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Generalized flow equation and kinetic coefficients in a reaction-diffusion system

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Based on Robertson's formalism, which can be applied to a system arbitrarily far from equilibruim, generalized flow and rate equations for a reaction-diffusion system are derived in nonlinear irreversible processes. The kinetic coefficients of the system are studied and the coupling between different flows and rates is discussed. Equations of the flow and rate and the kinetic coefficients obtained in the present paper are memory retaining and nonlocal. In particular, we relate the kinetic coefficients to the concrete microscopical mechanism of reaction diffusion. This enables us to calculate these kinetic coefficients.

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I. INTRODUCTION

The rate of reaction and the transport coefficient in a reaction-diffusion system are interesting problems. Some recent investigations have considered the transport coefficient [1–6] and the rate processes [7–9]. But the methods in those papers mentioned above cannot be applied arbitrarily far from equilibrium to the general reaction-diffusion system in which memory and nonlocality are retained. In this paper, based on Robertson's formalism [10], which can be applied to a system arbitrarily far from equilibrium, we derive generalized flow equations for a reaction-diffusion system with single and multiple components in nonlinear irreversible processes, and obtain the transport coefficients and the rates of the reactions. The kinetic coefficients are discussed in detail. In particular, the kinetic coefficients can be calculated by the formalism developed in this paper. The method is formulated in Sec. II. The transport coefficients and the rate constants of the reactions are given and discussed in Sec. III. In Sec. IV, there are some remarks.

II. GENERALIZED FLOW AND RATE EQUATIONS

We consider a general reaction-diffusion system with multiple components, in which there exist transport of heat, diffusion of different components, and a number of chemical reactions among different components of the mixture. The chemical potential of different components and the temperature depend not only on position in space but also on time. For the system under consideration, once the thermodynamic coordinates have been chosen, we choose a set of time-independent, quantum-mechanical operators corresponding to some of these thermodynamic coordinates. Let $F_n(\mathbf{r})$ denote these operators, whose expectations we wish to describe as a function of position and time. Here n takes the values $1,2,3,\ldots,m$ labeling the different operators, and these operators, whose expectations are some of the thermodynamic coordinates of the system, depend explicitly upon position.

A generalized differential conservation equation of those operators of the system which have corresponding thermodynamic coordinates (e.g., energy density, particle density, momentum density, etc.) can be given by [11]

$$\dot{F}_n(\mathbf{r},t)+\nabla\cdot\mathbf{j}_n(\mathbf{r},t)=J_n(\mathbf{r},t)\ , \tag{1}$$

where $\mathbf{j}_n(\mathbf{r},t)$ is the flow operator corresponding to $F_n(\mathbf{r})$. $J_n(\mathbf{r},t)$ is the source corresponding to the flow $\mathbf{j}_n(\mathbf{r},t)$. The equation of motion of the thermodynamic coordinates $F_n(\mathbf{r})$ is [10]

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t=\langle \dot{F}_n(\mathbf{r},t)\rangle_t + \int_0^t dt'\sum_{n'}\int d^3r' K_{nn'}(\mathbf{r},t,\mathbf{r}',t')\lambda_{n'}(\mathbf{r}',t')\ , \tag{2}$$

where the kernel is given by

$$K_{nn'}(\mathbf{r},t,\mathbf{r}',t')=\langle \dot{F}_n(\mathbf{r},t)T(t,t')[1-P(t')]\bar{\dot{F}}_{n'}(\mathbf{r}',t')\rangle_{t'} \tag{3}$$

and the symbols used here have the following definitions.

The angular brackets on the right of Eqs. (2) and (3) are defined by

$$\langle A\rangle_t=\mathrm{Tr}[A\sigma(t)]$$

and the bar over an operator is defined by

$$\bar{A}=\int_0^1 \sigma(t)^x A\sigma(t)^{-x}dx-\langle A\rangle_t\ , \tag{4}$$

where A may be any operator and the generalized canonical density operator $\sigma(t)$ is defined as

$$\sigma(t)=\frac{\exp\left[-\sum_n\int d^3r\,\lambda_n(\mathbf{r},t)F_n(\mathbf{r})\right]}{\mathrm{Tr}\left\{\exp\left[-\sum_n\int d^3r\,\lambda_n(\mathbf{r},t)F_n(\mathbf{r})\right]\right\}}\ . \tag{5}$$

$T(t,t')$ in Eq. (3) satisfies

$$\partial T(t,t')/\partial t'=iT(t,t')[1-P(t')]L(t')$$

with the initial condition $T(t,t)=1$. Here L is the Liouville operator and the operator $P(t)$ is defined as

1063-651X/96/53(4)/4194(4)/$10.00

$$P(t)A=\sum_n \int d^3r\, \mathrm{tr}\{F_n(\mathbf{r})A\}\delta\sigma(t)/\delta\langle F_n(\mathbf{r})\rangle_t\ .$$

The $\lambda_n(\mathbf{r},t)$ are called the thermodynamic conjugates of the $\langle F_n(\mathbf{r})\rangle_t$.

