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A Mode–Mode Coupling Theory of Chemical Reaction in a Dense Fluid

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A study is made of the coupling between chemical reaction and diffusion in a dense fluid. Our analysis utilizes the projection operator formalism and a generalized Langevin equation that is based on irreversible, phenomenological equations of motion instead of conventional Hamiltonian mechanics. It also is shown that this same "non-Hamiltonian" theory provides a simple way of deriving Kawasaki's mode–mode coupling theory of diffusion.

KEY WORDS: Projection operator; mode–mode coupling; non-Hamiltonian method; chemical reaction; bimolecular reaction; hydrodynamic mode; reactive mode; diffusion-controlled reaction.

1. INTRODUCTION

The bimolecular reaction A + B → C involves two distinct steps. The first of these is related to processes, associated with various hydrodynamic modes of the system, by which pairs of reactant molecules are prepared (brought together) under conditions suitable for reaction. The second is the elementary reactive event, the rate of which depends on chemical properties of the individual molecules and on the energetics at the moment collision occurs. The objective of the present investigation is to develop a theory of the coupling between these hydrodynamic and reactive modes(1–3) which is simpler and more flexible than the well-known mode–mode coupling theory of Kawasaki.(4) To accomplish this we construct a "non-Hamiltonian" version(5) of the familiar projection operator and generalized Langevin equation theory of Zwanzig(6) and Mori.(7)

The overall rates of the fast, condensed phase reactions (such as fluorescence quenching and radical reactions) that are of primary interest to us here

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usually are limited by the rates at which reactive pairs of molecules can diffuse together. Thus, diffusion is the dominant hydrodynamic mode contributing to the rate of this special class of reactions called "diffusion controlled."(8) This is the only hydrodynamic mode that we consider in this introductory paper.

Prior to applying the non-Hamiltonian theory to the specific problem of diffusion-controlled reactions we illustrate how the method works by performing a simple derivation of Kawasaki's well-known result for the coupling of viscous and diffusive hydrodynamic modes.

2. PROJECTION OPERATOR FORMALISM

In the first part of this section we review and summarize several aspects of the Zwanzig–Mori projection operator method and consider two identities that are needed for the applications treated in Sections 3 and 4. The second part is devoted to generalizing this projection operator formalism to situations where the exact, microscopic equations of motion have been replaced with irreversible, phenomenological equations.

2.1. Hamiltonian Method

We describe the macrostate of a system by a set of real-valued collective dynamical coordinates or field variables $\{A_i(\mathbf{r}, t)\}$ and assume for these variables the equations of change

$$\dot{A}_i = [\mathscr{H}, A_i]_{\mathrm{PB}} \equiv i\mathscr{L}A_i \tag{1}$$

Here $\mathscr{H}$ denotes the Hamiltonian function and $\mathscr{L}$ the associated Liouville operator. This operator will be Hermitian ($\mathscr{L} = \mathscr{L}^\dagger$) unless the system is immersed in an external magnetic field.

The formal solution of Eq. (1) can be written in the form $A_i(\mathbf{r}, t) = \exp(i\mathscr{L}t)A_i(\mathbf{r})$ with $A_i(\mathbf{r}) \equiv A_i(\mathbf{r}, t = 0)$ or as the ket $|A_i(t)\rangle = \exp(i\mathscr{L}t)|A_i\rangle$.

We define the inner product $\langle A(t)|B\rangle \equiv \langle A^*(t)B\rangle_{\mathrm{eq}}$, where $\langle A(t)| = \langle \exp(-i\mathscr{L}^\dagger t)A|$ is the adjoint of $|A(t)\rangle$ and where the bracket $\langle\cdots\rangle_{\mathrm{eq}}$ indicates an *equilibrium* ensemble average. Let us now assume that $\mathscr{L}$ is Hermitian. Then, because this ensemble is stationary, it follows that

$$\langle A^*(t)B\rangle_{\mathrm{eq}} \equiv \langle A(t)|B\rangle = \langle A|B(-t)\rangle \equiv \langle A^*B(-t)\rangle_{\mathrm{eq}} \tag{2}$$

The quantities on which we focus our attention are the Fourier–Laplace transforms,

$$\begin{aligned} G_{ij}(\mathbf{k}, z) &\equiv i\int_0^\infty dt\, \exp(izt) \int d^3r\, \exp(-i\mathbf{k}\cdot\mathbf{r})\, G_{ij}(\mathbf{r}, t) \\ &= -\langle A_i|(z - \mathscr{L})^{-1}|A_j\rangle, \qquad \mathrm{Im}\, z > 0 \end{aligned} \tag{3}$$

of the correlation functions $G_{ij}(\mathbf{r} - \mathbf{r}', t - t') = \langle A_i(\mathbf{r}, t) A_j(\mathbf{r}', t')\rangle_{\text{eq}}$. However, the observable associated with $G_{ij}(\mathbf{r}, t)$ is not $G_{ij}(\mathbf{k}, z)$ but the space and time Fourier transform

$$\begin{aligned} G_{ij}(\mathbf{k}, \omega) &\equiv \int_{-\infty}^{+\infty} dt \int d^3r \exp[i(\omega t - \mathbf{k}\cdot\mathbf{r})]\, G_{ij}(\mathbf{r}, t) \\ &= 2 \operatorname{Im} G_{ij}(\mathbf{k}, z = \omega + i0) \end{aligned} \tag{4}$$

Let us now introduce the projection operator $P = 1 - Q \equiv |A_i\rangle \chi_{ij}^{-1} \langle A_j|$, where $\chi_{ij}(\mathbf{k})$ denotes the space Fourier transform of the static correlation function $\langle A_i | A_j \rangle \equiv \langle A_i(\mathbf{r}) A_j(\mathbf{r}')\rangle_{\text{eq}}$. Here and henceforth the summation convention applies to repeated indices.

The generalized Langevin equations for the functions $G_{ij}(\mathbf{k}, z)$ are$^{(9,10)}$

$$[z\delta_{ik} - \Omega_{ik}(\mathbf{k}) - \Sigma_{ik}(\mathbf{k}, z)] G_{kj}(\mathbf{k}, z) = -\chi_{ij}(\mathbf{k}) \tag{5}$$

Because $\Omega_{ik}(\mathbf{k}) \equiv i\langle \dot{A}_i | A_l \rangle \chi_{lk}^{-1}$ is independent of z it can be interpreted as an instantaneous response due to interactions among the constituent particles of the system. It often is called the frequency matrix or mean field term. The dynamic response of the system is described by the damping term or memory matrix, $\Sigma_{ik}(\mathbf{k}, z) \equiv \langle \dot{A}_i | Q[z - Q\mathscr{L}Q]^{-1} Q | \dot{A}_l \rangle \chi_{lk}^{-1}$. The positive-semidefinite property of $\operatorname{Im} \det\{\Sigma(\mathbf{k}, z = \omega + i0)\}$ is related to the irreversible behavior of the many-body system.

