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용액중에서의 화학반응에 관한 동역학적 이론

신 국 조

서울대학교 자연과학대학 화학과 (1981. 5. 22. 접수)

Kinetic Theory for Chemical Reactions in Liquids

Kook Joe Shin

Department of Chemistry, Seoul National University, Seoul 151, Korea (Received May 22 1981)

요 약. 용액증에서 화학반응을 설명하기 위하여 한개의 대표적인 입자의 반복적 충돌현상까지 고 려한 동역학적인 이론을 경구모델을 사용하여 연구하였다. 반응성을 지닌 대표적인 입자의 상공간 밀도의 시간상관함수가 만족시키는 동역학방정식을 유도하였고 이로부터 비활성 용매 S중에서 일 이나는 A+B⇔C+D 형태의 가역반응에 관계되는 반응속도 계수의 인자를 투영연산자방법으로 구 하였다.

ABSTRACTS. A test particle kinetic theory for reaction dynamics in liquids is presented at the repeated ring collision level for the hard sphere model. A kinetic equation for the equilibrium time correlation function of the reactive test particle phase space density is derived and the rate kernel expression for the reversible chemical reaction of the type A+B=C+D in the presence of inert solvent S is obtained by the projection operator method.

1. INTRODUCTION

Several approaches for the microscopic theory of chemical reactions in liquids have been proposed recently. ^{1~5} The generalized Langevin equation approach at the singlet density level² and the repeated ring, renormalized kinetic theory at the doublet density level¹, among others, are successful in incorporating the static structure and the recollision events which characterize the description of reaction dynamics in dense media.

Since these two approaches are based on the same fundamental Liouville equation they should be equivalent although it is not very clear at present time how the equivalence can be shown unambiguously due to various approximations introduced at different levels. Also it is known that⁴ even in the same approach the formulation develops differently at different levels of description.

It is desirable, therefore, to compare aad analyze various formulations at different levels in the same approach and between different approaches at the same level. At present only two such formulations mentioned at the beginning are available and it is the purpose of this work to present another formulation to provide a missing piece of information.

In this work the repeated ring^{6,7}, renormalized kinetic theory^{8,9} at the singlet density level is presented. A kinetic equation for the 292

equilibrium time correlation function of the reactive test particle phase space density is derived in Section 2 and the corresponding rate kernel expression is obtained in Section 3. Comparision with other formulations and the direction for future development is suggested in Section 4.

2. THE PHASE SPACE KINETIC EQUATION

Definitions. The system of interest here is a classical simple fluid in equilibrium at temperature T, enclosed in a volume Ω , and comprised of N^{α} particles of species α , N^{β} particles of species β , *etc.* Our goal is to describe the thermal fluctuations of a test particle's motion in the fluid in the presence of a reversible reaction of the type

$$A + B \stackrel{\circ}{=} C + D$$
 (1)

where S represents an inert solvent. Reactants and products are assumed to be dilute in solution. The dynamical variable associated with a test particle of species A is the phase space density⁶

$$f_{i}^{A}(1,t) = \sqrt{N}\delta(1-\boldsymbol{q}_{i}(t)) \quad O_{i}^{A}$$
(2)

where the operator O_i^A selects a particular species A for the particle s. The phase space coordinates of the test particle s are $q_i(t) =$ $(\mathbf{R}_i(t), \mathbf{V}_i(t))$ and the field point, $1 = (\mathbf{r}_1, \mathbf{v}_1)$. Other singlet phase space densities whose fluctuations are correlated to the test particle are given by

$$f^{\alpha}(\mathbf{1}', t) = \sum_{i=1}^{N} \delta(\mathbf{1}' - \boldsymbol{q}_i(t)) O_i^{\alpha}, \quad (i \neq s) \quad (3)$$

where $\alpha = A$, B, C, D, and S.

The test particle phase space density is also coupled to the fluctuations of higher order phase space densities

$$f^{A\beta}(12, t) = \sqrt{N\delta}(1-\boldsymbol{q}_s(t))O^A_s$$

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$$\sum_{i=1}^{N} \delta(2-\boldsymbol{q}_{i}(t)) O_{i}^{\sharp}, \quad (i \neq s)$$

$$f^{\alpha\beta}(12, t) = \sum_{i,j=1}^{N} \delta(1-\boldsymbol{q}_{i}(t))$$

$$\delta(2-\boldsymbol{q}_{j}(t)) O_{i}^{\pi} O_{j}^{\beta} \qquad (4)$$

The static (equal time) correlation functions of the phase space densities are defined, for example, as

$$\widetilde{C}^{\alpha\beta,\,\alpha'\beta'}\left(12\,\,;\,1'2'\right) = \langle f^{\alpha\beta}(12)f^{\alpha'\beta'}(1'2')\rangle_0 \quad (5)$$

where $\langle \rangle_0$ denotes the thermal average and the tilde represents static quantities. These can be expressed in terms of the equilibrium correlation functions

$$\omega_0^{\alpha\beta}(12) = n_{\alpha}^{\alpha} n_{\alpha} f_0^{\alpha}(v_1) f_0^{\beta}(v_2) g^{\alpha\beta}(r_1, r_2) \quad (6)$$

where $n_{\alpha}^{\alpha} = N_{\alpha}^{\alpha}/Q$ and $f_0^{\alpha}(v_1)$ is the normalized
Maxwellian distribution

$$f_0^{\alpha}(v_1) = (2\pi m_{\alpha} kT)^{-3/2} \exp(-m_{\alpha} v_1^2/2kT)$$
(7)

and $g^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ is the two particle static distribution function. Above definitions can be generalized for the higher order correlation function in an obvious way.

