Memory Equations for Kinetics of Diffusion-Influenced Reactions

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A many-body master equation is constructed by incorporating stochastic terms responsible for chemical reactions into the many-body Smoluchowski equation. Two forms of Langevin-type of memory equations describing the time evolution of dynamical variables under the influence of time-independent perturbation with an arbitrary intensity are derived. One form is convenient in obtaining the dynamics approaching the steady-state attained by the perturbation and the other in describing the fluctuation dynamics at the steady-state and consequently in obtaining the linear response of the system at the steady-state to time-dependent perturbation. In both cases, the kinetics of statistical averages of variables is found to be obtained by analyzing the dynamics of time-correlation functions of the variables.

Key Words: Diffusion-influenced reaction, Memory equation, Linear response theory

Introduction

Chemical reactions in liquid occur under the influence of diffusive motion of reactants. Since the pioneering work was done by Smoluchowski, many theoretical studies have been proposed to explain the effects of molecular diffusion on the rates of chemical reactions.

One of the most popular approaches is based on reduced distribution functions of reactants. One-particle reduced distribution function is introduced in this method. Dynamics of the one-particle reduced distribution function is coupled to two-particle reduced distribution function via time-dependent rate coefficients which is determined by the dynamics of two-particle reduced distribution function. Such hierarchical structure extends to \( N \)-particle distribution function and solving the hierarchical problem is equivalent to solving the \( N \)-particle equations of motion. Thus in order to make the problem tractable, one should truncate the hierarchy at a certain level of reduced distribution function. Such truncation procedure often brings some uncontrollable errors in the framework.

Another popular approach is to employ memory kernel in the rate equation for one-particle reduced distribution function instead of time-dependent rate coefficient. The former is non-local in time while the latter is local. Examples which have been known powerful in a few cases of reactions include the integral encounter theory, the modified encounter theory, the memory equation approach developed by Yang, Lee, and Shin, the many-particle kernel theory, the relaxation time approximation, and the unified Smoluchowski approximation. Although the details of various forms of the memory equation approach are diverse, theoretical basis for the equations with time-nonlocal memory kernel may be found in the framework developed by Mori to derive the generalized Langevin equation for the motion of Brownian particle.

In this paper, we introduce a many-body reaction-Smoluchowski equation which describes the stochastic processes of microscopic chemical reactions as well as diffusive motion of reactants. From the reaction-Smoluchowski equation, using Mori’s projection operator technique, we derive two forms of memory equations for the time-evolution of density fields of reactants under time-independent perturbation. One form is suitable for obtaining the kinetics approaching the steady-state to be attained by continuous action of the perturbation on the system in equilibrium state. The other form is suitable for obtaining the fluctuation dynamics of the density fields at the steady-state. Attributed to the linear response theory, this equation can be utilized to determine the kinetics following time-dependent perturbation acted on the steady-state or on the equilibrium state.

Reactive Many-Body Smoluchowski Equation

We introduce a many-body probability distribution function \( \rho(q_1, \ldots, q_N; \theta_1, \ldots, \theta_N; t) \) that \( N \) molecules are found, respectively, at \( q_1, \ldots, q_N \) positions and their chemical species \( \theta_1, \ldots, \theta_N \) at time \( t \). A set of these dynamical variables is compactly denoted by \( \Gamma \). Due to the molecular motion caused by systematic intermolecular interaction and/or by incessant random collisions with solvents, the probability distribution function changes with time. In this case, the evolution equation for \( \rho(q_1, \ldots, q_N; \theta_1, \ldots, \theta_N; t) \) is assumed to satisfy the many-body Smoluchowski equation:

\[
\frac{\partial}{\partial t} \rho(\Gamma; t) - \sum_{i=1}^{N} \nabla_i \cdot D_i e^{V_i} \cdot \nabla e^{V_i} \rho(\Gamma; t) = 0
\]

