Response theory and reduced equations of motion

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(Received 23 September 2008; published 10 March 2009)

Nonlinear response theory for a relaxation experiment is used to derive classical and quantum-mechanical equations of motion for reduced distribution functions or density matrices, respectively. The classical equations are linear, but the quantum ones are not. The results are analyzed in the weak-coupling and separation-of-time-scales limits.

DOI: 10.1103/PhysRevE.79.031106 PACS number(s): 05.60.−k, 66.30.−h, 05.30.−d

I. INTRODUCTION

One of the classic problems in nonequilibrium statistical mechanics is the microscopic origin of equations of motion for reduced distribution functions, with applications to a wide variety of phenomena ranging from Brownian motion, to NMR or optical spectroscopies, etc. The earliest derivations of these reduced equations focused on hierarchical methods like the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy to derive the Boltzmann equation [1], Fokker-Planck equations, or Bloch-Redfield equations [2,3]. A large number of techniques have been applied to these problems, including various perturbation theories [2,3], projection operator methods [4–11], path-integral methods [12], etc., with the projection operator approach perhaps being the most popular.

In the projection operator approaches, using the techniques pioneered by Zwanzig [13] and Mori and co-worker [14,15], a generalized Langevin equation is obtained. The derivations depend on several assumptions: namely, (i) the choice of the projection operator; (ii) the choice of the initial distribution (this often linked to the first assumption); (iii) an assumption that there is a separation of time scales between the dynamics of the reduced system and the rest, thereby resulting in a random forcing term who's correlations decay on a short time scale (this is sometimes referred to as the "Markov" assumption); and finally, (iv) that the averages of the random force in general decays on a fast time scale, even for initial distributions other than that assumed in the derivation. What results, ignoring the random force, is a linear, generalized Fokker-Planck equation. Some of the differences arising from these choices, which seem to disappear in the weak-coupling, Markov limit, but which result in other problems, are discussed in Ref. [8].

In this work, a general derivation of such equations of motion is presented based on response theory for a relaxation experiment; i.e., a fairly general nonequilibrium initial state is assumed and allowed to freely relax back to equilibrium. The average reduced distribution functions and their time derivatives are calculated in terms of the parameters describing the initial distribution, and subsequently, these are eliminated in favor of the instantaneous reduced distribution, thereby resulting in a closed equation of motion. No assumptions about projection operators are made, although expressions that contain what look like Mori-Tokyuama projected quantities [15] arise naturally. Both classical and quantum systems will be examined. What is perhaps most interesting is the appearance of nonlinear terms in quantum-mechanical systems.

For classical systems, consider a system whose phase space can be decomposed into "subsystem" and "bath" parts, described by the phase vectors X_S and X_B, respectively, each containing their respective generalized coordinates q_i and conjugate momenta p_i. For quantum systems, it is assumed that the Hilbert space describing the entire system can be decomposed into the subspace of interest and its orthogonal complement, spanned by orthonormal basis vectors $|\mathsf{x}_s\rangle$ and $|\mathsf{x}_B\rangle$, respectively, where x_S and x_B denote the quantum numbers for the chosen representation. In particular, note the completeness relations

$$\sum_{\mathsf{x}_\alpha} |\mathsf{x}_\alpha\rangle\langle\mathsf{x}_\alpha| = \mathbb{1}_\alpha, \quad \alpha = S,B, \tag{1.1}$$

where $\mathbb{1}_{S(B)}$ is the identity operator in the subsystem (bath) space.

The total Hamiltonian governing the system is written as

$$H \equiv H_S + H_B + \lambda H_{S,B}, \tag{1.2}$$

where $H_{S(B)}$ depends only on $\mathsf{X}_{S(B)}$ (classically) or $|\mathsf{x}_{S(B)}\rangle$ (quantum mechanically); all interactions between the subsystem and bath are contained in $H_{S,B}$, whose strength is characterized by λ. The system's dynamics is governed by the Liouville equation, with Liouville operator

$$\begin{aligned} i\mathcal{L} &\equiv \begin{cases} \{\ldots,H\}, & \text{classically}, \\ [\ldots,H]/i\hbar, & \text{quantum mechanically}, \end{cases} \\ &\equiv i\mathcal{L}_S + i\mathcal{L}_B + \lambda i\mathcal{L}_{S,B}, \end{aligned} \tag{1.3}$$

where $\{\ldots,\ldots\}$ is a Poisson bracket [16], $[\ldots,\ldots]$ is a commutator, and the decomposition into subsystem, bath, and interaction parts follows trivially from Eq. (1.2). The reduced distribution functions can be obtained by averaging

$$\mathsf{A}(\mathsf{x},t) \equiv \delta(\mathsf{x} - \mathsf{X}_S(t)), \tag{1.4a}$$

classically, where $\delta(\mathsf{x})$ is a Dirac delta function and where $\mathsf{X}(t)$ is the phase point at time t given that it was X at $t=0$. Quantum mechanically, this becomes

$$\mathsf{A}(\mathsf{x}_S,\mathsf{x}'_S,t) \equiv e^{i\mathcal{L}t}(|\mathsf{x}'_S\rangle\langle\mathsf{x}_S| \otimes \mathbb{1}_B), \tag{1.4b}$$

where the S subscript will be dropped when the context is obvious.

In order to proceed, many authors start manipulating Liouville's equation for reduced distribution functions. In response theory, a slightly different approach can be taken—namely, to consider a relaxation experiment where the system and bath relax to equilibrium from an adiabatically prepared distribution. The exact form of this distribution is, of course, not really known, but as was argued in Ref. [17], it should not really matter as long as (i) a well-posed, closed, set of phenomenological equations of motion exist for some reduced set of variables A and (ii) the distribution gives expected initial average values of the phenomenological variables. To this end, it was assumed that the initial distribution has the form

$$\rho(t=0)=\begin{cases}\dfrac{e^{-\beta(H-\mathsf{A}*\mathsf{F})}}{\langle e^{\beta\mathsf{A}*\mathsf{F}}\rangle}, & \text{classically},\\ \dfrac{e^{-\beta(H-\mathsf{A}*\mathsf{F})}}{\mathrm{Tr}(e^{\beta(H-\mathsf{A}*\mathsf{F})})}, & \text{quantum mechanically},\end{cases} \tag{1.5}$$

where $\beta\equiv 1/k_BT$, $\langle\cdots\rangle$ denotes an equilibrium canonical average, "$*$" denotes a sum over the various variables contained in A and concomitant integrations, if necessary, and the F's are chosen to give the correct initial values of $\mathsf{a}(t=0)$, the average of the dynamical variables, using Eq. (1.5). The F's can viewed as real external fields that couple to the A's in preparing the system, or simply as Lagrange multipliers that enforce constraints on the initial averages in a maximum entropy formalism. In addition, note that no decoupling or factorization between the subsystem and bath degrees of freedom is assumed.

In the usual treatment [17], Eq. (1.5) is used to generate series expansions for $\mathsf{a}(t)$ and $\dot{\mathsf{a}}(t)$, the average and average rate of change of the dynamical variables, respectively, after which F is eliminated, thereby resulting in a nonlocal, nonlinear equations of motion. This idea will be applied here for a special choice of variables—i.e., for the generator of the subsystem's reduced distribution.

With these preliminary remarks, the derivations of classical and quantum-mechanical reduced equations of motion will be presented in Secs. II and III, respectively. One surprising result is that the classical equations are linear, exactly, while the quantum ones are not. Section IV contains some concluding remarks.