The static correlation function of the test particle phase space density is given by

$$\widetilde{C}_{i}^{A,A}(1, 1') = \langle f_{0}^{A}(1) f_{0}^{A}(1') \rangle_{0}$$

$$= n_{n}^{A} f_{0}^{A}(v_{1}) \delta(11') = \omega_{0}^{A}(1) \delta(11')$$

$$(8)$$

The dynamic correlation function of the test particle is defined in the Laplace transformed variable as

$$C_{i}^{A,A}(1, 1') = \int_{0}^{\infty} dt \cdot e^{-zt} \langle f_{i}^{A}(1, t) f_{i}^{A}(1') \rangle_{0} (9)$$

Pseudo-Liouville Operator. It is well known that the time evolution of a dynamical variable in the hard sphere system is given by¹⁰

$$f_{i}^{A}(1, t) = e^{t} \mathcal{L}_{+} f_{i}^{A}(1)$$
(10)

where the pseudo-Liouville operator \mathcal{L}_{\pm} is defined as

$$\mathcal{L}_{\pm} = \mathcal{L}_{0} \pm \mathcal{L}'_{\pm} \tag{11}$$

with the free streaming part

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(12)

$$\mathcal{L}_0 = \sum_{\alpha} \sum_{i=1}^{N} \boldsymbol{V}_i \cdot \boldsymbol{\nabla}_i O_i^{\alpha}$$

and the interaction part

$$\ell'_{\pm} = \sum_{\boldsymbol{\alpha}, \beta} \sum_{i > j} T_{\pm}^{\alpha\beta}(ij) \tag{13}$$

If a collision between species α and β is elastic, the hard sphere binary collision operator $T_{\pm}^{\alpha\beta}$ (ij) is given by⁷

$$T_{\pm}^{a\beta}(ij) = |V_{ij} \cdot \hat{R}_{ij}| \theta(\mp V_{ij} \cdot \hat{R}_{ij})$$

$$\delta (R_{ij} - \sigma_{\alpha\beta}) (\hat{b}_{ij} - 1) O_i^a O_j^\beta$$
(14)

where $\sigma_{\alpha\beta}$ is the mean diameter of the colliding species, \hat{R} is a unit vector along the line of centers at contact, and θ is the step function, $\theta(x)=0$ for x<1 and 1 for $x\geq 1$. The operator \hat{b}_{ij} converts the precollision velocities to their post collision values. When the collision can lead to reaction with probability α the collision operator may be expressed as¹¹

$$T_{\pm}^{\alpha\beta}(ij) = (1 - \alpha) \ T_{E\pm}^{\alpha\beta}(ij) + T_{R\pm}^{\alpha\beta}(ij)$$
(15)

with $\alpha\beta = AB$ or CD, and

$$T^{AB}_{R\pm}(ij) = \alpha | V_{ij} \cdot \hat{R}_{ij} | \theta (\mp V_{ij} \cdot \hat{R}_{ij}) \\ \delta(R_{ij} - \sigma_{AB}) (\hat{b}_{ij} \mathcal{P}^{AC}_i \mathcal{P}^{BD}_j - 1) O^A_i O^B_j (16)$$

where the operator \mathcal{P}_i^{AC} converts the species label of particle *i* from A to C.

Formal Kinetic Theory. The dynamics of a test particle in fluid can be described by the dynamic correlation function

$$C_{s}^{A,A}(1,1') = \langle f_{s}^{A}(1') \ (z - \mathcal{L}_{+})^{-1} \ f_{s}^{A}(1) \rangle_{\theta}(17)$$

The formalism used in the derivation of a kinetic equation for the above correlation function is along the same line as in our previous work. ¹ Using the identity $(z-\mathcal{L}_{+})^{-1}=z^{-1}+z^{-1}$ $(z-\mathcal{L}_{+})^{-1}\mathcal{L}_{+}$, Eq. (17) becomes

$$z C_{s}^{A,A}(1, 1') = \tilde{C}_{s}^{A,A}(1, 1') + \langle f_{s}^{A}(1') \\ (z - \mathcal{L}_{+})^{-1} \mathcal{L}_{+} f_{s}^{A}(1) \rangle_{0}$$
(18)

The effect of \mathcal{L}_+ acting on $f_i^A(1)$ is

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$$\mathcal{L}_{+}f_{*}^{A}(1) = -\mathcal{L}_{0}^{A}(1)f_{S}^{A}(1) + \tilde{T}_{R-}^{AB}(1\bar{2})f^{AB}(1\bar{2})$$

+
$$(1-\alpha) \, \bar{T}^{AB}_{\mathcal{E}^{-}}(1\bar{2}) f^{AB}(1\bar{2})$$

+ $\bar{T}^{AS}_{-}(1\bar{3}) f^{AS}(1\bar{3})$ (19)

in the low density limit of reacting species and the elastic collision between the test particle and the solvent particle is considered to be important other than the collision between the potential reactants. The field point free streaming operator $\mathcal{L}_{0}^{A}(1)$ is

$$\mathcal{L}_0^A(1) = \boldsymbol{v}_1^A \cdot \boldsymbol{\nabla}_n^A \tag{20}$$

and the elastic collision operator is1

$$\bar{T}_{-}^{A\alpha}(13) = T_{-}^{A\alpha}(13) + \boldsymbol{v}_{13} \cdot \hat{r}_{13}\delta(r_{13} - \sigma_{A\alpha})$$
(21)

where $T_{-}^{As}(13)$ is defined as in Eq. (14) but in the field point notation. The subscript E in $T_{E-}^{AB}(12)$ explicitly denotes the elastic collision but it is omitted in $T_{-}^{AS}(13)$ because of no reaction in the A-S collision. The reactive collision operator is

$$-\bar{T}_{R-}^{AB}(12) = T_{R-}^{AB}(12) + \alpha v_{12} \cdot \hat{r}_{12} \delta(r_{12} - \sigma_{AB}). \quad (22)$$

A short hand notation for integration over barred variables is introduced in Eq. (19).