where \( D_i \) is the diffusion constant of the \( i \)th molecule and \( V \) represents the potential of mean force in \( k_B T \) unit with the Boltzmann constant and \( T \) the absolute temperature. In addition to diffusive motion of the molecules, the probability distribution changes due to chemical reactions. In order to take into account such processes, we add kinetic transition
terms into Eq. (1):

\[
\frac{\partial}{\partial \tau} \rho(\Gamma, \tau) = - \sum_{i=1}^{N} \mathbf{\nabla}_i \cdot \mathbf{D}_i \rho(\Gamma, \tau) \mathbf{\nabla}_i \rho(\Gamma, \tau) \\
+ \left[ \mathbf{J}^* [W(\Gamma \leftarrow \Gamma') \rho(\Gamma') - W(\Gamma' \leftarrow \Gamma \rho(\Gamma))] \right] \equiv \hat{L}(\Gamma, t) \rho(\Gamma, t) \\
= \hat{L}^{eq}(\Gamma, t) \rho(\Gamma, t) \\
\tag{2}
\]

where \( \hat{J}^* \) denotes the classical trace implying the integration over \( q_i, \ldots, q_N \) and the summation over \( \theta_i, \ldots, \theta_N \). \( W(\Gamma \leftarrow \Gamma'; t) \) is the time-dependent transition rate for the system to change from the phase point \( \Gamma' \) to \( \Gamma \). The second and third terms of the right hand side (RHS) of Eq. (2) represent the rates of incoming and outgoing transfer of probability distribution function at the phase point \( \Gamma \) resulting from chemical reactions. The formal solution of Eq. (2) is given in terms of the forward-time ordered exponential operator, \( e^{\hat{L}^{eq} \tau} \), as \( \rho(\Gamma, t) = \exp \left\{ \int_{0}^{t} ds \hat{L}^{eq}(\Gamma; s) \right\} \rho_{eq}(\Gamma) \) with the initial equilibrium distribution function \( \rho_{eq}(\Gamma) \).

Time evolution of the mean value of a set of dynamical variables \( \Lambda(\Gamma, t) \) of the molecular system is obtained by the ensemble average over the probability distribution function

\[
\langle \Lambda \rangle_t = \left\langle \int d\Gamma \Lambda(\Gamma) \rho(\Gamma, t) \right\rangle. \\
\tag{3}
\]

The subscript \( t \) on \( \langle \cdot \rangle \) denotes an ensemble average over a distribution at time \( t \). Inserting the formal solution of \( \rho(\Gamma, t) \) into it, we obtain

\[
\langle \Lambda \rangle_t = \left\langle \int d\Gamma \Lambda(\Gamma) \exp \left\{ \int_{0}^{t} ds \hat{L}^{eq}(\Gamma; s) \right\} \rho_{eq}(\Gamma) \right\rangle. \\
\tag{4}
\]

We consider the integral \( \int d\Gamma A(\Gamma) \hat{L}(\Gamma; t) B(\Gamma) \) where \( A \) and \( B \) are arbitrary dynamical variables. Integrating by parts over the position variables for the Smoluchowski term and interchanging the dummy variables \( \Gamma \) and \( \Gamma' \) for the chemical reaction terms, the integral can be rewritten as

\[
\int d\Gamma A(\Gamma) \hat{L}(\Gamma; t) B(\Gamma) = \int d\Gamma B(\Gamma) \left[ \sum_{i=1}^{N} \mathbf{e}^\tau \mathbf{\nabla}_i \cdot \mathbf{D}_i \mathbf{e}^{-\tau} \mathbf{\nabla}_i A(\Gamma) + \int d\Gamma' W(\Gamma' \leftarrow \Gamma; t) \{ A(\Gamma') - A(\Gamma) \} \right] \\
= \int d\Gamma B(\Gamma) \mathbf{L}(\Gamma; t) A(\Gamma). \tag{5}
\]