Insert Eq. (1) into Eq. (2) to get the exact generalized flow equation of diffusional flows $\mathbf{j}_n(\mathbf{r},t)$ and the exact generalized rate equation of the reaction rates $J_n(\mathbf{r},t)$, respectively:

$$\mathrm{Tr}\{\rho(t)\mathbf{j}_n(\mathbf{r},t)\}=\langle \mathbf{j}_n(\mathbf{r},t)\rangle_t+\int_0^t dt'\sum_{n'}\int d^3r' K^{\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t')$$
$$+\int_0^t dt'\sum_{n'}\int d^3r' K^{\mathrm{j}-J}_{nn'}(\mathbf{r},t,\mathbf{r}',t')\lambda_{n'}(\mathbf{r}',t')\ , \tag{6}$$

where

$$K^{\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t')=\langle \mathbf{j}_n(\mathbf{r},t)T(t,t')[1-P(t')]\bar{\mathbf{j}}_{n'}(\mathbf{r}',t')\rangle_{t'}\ , \tag{7}$$

$$K^{\mathrm{j}-J}_{nn'}(\mathbf{r},t,\mathbf{r}',t')=\langle \mathbf{j}_n(\mathbf{r},t)T(t,t')[1-P(t')]\bar{J}_{n'}(\mathbf{r}',t')\rangle_{t'}\ , \tag{8}$$

and

$$\mathrm{Tr}\{\rho(t)J_n(\mathbf{r},t)\}=\langle J_n(\mathbf{r},t)\rangle_t+\int_0^t dt'\sum_{n'}\int d^3r' K^{J}_{nn'}(\mathbf{r},t,\mathbf{r}',t')\lambda_{n'}(\mathbf{r}',t')$$
$$+\int_0^t dt'\sum_{n'}\int d^3r' K^{J-\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t')\ , \tag{9}$$

where

$$K^{J}_{nn'}(\mathbf{r},t,\mathbf{r}',t')=\langle J_n(\mathbf{r},t)T(t,t')[1-P(t')]\bar{J}_{n'}(\mathbf{r}',t')\rangle_{t'}\ , \tag{10}$$

$$K^{J-\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t')=\langle J_n(\mathbf{r},t)T(t,t')[1-P(t')]\bar{\mathbf{j}}_{n'}(\mathbf{r}',t')\rangle_{t'}\ . \tag{11}$$

In deriving Eqs. (6) and (9), the condition $J_n(\mathbf{r},t)=0$ at $|\mathbf{r}|>\Omega$, where Ω is the region of space occupied by the system, has been used. Equations (6) and (9) are memory-retaining and nonlocal. These equations are coupled, nonlinear, integral equations. In fact, Eq. (6) involves not only the coupling between the diffusional flows of different components but also the coupling between the diffusion flows of different components and the reaction rates of different reactions. Similarly, Eq. (9) involves not only the coupling between the reaction rates of different reactions but also the coupling between the reaction rates of different reactions and the diffusion flows of different components. In particular, there exist the coupling between the diffusion flows and the energy flow and the coupling between the reaction rates and the energy flow. If the momentum flow is considered, there exist the coupling between the diffusional flows and the momentum flow and the coupling between the reaction rates and momentum flow. In the near-equilibrium approximation, the correlation functions (7) and (8) and (10) and (11) satisfy reciprocity relations. The first terms on the right of Eqs. (6) and (9) are called reversible terms since they do not directly change the entropy; the time integral terms are called irreversible terms since they do change the entropy.

