq 26. On the other hand, for small B, eq 37 gives

$$I_{\rm D}\tau_0=\frac{4\gamma^3}{\sqrt{\pi}}\frac{(2m+3)}{(m+3)^2}B \qquad (\gamma \ll 1, B \ll 1) \quad (40)$$

which takes its maximum $4\gamma^3B/3\sqrt{\pi}$ at $m=0$; then we recover eq 28. Finally, if we set $\varphi=1$, *i.e.*, $m=0$ in eq 37, we obtain the asymptotic expression of the closure approximation:[1,6]

$$I_{\rm D}\tau_0=\frac{20B\gamma^3}{\sqrt{\pi}\,(15+24B\gamma^2)} \qquad (\gamma \ll 1) \quad (41)$$

If we take the limit of $B\rightarrow 0$ in eq 41, we recover the exact result (eq 28). This is quite natural because the closure approximation gives the exact results in the limit of $k\rightarrow 0$.[2,3]

DISCUSSION

In the present paper, we have calculated the upper bound and the lower bound for k_1 by employing the variational principle of Rayleigh—Ritz and that of Doi.

As is observed from Table I, these bounds have very close values. The deviation is never more than 2.5%. Therefore these may be regarded as almost the exact values. Table I shows that the closure approximation produces good results in the range of small k, as expected from its nature. The deviation becomes larger as k increases, however, it never exceeds 20% even for the case of $k \rightarrow \infty$. Thus we again confirm the previous conclusion that the closure approximation is relatively satisfactory even if k is very large.

It is also observed that the two bounds become closer as $\gamma \rightarrow 0$. In fact, we can show that in the limit of $\gamma \rightarrow 0$, k_1 is exactly given by

$$k_1 = k_2 P_{\mathrm{eq}}(0) \tag{42}$$

where k_2 is the second-order reaction rate of the free particle system:[4]

$$k_2 = 4\pi DR\left(1 - \frac{\tanh \kappa R}{\kappa R}\right)\left(\kappa \equiv \sqrt{\frac{k}{D} \cdot \left(\frac{4\pi R^3}{3}\right)^{-1}}\right) \tag{43}$$

Euation 42 has a very simple meaning: if the potential $U(r)$ is flat near the reaction region, the particle behaves as a free particle. Then the first-order reaction rate k_1 is given by the product of k_2 and the local concentration, $P_{\mathrm{eq}}(0)$, near the origin. Equation 42 holds for any spherically symmetric system provided that its potential $U(r)$ is not singular near $r=0$. The proof of eq 42 is given Appendix II.

So far, our discussion has been limited to eq 1 because our purpose is to examine the validity of the closure approximation. However the finiteness of k can be taken into account by using a more tractable equation. If k is finite, the third term on the l.h.s. of eq 1 represents the situation that some fraction of the reactive sites in the reaction region can react. Physically, this is equivalent to including the fractional reflection of the reactive sites upon collision and can be expressed by the radiation boundary condition:[7,8]

$$kP(\boldsymbol{r}, t) = 4\pi r^2 \boldsymbol{n}\cdot\boldsymbol{J} \quad \text{at} \quad |\boldsymbol{r}| = R \tag{44}$$

where $\boldsymbol{n}\cdot\boldsymbol{J}$ is the normal component of the flux at the reaction surface and k in eq 44 has the same meaning as k in eq 1.[2] As was suggested by Wilemski,[9] the problem in this form can be rigorously solved by the method of I. This is simply discussed in Appendix III.

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APPENDIX I

Here, we derive the analytic expression for I_{D} in the limit of $\gamma \rightarrow 0$. In this limit, I_{D} becomes very small,[1] hence we may safely retain only the term $l=1$ in the summation in eq 34. Then I_{D} is solved as

$$I_{\mathrm{D}}[r^m] = \frac{kD_0}{\langle S\varphi^2\rangle + kC_1\tau_0} \qquad (\gamma \ll 1) \tag{A1}$$

The r.h.s. of eq A1 can be again calculated analytically for the case of $\gamma \rightarrow 0$: in a similar manner to that in eq 21, we have

$$\begin{aligned}\langle S\varphi^2\rangle &= \left(\frac{4\pi R^3}{3}\right)^{-1}\int_{r\leq R} \mathrm{d}^3 r P_{\mathrm{eq}}(r) r^{2m} \\ &\simeq \frac{3}{\pi\sqrt{\pi}}\frac{R^{2m-3}}{(2m+3)}\gamma^3\end{aligned} \tag{A2}$$

$$D_0 = \langle S\varphi\rangle^2 \simeq \frac{9}{\pi^3}\frac{R^{2m-6}}{(m+3)^2}\gamma^6 \tag{A3}$$