This separation of the response into the two parts, Ω and Σ, provides many valuable insights into the behavior of the many-body system but the price paid for this is the occurrence in the memory matrix of the modified Liouville operator $Q\mathscr{L}Q$. It would be delightful if this complicated operator could be eliminated from the formalism. Indeed, what one vastly would prefer to Eq. (5) are relationships among the correlation functions $G_{ij}(\mathbf{k}, z)$ and the elements $\Phi_{ij}(\mathbf{k}, z) \equiv \langle \dot{A}_i | Q(z - \mathscr{L})^{-1} Q | \dot{A}_k \rangle \chi_{kj}^{-1}$ [or $\Phi'_{ij}(\mathbf{k}, z) \equiv \langle \dot{A}_i | (z - \mathscr{L})^{-1} | \dot{A}_k \rangle \chi_{kj}^{-1} = -\langle \dot{A}_i(t) | \dot{A}_k \rangle(\mathbf{k}, z) \chi_{kj}^{-1}$] of a modified memory matrix.$^{(11)}$ The means for accomplishing this are provided in Appendix A, where we show that the matrices Φ and Σ are related to one another by the formula

$$\Sigma(\mathbf{k}, z) = [1 + \Phi(z1 - \Omega)^{-1}]^{-1}\Phi \tag{6}$$

This relationship has been used to transform the traditional Langevin equation into a renormalized form and it has played an essential role in the construction of the renormalized kinetic theory.$^{(12)}$ Several investigators have derived alternative forms of this relationship by using Zwanzig's projection operator techniques.$^{(13)}$ Because the Zwanzig and Mori methods differ only with respect to the observational point of view, as do the Schrödinger and Heisenberg pictures in quantum mechanics, the two representations are entirely equivalent.$^{(14)}$

Many previous studies of nonlinear transport theory have used the important identity (6) either explicitly or implicitly. Applications of this relationships can become extremely complicated. However, there are important special cases, unnoticed by previous investigators, for which it yields very simple connections between Φ and Σ. In illustrating this we shall avoid nonessential complexities by restricting our attention to the case of a single dynamical variable A. The generalized Langevin equation appropriate to this situation is given by

$$G_{AA}(\mathbf{k}, z) = -[z - \Omega_{AA} - \Sigma_{AA}(\mathbf{k}, z)]^{-1}\chi_{AA} \tag{7}$$

or, equivalently, by

$$\partial_t G_{AA}(\mathbf{k}, t) + i\Omega_{AA}G_{AA}(\mathbf{k}, t) - \int_0^t dt'\, \Sigma_{AA}(\mathbf{k}, t - t')G_{AA}(\mathbf{k}, t') = 0 \tag{7'}$$

where

$$\Sigma_{AA}(\mathbf{k}, z) = [1 + \Phi_{AA}(z - \Omega_{AA})^{-1}]^{-1}\Phi_{AA} \tag{8}$$

and

$$\Phi_{AA} = \langle \dot{A}|Q(z - \mathscr{L})^{-1}Q|\dot{A}\rangle\chi_{AA}^{-1} \tag{9}$$

In most cases $\Omega_{AA} = i\langle\dot{A}|A\rangle\chi_{AA}^{-1}$ vanishes because of time-reversal invariance. Consequently, $G_{AA} = -(z - \Sigma_{AA})^{-1}\chi_{AA}$,

$$\Sigma_{AA} = \langle\dot{A}|(z - Q\mathscr{L}Q)^{-1}|\dot{A}\rangle\chi_{AA}^{-1} = z(z + \Phi_{AA})^{-1}\Phi_{AA},$$

and $\Phi_{AA} = \langle\dot{A}|(z - \mathscr{L})^{-1}|\dot{A}\rangle\chi_{AA}^{-1} = -\langle\dot{A}(t)|\dot{A}\rangle(\mathbf{k}, z)\chi_{AA}^{-1}$. Suppose now that A is a "relevant variable,"(10,15) that is, a variable whose characteristic relaxation time is very long. Then A either must be (i) a conserved variable with an equation of motion of the form $\dot{A}(\mathbf{k}, t) = ik\mathscr{J}_A(\mathbf{k}, t)$ or (ii) a variable associated with a broken symmetry, in which case $\chi_{AA} \propto k^{-2}$. In either event both Σ_{AA} and Φ_{AA} are of order k^2 and so at long wavelengths, where the system is almost spatially uniform, Σ_{AA} and Φ_{AA} become equal. Thus, in the long-wavelength, long-time "hydrodynamic limit,"

$$\lim_{z\to i0}\lim_{k\to 0}\Sigma_{AA}(\mathbf{k}, z) = \lim_{z\to i0}\lim_{k\to 0}\Phi_{AA}(\mathbf{k}, z) \tag{10}$$

We shall encounter this case in Section 3 in connection with Kawasaki's mode–mode coupling theory. The order of the limits is important here (related to the "plateau-value" problem discussed in Ref. 7), whereas it is not in the following example.

The situation just described is the most familiar, but there are others, such as that considered in Section 4, where one is concerned with the hydrodynamic limit of a nonconserved variable for which $\Omega_{AA} \neq 0$. These problems often can be solved with the aid of the relationship $\Sigma_{AA}^{-1} = \Phi_{AA}^{-1} - \Omega_{AA}^{-1}$, which is the form of Eq. (8) that is applicable to all values of k when z is equal to zero. The theory of diffusion-controlled reactions presented in Section 4 provides an example of this sort.

Before proceeding further there are a few remarks that we would like to make about Eq. (6) or Eq. (8). Suppose that A is the velocity variable $\mathbf{v}$. Then $\dot{\mathbf{v}} = \mathbf{F}/m$, where $\mathbf{F}$ is the total force and $\exp(iQ\mathscr{L}Qt)|\dot{\mathbf{v}}(0)\rangle \equiv \mathbf{f}(t)$ is the fluctuating, random force. Therefore, Eq. (6) or (8) provides a connection between the autocorrelation function of the total force and the autocorrelation function of the random force. This makes it likely that Eq. (6) can be of aid in resolving the recent controversy over the calculation of the conductivity of liquid metals.(16)

We conclude this subsection by presenting a trivial but important identity. Let $P_1 \equiv 1 - Q_1 \equiv |A_1\rangle\chi_1^{-1}\langle A_1|$ and $P_2 \equiv 1 - Q_2 \equiv |A_1\rangle\chi_1^{-1}\langle A_1| + |A_2\rangle\chi_2^{-1}\langle A_2|$ with $\chi_1 = \langle A_1|A_1\rangle$ and $\chi_2 = \langle A_2|A_2\rangle$ and where $\langle A_1|A_2\rangle = 0$. Then, according to Appendix B, the memory function

$$\Sigma_{A_1A_1}(\mathbf{k}, z) \equiv \langle \dot{A}_1|Q_1(z - Q_1\mathscr{L}Q_1)^{-1}Q_1|\dot{A}_1\rangle\chi_1^{-1} \tag{11}$$

can be expressed in the form

$$\begin{aligned}\Sigma_{A_1A_1}(\mathbf{k}, z) = \sigma_{11}(\mathbf{k}, z) + [\omega_{12} + \sigma_{12}(\mathbf{k}, z)]&\\ \times [z - \omega_{22} - \sigma_{22}(\mathbf{k}, z)]^{-1}[\omega_{21} + \sigma_{21}(\mathbf{k}, z)]&\end{aligned} \tag{12}$$

with

$$\omega_{ij} = i\langle \dot{A}_i|A_j\rangle\chi_j^{-1} \tag{13}$$

$$\sigma_{ij}(\mathbf{k}, z) = \langle \dot{A}_i|Q_2(z - Q_2\mathscr{L}Q_2)^{-1}Q_2|\dot{A}_j\rangle\chi_j^{-1} \tag{14}$$

and where $i, j = 1$ or 2. In these last two formulas the repeated indices are not to be summed.