II. CLASSICAL SYSTEMS

When Eq. (1.4a) is used in (1.5), it follows that the nonequilibrium average of any mechanical quantity $B(t)$ is

$$\langle B(t)\rangle_{NE}=\frac{\langle B(t)e^{\beta\mathsf{A}*\mathsf{F}}\rangle}{\langle e^{\beta\mathsf{A}*\mathsf{F}}\rangle}=\frac{\langle B(t)\mathsf{A}(\mathsf{x})\rangle * e^{\beta\mathsf{F}(\mathsf{x})}}{\langle\mathsf{A}(\mathsf{x})\rangle * e^{\beta\mathsf{F}(\mathsf{x})}}, \tag{2.1}$$

where the last equality follows trivially from the definition of the δ function. The average in the denominator is just the equilibrium reduced distribution function—i.e.,

$$\rho_{eq}(\mathsf{x})=\int dX_B\frac{e^{-\beta H}|_{\mathsf{X}_S=\mathsf{x}}}{Q}\equiv e^{-\beta\Delta A(\mathsf{x})}, \tag{2.2}$$

where Q is the canonical partition function (without the usual $h^{3N}N!$ corrections) and $\Delta A(\mathsf{x})$ is the generalized potential of mean force for the subsystem in configuration x or, equivalently, the Helmholtz free energy required to put the subsystem into configuration x.

By setting $B=\mathsf{A}$ and $t=0$ in Eq. (2.1), it follows that

$$\rho_{NE}(\mathsf{x},t=0)=\frac{\exp[-\beta(\Delta A(\mathsf{x})-\mathsf{F}(\mathsf{x}))]}{\int d\mathsf{x}\exp[-\beta(\Delta A(\mathsf{x})-\mathsf{F}(\mathsf{x}))]}, \tag{2.3}$$

which gives

$$\mathsf{F}(\mathsf{x})=\Delta A(\mathsf{x})+k_BT\ln\rho_{NE}(\mathsf{x},t=0)+k_BT\ln\left(\int d\mathsf{x}e^{-\beta(\Delta A(\mathsf{x})-\mathsf{F}(\mathsf{x}))}\right). \tag{2.4}$$

This can be used to rewrite Eq. (2.1) as

$$\langle B(t)\rangle_{NE}=\langle B(t)\delta(\mathsf{x}-\mathsf{X}_S)\rangle * e^{\beta\Delta A(\mathsf{x})}\rho_{NE}(\mathsf{x}), \tag{2.5}$$

where, henceforth, the time arguments will be suppressed when $t=0$. Equation (2.5) is *exact*, given the assumption about the form of the initial distribution [cf. Eq. (1.5)] and the choice of variable [cf. Eq. (1.4a)]. Remarkably, it is also linear, even though no assumption about being near equilibrium has been made; indeed, it is basically a statement or proof of the Onsager regression hypothesis.

In order to proceed, we need to rewrite Eq. (2.5) in terms of $\rho_{NE}(\mathsf{x},t)$. Since Eq. (2.5) is linear, this can be done either in the time or frequency domains; here, the former will be considered. By using Eq. (2.5) for $B(t)=\delta(\mathsf{x}-\mathsf{X}_S(t))$, it follows that

$$\rho_{NE}(\mathsf{x})=e^{-\beta\Delta A(\mathsf{x})}\langle\delta(\mathsf{x}-\mathsf{X}_S(t))\delta(\mathsf{x}'-\mathsf{X}_S)\rangle^{-1} * \rho_{NE}(\mathsf{x}',t), \tag{2.6}$$

where an inverse kernel has been defined as

$$\int d\mathsf{x}'\langle\delta(\mathsf{x}-\mathsf{X}_S(t))\delta(\mathsf{x}'-\mathsf{X}_S)\rangle^{-1}\langle\delta(\mathsf{x}'-\mathsf{X}_S(t))\delta(\mathsf{x}''-\mathsf{X}_S)\rangle=\delta(\mathsf{x}-\mathsf{x}''). \tag{2.7}$$

Note that Eq. (2.7) implies that

$$\int d\mathsf{x}'\langle\delta(\mathsf{x}-\mathsf{X}_S(t))\delta(\mathsf{x}'-\mathsf{X}_S)\rangle^{-1}e^{-\beta\Delta A(\mathsf{x}')}=1. \tag{2.8}$$

In addition, when $t=0$ it is easy to see that

$$\langle\delta(\mathsf{x}-\mathsf{X}_S)\delta(\mathsf{x}'-\mathsf{X}_S)\rangle^{-1}=e^{\beta\Delta A(\mathsf{x})}\delta(\mathsf{x}-\mathsf{x}'). \tag{2.9}$$

By using Eq. (2.6) in (2.5) it follows that

$$\langle B(t)\rangle_{NE}=\langle B(t)\delta(\mathsf{x}-\mathsf{X}_S)\rangle * \langle\delta(\mathsf{x}-\mathsf{X}_S(t))\delta(\mathsf{x}'-\mathsf{X}_S)\rangle^{-1} * \rho_{NE}(\mathsf{x}',t) = \langle B\delta(\mathsf{x}-\mathsf{X}_S)\rangle e^{\beta\Delta A(\mathsf{x})} * \rho_{NE}(\mathsf{x},t) \tag{2.10a}$$

$$- \int_0^t ds \left\langle B^{\ddagger}(s) \frac{d\delta(\mathbf{x}-\mathbf{X}_S)}{dt} \right\rangle * \langle \delta(\mathbf{x}-\mathbf{X}_S(s))\delta(\mathbf{x}'-\mathbf{X}_S)\rangle^{-1} * \rho_{NE}(\mathbf{x}',t), \quad (2.10b)$$

where

$$B^{\ddagger}(t) \equiv B(t) - \langle B(t)\delta(\mathbf{x}'-\mathbf{X}_S)\rangle * \langle \delta(\mathbf{x}'-\mathbf{X}_S(t))\delta(\mathbf{x}''-\mathbf{X}_S)\rangle^{-1} * \delta(\mathbf{x}''-\mathbf{X}_S(t)). \quad (2.11)$$

In obtaining Eq. (2.10b) the time correlation functions were written as their $t=0$ values plus the integral of the time derivative. In addition, the fact that the equilibrium averages are stationary in time was used to move the time derivatives to the right. Note that $\langle B\delta(\mathbf{x}-\mathbf{X}_S)\rangle e^{\beta\Delta A(\mathbf{x})}$ is just the conditional average of B given that the subsystem is in configuration $\mathbf{x}$. In addition, $B^{\ddagger}(t)$ is orthogonal to the subspace in the sense that

$$\langle B^{\ddagger}(t)\delta(\mathbf{x}-\mathbf{X}_S)\rangle = 0 \quad (2.12)$$

and, indeed, Eq. (2.11) has the same form as the projection operators first introduced by Tokyuama and Mori [15]. Perhaps it is more important to note that [cf. Eq. (2.10a)] the second term in $B^{\ddagger}(t)$ subtracts the macroscopic, average behavior, applied to the microscopic variable, and thus, $B^{\ddagger}(t)$ represents the part of B *not* described by the average phenomenology. For systems with a so-called separation of time scales, this implies that $B^{\ddagger}(t)$ should vary on a short time scale. Henceforth, $B^{\ddagger}$ will be called the random or dissipative part of B.