Substitution of Eq. (19) into Eq. (18) gives the kinetic equation for $C_{I}^{A,A}(1,1')$:

$$\{z + \mathcal{L}_{0}^{A}(1)\} C_{s}^{A,A}(1, 1') - \tilde{C}_{s}^{A,A}(1, 1')$$

= $\tilde{T}_{R^{-}}^{AB}(1\bar{2}) C^{AB,A}(1\bar{2}, 1') + (1-\alpha) \tilde{T}_{E^{-}}^{AB}(1\bar{2})$
 $C^{AB,A}(1\bar{2}, 1') + \tilde{T}_{s}^{AS}(1\bar{3}) C^{AS,A}(1\bar{3}, 1')$ (23)

At this point it is convenient to introduce a matrix formulation to generalize Eq. (23):

$$\{z \underbrace{1}_{x} + \underbrace{L}_{=0}(1)\} \underbrace{C}_{=s}(1, 1') - \underbrace{\tilde{C}}_{=s}(1, 1')$$

$$= \underbrace{\bar{V}}_{=s}(1\overline{2}) \underbrace{C}_{=s}^{R}(1\overline{2}, 1') + \underbrace{\bar{T}}_{=s}(1\overline{3}) \underbrace{C}_{=s}^{S}(1\overline{3}, 1')$$

$$= \underbrace{V}_{=s}(1\overline{2}) \underbrace{C}_{=s}^{R}(1\overline{2}, 1') + \underbrace{T}_{=s}(1\overline{3}) \underbrace{C}_{=s}^{S}(1\overline{3}, 1')$$

where

$$\begin{split} \underline{\underline{I}}_{0}(1) &= \begin{pmatrix} \underline{\mathcal{I}}_{0}^{A}(1) & 0 \\ 0 & \underline{\mathcal{I}}_{0}^{C}(1) \end{pmatrix}, \quad \underline{\underline{I}}_{0}^{A}(1,1^{*}) &= \begin{pmatrix} c^{A}, A(1,1^{*}) & c^{A}, C(1,1^{*}) \\ c^{C}, A(1,1^{*}) & c^{C}, C(1,1^{*}) \end{pmatrix} \\ \underline{\underline{V}}_{1}(12) &= \begin{pmatrix} -\overline{1}_{RL_{1}}^{AB}(12) + (1-\alpha), \overline{1}_{L_{1}}^{AB}(12) \\ & \overline{1}_{RL_{1}}^{AB}(12) \\ & \overline{1}_{RL_{1}}^{AB}(12) \end{pmatrix}, \quad -\overline{1}_{RL_{1}}^{AB}(12) + (1-\alpha), \overline{1}_{L_{1}}^{AB}(12) \end{pmatrix}$$

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$$\begin{split} & \underline{\widetilde{T}}_{+}^{-}(1\,3) = \begin{pmatrix} \widetilde{T}_{+}^{AC}(1\,3) & c \\ c & \underline{T}_{+}^{CG}(1\,3) \end{pmatrix} \\ & \underline{\underline{C}}^{B}(12\,,1^{*}) = \begin{pmatrix} c^{Ab\,,A}(12\,,1^{*}) & c^{Ab\,,G}(12\,,1^{*}) \\ c^{Cb\,,A}(12\,,1^{*}) & c^{Cb\,,C}(12\,,1^{*}) \end{pmatrix} \\ & \underline{\underline{C}}^{S}(13\,,1^{*}) = \begin{pmatrix} c^{AC\,,A}(13\,,1^{*}) & 0 \\ 0 & c^{CD\,,C}(13\,,1^{*}) \end{pmatrix} \end{split}$$

The reactive collision operator $\bar{T}_{R^-}^{AB}$ is written here as the sum of two contributions, the forward and reverse reactions,

$$\bar{T}_{R-}^{AB}(12) = \bar{T}_{R-}^{AB}(12) - \bar{T}_{R-}^{AB}(12)$$

with the former term the part that changes species.

As it stands Eq. (24) is not in a closed form since the two point correlation function is coupled to the higher point correlation function. In order to make a closed kinetic equation the memory function formalism of renormalized kinetic theory is now introduced. The memory function matrix $\phi_{\pi S}(1, 1')$ is defined by

so that Eq. (24) can be rewritten as

$$\begin{aligned} & \{z \stackrel{1}{=} + \stackrel{L}{=} (1) \} \stackrel{C}{=} (1, 1') - \stackrel{\phi}{=} (1, \overline{2}) \stackrel{C}{=} (\overline{2}, 1') \\ &= \stackrel{C}{=} (1, 1') \end{aligned}$$
 (26)

The physical meaning of the memory function is apparent in Eq. (26). Since the first term on the left hand side is responsible for the free streaming of a test particle, the memory function contains all the information on the effects of the rest of the particles in solution. Hence it is expected that the structure of memory function is a manifestation of manybody interaction and its analysis is the key to understanding the reaction dynamics in liquids.