The identity (12) is useful in dealing with two coupled equations of motion that occur in the example studied in Section 4.

2.2. Non-Hamiltonian Method

Up to this point the analysis has dealt exclusively with systems whose dynamics are assumed to be governed by an exact Hamiltonian mechanics. The advantages of rigor which are enjoyed by this approach must be weighed against the very great mathematical and conceptual difficulties associated with these extremely complicated equations of motion. Thus, great cleverness and very powerful mathematical techniques are needed to extract even qualitatively correct results from such a detailed picture of the system's dynamics.

An alternative to this is the "non-Hamiltonian" method, which has been studied in connection with the superionic conductor problem.(5) The idea is to abandon the detailed dynamical equations of the exact theory in favor of a simpler, more tractable dynamics that incorporates some of the collective characteristics of the many-body system. Thus, in place of the exact, microdynamical equations of motion $\dot{A}_i = i\mathscr{L}A_i$ we adopt phenomenological equations $\dot{A}_i = -i\mathscr{U}A_i$, where $\mathscr{U} \neq \mathscr{U}^\dagger$ is non-Hermitian. This lack of Hermiticity is a consequence of the intrinsic irreversibility of the phenomenological equations of motion. Because of this irreversibility, the ensemble average, which we denote here by the double bracket $\langle\langle\cdots\rangle\rangle$, does not share the stationarity property, Eq. (2), of the Hamiltonian theory.

Analogous to $G_{ij}(z)$ we define the correlation function

$$\begin{aligned}\tilde{G}_{ij}(z) &\equiv \langle\langle A_i(0)|A_j(t)\rangle\rangle(z) = \langle\langle A_i|\exp(-i\mathscr{U}t)A_j\rangle\rangle(z)\\ &= -\langle\langle A_i|(z-\mathscr{U})^{-1}|A_j\rangle\rangle(z)\end{aligned}\tag{15}$$

and obtain in place of Eq. (5) the equations

$$[z\delta_{ik} - \tilde{\Omega}_{ik} - \tilde{\Sigma}_{ik}]\tilde{G}_{kj}(\mathbf{k}, z) = -\tilde{\chi}_{ij}\tag{16}$$

where

$$\tilde{\Omega}_{ij}(k) = \langle\langle A_i|\mathscr{U}A_k\rangle\rangle\tilde{\chi}_{kj}^{-1}\tag{17}$$

$$\tilde{\Sigma}_{ij}(\mathbf{k}, z) = \langle\langle A_i|\mathscr{U}Q(z-\mathscr{U}Q)^{-1}Q\mathscr{U}|A_k\rangle\rangle\tilde{\chi}_{kj}^{-1}\tag{18}$$

and $P \equiv 1 - Q \equiv |A_i\rangle\rangle\tilde{\chi}_{ij}^{-1}\langle\langle A_j|$. The static correlation function $\tilde{\chi}_{ij} = \langle\langle A_i|A_j\rangle\rangle$ is equal to $\chi_{ij} = \langle A_i|A_j\rangle$ because the former does not explicitly involve the irreversible, non-Hermitian operator $\mathscr{U}$.

It often happens that the operator $Q\mathscr{U}$ is either Hermitian or anti-Hermitian, that is, $Q\mathscr{U}A_k \equiv iQ\dot{A}_k = \mathscr{U}_h A_k$ or $Q\mathscr{U}A_k \equiv iQ\dot{A}_k = \mathscr{U}_a A_k$, where $\mathscr{U}_h$ and $\mathscr{U}_a$, respectively, are Hermitian and anti-Hermitian operators. In this event the matrices $\tilde{\Sigma}$ and $\tilde{\Phi}$ can be written in the forms

$$\tilde{\Sigma}_{ij}^{(\pm)} = \pm\langle\langle\dot{A}_i|Q(z-\mathscr{U}Q)^{-1}Q|\dot{A}_k\rangle\rangle\chi_{kj}^{-1}\tag{19}$$

and

$$\tilde{\Phi}_{ij}^{(\pm)} = \pm\langle\langle\dot{A}_i|Q(z-\mathscr{U})^{-1}Q|\dot{A}_k\rangle\rangle\chi_{kj}^{-1}\tag{20}$$

where the plus and minus signs apply to the Hermitian and anti-Hermitian cases, respectively.

In some cases $Q\mathscr{U}$ may coincide with either $\frac{1}{2}(\mathscr{U} + \mathscr{U}^\dagger)$ or $(1/2i)(\mathscr{U} - \mathscr{U}^\dagger)$,[2] the Hermitian and anti-Hermitian parts of the non-Hermitian operator $\mathscr{U}$. The operator $P\mathscr{U}$ then will exhibit symmetry opposite to that of its complement, $Q\mathscr{U}$. An example of this is provided in Section 3. However, it also is

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[2] When $(1/2i)(\mathscr{U} - \mathscr{U}^\dagger) > 0$, $\mathscr{U}$ is called a dissipative operator; see Ref. 17.

possible, as we shall see in Section 4, for $Q\mathscr{U}$ to be only a part of $\frac{1}{2}(\mathscr{U} + \mathscr{U}^\dagger)$ or $(1/2i)(\mathscr{U} - \mathscr{U}^\dagger)$. In this case $P\mathscr{U}$ may be Hermitian or anti-Hermitian or it may be neither. The operator $\mathscr{U}$ of Section 4 is anti-Hermitian and so, of course, are the corresponding operators $P\mathscr{U}$ and $Q\mathscr{U}$.

Let us suppose that $P\mathscr{U}$ is either Hermitian or anti-Hermitian. Then since $\langle\langle A_i|\mathscr{U}A_k\rangle\rangle = \langle\langle A_i|P\mathscr{U}A_k\rangle\rangle$, the frequency matrix defined by Eq. (17) becomes

$$\tilde{\Omega}_{ij}^{(\pm)} \equiv i\langle\langle A_i|\dot{A}_k\rangle\rangle\chi_{kj}^{-1} = \mp i\langle\langle \dot{A}_i|A_k\rangle\rangle\chi_{jk}^{-1} \tag{21}$$

Here the plus and minus (upper and lower) signs refer to the cases where $P\mathscr{U}$ is Hermitian and anti-Hermitian, respectively.