Repeatedly applying this equality to the expanded form of Eq. (4), we obtain

\[
\langle \Lambda \rangle_t = \left\langle \int d\Gamma \rho_{eq}(\Gamma) \Lambda(\Gamma; t) - \langle \Lambda(\Gamma) \rangle_{eq} \right\rangle \\
\tag{6}
\]

where

\[
\Lambda(\Gamma; t) = \exp \left\{ \int_{0}^{t} ds \mathbf{L}(\Gamma; s) \right\} \Lambda(\Gamma) \tag{7}
\]

which is the classical Heisenberg picture of the time-evolution corresponding to the classical Schrödinger picture of Eq. (4). Here \( \mathbf{L}^{eq} \) is the backward time-ordered exponential operator. \( \langle \cdot \rangle_{eq} = \int d\Gamma \rho_{eq}(\cdot) \) denotes an ensemble average over the equilibrium distribution \( \rho_{eq} \).

**Memory Equations**

**Dynamics approaching steady-state under time-independent perturbation.** If the transition rates are time-independent, the time-evolution of the dynamical variables is simply given, from Eq. (7), by \( \Lambda(t) = e^{\mathbf{L}^{eq} \tau} \). Here the subscript \( 0 \) denotes that the kinetic operator is time-independent. We split \( L_0 \) into two parts, equilibrium (\( L_{eq} \)) and time-independent perturbation (\( L_p \)) parts. Using Mori’s projection operator technique, we will derive an evolution equation for the set of dynamical variables \( \Delta \Lambda(t) = \Lambda(t) - \langle \Lambda \rangle_{eq} \) which describes the time evolution of the variables under the influence of the perturbation.

Differentiating \( \Delta \Lambda(t) \) with respect to time, we obtain the kinetic equation

\[
\frac{d}{dt} \Delta \Lambda(t) = e^{\mathbf{L}^{eq} \tau} (L_{eq} + L_p) \Delta \Lambda. \tag{8}
\]

We will consider the dynamical variables which is linear to the perturbation, i.e., \( L_p \Delta \Lambda = -L_{eq} \Delta \Lambda + F \Lambda \). Here \( F \) is an excitation matrix which depends on the intensity of the time-independent perturbation. In this case, Eq. (8) becomes

\[
\frac{d}{dt} \Delta \Lambda(t) = - F \cdot \Delta \Lambda(t) - e^{\mathbf{L}^{eq} \tau} L_{eq} \Delta \Lambda + F \cdot \langle \Lambda \rangle_{eq}. \tag{9}
\]

Following Mori’s procedure,\(^{12}\) we define projection operators \( P \) and \( Q \) as \( PA = \langle A \cdot \Delta \Lambda \rangle_{eq} \cdot \langle \Delta \Lambda \cdot \Delta \Lambda \rangle_{eq} \cdot \Delta \Lambda \) and \( Q = 1 - P \). Here the superscript \( T \) denotes the transpose of a vector. Inserting the identity \( P + Q = 1 \) into the first term of RHS of Eq. (9), we obtain

\[
\frac{d}{dt} \Delta \Lambda(t) = - F \cdot \Delta \Lambda(t) - \Omega \cdot \Delta \Lambda(t) + e^{\mathbf{L}^{eq} \tau} Q L_{eq} \Delta \Lambda + F \cdot \langle \Lambda \rangle_{eq} \tag{10}
\]

where \( \Omega = \langle L_{eq} \Delta \Lambda \cdot \Delta \Lambda \rangle_{eq} \cdot \langle \Delta \Lambda \cdot \Delta \Lambda \rangle_{eq}^{-1} \).

Inserting \( P + Q = 1 \) again into the exponent of the second term of RHS of Eq. (10) and using the operator identity \( e^{(A+B)t} = e^{Bt} + \int_{0}^{t} ds e^{B(s)} A e^{B(t-s)} \), we can rewrite the second term as

\[
e^{\mathbf{L}^{eq} \tau} Q L_{eq} \Delta \Lambda - \gamma(t) + \int_{0}^{t} d\tau e^{\mathbf{L}^{eq} \tau} Q L_{eq} \gamma(t-s) \tag{11}
\]