The time derivative appearing in Eq. (2.10b) is easily expressed in terms of the Liouville operators [cf. Eq. (1.3)] and thus

$$\langle B(t)\rangle_{NE} = \langle B\delta(\mathbf{x}-\mathbf{X}_S)\rangle e^{\beta\Delta A(\mathbf{x})} * \rho_{NE}(\mathbf{x},t) - \lambda \sum_{i\in S} \int_0^t ds \left(\left\langle B^{\ddagger}(s)\delta(\mathbf{x}-\mathbf{X}_S)\frac{\partial H_{S,B}}{\partial p_i}\right\rangle \frac{\partial}{\partial q_i} - \left\langle B^{\ddagger}(s)\delta(\mathbf{x}-\mathbf{X}_S)\frac{\partial H_{S,B}}{\partial q_i}\right\rangle \frac{\partial}{\partial p_i}\right) * \langle \delta(\mathbf{x}-\mathbf{X}_S(s))\delta(\mathbf{x}'-\mathbf{X}_S)\rangle^{-1} * \rho_{NE}(\mathbf{x}',t), \quad (2.13)$$

where the terms arising from $i\mathcal{L}_S$ vanish due to Eq. (2.12) as do those arising from $i\mathcal{L}_B$. At equilibrium, Eq. (2.8) implies that each of the terms in the sum in Eq. (2.13) vanishes, while the first term becomes the exact equilibrium average $\langle B\rangle$.

The macroscopic equation of motion for the reduced distribution function is now easily obtained by letting $B(t) = i\mathcal{L}\delta(x_S - X_S(t))$. In this case, it is easy to show that the first term on the right-hand side of Eq. (2.13) becomes

$$\langle [i\mathcal{L}\delta(\mathbf{x}-\mathbf{X}_S)]\delta(\mathbf{x}'-\mathbf{X}_S)\rangle e^{\beta\Delta A(\mathbf{x}')} * \rho_{NE}(\mathbf{x}',t) = -\{\rho_{NE}(\mathbf{x},t),\Delta A(\mathbf{x})\} \equiv -i\mathcal{L}_{eff}\rho_{NE}(\mathbf{x},t), \quad (2.14)$$

where $\Delta A(\mathbf{x})$ is the effective Hamiltonian and free energy defined in Eq. (2.2). These terms vanish at equilibrium, as expected.

The dissipative terms are slightly more complicated. It is easy to show that $[i\mathcal{L}_S\delta(x_S - X_S(t))]^{\ddagger} = 0$. The nonzero contributions can be written as

$$\lambda^2 \sum_{\substack{i,j\in S \\ \alpha,\gamma=p,q}} \int_0^t ds \frac{\partial}{\partial\alpha_i} L_{\alpha_i,\gamma_j}(\mathbf{x},\mathbf{x}';s)\frac{\partial}{\partial\gamma_j'} * \langle \delta(\mathbf{x}'-\mathbf{X}_S(s))\delta(\mathbf{x}''-\mathbf{X}_S)\rangle^{-1} * \rho_{NE}(\mathbf{x}'',t), \quad (2.15)$$

where a generalized Onsager coefficient is defined as

$$L_{\alpha_i,\gamma_j}(\mathbf{x},\mathbf{x}';s) \equiv \pm \left\langle \left[\left(\frac{\partial H_{S,B}}{\partial\bar{\alpha}_i}\right)(s)\delta(\mathbf{x}-\mathbf{X}_S(s))\right]^{\ddagger} \times \delta(\mathbf{x}'-\mathbf{X}_S)\frac{\partial H_{S,B}}{\partial\bar{\gamma}_j}\right\rangle, \quad (2.16)$$

where

$$\bar{\alpha} \equiv \begin{cases} q & \text{for } \alpha = p, \\ p & \text{for } \alpha = q, \end{cases} \quad (2.17)$$

and where the plus sign is used if $\alpha=\gamma$ and the minus otherwise.

Thus, by combining Eqs. (2.14) and (2.15) a generalized Fokker-Planck equation is obtained—namely,

$$\frac{\partial\rho_{NE}(\mathbf{x},t)}{\partial t} = -i\mathcal{L}_{eff}\rho_{NE}(\mathbf{x},t) + \lambda^2 \sum_{\substack{i,j\in S \\ \alpha,\gamma=p,q}} \int_0^t ds \frac{\partial}{\partial\alpha_i} L_{\alpha_i,\gamma_j}(\mathbf{x},\mathbf{x}';s)\frac{\partial}{\partial\gamma_j'} * \langle \delta(\mathbf{x}'-\mathbf{X}_S(s))\delta(\mathbf{x}''-\mathbf{X}_S)\rangle^{-1} * \rho_{NE}(\mathbf{x}'',t). \quad (2.18)$$

Equation (2.18) is exact, given the assumed form of the initial distribution. Again, note that each term in Eq. (2.18) vanishes at equilibrium. Note that it is nonlocal in $\mathbf{x}$ and has time-dependent coefficients; as such, anomalous diffusion phenomena [18] could arise if $L_{\alpha_i,\gamma_j}(\mathbf{x},\mathbf{x}';s)$ does not decay rapidly in time or in spatial separation (e.g., as would probably be the case near a critical point, or in some sort of disordered phase). For example, if the reduced subspace was the position of a tagged particle, this would generate a generalized diffusion equation, which, when Fourier transformed, has the form

$$\frac{\partial\rho(\mathbf{k},t)}{\partial t} = -k^2 D(k,t)\rho(\mathbf{k},t),$$

which has the solution $\rho(\mathbf{k},t) = \exp[-\int_0^t ds k^2 D(k,s)]\rho(\mathbf{k},0)$.

Next, consider the standard case where there is a separation of time scales, specifically where the system evolves on a slower time scale than the bath and where the coupling is weak. In this case, the dissipative correlation functions that appear in Eq. (2.16) are expected to decay on a fast-time scale, one in which the subsystem remains frozen for the most part. In addition, λ is assumed to be small. When both of these conditions hold, the time dependences associated with $\mathbf{X}_S(s)$ can be ignored for times long compared to the

bath correlation times, but small compared to the subsystem's, and Eq. (2.18) can be rewritten, to $O(\lambda^2)$, as

$$\frac{\partial \rho_{NE}(\mathsf{x},t)}{\partial t} = -i\mathcal{L}_{eff}\rho_{NE}(\mathsf{x},t) + \lambda^2 \sum_{\substack{i,j\in S \\ \alpha,\gamma=p,q}} \frac{\partial}{\partial \alpha_i} L_{\alpha_i,\gamma_j}(\mathsf{x}) e^{-\beta\Delta A(\mathsf{x})} \frac{\partial e^{\beta\Delta A(\mathsf{x})}\rho_{NE}(\mathsf{x},t)}{\partial \gamma_j}. \tag{2.19}$$

Henceforth,

$$L_{\alpha_i,\gamma_j}(\mathsf{x}) \equiv \pm \int_0^\infty ds \left\langle \left[\left(\frac{\partial H_{S,B}}{\partial \bar{\alpha}_i} \right)(s) \right]^{\ddagger} \frac{\partial H_{S,B}}{\partial \bar{\gamma}_j} \right\rangle_{\mathsf{x}}, \tag{2.20}$$

where $\langle \cdots \rangle_{\mathsf{x}}$ denotes an conditional average with the subsystem frozen in configuration x and

$$\left[\left(\frac{\partial H_{S,B}}{\partial \bar{\alpha}_i} \right)(s) \right]^{\ddagger} \equiv \left(\frac{\partial H_{S,B}}{\partial \bar{\alpha}_i} \right)(s) - \left\langle \frac{\partial H_{S,B}}{\partial \bar{\alpha}_i} \right\rangle_{\mathsf{x}}, \tag{2.21}$$

i.e., the fluctuations in the generalized coupling forces in the presence of the frozen subsystem. Note that the separation-of-time-scales assumption allows the upper limit of the integral to be extended to infinity for $t \gg \tau_{\text{bath}}$, where τ_{bath} is a typical bath relaxation time.