3. KAWASAKI'S MODE–MODE COUPLING THEORY

Here we demonstrate the efficacy of the formalism developed in the preceding section by using it to derive Kawasaki's(4) formula for the renormalized diffusion coefficient. The system is a dilute solution of tagged particles, the concentration and current of which we denote by $n(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r}, t)$, respectively. Our analysis of this system will be based on the continuity equation

$$\partial_t n(\mathbf{r}, t) = -\nabla\cdot\mathbf{j}(\mathbf{r}, t) \tag{22}$$

and on the phenomenological relationship

$$\mathbf{j}(\mathbf{r}, t) = -D_b\,\nabla n(\mathbf{r}, t) + \mathbf{j}_c(\mathbf{r}, t) + \mathbf{F}(\mathbf{r}, t) \tag{23}$$

The "bare" diffusion coefficient D_b is assumed to depend only on the density and temperature of the solvent. For the convective current $\mathbf{j}_c(\mathbf{r}, t)$ we choose the same function

$$\mathbf{j}_c(\mathbf{r}, t) = \mathbf{v}(\mathbf{r}, t)n(\mathbf{r}, t) \tag{24}$$

of the solvent velocity $\mathbf{v}(\mathbf{r}, t)$ as that used by previous investigators.(18,19) There is abundant evidence that in the hydrodynamic regime, Eqs. (23) and (24) provide an accurate approximation to the current of solute particles.

By discarding the fluctuating, random current $\mathbf{F}(\mathbf{r}, t)$, we obtain for $n(\mathbf{r}, t)$ the equation of motion

$$\partial_t n(\mathbf{r}, t) = D_b\,\nabla^2 n(\mathbf{r}, t) - \nabla\cdot[\mathbf{v}(\mathbf{r}, t)n(\mathbf{r}, t)] \tag{25}$$

Thus, this phenomenological treatment of diffusion in a dilute solution can be identified as an example to which the non-Hamiltonian formalism of

Section 2.2 is applicable. The single variable $n(\mathbf{r}, t)$ corresponds to the set of collective variables $\{A_i(\mathbf{r}, t)\}$, and $D_b\nabla^2 - \boldsymbol{\nabla}\cdot[\mathbf{v}(\mathbf{r}, t)$ corresponds to the operator $-i\mathscr{U}$. Accordingly, we introduce the projection operator $P = |n\rangle\rangle\tilde{\chi}^{-1}\langle\langle n|$ with $\tilde{\chi}(\mathbf{k}) = \langle\langle n|n\rangle\rangle(\mathbf{k})$ and so conclude that

$$P|\dot{n}\rangle\rangle = |n\rangle\rangle\chi^{-1}\langle\langle n|\dot{n}\rangle\rangle = |\{-D_b\, \nabla^2 n(\mathbf{r}, t)\}_{t=0}\rangle\rangle \tag{26a}$$

and

$$Q|\dot{n}\rangle\rangle = (1 - P)|\dot{n}\rangle\rangle = |\{-\boldsymbol{\nabla}\cdot[\mathbf{v}(\mathbf{r}, t)n(\mathbf{r}, t)]\}_{t=0}\rangle\rangle \tag{26b}$$

Consequently, $Q\mathscr{U}$ is Hermitian and $P\mathscr{U}$ is anti-Hermitian.

From the first of these equations we see that in the present example the (1 by 1) matrix $\tilde{\Omega}(\mathbf{k})$, defined by Eq. (18), is given by

$$\begin{aligned}\tilde{\Omega}(\mathbf{k}) = i\langle\langle n|\dot{n}\rangle\rangle(\mathbf{k})\tilde{\chi}^{-1}(\mathbf{k}) &= -k^2D_b\langle\langle n|n\rangle\rangle(k)\tilde{\chi}^{-1}(\mathbf{k})\\ &= -ik^2D_b\end{aligned} \tag{27}$$

Furthermore, because the equation of motion, Eq. (25), ensures that $\dot{n}(\mathbf{k}, t) \propto k$, the identity (8) implies that the two memory functions

$$\tilde{\Sigma}^{+}(\mathbf{k}, z) = \langle\langle \dot{n}|Q(z - Q\mathscr{U}Q)^{-1}Q|\dot{n}\rangle\rangle(\mathbf{k}, z)\tilde{\chi}^{-1}(\mathbf{k}) \tag{28}$$

and

$$\tilde{\Phi}^{+}(\mathbf{k}, z) = \langle\langle \dot{n}|Q(z - \mathscr{U})^{-1}Q|\dot{n}\rangle\rangle(\mathbf{k}, z)\tilde{\chi}^{-1}(\mathbf{k}) \tag{29}$$

will be equal in the long-wavelength limit. Thus, in this limit

$$\begin{aligned}\tilde{\Sigma}^{+}(\mathbf{k}, z) &\approx \tilde{\Phi}^{+}(\mathbf{k}, z)\\ &= \langle\langle\boldsymbol{\nabla}\cdot[\mathbf{v}(\mathbf{r}, 0)n(\mathbf{r}, 0)]|(z - \mathscr{U})^{-1}|\boldsymbol{\nabla}'\cdot[\mathbf{v}(\mathbf{r}', 0)n(\mathbf{r}', 0)]\rangle\rangle(\mathbf{k}, z)\tilde{\chi}^{-1}(\mathbf{k})\\ &= k_ik_j\langle\langle v_i(\mathbf{r}, 0)n(\mathbf{r}, 0)|(z - \mathscr{U})^{-1}|v_j(\mathbf{r}', 0)n(\mathbf{r}', 0)\rangle\rangle(\mathbf{k}, z)\tilde{\chi}^{-1}(\mathbf{k})\\ &= -k_ik_j\langle\langle v_i(\mathbf{r}, 0)n(\mathbf{r}, 0)|v_j(\mathbf{r}', t)n(\mathbf{r}', t)\rangle\rangle(\mathbf{k}, z)\tilde{\chi}^{-1}(\mathbf{k})\\ &\doteq -ik_ik_j\int\frac{d^3k'}{(2\pi)^3}\int_0^\infty dt\, e^{izt}\tilde{G}_{v_iv_j}(\mathbf{k} - \mathbf{k}', t)\tilde{G}_{nn}(\mathbf{k}', t)\tilde{\chi}^{-1}(\mathbf{k})\end{aligned} \tag{30}$$

where $\tilde{G}_{AB}(\mathbf{k}, t)$ denotes the space Fourier transform of the correlation function $\langle\langle A(\mathbf{r}, 0)|B(\mathbf{r}', t)\rangle\rangle$. To obtain this result use has been made of Eq. (15), of the factorization approximation $\langle\langle v_in|v_jn\rangle\rangle \doteq \langle\langle v_i|v_j\rangle\rangle\langle\langle n|n\rangle\rangle$, and of the convolution theorem for Laplace transforms.