where \( \gamma(t) = e^{Q L_{eq} \tau} Q L_{eq} \Delta \Lambda \). Inserting Eq. (11) into Eq. (10) and noting that \( P L_{eq} \gamma(s) - \langle L_{eq} \gamma(s) \rangle_{eq} \cdot \langle \Delta \Lambda \cdot \Delta \Lambda \rangle_{eq}^{-1} \cdot \Delta \Lambda \), we obtain the kinetic equation with a memory kernel matrix defined by

\[
\phi(t) = -\Omega \delta(t) - \langle L_{eq} \gamma(t) \rangle_{eq} \cdot \langle \Delta \Lambda \cdot \Delta \Lambda \rangle_{eq}^{-1} \cdot \Delta \Lambda \tag{12}
\]

as

\[
\frac{d}{dt} \Delta \Lambda(t) = - F \cdot \Delta \Lambda(t) - \int_{0}^{t} d\tau \phi(t-s) \cdot \Delta \Lambda(s) + \gamma(t) + F \cdot \langle \Lambda \rangle_{eq} \tag{13}
\]

This is the formally exact expression of the kinetic
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equation with a memory kernel under an arbitrary intensity of perturbation. Since the evolution of the memory kernel matrix is governed by \( \mathbf{L}_0 \), it should depend on the time-independent perturbation \( \varepsilon_p \) as well as the equilibrium dynamics of the system \( \mathbf{L}_{eq} \).

We note here two properties of \( \gamma_0(t) \): orthogonality and randomness. As one can see from its definition, \( \gamma_0(t) \) is projected by the operator \( Q \) and it should be orthogonal to the vector \( \Delta \Lambda \), i.e., \( \langle \gamma_0(t) \cdot \Delta \Lambda \rangle_{eq} - \langle Q \gamma_0(t) \cdot \Delta \Lambda \rangle_{eq} = 0 \). In addition, the average of \( \gamma_0(t) \) over the initial equilibrium distribution should be zero as shown below:

\[
\langle \gamma_0(t) \rangle_{eq} = 0.
\]

First we expand the exponential operator in the definition of \( \gamma_0(t) \) as follows:

\[
\gamma_0(t) - \left[ 1 + \mathbf{L}_0 t + \frac{1}{2!} \mathbf{L}_0^2 t^2 + \cdots \right] \mathbf{L}_{eq} \mathbf{A} = \mathbf{L}_{eq} \mathbf{A}.
\] (14)

The equilibrium average of the first term is zero since \( \langle \mathbf{L}_{eq} \mathbf{A} \rangle_{eq} = 0 \). The last equality holds owing to the time-invariance of the equilibrium distribution function in the absence of any perturbation. The equilibrium averages of the other terms have the form of \( \langle Q \mathbf{L} \mathbf{L}_{eq} \mathbf{A} \rangle_{eq} = 0 \). The last equality holds owing to the time-invariance of the equilibrium distribution function in the absence of any perturbation. The last term is zero if and only if the \( Q \)-projected part of dynamical variables, \( Q \mathbf{\Phi} \), is uncorrelated with the time-independent perturbation. In other words, if the set of the selected variables \( \mathbf{A} \) includes all variables correlated with the time-independent perturbation, then the equilibrium ensemble average of \( \gamma_0(t) \) in the memory equation for the variables is zero and is called random force term. Therefore, in order to fully utilize the memory equation formulation, we should include all dynamical variables coupled to the time-independent perturbation in \( \mathbf{A} \). When \( \mathbf{A} \) is an incomplete set where some variables correlated with the perturbation are missing, Eq. does not hold and the equilibrium ensemble average of \( \gamma_0(t) \) does not vanish.