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Using the techniques of the renormalized kinetic theory ^{8,9} one can separate the memory function into static and dynamic parts. The static memory function is given by

$$\Phi^{S}(\mathbf{1}, \ \overline{2}) \widetilde{C}(\overline{2}, \ \mathbf{1}') = \widetilde{V}(\mathbf{1}\overline{2}) \widetilde{C}^{R}(\mathbf{1}\overline{2}, \ \mathbf{1}') + \overline{T}(\mathbf{1}\overline{3}) \widetilde{C}^{S}(\mathbf{1}\overline{3}, \ \mathbf{1}')$$
(27)

and the dynamic memory function is

$$\begin{split} \phi^{4}(1, \bar{2})\tilde{C}(\bar{2}, 1') \\ &= \tilde{V}(1\bar{2})G^{RR}(1\bar{2}, 1'\bar{2}')\tilde{V}^{T}(1'\bar{2}') \\ &+ \tilde{T}(1\bar{3})G^{SS}(1\bar{3}, 1'\bar{3}')\tilde{T}^{T}(1'\bar{3}') \\ &+ \tilde{V}(1\bar{2})G^{RS}(1\bar{2}, 1'\bar{3}')\tilde{T}^{T}(1'\bar{3}') \\ &+ \tilde{T}(1\bar{3})G^{SR}(1\bar{3}, 1'\bar{2}')\tilde{V}^{T}(1'\bar{2}') \end{split}$$
(28)

The four-point correlation functions appeared above are defined as

$$\begin{split} & G^{RR}(12, 1'2') = C^{RR}(12, 1'2') - C^{R}(12, \bar{1}') \\ & C_{s}^{-1}(\bar{1}', \bar{2}'')C^{R}(\bar{2}'', 1'2') \\ & G^{RS}(12, 1'3') = C^{RS}(12, 1'3') - C^{R}(12, \bar{1}') \\ & C_{s}^{-1}(\bar{1}', \bar{2}'')C^{S}(\bar{2}'', 1'3') \\ & G^{SR}(13, 1'2') = C^{SR}(13, 1'2') - C^{S}(13, \bar{1}') \\ & C_{s}^{-1}(\bar{1}', \bar{2}'')C^{R}(\bar{2}'', 1'2') \\ & G^{SS}(13, 1'3') = C^{SS}(13, 1'3') - C^{S}(13, \bar{1}') \\ & C_{s}^{-1}(\bar{1}', \bar{2}'')C^{S}(\bar{2}'', 1'3') \\ & C_{s}^{-1}(\bar{1}', \bar{2}'')C^{S}(\bar{2}'', 1'3') \\ \end{split}$$

with

$$\begin{split} \underline{c}^{\text{RR}}(12,1^{1}2^{*}) &= \begin{pmatrix} c^{\text{AB},\text{AB}}(12,1^{1}2^{*}) & c^{\text{AB},\text{CD}}(12,1^{*}2^{*}) \\ c^{\text{CD},\text{AB}}(12,1^{*}2^{*}) & c^{\text{CD},\text{CD}}(12,1^{*}2^{*}) \end{pmatrix} \\ \underline{c}^{\text{RS}}(12,1^{*}3^{*}) &= \begin{pmatrix} c^{\text{AB},\text{AS}}(12,1^{*}3^{*}) & c^{\text{AB},\text{CS}}(12,1^{*}3^{*}) \\ c^{\text{CD},\text{AS}}(12,1^{*}3^{*}) & c^{\text{CD},\text{CS}}(12,1^{*}3^{*}) \end{pmatrix} \\ \underline{c}^{\text{SR}}(13,1^{*}2^{*}) &= \begin{pmatrix} c^{\text{AS},\text{AB}}(13,1^{*}2^{*}) & 0 \\ 0 & c^{\text{CS},\text{CD}}(13,1^{*}2^{*}) \end{pmatrix} \\ \underline{c}^{\text{SS}}(13,1^{*}3^{*}) &= \begin{pmatrix} c^{\text{AS},\text{AS}}(13,1^{*}3^{*}) & 0 \\ 0 & c^{\text{CS},\text{CS}}(12,1^{*}3^{*}) \end{pmatrix} \end{split}$$

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The superscript T denotes the matrix transpose and $C_{=s}^{-1}(1', 2'')$ is the inverse of $C_{s}(1', 2'')$.

The Static Memory Function. The static correlation functions in Eq. (27) may be approximated in the low density limit of reactants as

$$\widetilde{C}(1, 1') = \delta(11') \underbrace{\omega(1)}_{=} \\
\widetilde{C}^{R}(12, 1') = \delta(11') \underbrace{\omega(12)}_{=} \\
\widetilde{C}^{S}(13, 1') = \delta(11') \underbrace{\omega(13)}_{=} \\
\widetilde{C}^{S}(13, 1') = \delta(11') \underbrace{\omega(13)}_{=} \\$$

where the diagonal matrices of equilibrium correlation functions are given by

$$\begin{split} & \omega(1) = \begin{bmatrix} \omega_0^A(1) & 0 \\ 0 & \omega_0^C(1) \end{bmatrix}, \\ & \omega_{=0}^{(12)} = \begin{bmatrix} \omega_0^{AB}(12) & 0 \\ 0 & \omega_0^{CD}(12) \end{bmatrix}, \end{split}$$