Because the fluid is isotropic the velocity autocorrelation function can be resolved into the sum,

$$\tilde{G}_{v_iv_j}(\mathbf{k}, t) = (\delta_{ij} - k_ik_j/k^2)\tilde{G}_{vv}^{\mathrm{tr}}(k, t) + (k_ik_j/k^2)\tilde{G}_{vv}^{l}(k, t)$$

of transverse and longitudinal contributions. Consequently, the hydrodynamic limit of the memory function $\tilde{\Sigma}^+(\mathbf{k}, z)$ is given by

$$\begin{aligned}\lim_{z\to i0}\lim_{k\to 0} \tilde{\Sigma}^+(\mathbf{k}, z) &\doteq -ik_ik_j \int \frac{d^3k'}{(2\pi)^3} \int_0^\infty dt\, \tilde{G}_{v_iv_j}(-\mathbf{k}', t)\tilde{G}_{nn}(\mathbf{k}', t)\chi^{-1}(0) \\ &= -ik^2[\Delta D_{\text{tr}} + \Delta D_l] \end{aligned} \tag{31}$$

with

$$\Delta D_{\text{tr}} = \int \frac{d^3k'}{(2\pi)^3} \int_0^\infty dt\, (1 - \mu^2)\tilde{G}^{\text{tr}}_{vv}(-k', t)\tilde{G}_{nn}(k', t)\chi^{-1}(0) \tag{32a}$$

$$\Delta D_l = \int \frac{d^{3\prime}k}{(2\pi)^3} \int_0^\infty dt\, \mu^2\tilde{G}^{l}_{vv}(-k', t)\tilde{G}_{nn}(k', t)\chi^{-1}(0) \tag{32b}$$

and where $\mu = \mathbf{k}'\cdot\mathbf{k}/k'k$.

According to Eq. (16), the density autocorrelation function associated with this phenomenological theory is equal to

$$\tilde{G}_{nn}(\mathbf{k}, z) = -[z - \tilde{\Omega}(\mathbf{k}) - \tilde{\Sigma}(\mathbf{k}, z)]^{-1}\chi(\mathbf{k}).$$

By using Eqs. (27) and (31), we therefore conclude that the hydrodynamic limit of this correlation function is $-[z + ik^2D]^{-1}\chi(0)$ with $D = D_b + \Delta D_{\text{tr}} + \Delta D_l$. This would be identical to Kawasaki's result, $D = D_b + \Delta D_{\text{tr}}$, were it not for the longitudinal term ΔD_l. In most cases of interest ΔD_l can, indeed, be neglected in comparison with ΔD_{tr}. Thus, in the vicinity of the critical point ΔD_l diverges less strongly than ΔD_{tr} and, far from the critical point, ΔD_{tr} produces the dominant $t^{-3/2}$ contribution to the long-time tail of the nonlinear hydrodynamic theory, whereas ΔD_l varies asymptotically as $t^{-5/2}$.(19)

4. THE COUPLING BETWEEN REACTION AND DIFFUSION

Here we examine a single-phase system in which the reversible reaction

$$\mathrm{A} + \mathrm{B} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{C}$$

occurs. The dynamical variables are taken to be the displacements $\delta n_i = n_i - n_i^{\text{eq}}$ (i = A, B, C) of the species concentrations from their equilibrium values. In terms of these the rate of reaction is given by

$$r = -k_f n_{\mathrm{A}} n_{\mathrm{B}} + k_r n_{\mathrm{C}} = -k_f n_{\mathrm{A}}^{\text{eq}} \delta n_{\mathrm{B}} - k_f n_{\mathrm{B}}^{\text{eq}} \delta n_{\mathrm{A}} + k_r \delta n_{\mathrm{C}} - k_f \delta n_{\mathrm{A}} \delta n_{\mathrm{B}} \tag{33}$$

We adopt for the variables $\delta n_i(k, t)$ the phenomenological equations of motion

$$\begin{aligned}\partial_t(\delta n_\mathrm{A}) &= -k^2[D_\mathrm{AA}\delta n_\mathrm{A} + D_\mathrm{AB}\delta n_\mathrm{B} + D_\mathrm{AC}\delta n_\mathrm{C}] + r\\ \partial_t(\delta n_\mathrm{B}) &= -k^2[D_\mathrm{BA}\delta n_\mathrm{A} + D_\mathrm{BB}\delta n_\mathrm{B} + D_\mathrm{BC}\delta n_\mathrm{C}] + r\\ \partial_t(\delta n_\mathrm{C}) &= -k^2[D_\mathrm{CA}\delta n_\mathrm{A} + D_\mathrm{CB}\delta n_\mathrm{B} + D_\mathrm{CC}\delta n_\mathrm{C}] - r\end{aligned} \tag{34}$$

with diffusion coefficients D_{ij} that satisfy the relationships $D_{ij} = D_{ji}$, $\sum_j m_j D_{ji} = 0$. (The first of these are the familiar reciprocal relations. The second ensure that the total *diffusive* flux of mass is identically zero.)

4.1. Single-Variable Analysis

The simplest, most primitive analysis of this system can be based on the single variable δn_A and on the simplified equation of motion

$$\partial_t(\delta n_\mathrm{A}) = -(k^2 D_\mathrm{AA} + k_f n_\mathrm{B}^\mathrm{eq})(\delta n_\mathrm{A}) - k_f(\delta n_\mathrm{A})(\delta n_\mathrm{B}) \equiv -i\mathscr{U}(\delta n_\mathrm{A}) \tag{35}$$

We then identify P with the projection operator $|\delta n_\mathrm{A}\rangle\rangle\chi_\mathrm{AA}^{-1}\langle\langle\delta n_\mathrm{A}|$, where $\chi_\mathrm{AA}(\mathbf{k}) \equiv \langle\delta n_\mathrm{A}|\delta n_\mathrm{A}\rangle(\mathbf{k}) = [n_\mathrm{A}^\mathrm{eq}\delta(\mathbf{r} - \mathbf{r}')](\mathbf{k}) = n_\mathrm{A}^\mathrm{eq}$. From this and Eq. (35) it follows that, at $t = 0$, $P\partial_t(\delta n_\mathrm{A}) = -(k^2 D_\mathrm{AA} + k_f n_\mathrm{B}^\mathrm{eq})(\delta n_\mathrm{A})$ and $Q\partial_t(\delta n_\mathrm{A}) = -k_f(\delta n_\mathrm{A})(\delta n_\mathrm{B})$. Consequently, both $P\mathscr{U}$ and $Q\mathscr{U}$ are anti-Hermitian.