Another interesting case is that where the subsystem-bath interaction is weak and separable (in the integral-equation sense), specifically where

$$H_{S,B} = \sum_k \mathcal{S}^{(k)}(\mathsf{X}_S)\mathcal{B}^{(k)}(\mathsf{X}_B), \tag{2.22}$$

where the sum over k could be replaced by an integral (e.g., as in the case of a Fourier representation of the generalized forces). Since the dissipative term in Eq. (2.18) is explicitly $O(\lambda^2)$, to that order the system-bath coupling can be ignored and the generalized Onsager coefficient [cf. Eq. (2.16)] becomes

$$L_{\alpha_i,\gamma_j}(\mathsf{x},\mathsf{x}';s) \sim \pm \sum_{k,k'} \left(\frac{\partial \mathcal{S}^{(k)}(\mathsf{x})}{\partial \bar{\alpha}_i} \right) \left(\frac{\partial \mathcal{S}^{(k')}(\mathsf{x}')}{\partial \bar{\gamma}'_j} \right) \langle \delta(\mathsf{x} - \mathsf{X}_S(s))\delta(\mathsf{x}' - \mathsf{X}_S) \rangle \langle \hat{\mathcal{B}}^{(k)}_{\bar{\alpha}_i}(s) \hat{\mathcal{B}}^{(k')}_{\bar{\gamma}_j} \rangle, \tag{2.23}$$

where the $\hat{B}$ denotes the deviation of B from its equilibrium average. Clearly Eq. (2.23) will further simplify when there is a separation of time scales (with the bath fluctuations decaying faster). In this case, Eq. (2.20) becomes

$$L_{\alpha_i,\gamma_j}(\mathsf{x}) \sim \pm \sum_{k,k'} \left(\frac{\partial \mathcal{S}^{(k)}(\mathsf{x})}{\partial \bar{\alpha}_i} \right) \left(\frac{\partial \mathcal{S}^{(k')}(\mathsf{x})}{\partial \bar{\gamma}_j} \right) \int_0^\infty ds \langle \hat{\mathcal{B}}^{(k)}_{\bar{\alpha}_i}(s) \hat{\mathcal{B}}^{(k')}_{\bar{\gamma}_j} \rangle. \tag{2.24}$$

Classical Brownian motion

As an example, consider the Brownian motion of a heavy particle in a bath of light ones, one of the workhorse problems in statistical mechanics. In this case,

$$H_S = \frac{P^2}{2M}, \quad H_{S,B} = \sum_{j\in B} u_{SB}(\mathbf{R} - \mathbf{r}_j), \tag{2.25}$$

where $\mathbf{R}$ and $\mathbf{P}$ denote the position and momentum of the Brownian particle, M is its mass, and a pairwise additive, velocity-independent potential has been assumed for the interaction with the bath. With this choice, assuming that the system is uniform at equilibrium, it follows that $\Delta A(\mathbf{R},\mathbf{P}) = P^2/2M$ up to unimportant additive constants. Evaluating the various terms in Eq. (2.18) results in the following generalized Fokker-Planck equation for the Brownian particle:

$$\frac{\partial \rho_{NE}(\mathbf{R},\mathbf{P},t)}{\partial t} = -\frac{\mathbf{P}}{M} \cdot \frac{\partial \rho_{NE}(\mathbf{R},\mathbf{P},t)}{\partial \mathbf{R}} + \lambda^2 \int_0^t ds \frac{\partial}{\partial \mathbf{P}} \cdot \overleftrightarrow{L}_{\mathbf{P},\mathbf{P}}(s) \cdot \frac{\partial}{\partial \mathbf{P}'} * \langle \delta(\mathsf{x}' - \mathsf{X}_S(s))\delta(\mathsf{x}'' - \mathsf{X}_S) \rangle^{-1} * \rho_{NE}(\mathbf{R}'',\mathbf{P}'',t), \tag{2.26}$$

where

$$\overleftrightarrow{L}_{\mathbf{P},\mathbf{P}}(s) \equiv \langle [\mathbf{F}_B(s)\delta(\mathsf{x} - \mathsf{X}_S(s))]^{\ddagger} \mathbf{F}_B \delta(\mathsf{x}' - \mathsf{X}_S) \rangle, \tag{2.27}$$

where $\mathbf{F}_B$ is the force exerted on the Brownian particle by the bath. At this point, this exact expression differs from that obtained by Romero-Rochin and Oppenheim [6] using projection operator techniques. It is not clear if the differences are more than formal and, in part, stem from the choice of staying completely in the time domain, leading to differences analogous to those arising between the Zwanzig-Mori [13,14] and Tokuyama-Mori [15] formalisms. Of course, no separation of weak-coupling and time-scale assumptions has been made yet; when these are invoked [cf. Eq. (2.19)], Eq. (2.26) becomes

$$\frac{\partial \rho_{NE}(\mathbf{R},\mathbf{P},t)}{\partial t} = -\frac{\mathbf{P}}{M} \cdot \frac{\partial \rho_{NE}(\mathbf{R},\mathbf{P},t)}{\partial \mathbf{R}} + \lambda^2 D \frac{\partial}{\partial \mathbf{P}} \cdot \left(\frac{\partial}{\partial \mathbf{P}} + \frac{\beta}{M}\mathbf{P} \right) \rho_{NE}(\mathbf{R},\mathbf{P},t), \tag{2.28}$$

where

$$D \equiv \frac{1}{3} \int_0^\infty ds \langle \mathbf{F}_B(s) \cdot \mathbf{F}_B \rangle_{\mathsf{x}}, \tag{2.29}$$

which is the usual result [4,6].

III. QUANTUM SYSTEMS

Moving from classical to quantum dynamics introduces several changes. The simplest are basically notational as was detailed in the Introduction. For relaxation experiments, it is

still reasonable to assume that the initial density matrix has the form given by Eq. (1.5), simply replacing the distribution function by the density matrix ρ and phase-space integrations by quantum mechanical traces, and where the "$*$" now denotes integrations (or sums) over both x_S and x'_S [cf. Eq. (1.4b)]. With this initial form of the density matrix, it follows that

$$\langle B(t)\rangle_{NE} = \frac{\mathrm{Tr}(B(t)e^{-\beta(H-\mathsf{A}*\mathsf{F})})}{\mathrm{Tr}(e^{-\beta(H-\mathsf{A}*\mathsf{F})})}, \tag{3.1}$$

where $B(t)=e^{iHt/\hbar}Be^{-iHt/\hbar}$ is a Heisenberg operator. This leads to the first difference with the classical development; namely, since A and H do not commute in general, the second equality in Eq. (2.1) will not hold and nonlinear corrections to the quantum-mechanical analog of Eq. (2.5) can arise. In order to examine this in detail, note the well-known operator identity

$$e^{-\beta(H-\mathsf{A}*\mathsf{F})} = e^{-\beta H} + \int_0^\beta ds e^{-(\beta-s)H}\mathsf{A}*\mathsf{F}e^{-s(H-\mathsf{A}*\mathsf{F})}, \tag{3.2}$$

which can be iterated to give a formal expansion of the distribution function around equilibrium. This is used to rewrite Eq. (3.1) as

$$\langle B(t)\rangle_{NE} \sim \langle B\rangle + \langle\langle B_K(t)\mathsf{A}\rangle\rangle * \beta\mathsf{F} + \int_0^\beta ds\int_0^s ds' \times\langle\langle B(t-i\beta\hbar)\mathsf{A}(-i\hbar s)\mathsf{A}(-i\hbar s')\rangle\rangle \underset{*}{*}\mathsf{F}\mathsf{F} + O(\mathsf{F}^3), \tag{3.3}$$

where $\langle\langle\cdots\rangle\rangle$ denote cumulant averages [19] and

$$B_K(t) \equiv \int_0^1 ds B(t-i\beta\hbar s) \tag{3.4}$$

is the Kubo transform of the Heisenberg operator $B(t)$ [20].