III. KINETIC COEFFICIENTS AND THE RATE CONSTANT

If we neglect the retardations in Eqs. (6) and (9), i.e., assume that $\lambda_{n'}(\mathbf{r}',t')$ change little in the attenuation time of the correlation between the flows, then we can take the thermodynamic forces at time $t'=t$ outside the integral over the time. We then obtain a linear relation between the thermodynamic forces and flows that are without retardation, but nonlocal in character:

$$\mathrm{Tr}\{\rho(t)\mathbf{j}_n(\mathbf{r},t)\}=\langle \mathbf{j}_n(\mathbf{r},t)\rangle_t+\sum_{n'}\int d^3r' L^{\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t)+\sum_{n'}\int d^3r' L^{\mathrm{j}-J}_{nn'}(\mathbf{r},t,\mathbf{r}')\lambda_{n'}(\mathbf{r}',t)\ , \tag{12}$$

$$\mathrm{Tr}\{\rho(t)J_n(\mathbf{r},t)\}=\langle J_n(\mathbf{r},t)\rangle_t+\sum_{n'}\int d^3r' L^{J}_{nn'}(\mathbf{r},t,\mathbf{r}')\lambda_{n'}(\mathbf{r}',t)+\sum_{n'}\int d^3r' L^{J-\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t)\ , \tag{13}$$

where

$$L(\mathbf{r},\mathbf{r}',t)=\begin{bmatrix} L^{\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t) & L^{\mathrm{j}-J}_{nn'}(\mathbf{r},\mathbf{r}',t) \\ L^{J}_{nn'}(\mathbf{r},\mathbf{r}',t) & L^{J-\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t) \end{bmatrix} = \begin{bmatrix} \int_0^t dt' K^{\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t') & \int_0^t dt' K^{\mathrm{j}-J}_{nn'}(\mathbf{r},t,\mathbf{r}',t') \\ \int_0^t dt' K^{J}_{nn'}(\mathbf{r},t,\mathbf{r}',t') & \int_0^t dt' K^{J-\mathrm{j}}_{nn'}(\mathbf{r},t,\mathbf{r}',t') \end{bmatrix} \tag{14}$$

can be defined as the kinetic coefficients. If we neglect the nonlocal character, i.e., assume that the thermodynamic forces vary little over the correlation length over which $L(\mathbf{r},\mathbf{r}',t)$ differs appreciably from zero, then in Eqs. (12) and (13) we can take $\lambda_{n'}(\mathbf{r}',t)$ at the point $\mathbf{r}'=\mathbf{r}$ outside the integral over space. We get, then

$$\mathrm{Tr}\{\rho(t)\mathbf{j}_n(\mathbf{r},t)\}=\langle \mathbf{j}_n(\mathbf{r},t)\rangle_t+\sum_{n'} L^{\mathrm{j}}_{nn'}(\mathbf{r},t)\cdot\nabla'\lambda_{n'}(\mathbf{r},t) + \sum_{n'} L^{\mathrm{j}-J}_{nn'}(\mathbf{r},t)\lambda_{n'}(\mathbf{r},t)\ , \tag{15}$$

$$\mathrm{Tr}\{\rho(t)J_n(\mathbf{r},t)\}=\langle J_n(\mathbf{r},t)\rangle_t+\sum_{n'} L^{J}_{nn'}(\mathbf{r},t)\lambda_{n'}(\mathbf{r},t) + \sum_{n'} L^{J-\mathrm{j}}_{nn'}(\mathbf{r},t)\cdot\nabla'\lambda_{n'}(\mathbf{r},t) \tag{16}$$

where

$$L(\mathbf{r},t)=\begin{bmatrix} L^{j}_{nn'}(\mathbf{r},t) & L^{\mathrm{j}-J}_{nn'}(\mathbf{r},t) \\ L^{J}_{nn'}(\mathbf{r},t) & L^{J-\mathrm{j}}_{nn'}(\mathbf{r},t) \end{bmatrix} = \begin{bmatrix} \int d^3r' L^{\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t) & \int d^3r' L^{\mathrm{j}-J}_{nn'}(\mathbf{r},\mathbf{r}',t) \\ \int d^3r' L^{J}_{nn'}(\mathbf{r},\mathbf{r}',t) & \int d^3r' L^{J-\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t) \end{bmatrix} \tag{17}$$

can be called transport coefficients and the constants of the rate for the diffusion and for the reaction, respectively. It is clear that the transport coefficients are more general than those of Refs. [1–3] since the operator P does not appear in their expressions. In particular, we obtain the generalized rate constants $L^{J}_{nn'}(\mathbf{r},t)$ which obviously depend on temperature, and in general, on time. From Eq. (17) we can obtain the diffusional coefficients, the rate coefficients of the reaction, and the reaction-diffusion coefficients, respectively, in which all traces are to be calculated using the local equilibrium statistical density operator $\sigma(t)$ as in Eq. (5). In linear approximation, if we neglect the coupling between the reaction and the diffusion, the flows given in Eq. (6) can be reduced to those of Ref. [1].