From the non-Hamiltonian theory of Section 2.2 we conclude that

$$\tilde{\Omega}_\mathrm{AA} = i\langle\langle\delta n_\mathrm{A}|\delta\dot{n}_\mathrm{A}\rangle\rangle\chi_\mathrm{AA}^{-1} = -i(k^2 D_\mathrm{AA} + k_f n_\mathrm{B}^\mathrm{eq}) \tag{36a}$$

and

$$\begin{aligned}\tilde{\Phi}_\mathrm{AA} &= \langle\langle\delta n_\mathrm{A}|\mathscr{U}Q(z - \mathscr{U})^{-1}Q\mathscr{U}|\delta n_\mathrm{A}\rangle\rangle\chi_\mathrm{AA}^{-1}\\ &= -\langle\langle\delta\dot{n}_\mathrm{A}|Q(z - \mathscr{U})^{-1}Q|\delta\dot{n}_\mathrm{A}\rangle\rangle\chi_\mathrm{AA}^{-1}\\ &= k_f{}^2\langle\langle\delta n_\mathrm{A}\delta n_\mathrm{B}|\delta n_\mathrm{A}(t)\delta n_\mathrm{B}(t)\rangle\rangle(\mathbf{k}, z)\chi_\mathrm{AA}^{-1}\\ &\doteq ik_f{}^2\int\frac{d^3k'}{(2\pi)^3}\int_0^\infty dt\, e^{izt}S_{n_\mathrm{A}n_\mathrm{A}}(\mathbf{k} - \mathbf{k}', t)S_{n_\mathrm{B}n_\mathrm{B}}(\mathbf{k}', \mathbf{t})\chi_\mathrm{AA}^{-1}\end{aligned} \tag{36b}$$

where $S_{n_\gamma n_\gamma}(\mathbf{k}, t) = \langle\langle n_\gamma(\mathbf{r}, 0)|n_\gamma\mathbf{r}', t)\rangle\rangle(\mathbf{k})$ is the density autocorrelation function of the chemical species γ. To obtain the last of the expressions in (36b) we have used the factorization approximation.

In order to generate an estimate of this integral we use for $S_{n_\gamma n_\gamma}(\mathbf{k}, t)$ the approximation $n_\gamma^\mathrm{eq}\exp(-D_{\gamma\gamma}k^2 t)$. Then, in the long-wavelength, low-frequency limit

$$\begin{aligned}\tilde{\Phi}_\mathrm{AA} &\doteq ik_f{}^2 n_\mathrm{B}^\mathrm{eq}\int\frac{d^3k}{(2\pi)^3}\int_0^\infty dt\exp[-k^2(D_\mathrm{AA} + D_\mathrm{BB})t]\\ &= ik_f{}^2 n_\mathrm{B}^\mathrm{eq}\int_0^{k_c}\frac{4\pi k^2 dk}{(2\pi)^3}\frac{1}{k^2(D_\mathrm{AA} + D_\mathrm{BB})}\end{aligned} \tag{37}$$

Here k_c is the short-wavelength cutoff value of the wave number. If R $(=R_A + R_B)$ is the molecular separation at which reaction occurs, then the lower limit on the wavelength scale is $\lambda = 4R$. This corresponds to a largest wave number $k_c = 2\pi/4R$. Consequently,

$$\lim_{z\to i0}\lim_{k\to 0}\tilde{\Phi}_{AA} \doteq i n_B^{eq} k_f{}^2/k_D \tag{38}$$

with

$$k_D = 4\pi(R_A + R_B)(D_{AA} + D_{BB}) \tag{39}$$

To obtain the first-order approximation to the correlation function $\tilde{G}_{AA}(\mathbf{k}, z) = -\chi_{AA}/(z - \tilde{\Omega}_{AA} - \tilde{\Sigma}_{AA})$ we ignore the resonance structure of the memory function $\tilde{\Sigma}_{AA}(\mathbf{k}, \mathbf{z})$ by replacing it with

$$\tilde{\Sigma}_{AA}(\mathbf{k}, 0) = [\tilde{\Phi}_{AA}^{-1}(\mathbf{k}, 0) - \tilde{\Omega}_{AA}^{-1}(\mathbf{k})]^{-1}.$$

Thus, in the hydrodynamic limit,

$$\tilde{G}_{AA}(\mathbf{k}, z) \approx -\frac{\chi_{AA}}{z - [\tilde{\Omega}_{AA}^2/(\tilde{\Omega}_{AA} - \tilde{\Phi}_{AA})](k = 0, z = 0)} = -\frac{n_A^{eq}}{z + ik_f{}^R n_B^{eq}} \tag{40}$$

where $k_f{}^R$, given by

$$1/k_f{}^R = 1/k_f + 1/k_D \tag{41}$$

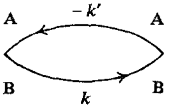
is the renormalized rate constant for the forward reaction.

This expression for the renormalized rate also can be written as the sum

$$\begin{aligned} ik_f{}^R n_B^{eq} &\equiv \tilde{\Omega}_{AA}^2/(\tilde{\Omega}_{AA} - \tilde{\Phi}_{AA}) = \tilde{\Omega}_{AA}[1 + \tilde{\Omega}_{AA}^{-1}\tilde{\Phi}_{AA} + (\tilde{\Omega}_{AA}^{-1}\tilde{\Phi}_{AA})^2 + \cdots] \\ &= \tilde{\Omega}_{AA}[1 + \bigcirc + \bigcirc\!\bigcirc + \bigcirc\!\bigcirc\!\bigcirc + \cdots] \end{aligned} \tag{42}$$

of repeated contributions from the "ring"

$$\tilde{\Omega}_{AA}^{-1}\tilde{\Phi}_{AA} \approx$$



composed of two diffusive elements. Thus, in this theory higher order mode couplings are represented approximately in terms of the single mode–mode coupling diagram ◯. This is analogous to the repeated ring approximation of kinetic theory.(3) It is remarkable that the simple identity $\tilde{\Sigma}(\mathbf{k}, 0) = \tilde{\Omega}_{AA}(\mathbf{k})\tilde{\Phi}(\mathbf{k}, 0)/[\tilde{\Omega}_{AA}(\mathbf{k}) - \tilde{\Phi}_{AA}(\mathbf{k}, 0)]$ generates this special class of higher order mode coupling diagrams.

4.2. Two-Variable Analysis

This more thorough analysis of the problem will be based on the two equations of motion

$$\partial_t(\delta n_{\mathrm{A}}) = -(k^2 D_{\mathrm{AA}} + k_f n_{\mathrm{B}}^{\mathrm{eq}})(\delta n_{\mathrm{A}}) - (k^2 D_{\mathrm{AB}} + k_f n_{\mathrm{A}}^{\mathrm{eq}})(\delta n_{\mathrm{B}}) - k_f(\delta n_{\mathrm{A}})(\delta n_{\mathrm{B}}) \tag{43a}$$

$$\partial_t(\delta n)_{\mathrm{B}} = -(k^2 D_{\mathrm{BA}} + k_f n_{\mathrm{B}}^{\mathrm{eq}}) - (k^2 D_{\mathrm{BB}} + k_f n_{\mathrm{A}}^{\mathrm{eq}})(\delta n_{\mathrm{B}}) - k_f(\delta n_{\mathrm{A}})(\delta n_{\mathrm{B}}) \tag{43b}$$

and the projection operator $P = |\delta n_{\mathrm{A}}\rangle\rangle\chi_{\mathrm{AA}}^{-1}\langle\langle\delta n_{\mathrm{A}}| + |\delta n_{\mathrm{B}}\rangle\rangle\chi_{\mathrm{BB}}^{-1}\langle\langle\delta n_{\mathrm{B}}|$; $\chi_{\mathrm{AB}} \equiv \langle\delta n_{\mathrm{A}}|\delta n_{\mathrm{B}}\rangle = 0$.