Since the random force term is orthogonal to the vector \( \Delta \Lambda \), we multiply \( \Delta \Lambda^T \) on the RHS of Eq. and take the average over the equilibrium distribution

\[
\left\{ \frac{d}{dt} \mathbf{A} \right\} \langle \Delta \Lambda_0(t) \cdot \Delta \Lambda^T \rangle_{eq} - \mathbf{L}_0 \mathbf{A} = - \int_0^t ds \phi_0(t-s) \cdot \langle \Delta \Lambda_0(s) \cdot \Delta \Lambda^T \rangle_{eq}.
\] (15)

We define a relaxation function matrix in terms of the normalized correlation function

\[
S_0(t) = \langle \Delta \Lambda_0(t) \cdot \Delta \Lambda^T \rangle_{eq} \cdot \langle \Delta \Lambda \cdot \Delta \Lambda^T \rangle_{eq}^{-1}.
\] (16)

Kinetics of the time correlation function may be studied by various tools such as the fully renormalized kinetic theory developed by Mazenko and later applied to diffusion influenced reactions by Yang, Lee, and Shin. The time correlation function reflects the dynamics occurring under the time-independent perturbation in the equilibrium ensemble.

Solving Eq. (13) in the Laplace transform domain, we obtain the dynamics of \( \Delta \Lambda_0(t) \) in terms of the relaxation function matrix:

\[
\Delta \Lambda_0(t) = \int_0^t d\tau \mathbf{S}_0(t-\tau) \cdot [\Delta \mathbf{A} \delta(t) + \gamma_0(t) + F \cdot \langle \Lambda \rangle_{eq}] .
\] (17)

Utilizing the randomness of \( \gamma_0(t) \), the time evolution of mean value of \( \Delta \Lambda \) is obtained from Eq. (17)

\[
\langle \Delta \Lambda_0(t) \rangle_{eq} = \int_0^t d\tau \mathbf{S}_0(t-\tau) \cdot F \cdot \langle \Lambda \rangle_{eq} .
\] (18)

As one can see in Eq. (18), the key quantity to predict the time evolution of mean value of dynamical variables developing under the influence of the time-independent perturbation is the time correlation function \( \mathbf{S}_0(t) \) which reflects the fluctuation dynamics of equilibrium ensemble affected by the perturbation. This relation illustrates a special case of the fluctuation-dissipation theorem holding for an arbitrary intensity of perturbation with the particular linear property \( \varepsilon_p \mathbf{A} = F \cdot \mathbf{A} \). The formal relation (18) with \( t \to \infty \) may be employed in the study of steady-state kinetics of chemical reaction systems such as the Stern-Volmer kinetics of fluorescence quenching reaction.

**Fluctuation dynamics at steady-state.** In the previous section, we derived a formal expression of the memory equation describing the evolution of dynamical variables under a time-independent perturbation. As the perturbation keeps on, the system will approach a non-equilibrium steady-state. In this subsection, we derive another memory equation which is convenient for describing the fluctuation dynamics of the dynamical variables at the steady state. We consider the deviation of variables: \( \delta \Lambda_0(t) = \Lambda_0(t) - \langle \Lambda \rangle_{ss} \), where \( \langle \cdot \rangle_{ss} = \int_0^\infty d\tau \rho_{ss} \langle \cdot \rangle \) with the probability distribution function at the steady state, \( \rho_{ss} = \lim_{t \to \infty} \rho_{eq} \), denotes the ensemble average at long times under the influence of the time-independent perturbation.

Differentiating \( \delta \Lambda_0(t) \) with respect to time, we obtain the kinetic equation

\[
\frac{d}{dt} \delta \Lambda_0(t) = e^{\mathbf{L}_0 t} \mathbf{L}_0 \delta \Lambda_t .
\] (19)

Now, projection operators \( \mathbf{P} \) and \( \mathbf{Q} \) are defined as \( \mathbf{P} \mathbf{A} = \langle \mathbf{A} \cdot \delta \mathbf{A} \rangle_{ss} \cdot \langle \delta \mathbf{A} \cdot \delta \mathbf{A} \rangle_{ss}^{-1} \cdot \delta \mathbf{A} \) and \( \mathbf{Q} = \mathbf{I} - \mathbf{P} \). Repeating Mori's procedure discussed in the previous section with the new projection operators, we obtain the kinetic equation

\[
\frac{d}{dt} \delta \Lambda_0(t) = - \int_0^t ds \phi_0(t-s) \cdot \delta \Lambda_0(s) + \gamma_0(t)
\] (20)

where

\[
\phi_0(t) = - \mathbf{Q} \mathbf{\Phi} \langle \cdot \rangle \cdot \langle \delta \mathbf{A} \cdot \delta \mathbf{A} \rangle_{ss}^{-1}, \quad \gamma_0(t) = e^{Q \mathbf{L}_0 Q} \mathbf{L}_0 \mathbf{Q} \mathbf{\Lambda} .
\]