Equation (3.3) is the usual nonlinear response theory result for a relaxation experiment. At this point the F's are eliminated in favor of $\langle\mathsf{A}(t)\rangle_{NE}$. In Ref. [17] this was done by treating the nonlinear terms in Eq. (3.3) as perturbations and iterating, thereby obtaining an expansion in powers of $\langle\mathsf{A}(t)\rangle_{NE}-\langle\mathsf{A}\rangle$. Unfortunately, this approach cannot be applied without modification since, for the choice of A given by Eq. (1.4b), $\langle\langle\mathsf{A}_K(t)\mathsf{A}\rangle\rangle$ is singular, i.e.,

$$\int d\mathsf{x}_1\langle\langle\mathsf{A}_K(\mathsf{x},\mathsf{x}';t)\mathsf{A}(\mathsf{x}_1,\mathsf{x}_1)\rangle\rangle = 0 \tag{3.5}$$

[cf. Eq. (1.1)], and implies that the $F's$ are only determined up to an additive constant [cf. Eq. (3.1)]. Instead, Eq. (3.3), for $B=\mathsf{A}$, is rewritten as

$$\beta\mathsf{F}(\mathsf{x}_1,\mathsf{x}_2) \sim -\delta(\mathsf{x}_1-\mathsf{x}_2)(1-\rho_{eq}*\beta\mathsf{F}) + \langle\mathsf{A}_K(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle^{-1} * \Bigg(\rho_{NE}(\mathsf{x}_3,\mathsf{x}_4,t) - \int_0^\beta ds\int_0^s ds'\langle\langle\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4;t-i\beta\hbar) \times\mathsf{A}(-i\hbar s)\mathsf{A}(-i\hbar s')\rangle\rangle \underset{*}{*}\mathsf{F}\mathsf{F}\Bigg) + O(\mathsf{F}^3), \tag{3.6}$$

where, in analogy to Eq. (2.7), the inverse kernel satisfies

$$\int d\mathsf{x}_3\mathsf{x}_4\langle\mathsf{A}_K(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle^{-1}\langle\mathsf{A}_K(\mathsf{x}_3,\mathsf{x}_4;t)\mathsf{A}(\mathsf{x}_5,\mathsf{x}_6)\rangle = \delta(\mathsf{x}_1-\mathsf{x}_5)\delta(\mathsf{x}_2-\mathsf{x}_6). \tag{3.7}$$

Note that in obtaining Eq. (3.6) the identity

$$\int d\mathsf{x}_3\mathsf{x}_4\langle\mathsf{A}_K(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle^{-1}\rho_{eq}(\mathsf{x}_3,\mathsf{x}_4) = \delta(\mathsf{x}_1-\mathsf{x}_2), \tag{3.8}$$

which follows from Eqs. (3.7) and (1.1), was used. Equation (3.8) is the quantum-mechanical analog of Eq. (2.8).

By treating the quadratic term in Eq. (3.6) as a perturbation, iterating, and using the result in Eq. (3.3), the latter becomes

$$\langle B(t)\rangle_{NE} \sim \langle B_K(t)\mathsf{A}\rangle * \langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t) + \int_0^1 ds\int_s^1 ds'\langle\langle B^{\ddagger}(t)\mathsf{A}(i\beta\hbar s)\mathsf{A}(i\beta\hbar s')\rangle\rangle \underset{*}{*}[\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)][\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)] + O(\mathsf{F}^3), \tag{3.9}$$

where

$$B^{\ddagger}(t) \equiv B(t) - \langle B_K(t)\mathsf{A}\rangle * \langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \mathsf{A}(t). \tag{3.10}$$

Note that unlike its classical analog [cf. Eq. (2.11)], $B^{\ddagger}(t)$ is not orthogonal to A [$B^{\ddagger}_K(t)$ is], although $\langle B^{\ddagger}(t)\rangle=0$. The first term in Eq. (3.9) is the expected generalization of the classical result, Eq. (2.10a), by the introduction of the Kubo transforms. By using Eq. (3.8), it is easy to show that this term becomes $\langle B\rangle$ at equilibrium. Similarly, the quadratic terms can be shown to vanish at equilibrium and are second order in deviations from equilibrium. Perhaps more interesting is that they are purely quantum mechanical in origin.

By repeating the steps that led to Eq. (2.10b), Eq. (3.9) can be rewritten as

$$\langle B(t)\rangle_{NE} \sim \langle B_K \mathsf{A}\rangle * \langle \mathsf{A}_K \mathsf{A}\rangle^{-1} * \rho_{NE}(t) - \int_0^t ds \langle B_K^{\ddagger}(s)\dot{\mathsf{A}}^{\ddagger}\rangle * \langle \mathsf{A}_K(s)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)$$
$$+ \int_0^1 ds \int_s^1 ds' \langle\langle B^{\ddagger}(t)\mathsf{A}(i\beta\hbar s)\mathsf{A}(i\beta\hbar s')\rangle\rangle \overset{*}{*}[\langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)][\langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)] + O(\mathsf{F}^3). \tag{3.11}$$

As in Sec. II, Eq. (3.11) can be used to derive an equation of motion for the reduced density matrix. The A's obey the quantum-mechanical Heisenberg equation

$$\frac{\partial \mathsf{A}}{\partial t} = \frac{[\mathsf{A},H]}{i\hbar} \equiv i\mathcal{L}\mathsf{A}; \tag{3.12}$$

hence, Eq. (3.11) implies that

$$\frac{\partial \rho_{NE}(t)}{\partial t} \sim \langle \dot{\mathsf{A}}_K \mathsf{A}\rangle * \langle \mathsf{A}_K \mathsf{A}\rangle^{-1} * \rho_{NE}(t) - \int_0^t ds \langle \dot{\mathsf{A}}_K^{\ddagger}(s)\dot{\mathsf{A}}^{\ddagger}\rangle * \langle \mathsf{A}_K(s)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)$$
$$+ \int_0^1 ds \int_s^1 ds' \langle\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}(i\beta\hbar s)\mathsf{A}(i\beta\hbar s')\rangle\rangle \overset{*}{*}[\langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)][\langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \rho_{NE}(t)] + O(\mathsf{F}^3), \tag{3.13}$$

where note that the second- and higher-order corrections in deviation from equilibrium all vanish in the classical limit.