To calculate C_1, we utilize the relation[1]

$$\begin{aligned}&\sum_{n=0}^{\infty} P_{\mathrm{eq}}(\boldsymbol{r}_2)\varphi_n(\boldsymbol{r}_2)\varphi_n(\boldsymbol{r}_1)\exp(-nt/\tau_0) \equiv G(\boldsymbol{r}_2, \boldsymbol{r}_1, t) \\ &= \left\{\frac{2\pi L^2}{3}(1-\mathrm{e}^{-t/\tau_0})\right\}^{-3/2} \\ &\quad \times \exp\left\{-\frac{3}{2L^2}\frac{|\boldsymbol{r}_2 - \boldsymbol{r}_1\mathrm{e}^{-t/2\tau_0}|^2}{(1-\mathrm{e}^{-t/\tau_0})}\right\}\end{aligned} \tag{A4}$$

Then we can obtain the following identity

$$C_1=\sum_{n=1}^{\infty}\frac{\langle S\varphi_n\varphi\rangle^2}{n}$$
$$\equiv\frac{1}{\tau_0}\int_0^{\infty}dt\Big[\int d^3r_1\int d^3r_2\varphi(\boldsymbol{r}_1)\varphi(\boldsymbol{r}_2)S(\boldsymbol{r}_1)S(\boldsymbol{r}_2)\times G(\boldsymbol{r}_2,\boldsymbol{r}_1,t)P_{eq}(\boldsymbol{r}_1)-\Big\{\int d^3r\varphi(\boldsymbol{r})S(\boldsymbol{r})\varphi_0(\boldsymbol{r})P_{eq}(\boldsymbol{r})\Big\}^2\Big] \quad \text{(A5)}$$

In the integral of eq A5, the contribution of the short time region is dominant in case of $\gamma\ll 1$,[6] so we can replace the Green's function by that for the short time form:

$$G_f(\boldsymbol{r}_2,\boldsymbol{r}_1,t)=\left(\frac{3\tau_0}{2\pi L^2 t}\right)^{3/2}\exp\left(-\frac{3\tau_0|\boldsymbol{r}_2-\boldsymbol{r}_1|^2}{2L^2t}\right)=\left(\frac{1}{4\pi Dt}\right)^{3/2}\exp\left(-\frac{|\boldsymbol{r}_2-\boldsymbol{r}_1|^2}{4Dt}\right) \quad (t\ll 1) \quad \text{(A6)}$$

which has the same form as that of a free particle. Further, in this limit of $\gamma\to 0$, the second term of the integral can be neglected (it is of the order of γ^6). Thus

$$C_1\simeq\frac{1}{\tau_0}\int_0^{\infty}dt\left(\frac{4\pi R^3}{3}\right)^{-2}\int_{|r_1|\le R}d^3r_1\int_{|r_2|\le R}d^3r_2\boldsymbol{r}_1^{\,m}\boldsymbol{r}_2^{\,m}\times G_f(\boldsymbol{r}_2,\boldsymbol{r}_1,t)P_{eq}(\boldsymbol{r}_1)$$
$$=\left(\frac{4\pi R^3}{3}\right)^{-2}\int_{|r_1|\le R}d^3r_1\int_{|r_2|\le R}d^3r_2\boldsymbol{r}_1^{\,m}\boldsymbol{r}_2^{\,m}\times P_{eq}(\boldsymbol{r}_1)\left(\frac{3}{2\pi L^2}\right)^{3/2}\frac{\sqrt{6\pi}\,L}{3}\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$
$$=\frac{18}{\pi^2\sqrt{\pi}}\frac{R^{2m-6}}{(m+3)(2m+5)}\gamma^5 \quad (\gamma\ll 1) \quad \text{(A7)}$$

Substituting eq A2, A3, and A7 into eq A1, we obtain the analytic expression for I_D (eq 37).

APPENDIX II

In this Appendix, we prove that in the case of $R\ll L\equiv\sqrt{\langle r^2\rangle}$, eq 42 holds for any spherically symmetric system, provided that its potential $U(r)$ is not singular near the origin. For this purpose, we shall show that the upper bound I_R (see eq 20)

$$k_1\le I_R=\frac{\left\langle\varphi\frac{D}{k_BT}\frac{dU}{dr}\frac{d\varphi}{dr}\right\rangle}{\langle\varphi^2\rangle} \quad \text{(A8)}$$

and the lower bound I_D

$$k_1\ge I_D=\frac{kD_0}{\langle S\varphi^2\rangle+k\tilde{C}_1}\left(\tilde{C}_1\equiv\sum_p\frac{\langle S\varphi_p\varphi\rangle^2}{\varepsilon_p}\right) \quad \text{(A9)}$$

become equal if we take the distribution function of a free particle system under reaction (eq 18) as the trial function. Equation A9 is derived in the same manner as eq A1.