Because $P\mathscr{U}$ is anti-Hermitian the frequency matrix can be written as $\tilde{\Omega}_{ij} = i\langle\langle\dot{A}_i|A_k\rangle\rangle\chi_{kj}^{-1}$ or, more explicitly,

$$\tilde{\Omega} = -ik^2\mathsf{D} + \omega_0\begin{bmatrix} 1 & \xi \\ 1 & \xi \end{bmatrix} \tag{44}$$

Here, $\omega_0 \equiv -ik_f n_{\mathrm{B}}^{\mathrm{eq}}$, $\xi \equiv n_{\mathrm{A}}^{\mathrm{eq}}/n_{\mathrm{B}}^{\mathrm{eq}}$, and D is the matrix of diffusion coefficients for this quasi-two-component fluid mixture. If we interpret the absence of product (C) diffusive terms from Eqs. (43) as equivalent to the approximation that all diffusion coefficients for the species C are zero, then the formulas $D_{ij} = D_{ji}$ and $\sum_j m_j D_{ji} = 0$ imply that $D_{\mathrm{AB}} = D_{\mathrm{BA}} = -\vartheta D_{\mathrm{AA}}$ and $D_{\mathrm{BB}} = \vartheta^2 D_{\mathrm{AA}}$ with $\vartheta \equiv m_{\mathrm{A}}/m_{\mathrm{B}}$. Hence

$$\mathsf{D} = D_{\mathrm{AA}}\begin{bmatrix} 1 & \vartheta \\ -\vartheta & \vartheta^2 \end{bmatrix}$$

This approximation is used throughout the remainder of this section.

Since $Q\mathscr{U}$ also is anti-Hermitian, $\tilde{\Phi}_{ij} = -\langle\langle\dot{A}_i|Q(z - \mathscr{U})^{-1}Q|\dot{A}_k\rangle\rangle\chi_{kj}^{-1}$ or

$$\tilde{\Phi} = \alpha\begin{bmatrix} 1 & \xi \\ 1 & \xi \end{bmatrix} \tag{45}$$

where $\alpha \equiv -\langle\langle\delta\dot{n}_{\mathrm{A}}|Q(z - \mathscr{U})^{-1}Q|\delta\dot{n}_{\mathrm{A}}\rangle\rangle = k_f{}^2\langle\langle\delta n_{\mathrm{A}}\delta n_{\mathrm{B}}|\delta n_{\mathrm{A}}(t)\delta n_{\mathrm{B}}(t)\rangle\rangle(\mathbf{k}, z)$. According to Eqs. (37) and (38), $\alpha \doteq in_{\mathrm{B}}^{\mathrm{eq}}(k_f{}^2/k_{\mathrm{D}})\phi(k, z)$ with $\phi(0, 0) = 1$.

When Eqs. (43) and (44) are substituted into Eq. (6) it is found that

$$\tilde{\Sigma}(\mathbf{k}, z) = \Gamma(\mathbf{k}, z)\begin{bmatrix} 1 & \xi \\ 1 & \xi \end{bmatrix} \tag{46a}$$

where

$$\Gamma(\mathbf{k}, z = 0) = \omega_0\alpha/(\omega_0 - \alpha) \tag{46b}$$

To determine $\tilde{G}_{\mathrm{AA}}(\mathbf{k}, z) = -\chi_{\mathrm{AA}}/(z - \tilde{\Omega}_{\mathrm{AA}} - \tilde{\Sigma}_{\mathrm{AA}})$ we identify $\tilde{\Omega}$ and $\tilde{\Sigma}$ given by Eqs. (44) and (45) with the matrices ω and σ that appear in Eq. (12).

Next, we set z equal to zero in $\Gamma(\mathbf{k}, z)$ in order to eliminate complexities associated with the resonance structure of $\tilde{\Sigma}$. It then is easy to verify that

$$\tilde{G}_{\mathrm{AA}}(\mathbf{k}, z) \approx -n_{\mathrm{A}}^{\mathrm{eq}}\left[\frac{\xi/(1+\xi)}{z + ik^2 D_{\mathrm{AA}} f(\xi, \vartheta)} + \frac{1/(1+\xi)}{z + ik_f{}^R n_{\mathrm{B}}^{\mathrm{eq}}(1+\xi) + ik^2 D_{\mathrm{AA}} g(\xi, \vartheta)}\right] \tag{47}$$

with $f(\xi, \vartheta) \equiv (\xi + \vartheta)(1 + \vartheta)(1 + \xi)^{-1}$ and

$$g(\xi, \vartheta) \equiv (1 - \vartheta)(1 - \xi\vartheta)(1 + \xi)^{-1}.$$

The first of the two terms in Eq. (47) is associated with a pure hydrodynamic pole, whereas the second pole is reactive.

The results generated by the more complicated and complete three-variable analysis differ only slightly from those derived here. Thus, in place of Eq. (47) one obtains

$$\tilde{G}_{\mathrm{AA}}(\mathbf{k}, z) \approx -n_{\mathrm{A}}^{\mathrm{eq}}\left[\frac{(\xi + \eta)/(1 + \xi + \eta)}{z + O(k^2)} + \frac{1/(1 + \xi + \eta)}{z + ik_f{}^R n_{\mathrm{B}}^{\mathrm{eq}}(1 + \xi + \eta) + O(k^2)}\right] \tag{48}$$

where

$$\eta \equiv k_r/k_f n_{\mathrm{B}}^{\mathrm{eq}} = n_{\mathrm{A}}^{\mathrm{eq}}/n_{\mathrm{C}}^{\mathrm{eq}}$$

Although it might appear that our results would be equally valid for all values of $\xi = n_{\mathrm{A}}^{\mathrm{eq}}/n_{\mathrm{B}}^{\mathrm{eq}}$, $\eta = n_{\mathrm{A}}^{\mathrm{eq}}/n_{\mathrm{C}}^{\mathrm{eq}}$, and $\vartheta = m_{\mathrm{A}}/m_{\mathrm{B}}$, they are in fact reliable only for the extreme limiting values of these parameters, namely, $\xi, \eta \ll 1$ or $\xi, \eta \gg 1$. The reason for this is that we have limited our considerations to coupling between the reactive and diffusive modes. A more thorough analysis would include the coupling of the reactive mode to other hydrodynamic coordinates such as the viscous and thermal modes.(1)

5. CONCLUDING REMARKS

We have shown how to modify the projection operator formalism and generalized Langevin equations of Zwanzig and Mori so that they are applicable when the exact dynamical equations of motion are replaced by intrinsically irreversible, phenomenological equations of motion. Although this "non-Hamiltonian" theory is based on a cruder, less precise mechanics than the conventional, dynamically exact theory, many benefits are gained in exchange for this loss of microscopic accuracy. Thus, computations are relatively simple even for very complicated systems and one is able to incorporate directly into this theory approximate, phenomenological descriptions of the relevant physical processes or events. This theory paves the way for applications of statistical mechanical techniques to systems consisting of aggregates which are much more complicated than small molecules and for which a detailed microscopic characterization would be either irrelevant or hopelessly impractical to conduct.