The linear terms will be examined first. If the potential is decomposed as in Eq. (1.2), it is easy to see that

$$\langle([\mathsf{A}(\mathsf{x}_1,\mathsf{x}_2),H_S])_K(t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle * \langle \mathsf{A}_K(\mathsf{x}_3,\mathsf{x}_4;t)\mathsf{A}(\mathsf{x}_5,\mathsf{x}_6)\rangle^{-1}$$
$$= [\langle \mathsf{x}_1|H_S|\mathsf{x}_5\rangle\delta(\mathsf{x}_2-\mathsf{x}_6) - \langle \mathsf{x}_6|H_S|\mathsf{x}_2\rangle\delta(\mathsf{x}_1-\mathsf{x}_5)], \tag{3.14}$$

which, when used in the first term on the right-hand side of Eq. (3.9) with $B=\dot{\mathsf{A}}$, gives the quantum Liouville equation for an isolated subsystem—i.e.,

$$\frac{\partial \rho_{NE}(t)}{\partial t} = -i\mathcal{L}_S \rho_{NE}(t). \tag{3.15}$$

In addition, by using Eqs. (3.12) and (3.14), it is easy to see that the explicit contribution of H_S to $\dot{\mathsf{A}}^{\ddagger}$ [cf. Eq. (3.10)] vanishes, as it must if there are to be no corrections to an isolated subsystem's Liouville equation [cf. Eq. (3.15)]. Also, the explicit contributions of H_B to $\dot{\mathsf{A}}$ obviously vanish, and hence, what remains are the contributions arising from $H_{S,B}$—namely,

$$\frac{\lambda}{i\hbar}\langle([\mathsf{A},H_{SB}])_K(t)\mathsf{A}\rangle * \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} \tag{3.16}$$

and

$$\dot{\mathsf{A}}^{\ddagger}(t) = \frac{\lambda}{i\hbar}\{([\mathsf{A},H_{SB}])(t) - \langle([\mathsf{A},H_{SB}])_K(t)\mathsf{A}\rangle * \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \mathsf{A}(t)\}. \tag{3.17}$$

Unfortunately, Eq. (3.16) does not simplify significantly, even for $t=0$, because of the Kubo transform. In order to deal with this problem, as in Ref. [7], the weak-coupling limit (i.e., $\lambda \ll 1$) to $O(\lambda^2)$ will be examined for a separable $H_{S,B}$ of the form given in Eq. (2.22), generalized to quantum-mechanical operators in the S and B subspaces. By noting that

$$e^{sH} \sim e^{sH_0} + \lambda \int_0^s ds' e^{(s-s')H_0} H_{S,B} e^{s'H_0} + O(\lambda^2) \tag{3.18a}$$

and

$$e^{i\mathcal{L}t} \sim e^{i\mathcal{L}_0 t} + \lambda \int_0^s dt' e^{i\mathcal{L}_0(t-t')} i\mathcal{L}_{S,B} e^{i\mathcal{L}_0 t'} + O(\lambda^2), \tag{3.18b}$$

where $H_0 \equiv H_S + H_B$, etc., it follows that

$$\frac{\lambda}{i\hbar}\langle([\mathsf{A},H_{S,B}])_K\mathsf{A}\rangle * \langle \mathsf{A}_K\mathsf{A}\rangle^{-1} \sim \frac{\lambda}{i\hbar}\Bigg[\sum_\alpha (\langle \mathsf{x}_1|\mathcal{S}^{(\alpha)}|\mathsf{x}_5\rangle\delta(x_2-\mathsf{x}_6) - \langle \mathsf{x}_6|\mathcal{S}^{(\alpha)}|\mathsf{x}_2\rangle\delta(\mathsf{x}_1-\mathsf{x}_5))\langle \mathcal{B}^{(\alpha)}\rangle$$
$$- \int_0^\beta \frac{ds}{\beta}\int_0^s ds' \langle[\dot{\mathsf{A}}_0^{\ddagger}(-i\hbar s)H_{S,B}(-i\hbar s') + H_{S,B}(-i\hbar s)\dot{\mathsf{A}}_0^{\ddagger}(-i\hbar s')]\mathsf{A}\rangle * \langle \mathsf{A}_K\mathsf{A}\rangle^{-1}\Bigg] + O(\lambda^3), \tag{3.19}$$

where all averages on the right-hand side are evaluated for the noninteracting subsystem-bath Hamiltonian,

$$\dot{\mathsf{A}}_0^{\ddagger}(\mathsf{x}_1,\mathsf{x}_2) \equiv \frac{\lambda}{i\hbar}\sum_{\alpha}[\mathsf{A}(\mathsf{x}_1,\mathsf{x}_2),\mathcal{S}^{(\alpha)}]\hat{\mathcal{B}}^{(\alpha)}$$

$$= \frac{\lambda}{i\hbar}\sum_{\alpha,\mathsf{x}}(\langle \mathsf{x}_1|\mathcal{S}^{(\alpha)}|\mathsf{x}\rangle \mathsf{A}_{\mathsf{x},\mathsf{x}_2} - \mathsf{A}_{\mathsf{x}_1,\mathsf{x}}\langle \mathsf{x}|\mathcal{S}^{(\alpha)}|\mathsf{x}_2\rangle)\hat{\mathcal{B}}^{(\alpha)}, \tag{3.20}$$

which is just Eq. (3.17) to leading order in λ for the assumed $H_{S,B}$. The remaining linear term in Eq. (3.13) is explicitly $O(\lambda^2)$, and thus

$$\frac{\partial \rho_{NE}(t)}{\partial t} \sim -i\mathcal{L}_{eff}\rho_{NE}(t) - \left(\frac{\lambda}{i\hbar}\right)^2 \sum_{\alpha,\alpha'}\left[\int_0^\beta \frac{ds}{\beta}\int_0^s ds'\langle\{[\mathsf{A},\mathcal{S}^{(\alpha)}]\right.$$

$$\times(-i\hbar s)\mathcal{S}^{(\alpha')}(-i\hbar s') + \mathcal{S}^{(\alpha)}(-i\hbar s)[\mathsf{A},\mathcal{S}^{(\alpha')}]$$

$$\times(-i\hbar s')\}\mathsf{A}\rangle * \langle \mathsf{A}_K\mathsf{A}\rangle^{-1}\langle \hat{\mathcal{B}}^{(\alpha)}(-i\hbar s)\hat{\mathcal{B}}^{(\alpha')}(-i\hbar s')\rangle$$

$$+ \int_0^t dt'\int_0^\beta \frac{ds'}{\beta}\langle[\mathsf{A},\mathcal{S}^{(\alpha)}](t'-i\hbar s')$$

$$\times[\mathsf{A},\mathcal{S}^{(\alpha')}]\rangle * \langle \mathsf{A}_K(t')\mathsf{A}\rangle^{-1}$$

$$\left.\times\langle \hat{\mathcal{B}}^{(\alpha)}(t'-i\hbar s')\hat{\mathcal{B}}^{(\alpha')}\rangle\right] * \rho_{NE}(t) + O(\lambda^3), \tag{3.21}$$

where $i\mathcal{L}_{eff}$ is an effective subsystem Liouville operator defined in terms of an effective Hamiltonian

$$H_{eff} \equiv H_S + \lambda\sum_{\alpha}\mathcal{S}^{(\alpha)}\langle\mathcal{B}^{(\alpha)}\rangle \tag{3.22}$$

and where the independence of the subsystem and bath (to leading order in λ) was used to factorize the various correlations into bath and subsystem parts. Since the subsystem parts now only depend on the isolated subsystem degrees of freedom, to the extent that they are simple, they can be evaluated explicitly. Indeed, by using Eq. (3.20) in Eq. (3.21), it is easy to see that the system parts can all be expressed in terms of the two-point Green's function

$$\mathcal{G}(\mathsf{x}_1,\mathsf{x}_2;t) \equiv \langle \mathsf{x}_1|e^{-itH_S/\hbar}|\mathsf{x}_2\rangle \tag{3.23}$$

and its analytic continuation to imaginary time (or equivalently in terms of the isolated subsystem density matrix and its analytic continuation to imaginary temperature).

Note that the reduced equilibrium density matrix to first order in λ is easily shown to be given by

$$\rho_{eq}(\mathsf{x}_1,\mathsf{x}_2) \sim \rho_{eq}^{(0)}(\mathsf{x}_1,\mathsf{x}_2) - \beta\lambda\sum_{\alpha}\langle \hat{\mathsf{A}}_K(\mathsf{x}_1,\mathsf{x}_2)\hat{S}^{(\alpha)}\rangle\langle\mathcal{B}^{(\alpha)}\rangle$$

$$+ O(\lambda^2), \tag{3.24}$$

where $\rho_{eq}^{(0)}$ is the subsystem density matrix for the noninteracting system. Since the separation of the Hamiltonian into subsystem and bath is arbitrary up to additive constants (in the degrees of freedom of each part), the terms in $\langle B^{(\alpha)}\rangle$ can be incorporated into the system part—i.e., $H_S \to H_S + \lambda\Sigma_\alpha \mathcal{S}^{(\alpha)}\langle\mathcal{B}^{(\alpha)}\rangle$—which makes the first-order corrections in ρ_{eq} and in Eq. (3.21) vanish.