First we calculate I_R. In the following, the trial function φ for $r<R$ is denoted by φ_i and that for $r>R$ by φ_0. Substituting eq 18 into eq A8, we have

$$\left\langle\varphi\frac{D}{k_BT}\frac{dU}{dr}\frac{d\varphi}{dr}\right\rangle=\int_{r>R}d^3rP_{eq}(r)\varphi_i\frac{D}{k_BT}\frac{dU}{dr}\frac{d\varphi_i}{dr}+\int_{r>R}d^3rP_{eq}(r)\varphi_0\frac{D}{k_BT}\frac{dU}{dr}\frac{d\varphi_0}{dr}$$
$$=D\int d^3rP_{eq}(r)\frac{1}{k_BT}\frac{dU}{dr}\frac{R\alpha}{r^2}+O(R^2/L^2)$$
$$=-4\pi DR\alpha\int_0^{\infty}dr\frac{dP_{eq}}{dr}+O(R^2/L^2)$$
$$=4\pi DR\alpha P_{eq}(0)+O(R^2/L^2) \quad \text{(A10)}$$

$$\langle\varphi^2\rangle=\int_{r<R}d^3rP_{eq}(r)\varphi_i^{\,2}+\int_{r>R}d^3rP_{eq}(r)\varphi_0^{\,2}=\langle 1\rangle+0(R/L)=1+O(R/L) \quad \text{(A11)}$$

Then I_R becomes

$$I_R=4\pi DR\alpha P_{eq}(0)+O(R/L)\left(\alpha\equiv 1-\frac{\tanh\kappa R}{\kappa R}\right) \quad \text{(A12)}$$

Similarly for eq A9, we have

$$\langle S\varphi^2\rangle=\left(\frac{4\pi R^3}{3}\right)^{-1}\int_{r<R}d^3rP_{eq}(r)\varphi_i^{\,2}\simeq\left(\frac{4\pi R^3}{3}\right)^{-1}P_{eq}(0)\int_{r<R}d^3r\varphi_i^{\,2}$$
$$=\left(\frac{4\pi R^3}{3}\right)^{-1}P_{eq}(0)\frac{2\pi}{\kappa^3}(\kappa R\tanh^2\kappa R+\tanh\kappa R-\kappa R) \quad \text{(A13)}$$

$$D_0=\langle S\varphi\rangle^2=\left[\left(\frac{4\pi R^3}{3}\right)^{-1}\int_{r<R}d^3rP_{eq}(r)\varphi_i\right]^2\simeq\left(\frac{4\pi R^3}{3}\right)^{-2}P_{eq}^2(0)\left[\int_{r<R}d^3r\varphi_i\right]^2$$
$$=\left(\frac{4\pi R^3}{3}\right)^{-2}P_{eq}^2(0)\frac{16\pi^2}{\kappa^6}(\kappa R-\tanh\kappa R)^2 \quad \text{(A14)}$$

$$\tilde{C}_1=\int_0^{\infty}\mathrm{d}t\int_{|r_1|\le R}\mathrm{d}^3r_1\int_{|r_2|\le R}\mathrm{d}^3r_2\varphi_i(\boldsymbol{r}_1)\varphi_i(\boldsymbol{r}_2)$$
$$\times G_{\mathrm{f}}(\boldsymbol{r}_2,\ \boldsymbol{r}_1,\ t)P_{\mathrm{eq}}(\boldsymbol{r}_1)\left(\frac{4\pi R^3}{3}\right)^{-2}$$
$$\simeq\left(\frac{4\pi R^3}{3}\right)^{-2}\frac{1}{4\pi D}P_{\mathrm{eq}}(0)\int_{|r_1|\le R}\mathrm{d}^3r_1$$
$$\times\int_{|r_2|\le R}\mathrm{d}^3r_2\varphi_i(\boldsymbol{r}_1)\varphi_i(\boldsymbol{r}_2)\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$
$$=\left(\frac{4\pi R^3}{3}\right)^{-2}\frac{P_{\mathrm{eq}}(0)}{4\pi D}\frac{8\pi^2}{\kappa^5}$$
$$\times(-\kappa R\tanh^2\kappa R-3\tanh\kappa R+3\kappa R) \qquad \text{(A15)}$$

In the calculation of $\tilde{C}_1$, we have used the technique of Appendix I. From eq A9, A13, A14, and A15, I_{D} becomes

$$I_{\mathrm{D}}=4\pi DR\alpha P_{\mathrm{eq}}(0)+\mathrm{O}(R/L) \qquad \text{(A16)}$$

Thus eq 42 is verified.