$$\begin{split} & \underset{=-}{A}(1) = \begin{bmatrix} \overline{T}_{kl^{-}}^{AB}(1\overline{2}) \ \omega_{0}^{AB}(1\overline{2}) \ \omega_{0}^{A^{-1}}(1) & -\overline{T}_{kl^{-}}^{AB}(1\overline{2}) \ \omega_{0}^{C^{-1}}(1\overline{2}) \ \omega_{0}^{C^{-1}}(1) \\ -\overline{T}_{kl^{-}}^{CD}(1\overline{2}) \ \omega_{0}^{AB}(1\overline{2}) \ \omega_{0}^{A^{-1}}(1) & \overline{T}_{kl^{-}}^{CD}(1\overline{2}) \ \omega_{0}^{C^{-1}}(1) \end{bmatrix} \\ & \underset{=-}{A}(1) = \begin{bmatrix} \overline{T}_{kl^{-}}^{AB}(1\overline{2}) \ \omega_{0}^{AB}(1\overline{2}) \ \omega_{0}^{A^{-1}}(1) + \overline{T}_{-}^{AS}(1\overline{3}) \ \omega_{0}^{AS}(1\overline{3}) \ \omega_{0}^{A^{-1}}(1) & 0 \\ & 0 & \overline{T}_{kl^{-}}^{CD}(1\overline{2}) \ \omega_{0}^{C^{-1}}(1) + \overline{T}_{-}^{CS}(1\overline{3}) \ \omega_{0}^{CS}(1\overline{3}) \ \omega_{0}^{C^{-1}}(1) \end{bmatrix} \end{split}$$

and the identity¹

$$\bar{T}_{kJ^{-}}^{AB}(12) - (1-\alpha) \, \bar{T}_{k^{-}}^{AB}(12) \\
= \bar{T}_{kJ^{-}}^{AB}(12) - \bar{T}_{k^{-}}^{AB}(12)$$

with

$$\bar{T}_{Rf-}^{AB}(12) = \alpha |v_{12} \cdot \hat{r}_{12}| \theta(v_{12} \cdot \hat{r}_{12}) \delta(r_{12} - \sigma_{AB}) \hat{b}_{12}O_1^A O_2^B$$

has been used.

The Dynamic Memory Function. Up to the static memory function level approximation, the free streaming of the test particle and statically correlated collisions, either reactive or elastic, between the test particle and its partner are accounted for. Another important contribution due to dynamically correlated collision phenomenon which is absent in the Enskog-like theories is contained in the dynamic memory function. As shown in Eq. (28) the dynamic memory function has a rather

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complex structure. It has four contributions; the first two of them may be put together as "diagonal" terms and the other two terms as "cross" terms. In this work the "diagonal" terms are assumed to be major contributions to the dynamic memory function and further analysis is carried out for these two terms. This is in the same spirit as the repeated ring approximation introduced earlier^{6,7}.

The dynamic memory function becomes in this approximation

$$\begin{split} & \phi_{=s}^{d}(1, \ \bar{2}) \ \tilde{C}_{(2)}(\bar{2}, \ 1') \\ &\approx \tilde{V}(1\bar{2}) G^{RR}(1\bar{2}, \ 1'\bar{2}') \ \tilde{V}^{T}(1'\bar{2}') \\ &+ \ \tilde{T}_{-}(1\bar{3}) \ \tilde{G}^{SS}(1\bar{3}, \ 1'\bar{3}') \ \tilde{T}_{+}^{T}(1'\bar{3}') \end{split}$$
(29)

The repeated ring operators can be constructed from the above expression such that

and

Substitution of Ec combining with Eq. (25) gives

 $\omega_{=0}^{(13)} = \begin{bmatrix} \omega_0^{AS}(13) & 0\\ 0 & \omega_0^{CS}(13) \end{bmatrix}$

At the static memory function level the kinetic equation for $C_{1}(1, 1')$ becomes

$$\{z \underset{=}{1 + L(1) + \Lambda}_{=R^{-}}(1) - \Lambda_{=-}(1) \} \underset{=s}{C}(1, 1')$$

= $\tilde{C}_{=s}(1, 1')$ (31)

where

$$\begin{split} & R(1) = \bar{V}(1\bar{2}) \left\{ z \ 1 + L(1\bar{2}) \\ & - \bar{T}(1\bar{2}\bar{3}) \ \omega(1\bar{2}\bar{3}) \ \omega^{-1}(1\bar{2}) \\ & - \bar{V}(1\bar{2}) \right\}^{-1} V(1\bar{2}) \ \omega^{-1}(1\bar{2}) \ \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \left\{ z \ 1 + L(1\bar{3}) \\ & - \bar{T}(1\bar{2}) \ \omega(1\bar{2}\bar{3}) \ \omega^{-1}(1\bar{3}) - \bar{T}(1\bar{3}) \\ & - \bar{T}(1\bar{3}\bar{4}) \ \omega(1\bar{3}\bar{4}) \ \omega^{-1}(1\bar{3}) \right\}^{-1} \\ & \bar{T}(1\bar{3}) \ \omega(1\bar{3}) \ \omega^{-1}(1\bar{3}) \\ & - \bar{T}(1\bar{3}) \ \omega(1\bar{3}) \ \omega^{-1}(1\bar{3}) \right\}^{-1} \end{split}$$

with

$$\underline{I}_{=0}^{-}(12) = \begin{pmatrix}
\mathbf{v}_{1}^{A} \cdot \vec{\nabla}_{r_{1}}^{A} + \mathbf{v}_{2}^{B} \cdot \vec{\nabla}_{r_{2}}^{B} & 0 \\
0 & \mathbf{v}_{1}^{C} \cdot \vec{\nabla}_{r_{1}}^{C} + \mathbf{v}_{2}^{D} \cdot \vec{\nabla}_{r_{2}}^{D}
\end{pmatrix}$$