Finally, consider the case where there is a separation of time scales between the bath and system, specifically where the correlation times $\tau_S \gg \tau_B$ *and* where $\tau_S \gg \beta\hbar$ ($\beta\hbar \sim 2.5 \times 10^{-14}$ s at 300 K). This last condition allows the Kubo transforms to be ignored in the subsystem correlation functions, and Eq. (3.21) becomes

$$\frac{\partial \rho_{NE}(t)}{\partial t} \sim -i\mathcal{L}_{eff}\rho_{NE}(t) - \left(\frac{\lambda}{i\hbar}\right)^2 \sum_{\alpha,\alpha'}\left[\int_0^\beta \frac{ds}{\beta}(\beta - s)\right.$$

$$\times\langle \hat{\mathcal{B}}^{(\alpha)}(-i\hbar s)\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[\mathsf{A},\mathcal{S}^{(\alpha)}\mathcal{S}^{(\alpha')}]\mathsf{A}\rangle$$

$$\left.+\int_0^\infty dt'\langle \hat{\mathcal{B}}_K^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[\mathsf{A},\mathcal{S}^{(\alpha)}][\mathsf{A},\mathcal{S}^{(\alpha')}]\rangle\right]$$

$$* [\rho_{NE}(t) * \rho_{eq}^{-1}]^T + O(\lambda^3) \tag{3.25a}$$

$$\sim -i\mathcal{L}_{eff}\rho_{NE}(t) - \left(\frac{\lambda}{i\hbar}\right)^2 \sum_{\alpha,\alpha'}\left[\int_0^\beta \frac{ds}{\beta}(\beta - s)\right.$$

$$\times\langle \hat{\mathcal{B}}^{(\alpha)}(-i\hbar s)\hat{\mathcal{B}}^{(\alpha')}\rangle[\mathcal{S}^{(\alpha)}\mathcal{S}^{(\alpha')},\rho_{NE}(t)]$$

$$\left.+\int_0^\infty dt'\langle \hat{\mathcal{B}}_K^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[\mathsf{A},\mathcal{S}^{(\alpha)}][\mathsf{A},\mathcal{S}^{(\alpha')}]\rangle\right]$$

$$* [\rho_{NE}(t) * \rho_{eq}^{-1}]^T + O(\lambda^3), \tag{3.25b}$$

where T denotes a transpose and where the inverse density matrix is defined by

$$\rho_{eq}(\mathsf{x},\mathsf{x}_1) * \rho_{eq}^{-1}(\mathsf{x}_1,\mathsf{x}') = \delta(\mathsf{x}-\mathsf{x}'). \tag{3.26}$$

In addition, the easily proven relations

$$\langle \mathsf{A}(\mathsf{x}_1,\mathsf{x}_2)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle = \delta(\mathsf{x}_1-\mathsf{x}_4)\rho_{eq}(\mathsf{x}_3,\mathsf{x}_2) \tag{3.27}$$

and

$$\langle \mathsf{A}(\mathsf{x}_1,\mathsf{x}_2)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle^{-1} = \delta(\mathsf{x}_2-\mathsf{x}_3)\rho_{eq}^{-1}(\mathsf{x}_4,\mathsf{x}_1) \tag{3.28}$$

were used in obtaining Eq. (3.25).

The quadratic terms are considerably more complicated and are analyzed in detail in the Appendix. Here only the final result, when the isolated subsystem energy representation is used for the $|x_S\rangle$'s and when there is a separation of time scales [see the discussion before Eq. (3.25a)], is reported—namely,

$$\left(\frac{\lambda}{i\hbar}\right)^2 \sum_{\alpha,\alpha'} \int_0^\infty dt' \langle \hat{\mathcal{B}}^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle \langle \mathsf{x}_5|[[\mathsf{A}(\mathsf{x}_1,\mathsf{x}_2),\mathcal{S}^{(\alpha)}],\mathcal{S}^{(\alpha')}]$$

$$\times|\mathsf{x}_4\rangle e^{\beta\varepsilon_{\mathsf{x}_3}} q\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4}\rho_{NE}(\mathsf{x}_3,\mathsf{x}_5;t)\rho_{NE}(\mathsf{x}_4,\mathsf{x}_3;t), \tag{3.29}$$

which, given that the commutators are each $O(\hbar)$, shows that the quadratic terms are $O(\lambda^2\hbar)$. More generally, the quadratic terms vanish when $\rho_{NE}(t)$ is diagonal in the energy representation—e.g., as it is in equilibrium to leading order in λ. In addition, note that there are several transient quadratic terms that vanish on the τ_B time scale [cf. Eq. (A9)] that have been omitted.

IV. DISCUSSION

Perhaps the most interesting result of this work is the fundamental difference between quantum and classical systems; namely, given the form of the initial distribution, in general, the reduced equations of motion are exactly linear for the classical systems, but are nonlinear for quantum ones. These quantum-mechanical nonlinearities do not seem to arise in the projection operator methods [4–11]. They would arise from the average of the random noise term which is either thrown out (arguing that it would decay on a fast time scale) or vanishes for the special choices of projection operator and initial distribution. To be sure (cf. the Appendix), some of the nonlinear terms are clearly transient (assuming the bath dynamics is fast), but some seem to persist. They are second order in couplings between system and bath and $O(\hbar)$ and in part stem from the nonseparability of the full distribution function (both initially and as time progresses) into bath and system parts. Classically, since everything commutes, this this is not an issue, but is one quantum mechanically.

At first glance this result may appear to be strange from several points of view. For example, there are many examples of classical nonlinear reduced equations of motion (e.g., the classical Boltzmann equation is one), so why do the nonlinearities drop out classically? Of course, the derivations presented here were largely formal, and physical considerations can easily lead to nonlinearities, even classically.

For example, it was shown some time ago [21] that all slow variables must be included in the initial distribution function when choosing the variables that describe the reduced problem. If not, then differences between the real initial distribution function and the form assumed by Eq. (1.5) will not decay. This is a key difference between projection operator identities for equilibrium time correlation functions and a nonequilibrium averages. Here, as is well known, this means that minimally the densities of conserved collective variables should have been included and it is easy to see that that this will result in nonlinear terms in the classical reduced equations of motion (e.g., by using the techniques of Ref. [17]). Nonetheless, to the extent that the bath remains approximately at equilibrium (e.g., when the subsystem is weakly coupled or very dilute), these extra terms will drop out.

In a similar, albeit more trivial, vein, in a dilute gas, to the extent that pair interactions are important it is reasonable that at least a two-particle subspace be considered (so that average properties of the pair potentials arise). Nonlinear equations will be obtained by writing the two-particle reduced distribution function as a product of one-particle ones plus a two-particle variance. Indeed, the classic microscopic derivations of the Boltzmann equation typically start with the BBGKY hierarchy, which is linear, but in which the pair distribution function arises naturally [1]. In any event, while the effects discussed in this and the preceding paragraph can lead to nonlinearities, they will do so for both quantum and classical systems, and are not the origin of the quadratic terms found here.