IV. SOME REMARKS

(1) The key to solving Eqs. (6) and (9) is to deal with the kernels in the integrals. Some methods of dealing with the kernels have been developed [12–14]. We here make the Markov approximation, namely,

$$\sigma(t')=\exp[iL(t-t')]\sigma(t)\ ,$$

$$Q(t')=\exp[iL(t-t')]Q(t)\exp[-iL(t-t')]\ , \tag{18}$$

$$T(t,t')=\exp[-iL(t-t')]\ ,$$

where L is the Liouville operator, and $Q(t)=1-P(t)$. For more details of the above approximations the reader is recommended to Ref. [13]. Consider the case of steady state characterized by the flows $\mathbf{j}_n(\mathbf{r})$ and $J_n(\mathbf{r})$, and insert Eq. (18) into Eqs. (6) and (9) to get, respectively,

$$\mathrm{Tr}\{\rho\mathbf{j}_n(\mathbf{r})\}=\langle \mathbf{j}_n(\mathbf{r})\rangle+\int_0^\infty dt'\sum_{n'}\int d^3r' K^{\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t') + \int_0^\infty dt'\sum_{n'}\int d^3r' K^{\mathrm{j}-J}_{nn'}(\mathbf{r},\mathbf{r}',t')\lambda_{n'}(\mathbf{r}',t')\ , \tag{19}$$

where

$$K^{\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t')=\mathrm{Tr}\{\mathbf{j}_n(\mathbf{r},t)Q\exp[iLt']\bar{\mathbf{j}}_{n'}(\mathbf{r}')\exp[-iLt']\sigma\}\ , \tag{20}$$

$$K^{\mathrm{j}-J}_{nn'}(\mathbf{r},\mathbf{r}',t')=\mathrm{Tr}\{\mathbf{j}_n(\mathbf{r})Q\exp[iLt']\bar{J}_{n'}(\mathbf{r}')\exp[-iLt']\sigma\}\ , \tag{21}$$

and

$$\mathrm{Tr}\{\rho J_n(\mathbf{r})\}=\langle J_n(\mathbf{r})\rangle+\int_0^\infty dt'\sum_{n'}\int d^3r' K^{J}_{nn'}(\mathbf{r},\mathbf{r}',t')\lambda_{n'}(\mathbf{r}',t') + \int_0^\infty dt'\sum_{n'}\int d^3r' K^{J-\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t')\cdot\nabla'\lambda_{n'}(\mathbf{r}',t')\ , \tag{22}$$

where

$$K^{J}_{nn'}(\mathbf{r},\mathbf{r}',t')=\mathrm{Tr}\{\mathbf{j}_n(\mathbf{r})Q\exp[iLt']\bar{J}_{n'}(\mathbf{r}')\exp[-iLt']\sigma\}\ , \tag{23}$$

$$K^{J-\mathrm{j}}_{nn'}(\mathbf{r},\mathbf{r}',t')=\mathrm{Tr}\{J_n(\mathbf{r})Q\exp[iLt']\bar{\mathbf{j}}_{n'}(\mathbf{r}')\exp[-iLt']\sigma\}\ . \tag{24}$$

It is clear that one can calculate the transport coefficients and the rate constant of the reaction from Eqs. (19) and (22) when the Hamiltonian and the relevant parameters $\lambda_n(\mathbf{r},t)$ in the system are given.

(2) The method developed in the present paper can be applied to study not only chemical reaction-diffusion systems but also various birth-death processes. In particular, we relate kinetic coefficients to the concrete microscopic mechanism of reaction diffusion. This enables us to understand the inherent rule of chemical reaction diffusion at a deeper level, i.e., the microscopic field, and to calculate kinetic coefficients and transport coefficients.

(3) Although the present formalism is exact, one must make some approximations when dealing with the kernels. In fact, expressing macroscopic phenomenological coefficients by a microscopic formalism is the primary difficulty in investigating dynamic processes, and also the interest of dealing with the processes. Generally speaking, it is inevitable to make approximations when dealing with dynamic processes with memory retention and nonlocality.

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