$$\underline{I}_{=0}^{-}(13) = \begin{pmatrix}
\mathbf{v}_{1}^{A} \cdot \vec{\nabla}_{r_{1}}^{A} + \hat{\mathbf{v}}_{3}^{S} \cdot \vec{\nabla}_{r_{3}}^{S} & 0 \\
0 & \mathbf{v}_{1}^{C} \cdot \vec{\nabla}_{r_{2}}^{C} + \mathbf{v}_{3}^{S} \cdot \vec{\nabla}_{r_{3}}^{S}
\end{pmatrix}$$

$$\underline{\overline{T}}_{=-}^{-}(123) = \begin{pmatrix}
\overline{T}_{-}^{AS}(13) + \overline{T}_{-}^{BS}(23) & 0 \\
0 & \overline{T}_{-}^{CS}(13) + \overline{T}_{-}^{DS}(23)
\end{pmatrix}$$

$$\underline{\overline{T}}_{=-}^{-}(134) = \begin{pmatrix}
\overline{T}_{-}^{AS}(14) + \overline{T}_{-}^{SS}(34) & 0 \\
0 & \overline{T}_{-}^{CS}(14) + \overline{T}_{-}^{SS}(34)
\end{pmatrix}$$

$$\underline{\omega}_{0}^{-}(123) = \begin{pmatrix}
\omega_{0}^{ABS}(123) & 0 \\
0 & \omega_{0}^{CDS}(123)
\end{pmatrix}$$

$$\underline{\omega}_{0}^{-}(134) = \begin{pmatrix}
\omega_{0}^{ASS}(134) & 0 \\
0 & \omega_{0}^{CSS}(134)
\end{pmatrix}$$
Invoking another identity¹

$$\begin{aligned} \bar{T}_{E^{B}}^{AB}(12) + \{\bar{T}_{-}^{AS}(1\bar{3}) + \bar{T}_{-}^{BS}(2\bar{3})\} \\ \omega_{0}^{ABS}(12\bar{3}) \,\omega_{0}^{AB^{-1}} = T_{E^{-}}^{AB}(12) + \tilde{A}_{-}^{AS}(12) \\ + A_{-}^{BS}(12) - \boldsymbol{v}_{12} \cdot \bar{\boldsymbol{V}}_{r_{12}} \beta W^{AB}(r_{12}) \end{aligned} \tag{33}$$

where

$$\tilde{A}^{AS}_{-}(12) = n_{s}^{S} \int d3 \ g^{ABS}(r_{1}, r_{2}, r_{3})$$

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$$\begin{array}{rl} \cdot g^{AB}(r_{12})^{-1} \ T^{AS}_{-}(13) \ f^{S}_{0}(v_{3}) \\ \text{and} \qquad \beta \ W^{AB}(r_{12}) = -\ln g^{AB}(r_{12}), \end{array}$$

the repeated ring operators can be rearranged to give

$$\begin{split} & \underset{=1}{R}(1) = \bar{V}(1\bar{2}) \{z \ 1 + \underset{=0}{L}(1\bar{2}) + \underset{=k^{-}}{\bar{T}}(1\bar{2}) \\ & - T_{=E^{-}}(1\bar{2}) - \tilde{A}(1\bar{2}) + \underset{=k^{-}}{\bar{W}}'(1\bar{2})\}^{-1} \\ & \underbrace{V(1\bar{2})}_{=0} \omega(1\bar{2}) \omega^{-1}(1) \\ & \equiv \bar{V}(1\bar{2}) \underbrace{G}_{=1}(1\bar{2}, z) \underbrace{V}_{=0}(1\bar{2}) \omega^{-1}(1) \\ & = \bar{V}(1\bar{2}) \underbrace{G}_{=1}(1\bar{2}, z) \underbrace{V}_{=-}(1\bar{2}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \{z \ 1 + L(1\bar{3}) \\ & - \bar{T}_{=k^{-}}(1\bar{2}) \omega(1\bar{2}\bar{3}) \omega^{-1}(1\bar{3}) - T(1\bar{3}) \\ & - \tilde{A}(1\bar{3}) + \underbrace{W'(1\bar{3})}_{=1}^{-1} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & \equiv \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=2} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \omega(1\bar{3}) \omega^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) u(1\bar{3}) u^{-1}(1) \\ & = \bar{T}(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} T(1\bar{3}) u(1\bar{3}) \underbrace{G(1\bar{3}, z)}_{=-} U(1\bar{3}) u($$