With
\[ \Omega = \langle \delta \rho \cdot \delta \Lambda \rangle^T_{ss} \cdot \langle \delta \rho \cdot \delta \Lambda \rangle^T_{ss} \cdot \langle \delta \rho \cdot \delta \Lambda \rangle_{ss} \cdot \langle \delta \rho \cdot \delta \Lambda \rangle_{ss}^T \cdot \langle \delta \rho \cdot \delta \Lambda \rangle_{ss}^T \cdot \langle \delta \rho \cdot \delta \Lambda \rangle_{ss} \].

This is the formally exact kinetic equation describing the fluctuation dynamics occurring at the steady-state under the time-independent perturbation. When \( \rho_0 = 0 \) (no time-independent perturbation), Eqs. (13) and (20) become identical as it should be.

As one can see from its definition, \( \tilde{\gamma}_0(t) \) is projected by the operator \( \tilde{Q} \) and it should be orthogonal to the vector \( \delta \rho \), i.e., \( \langle \tilde{\gamma}_0(t) \cdot \delta \Lambda \rangle_{ss} \cdot \langle \tilde{Q} \tilde{\gamma}_0(t) \cdot \delta \Lambda \rangle_{ss} = 0 \). In addition, similarly in the previous section, the average over the steady-state distribution should be zero as shown below. We expand the exponential operator in the definition of \( \tilde{\gamma}_0(t) \) as follows:

\[
\tilde{\gamma}_0(t) = \left( 1 + \tilde{Q} \tilde{\gamma}_0 + \frac{1}{2} \tilde{Q} \tilde{\gamma}_0 \tilde{\gamma}_0^2 + \cdots \right) \tilde{Q} \tilde{\gamma}_0 \delta \Lambda. \quad (21)
\]

The average of the first term over the steady-state distribution is zero since \( \langle \tilde{Q} \tilde{\gamma}_0 \delta \Lambda \rangle = \int d\tau \tilde{\gamma}_0 \tilde{\Lambda}_0 \rho_0 \delta \rho - 0 \). The last equality holds owing to the time-invariance of the steady-state distribution function. The other terms have the form of \( \langle \tilde{Q} \tilde{\gamma}_0 \tilde{\gamma}_0 (\cdot) \rangle_{ss} \). Noting that the average of the \( \tilde{P} \)-projected part over \( \rho_0 \) must be zero by definition, we get the equalities \( \langle \tilde{Q} \tilde{\gamma}_0 \tilde{\gamma}_0 (\cdot) \rangle_{ss} = \langle \tilde{Q} \tilde{\gamma}_0 \tilde{\gamma}_0 (\cdot) \rangle_{ss} \).

Although the two kinetic equations (13) and (20) contain the same dynamical information governed by the operator \( \tilde{Q} \tilde{\gamma}_0 \), the statistical properties of the random force terms \( \tilde{\gamma}_0 (t) \) in Eq. (13) and \( \tilde{\gamma}_0 (t) \) in Eq. (20) are different. \( \tilde{\gamma}_0(t) \) is random and orthogonal to \( \tilde{\Lambda} \) over the equilibrium distribution while \( \tilde{\gamma}_0(t) \) over the steady-state distribution.