Both of the applications considered in this paper are based on phenomenological equations of motion. However, the theory also is suitable for systems characterized by "effective" Hamiltonian operators, in which case the non-Hermitian operator $\mathscr{U}$ is related to the effective Hamiltonian $\mathscr{H}^{\text{eff}}$ by $-i\mathscr{U} = [\mathscr{H}^{\text{eff}}]_{\text{PB}}$. This permits application of the theory to systems for which phenomenological model Hamiltonians exist.

APPENDIX A

Here we shall derive the relationship, Eq. (6), between the two memory function matrices

$$\Sigma_{ij} = \langle \dot{A}_i | Q(z - Q\mathscr{L})^{-1} Q | \dot{A}_k \rangle \chi_{kj}^{-1} \tag{A1}$$

and

$$\Phi_{ij} = \langle \dot{A}_i | Q(z - \mathscr{L})^{-1} Q | \dot{A}_k \rangle \chi_{kj}^{-1} \tag{A2}$$

From these definitions and the identity $(z - \mathscr{L})^{-1} - (z - Q\mathscr{L})^{-1} = (z - \mathscr{L})^{-1} P\mathscr{L}(z - Q\mathscr{L})^{-1}$ it follows that

$$\begin{aligned} z[\Phi_{ij} - \Sigma_{ij}] &= \langle \dot{A}_i | Qz\{(z - \mathscr{L})^{-1} P\mathscr{L}(z - Q\mathscr{L})^{-1}\} Q | \dot{A}_k \rangle \chi_{kj}^{-1} \\ &= \langle \dot{A}_i | Q(z - \mathscr{L})^{-1}[(z - \mathscr{L}) + \mathscr{L}] P\mathscr{L}(z - Q\mathscr{L})^{-1} Q | \dot{A}_k \rangle \chi_{kj}^{-1} \end{aligned}$$

Then, since $PQ = 0$, $P \equiv |A_l\rangle \chi_{lm}^{-1} \langle A_m|$, and $\dot{A}_k = i\mathscr{L} A_k$ we see that

$$\begin{aligned} z[\Phi_{ij} - \Sigma_{ij}] &= \langle \dot{A}_i | Q(z - \mathscr{L})^{-1} \mathscr{L} | A_l \rangle \chi_{lm}^{-1} \langle A_m | \mathscr{L}(z - Q\mathscr{L})^{-1} | \dot{A}_k \rangle \chi_{kj}^{-1} \\ &= \alpha_{im} \Sigma_{mj} \end{aligned} \tag{A3}$$

where

$$\begin{aligned} \alpha_{im} &\equiv \langle \dot{A}_i | Q(z - \mathscr{L})^{-1} | \dot{A}_l \rangle \chi_{lm}^{-1} \\ &= \langle \dot{A}_i | Q(z - \mathscr{L})^{-1}(P + Q) | \dot{A}_l \rangle \chi_{lm}^{-1} \\ &= \Phi_{im} + z^{-1} \langle \dot{A}_i | Q(z - \mathscr{L})^{-1}(z - \mathscr{L} + \mathscr{L}) P | \dot{A}_l \rangle \chi_{lm}^{-1} \\ &= \Phi_{im} + z^{-1} \langle \dot{A}_i | Q(z - \mathscr{L})^{-1} \mathscr{L} | A_j \rangle \chi_{jk}^{-1} \langle A_j | \dot{A}_l \rangle \chi_{lm}^{-1} \\ &= \Phi_{im} + z^{-1} \alpha_{ik} \Omega_{km} \end{aligned} \tag{A4}$$

The matrix forms of Eqs. (A3) and (A4) are $z(\Phi - \Sigma) = \alpha\Sigma$ and $z(\alpha - \Phi) = \alpha\Omega$, respectively. From the second of these it follows that $\alpha = z\Phi(z - \Omega)^{-1}$. When this is substituted into the first we find that $z(\Phi - \Sigma) = z\Phi(z - \Omega)^{-1}\Sigma$ or

$$\Sigma = [1 + \Phi(z - \Omega)^{-1}]^{-1} \Phi \tag{A5}$$

APPENDIX B

Our objective here is to derive the identity (12) of Section 2.1. To accomplish this we begin with two orthogonal dynamical variables A_1 and A_2 and the associated projection operator $P_2 = |A_1\rangle\chi_1^{-1}\langle A_1| + |A_2\rangle\chi_2^{-1}\langle A_2|$. Because $\langle A_1|A_2\rangle = 0$ we adopt the condensed notation $\chi_i \equiv \chi_{ii} \equiv \langle A_i|A_i\rangle$ for $i = 1, 2$.

The generalized Langevin equations (5) appropriate to this situation may be written in the matrix representation

$$\begin{bmatrix} \Gamma_{11}^{-1} & \Gamma_{12}^{-1} \\ \Gamma_{21}^{-1} & \Gamma_{22}^{-1} \end{bmatrix}\begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix} = -\begin{bmatrix} \chi_1 & 0 \\ 0 & \chi_2 \end{bmatrix} \tag{B1}$$

Here $\Gamma_{11}^{-1} = z - (\omega_{11} + \sigma_{11})$, $\Gamma_{12}^{-1} = -(\omega_{12} + \sigma_{12})$, $\Gamma_{21}^{-1} = -(\omega_{21} + \sigma_{21})$, and $\Gamma_{22}^{-1} = z - (\omega_{22} + \sigma_{22})$ and the integrals ω_{ij} and σ_{ij} are those defined by Eqs. (13) and (14) of the text.

From Eq. (B1) we immediately conclude that $\Gamma_{21}^{-1}G_{11} + \Gamma_{22}^{-1}G_{21} = 0$ or $G_{21} = -\Gamma_{22}\Gamma_{21}^{-1}G_{11}$. Consequently, the relationships $\Gamma_{11}^{-1}G_{11} + \Gamma_{12}^{-1}G_{21} = -\chi_1$ can be written in the form

$$[\Gamma_{11}^{-1} - \Gamma_{12}^{-1}\Gamma_{22}\Gamma_{21}^{-1}]G_{11} = -\chi_1 \tag{B2}$$

or

$$(z - \omega_{11} - \Sigma_{11})G_{11} = -\chi_1 \tag{B3}$$

where

$$\Sigma_{11} = \sigma_{11} + (\omega_{12} + \sigma_{12})(z - \omega_{22} - \sigma_{22})^{-1}(\omega_{21} + \sigma_{21}) \tag{B4}$$

is the same as $\Sigma_{A_1A_1}$ of the text.

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