where

$$\begin{split} \bar{\underline{T}}_{R_{r}}^{-}(12) &= \begin{pmatrix} \bar{T}_{R_{r}}^{AB}(12) & -\bar{T}_{R_{r}}^{AB}(12) \\ -\bar{T}_{R_{r}}^{CD}(12) & \bar{T}_{R_{r}}^{CD}(12) \end{pmatrix} \\ \bar{\underline{T}}_{R_{r}}^{-}(12) &= \begin{pmatrix} T_{-}^{AB}(12) & 0 \\ 0 & T_{E-}^{CD}(12) \end{pmatrix} \\ \bar{\underline{T}}_{-}^{-}(13) &= \begin{pmatrix} T_{-}^{AS}(13) & 0 \\ 0 & T_{-}^{CS}(13) \end{pmatrix} \\ \bar{\underline{\Lambda}}_{-}^{-}(12) &= \begin{pmatrix} \bar{\Lambda}_{-}^{AS}(12) + \bar{\lambda}_{-}^{BS}(12) & 0 \\ 0 & \bar{\Lambda}_{-}^{CS}(12) + \bar{\Lambda}_{-}^{DS}(12) \end{pmatrix} \\ \bar{\underline{\Lambda}}_{-}^{-}(13) &= \begin{pmatrix} \bar{\Lambda}_{-}^{AS}(12) + \bar{\Lambda}_{-}^{SS}(13) & 0 \\ 0 & \bar{\Lambda}_{-}^{CS}(12) + \bar{\Lambda}_{-}^{DS}(12) \end{pmatrix} \\ \bar{\underline{\Lambda}}_{-}^{-}(13) &= \begin{pmatrix} \bar{\Lambda}_{-}^{AS}(13) + \bar{\Lambda}_{-}^{SS}(13) & 0 \\ 0 & \bar{\Lambda}_{-}^{CS}(13) + \bar{\Lambda}_{-}^{SS}(13) \end{pmatrix} \\ \bar{\underline{M}}_{-}^{+}(12) &= \begin{pmatrix} v_{12}, \bar{\overline{V}}_{r_{12}}/\bar{\mathcal{I}}^{W^{AB}}(r_{12}) & 0 \\ 0 & v_{12}, \bar{\overline{V}}_{r_{12}}/\bar{\mathcal{I}}^{W^{CD}}(r_{12}) \end{pmatrix} \\ \bar{\underline{M}}_{-}^{+}(13) &= \begin{pmatrix} v_{13}, \bar{\overline{V}}_{r_{13}}/\bar{\mathcal{I}}^{W^{AS}}(r_{13}) & 0 \\ 0 & v_{13}, \bar{\overline{V}}_{r_{13}}/\bar{\mathcal{I}}^{W^{CS}}(r_{13}) \end{pmatrix} \end{split}$$

Combining Eqs. (31), (34), and (35), one Journal of the Korean Chemical Society can obtain the final kinetic equation in the repeated ring approximation:

$$\{z \ \underline{1} + \underline{L}_{=0}^{(1)} + \underline{A}_{=R^{-}}^{(1)} - \underline{A}_{=1}^{(1)} - \underline{R}_{=1}^{(1)} \\ - \underline{R}_{=2}^{(1)} \{\underline{L}_{=s}^{(1)}(1, 1') = \widetilde{\underline{C}}_{=s}^{(1)}(1, 1')$$

or

$$\{z = -L_{=R}(1)\} C_{=S}(1, 1') = \tilde{C}_{=S}(1, 1')$$
(36)

which describes the dynamics of a test particle in phase space. The general structure of the kinetic equation is similar to the one derived earlier using the generalized Langevin equation approach² but the detailed structure is different because the dynamical variables of interest are different. This point will be discussed further in Section 4.

3. THE RATE KERNEL

In order to obtain the rate kernel from the final kinetic equation the velocity and the coordinate dependences are projected out by a diagonal matrix projection operator $\mathcal{P} = \begin{bmatrix} \mathcal{P}_A & 0 \\ 0 & \mathcal{P}_C \end{bmatrix}$ and its transpose \mathcal{P}^T . The elements of the projection operator matrices are defined, for example, by

$$\mathcal{P}_{A}C^{A,A}(1, 1') = \Omega^{-1} f_{0}^{A}(v_{1}) \int d1 \ C^{A,A}(1, 1')$$

$$C^{A,A}(1, 1') \mathcal{P}_{A}^{T} = \left\{ \int d1' \ C^{A,A}(1, 1') \right\}$$

$$\Omega^{-1} f_{0}^{A}(v_{1}')$$
(37)

The projected kinetic equation becomes

$$\begin{aligned} & \{z \stackrel{1}{=} - \stackrel{\mathcal{P}}{\xrightarrow{}} \stackrel{L}{\underset{R}{}} (1) \stackrel{\mathcal{P}}{\xrightarrow{}} - \stackrel{\mathcal{P}}{\underset{R}{}} \stackrel{L}{\underset{R}{}} (1) [z \stackrel{1}{=} - \stackrel{\mathcal{Q}}{\xrightarrow{}} \stackrel{L}{\underset{R}{}} (1)]^{-1} \\ & Q \stackrel{L}{\underset{R}{}} (1) \} \stackrel{\mathcal{P}}{\xrightarrow{}} \stackrel{C}{\underset{R}{}} (1, 1') \stackrel{\mathcal{P}}{\underset{R}{}}^{T} = \stackrel{\mathcal{P}}{\xrightarrow{}} \stackrel{\tilde{C}}{\underset{R}{}} (1, 1') \stackrel{\mathcal{P}}{\underset{R}{}}^{T} \\ & (38) \end{aligned}$$

which can be further reduced to an equation of the form of the macroscopic rate law expression using the number conservation in elastic collision:

$$\{z_{1} + k(z)n'\} P = \tilde{P}_{=S}$$
 (39)

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where $P_{=s} = \int d1 \ d1' \ C_{s}(1, 1'), \ Q = 1 - \mathcal{P}$, and $n'_{=s} = \begin{bmatrix} n_{s_{1}}^{s} & 0\\ 0 & n_{s} \end{bmatrix}$. The rate kernel k(z) has three contributions

$$\underset{=}{\overset{k}{z}}(z) = \underset{=}{\overset{k}{z}} + \underset{=}{\overset{kRR}{z}} + \underset{=}{\overset{kNE}{z}}$$
(40)

with

and

 $f_{x}(v_{1}) = \begin{bmatrix} f_{0}^{A}(v_{1}) & 0\\ 0 & f_{0}^{C}(v_{1}) \end{bmatrix}.$