Multiplying \( \delta \Lambda \) on the RHS of Eq. (20) and taking the average over the steady-state distribution \( \rho_0 \), we obtain the kinetic equation for the time-correlation function describing the fluctuation dynamics of the variable \( \Lambda \) at the steady-state

\[
\frac{d}{dt} \langle \delta \Lambda_0(t) \cdot \delta \Lambda \rangle_{ss} = - \int_0^t ds \int_0^t \tilde{\gamma}_0(t - s) \cdot \langle \delta \Lambda_0(s) \cdot \delta \Lambda \rangle_{ss}.
\]

We define a relaxation function matrix

\[
\tilde{S}_0(t) = \langle \delta \Lambda_0(t) \cdot \delta \Lambda \rangle^T_{ss}, \langle \delta \Lambda \cdot \delta \Lambda \rangle^T_{ss}.
\]

Similarly in Eq. (16), kinetics of the time correlation function \( \tilde{S}_0(t) \) may be studied by various tools. The time correlation function reflects the fluctuation dynamics of the variables \( \Lambda \) occurring at the steady-state attained by the action of the time-independent perturbation.

Solving Eq. (20) in the Laplace transform domain, we obtain the dynamics of \( \delta \Lambda_0(t) \) in terms of the relaxation function matrix and random force term

\[
\delta \Lambda_0(t) = \int_0^t \frac{d \tau \tilde{S}_0(t - \tau) \cdot [ \delta \Lambda \cdot \tilde{Y}_0(\tau) ]}{d \tau} \cdot \delta \Lambda + \tilde{Y}_0(\tau).
\]

The mean value of \( \delta \Lambda_0(t) \) over the steady-state distribution is zero, since \( \langle \delta \Lambda \rangle_{ss} = \langle \tilde{Y}_0(t) \rangle_{ss} = 0 \), as it should be.

**Summary**

We derived two exact formal expressions of memory equations for the time-evolution of dynamical variables for the systems of chemical reactions occurring in liquid under time-independent perturbation with an arbitrary intensity. One form is suitable for obtaining the information of

**Linear Response to Time-Dependent Perturbation:**

Fluctuation-Dissipation. When a time-dependent perturbation is acted on the system, it is not possible to solve the kinetic equation (2) exactly. The kinetic operator for the time-dependent perturbation is denoted by \( \tilde{\gamma}_1(t) \) and the total kinetic operator is given by \( \tilde{\gamma}_1(t) \). Applying the first order perturbation theory with respect to \( \tilde{\gamma}_1(t) \), the probability distribution function is obtained within the linear response theory as \( \rho_1(t) = \rho_0 + \rho_1(t) \) where \( \rho_1(t) \) involves the effect of the perturbation which is obtained by solving the kinetic equation

\[
\frac{d}{dt} \rho_1(t) - \tilde{\gamma}_1(t) \rho_1(t) = \tilde{\gamma}_1(t) \rho_0,
\]

with \( \rho_1(t - 0) = 0 \). Eq. (25) is solved to

\[
\rho_1(t) = \int_0^t ds e^{\tilde{\gamma}_1(t - s)} \tilde{\gamma}_1(s) \rho_{ss}.
\]

Inserting Eq. (26) along with \( \rho_1(t) \) into Eq. (3) and noting that \( \langle \delta \Lambda \rangle_{ss} = 0 \), we obtain time-dependence of the dynamical variables responding to the time-dependent perturbation

\[
\langle \delta \Lambda \rangle_1 = \int_0^t ds \int d\tau \tilde{L}_1(\tau) \tilde{L}_1^{\dagger}(\tau) \tilde{L}_1(\tau) \rho_{ss}.
\]

Applying the property (5), we rewrite Eq. (27) as

\[
\langle \delta \Lambda \rangle_1 = \int_0^t ds \int d\tau \tilde{L}_1(\tau) \delta \Lambda_0(\tau - s) \rho_{ss}.
\]