APPENDIX III

With a sink function $\rho(\boldsymbol{r}, t)$ representing the reaction rate on the reaction surface ($|\boldsymbol{r}|=R$), the diffusion equation in I reads

$$\left\{\frac{\partial}{\partial t}+\mathscr{L}(\boldsymbol{r})\right\}P(\boldsymbol{r},\ t)=-\rho(\boldsymbol{r},\ t) \qquad \text{(A17)}$$

In I, $\rho(\boldsymbol{r}, t)$ was chosen as $\rho=\delta(|\boldsymbol{r}|-R)\xi(t)$; however, as is pointed out by Wilemski,[9] the simplest choice will be $\rho=\delta(\boldsymbol{r})\xi(t)$, which also enables $P(\boldsymbol{r}, t)$ to satisfy the boundary condition at $|\boldsymbol{r}|=R$.

A formal solution of eq A17 can then be written as

$$P(\boldsymbol{r},\ t)=\int\mathrm{d}^3rG(\boldsymbol{r},\ \boldsymbol{r}',\ t)P(\boldsymbol{r}',\ 0)$$
$$-\int_0^t\mathrm{d}s\int\mathrm{d}^3r'G(\boldsymbol{r},\ \boldsymbol{r}',\ t-s)\delta(\boldsymbol{r}')\xi(s)$$
$$=P_{\mathrm{eq}}(\boldsymbol{r})-\int_0^t\mathrm{d}sG(\boldsymbol{r},\ 0,\ t-s)\xi(s) \qquad \text{(A18)}$$

where G is the Green's function (eq A4) and $P(\boldsymbol{r}, 0)=P_{\mathrm{eq}}(\boldsymbol{r})$ has been assumed.

The radiation boundary condition (eq 44) in a spherically symmetric form now becomes

$$kP(r,\ t)=4\pi r^2D\left(\frac{\partial P}{\partial r}+\frac{3r}{L^2}P\right)\quad \text{at}\quad r=R \qquad \text{(A19)}$$

Substituting eq A18 into eq A19, we obtain an integral equation for $\xi(t)$:

$$P_{\mathrm{eq}}(R)=\int_0^t\mathrm{d}S\left[\left(1-\frac{3}{2B}\right)B(t-s)-\frac{3R}{4\gamma^2B}B'(t-s)\right]\xi(s) \qquad \text{(A20)}$$

where the definitions of B (eq 19) and γ (below eq 20) has been used and

$$B(t)=G(R,\ 0,\ t) \qquad \text{(A21)}$$

$$B'(t)=\left.\frac{\partial G(r,\ 0,\ t)}{\partial r}\right|_{r=R} \qquad \text{(A22)}$$

Taking the Laplace transform of eq A20, we have

$$\hat{\xi}(p)\equiv\int_0^{\infty}\mathrm{d}t\xi(t)\mathrm{e}^{-pt}$$
$$=\frac{P_{\mathrm{eq}}(R)}{p}\frac{1}{\left[\left(1-\frac{3}{2B}\right)\hat{B}(p)-\frac{3R}{4\gamma^2B}\hat{B}'(p)\right]} \qquad \text{(A23)}$$

As in *I*, k_1 is given by the largest (or the smallest in the absolute value) root of the equation:

$$\left(1-\frac{3}{2B}\right)\hat{B}(p)-\frac{3R}{4\gamma^2B}\hat{B}'(p)=0 \qquad \text{(A24)}$$

In terms of the eigenfunction expansion of the Green's function (eq A4), eq A24 is reduced to

$$\left(1-\frac{3}{2B}\right)\left(\sum_{n=0}^{\infty}\frac{B_n}{p+n/\tau_0}\right)-\frac{3R}{4\gamma^2B}\left(\sum_{n=0}^{\infty}\frac{B_n'}{p+n/\tau_0}\right)=0 \qquad \text{(A25)}$$

where

$$B_n=P_{\mathrm{eq}}(R)\varphi_n(R) \qquad \text{(A26)}$$

$$B_n'=\left.\frac{\partial P_{\mathrm{eq}}(r)\varphi_n(r)}{\partial r}\right|_{r=R} \qquad \text{(A27)}$$

In case of small γ, we can obtain an analytic expression for k_1 in a manner similar to that used in Appendix I:

$$k_1\tau_0=\frac{\frac{\gamma}{\sqrt{\pi}}}{1+\frac{3}{2B}+\frac{3}{4\gamma^2B}}\qquad(\gamma\ll1) \qquad \text{(A28)}$$

As is easily seen, eq A28 has exact asymptotic forms in both limits of $k\rightarrow0$ and $k\rightarrow\infty$ (see eq 26 and 28).

For the general case, we solved eq A25

numerically by employing a similar procedure to that used in I. The results are listed in Table I. It is observed that k_1 of the radiation boundary condition is very close to the exact value. Thus we may use this formalism to calculatie k_1 because it is more tractable.

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