The equilibrium forward and reverse reactive collision frequencies are defined by

$$k_{f}^{0} = \int dr_{12} \int dv_{1} dv_{2} \,\bar{\bar{T}}_{Rf-}^{AB}(12) f_{0}^{A}(v_{1}) f_{0}^{B}(v_{2})$$

$$k_{r}^{0} = \int dr_{12} \int dv_{1} dv_{2} \,\bar{\bar{T}}_{Rf-}^{CD}(12) f_{0}^{C}(v_{1}) f_{0}^{D}(v_{2})$$

The first term in Eq. (40) is the equilibrium contribution which incorporates the static correlation through the radial distribution function and the second term is due to the repeated ring collision event which is important in describing the dynamics of particles in dense media. The last term is a nonequilibrium correction to the rate kernel which has been known to have small contribution in certain circumstances¹².

When the reverse reaction is ignored the rate kernel expression can be decoupled and the matrix formulation is no longer necessary. The resulting expression becomes, neglecting 신 국 조

the nonequilibrium correction,

$$k_{f}(z) = k_{f}^{0} g^{AB}(\sigma_{AB}) - Q^{-1} \int d1 \, d2 \, \vec{T}_{kf-}^{AB}(12)$$

$$G_{1}^{AB}(12, z) \, T_{kf-}^{AB}(12) \, g^{AB}(r_{12}) \, f_{0}^{A}(v_{1})$$

$$f_{0}^{B}(v_{2}) \qquad (41)$$

with

$$G_{1}^{AB}(12, z) = \{z + \mathcal{L}_{0}^{AB}(12) + \bar{T}_{Rf}^{AB}(12) - T_{E}^{AB}(12) - \bar{\Lambda}_{-}^{AS}(12) + v_{12} \cdot \bar{V}_{r_{12}}\beta W^{AB}(r_{12})\}^{-1}$$

4. DISCUSSION

In this work the repeated ring, renormalized kinetic theory for a reactive test particle in liquid at the singlet density level is presented. This formulation should be compared with the same approach at the doublet level¹ and then with the generalized Langevin equation approach at the singlet level² both of them presented earlier. The doublet level of the generalized Langevin equation approach is yet to be formulated but it is expected that its formulation would be rather complex due to more complicated couplings between higher density fields.

The kinetic equation derived in the doublet level repeated ring, renormalized kinetic theory has the form¹

$$\begin{aligned} & \{z \stackrel{1}{=} + \stackrel{L}{\underset{=0}{L}}(12) + \stackrel{T}{\underset{=R^{-}}{T}}(12) - \stackrel{T}{\underset{=R^{-}}{T}}(12) - \stackrel{A}{\underset{=R^{-}}{T}}(12) \\ & + \stackrel{W'}{\underset{=}{V}}(12) - \stackrel{R}{\underset{=}{R}}(12)\} \stackrel{C}{\underset{=}{C}}(12, 1'2') \\ & = \stackrel{\tilde{C}}{\underset{=}{C}}(12, 1'2') \end{aligned}$$

$$\end{aligned}$$

Since Eq. (42) is derived for a reactive test *pair* of particles it contains (contributions due to direct collision of the pair and the potential of mean force for the pair which are absent in the kinetic equation for a test particle, Eq. (36). On the other hand, the reactive collision effect appears in Eq. (36) at the Enskog level and in the repeated ring operator.

The kinetic equation derived in the generalized Langevin equation approach at the singlet level has the same structure as Eq. (36) when the couplings between the test particle field density and the doublet field densities are properly taken into account. This shows the equivalence of two approaches at the singlet level provided various approximations are introduced at proper stages as shown.

The rate kernel expression obtined in the repeated ring, renormalized kinetic theory at the doublet level is given by¹

$$\underbrace{k}_{=}(z) = \underbrace{k}_{=} - \Omega^{-1} \int d1 \, d2 \, \underbrace{T}_{=R-}(12) [z_{=}^{1} - L_{=}(12)]^{-1} \\ \cdot \underbrace{T}_{=R-}(12) g(r_{12}) \, \underbrace{f}_{=0}(v_{1}) \, \underbrace{f}_{=0}(v_{2}) \quad (43)$$

with

$$\underline{g}(r_{12}) = \begin{bmatrix} g^{AB}(r_{12}) & 0\\ 0 & g^{CD}(r_{12}) \end{bmatrix}$$

$$\underline{f}_{=0}(v_2) = \begin{bmatrix} f_0^B(v_2) & 0\\ 0 & f_0^D(v_2) \end{bmatrix}$$

which is similar to the expression Eq. (40) without the nonequilibrium correction term. It is interesting to notice that the first two terms in Eq. (40) come from $\mathcal{P}_{\underline{z}}(1) \mathcal{P}_{\underline{z}}$ term in Eq. (38) whereas only k term in Eq. (43) is originated from $\mathcal{P}_{\underline{z}}(12) \mathcal{P}$ type term. The second term in Eq. (43) comes from the term containing the complementary projection operator Q.

The generalized Langevin equation approach at the singlet level gives the same expression for the rate kernel as in Eq. (41) when the reverse reaction is neglected but the propagator between two reactive collision operators is slightly different. This difference may be attributed to the fact that the effects of doublet fields on the propagation between two reactive collisions are different due to the different constructions of doublet density fields in two approaches. This point may be further clarified when the generalized Langevin equation approach at the doublet level is properly formulated.

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