Inserting Eq. (24) describing the dynamics of \( \delta \Lambda_0(t) \) into Eq. (28), we obtain

\[
\langle \delta \Lambda \rangle_1 = \int_0^t ds \int d\tau \tilde{L}_1(\tau) \tilde{S}_0(\tau) \tilde{L}_1^{\dagger}(\tau) \delta \Lambda_0(\tau - s) \rho_{ss}.
\]

where \( F(\tau) \) is an excitation matrix which depends on the intensity of the time-dependent perturbation. In order to obtain the response of system within the linear order with respect to time-dependent perturbation, one should have the fluctuation dynamics of the time-correlation function occurring at the steady-state which can be studied by other theoretical methods. Eq. (29) illustrates the fluctuation-dissipation theorem stemmed from the linear response theory. The formal exact relation (29) may be utilized in the study of frequency-domain kinetics of various chemical reactions. The results will be published elsewhere.
dynamics approaching the steady-state to be attained by the continuous action of the perturbation on the system which was in equilibrium. The other form is suitable for obtaining the fluctuation dynamics of the variables occurring at the steady-state. Attributed to the linear response theory, this equation can be utilized to determine the kinetics following time-dependent perturbation acted on the steady-state or on the equilibrium state.

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Appendix. Dynamical Variable Representation of $\dot{L}_p\rho_{eq}$

By the principle of the maximum uncertainty measure of the information theory,$^9$ the statistical distribution of a system at time $t$ is written regardless of whether the system is in the equilibrium or not as

$$\rho_\lambda(\Gamma; \lambda(t)) = \frac{1}{Z_t(\lambda)} \exp(-\Lambda_t^\top \cdot \lambda(t))$$  \hfill (A1)

where the generalized partition function $Z(t)$ is defined by

$$Z(t) = \int d\Gamma \exp(-\Lambda_t^\top \cdot \lambda(t)).$$  \hfill (A2)

Here $\Lambda$ is a set of dynamical variables specifying the macrostate of the system and $A(t)$ is the set of the parameters conjugated to $A$ at time $t$ which is related to experimental measurements of $A$. For an equilibrium distribution, $\Lambda(t) = \Lambda_{eq}$ is constant in time and in this case $\rho_{eq}(\Gamma; \Lambda_{eq}) = \exp(-\Lambda_{eq}^\top \cdot \lambda_{eq})/Z_{eq}$ is time-independent. For example, $\Lambda$ is energy and $\lambda_{eq} = \frac{1}{k_B} T$ for the canonical distribution function.

When an external perturbation giving rise to change of expectation values of dynamical variables is acted on the system, the rate of change of the distribution function induced by the external perturbation is related to the changing rates of the conjugated variables $\dot{\lambda}(t)$ as follows:

$$\dot{L}_p\rho_{eq} = \frac{d}{dt}\rho_{eq} - \sum_i \dot{\lambda}_i \frac{\partial}{\partial \lambda_i} \left\{ \exp(-\Lambda_{eq}^\top \cdot \lambda_{eq})/Z_{eq} \right\}$$

$$= -\sum_i \dot{\lambda}_i (\Lambda_i - \langle \Lambda_i \rangle_{eq} \cdot \exp(-\Lambda_{eq}^\top \cdot \lambda_{eq})/Z_{eq})$$

$$= -\sum_i \dot{\lambda}_i (\Lambda_i - \langle \Lambda_i \rangle_{eq}) \exp(-\Lambda_{eq}^\top \cdot \lambda_{eq})/Z_{eq}$$  \hfill (A3)

The subscript $p$ on both $\Lambda$ and $\lambda$ denotes the subset of the variables correlated with the external perturbation.

Using the formula (A3), we can show that $\langle L_p Q(\cdot) \rangle_{eq} = 0$ under the condition discussed in the above subsection:

$$\langle L_p Q(\cdot) \rangle_{eq} = \int d\Gamma \rho_{eq} \frac{d}{dt}\rho_{eq} - \int d\Gamma \rho_{eq} \frac{d}{dt}Q(\cdot)$$

$$= -\langle Q(\cdot) \Delta \Lambda_{eq}^\top \cdot \lambda_{eq} \rangle_{eq} = 0$$  \hfill (A4)

if and only if the set of variables $A$ defined in the projection operator coincides with $A_{eq}$.

References