As was mentioned above, each of the terms in the exact equations of motion—i.e., Eqs. (2.18) (classically) or (3.13) (quantum mechanically)—vanishes separately at equilibrium. Not surprisingly, this is only true to the order of perturbation theory used in the weak-coupling expansion. Nonetheless, this property can be restored by using a $\langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1}$ that still satisfies Eq. (3.8), etc., in the approximate equations of motion.

As was mentioned in the Introduction, earlier works have largely been based on projection operator methods. In this approach, the equations of motion naturally arise as memory equations. Here, no *a priori* assumptions were made about a projection operator, even though they arise naturally in the course of the derivation. Since the derivation was carried out in the time representation, it is not surprising that the projection operator of the form given in Ref. [15] arises, but nonetheless, the real underlying assumptions of the calculation were that a closed phenomenological set of equations of motion for the averages (perhaps with time-dependent coefficients) exists and that it does not depend on the precise details of the initial distribution function, at least for times longer than the bath correlation times. Clearly, it is very unlikely that any real experiment has an initial full distribution corresponding to *any* of the model distributions assumed in the literature, and if the details matter, it is highly unlikely that a general reduced equation of motion exists.

ACKNOWLEDGMENTS

I thank Irwin Oppenheim for useful discussions. A portion of this work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

APPENDIX: THE QUADRATIC TERMS

By noting that $\langle \dot{B}^{\ddagger}(t)\rangle = 0$ and that $\langle \dot{B}_K^{\ddagger}(t)\mathsf{A}\rangle = 0$, it is easy to show that

$$\int_0^1 ds \int_s^1 ds' \langle\langle B^{\ddagger}(t)\mathsf{A}(i\beta\hbar s)\mathsf{A}(i\beta\hbar s')\rangle\rangle = \int_0^\beta \frac{ds}{\beta}\int_s^\beta \frac{ds'}{\beta}\langle B^{\ddagger}(t)\mathsf{A}(i\hbar s)\mathsf{A}(i\hbar s')\rangle. \tag{A1}$$

With this, taking $B=\dot{\mathsf{A}}$, using the invariance of the trace under cyclic permutation of the arguments, writing

$$\mathsf{A}(i\hbar s) = \mathsf{A}(0) + i\hbar\int_0^s ds_1 \dot{\mathsf{A}}(i\hbar s_1),$$

and rearranging the orders of integration, it follows that

$$\int_0^\beta \frac{ds}{\beta}\int_s^\beta \frac{ds'}{\beta}\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}(i\hbar s)\mathsf{A}(i\hbar s')\rangle = \frac{i\hbar}{2\beta^2}\int_0^\beta ds\left(\int_0^{\beta-s} ds'(\beta - s - s')\langle \dot{\mathsf{A}}^{\ddagger}(t - i\hbar s)\times \mathsf{A}\dot{\mathsf{A}}(i\hbar s')\rangle - \int_{-s}^0 ds' s'\langle \dot{\mathsf{A}}^{\ddagger}(t - i\hbar s)\dot{\mathsf{A}}(i\hbar s')\mathsf{A}\rangle\right), \tag{A2}$$

which shows that the quadratic terms are intrinsically quantum mechanical [i.e., $O(\hbar)$] and at least second order in subsystem-bath coupling [cf. Eq. (3.20)]. In order to see the leading-order behavior of this term, Eq. (3.10), for $B=\dot{\mathsf{A}}$, is solved formally for $\mathsf{A}(t)$—i.e.,

$$\mathsf{A}(t) = \mathsf{G}(t;0) * \mathsf{A}(0) + \int_0^t ds\, \mathsf{G}(t;s) * \dot{\mathsf{A}}^{\ddagger}(s), \tag{A3}$$

where

$$\mathsf{G}(t;s) \equiv \langle \mathsf{A}_K(t)\mathsf{A}\rangle * \langle \mathsf{A}_K(s)\mathsf{A}\rangle^{-1} \tag{A4}$$

is a Green's function. This result is used to rewrite Eq. (A1) as

$$\begin{aligned}\int_0^\beta \frac{ds}{\beta}\int_s^\beta \frac{ds'}{\beta}\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}(i\hbar s)\mathsf{A}(i\hbar s')\rangle &= \int_0^\beta \frac{ds}{\beta}\int_s^\beta \frac{ds'}{\beta}\Big(\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}\mathsf{A}\rangle \,{}^{*}_{*}\mathsf{G}^T(i\hbar s';0)\mathsf{G}^T(i\hbar s;0) \\ &+ i\hbar\int_0^s ds''\langle \dot{\mathsf{A}}^{\ddagger}(t)\dot{\mathsf{A}}^{\ddagger}(i\hbar s'')\mathsf{A}\rangle \,{}^{*}_{*}\mathsf{G}^T(i\hbar s';0)\mathsf{G}^T(i\hbar s;i\hbar s'') \\ &+ i\hbar\int_0^{s'} ds''\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}\dot{\mathsf{A}}^{\ddagger}(i\hbar s'')\rangle \,{}^{*}_{*}\mathsf{G}^T(i\hbar s';i\hbar s'') \\ &\times \mathsf{G}^T(i\hbar s';0) - \hbar^2\int_0^s ds''\int_0^{s'} ds'''\langle \dot{\mathsf{A}}^{\ddagger}(t)\dot{\mathsf{A}}^{\ddagger}(i\hbar s''') \\ &\times \dot{\mathsf{A}}^{\ddagger}(i\hbar s'')\rangle \,{}^{*}_{*}\mathsf{G}^T(i\hbar s';i\hbar s'')\mathsf{G}^T(i\hbar s;i\hbar s''')\Big).\end{aligned} \tag{A5}$$

Equation (3.20) implies that the middle two terms on the right are explicitly $O(\lambda^2)$, while the last one is $O(\lambda^3)$ [or $O(\lambda^4)$ if the odd order moments of $\mathcal{B}^{(\alpha)}$ vanish]. The first term is more slightly more complicated.

First, note that

$$\langle \dot{\mathsf{A}}^{\ddagger}(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\mathsf{A}(\mathsf{x}_5,\mathsf{x}_6)\rangle = \delta(\mathsf{x}_3 - \mathsf{x}_6)\times\langle \dot{\mathsf{A}}^{\ddagger}(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_5,\mathsf{x}_4)\rangle \tag{A6}$$

[cf. Eq. (1.4b)]. By using Eq. (3.18) it follows that

$$\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}\rangle \sim -\lambda\int_0^\beta ds\langle \dot{\mathsf{A}}_0^{\ddagger}(t)\mathsf{A}e^{-sH_0}H_{S,B}e^{sH_0}\rangle * [\mathbb{1} - \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \langle \mathsf{A}(t)\mathsf{A}\rangle] + \frac{\lambda}{i\hbar}\int_0^t dt'\langle [\dot{\mathsf{A}}^{\ddagger}(t',t),H_{S,B}]\mathsf{A}(t'-t)\rangle * [\mathbb{1} - \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \langle \mathsf{A}(t)\mathsf{A}\rangle] + \lambda\int_0^\beta \frac{ds}{\beta}\int_0^s ds'\langle [\dot{\mathsf{A}}^{\ddagger}(t - i\hbar s',t),H_{S,B}]\mathsf{A}(i\hbar(s-s'))\rangle * \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \langle \mathsf{A}(t)\mathsf{A}\rangle, + O(\lambda^3), \tag{A7}$$

where $\mathbb{1}$ is the identity operator,

$$B^{\ddagger}(t',t) \equiv B(t') - \langle B_K(t)\mathsf{A}\rangle * \langle \mathsf{A}_K(t)\mathsf{A}\rangle^{-1} * \mathsf{A}(t'), \tag{A8}$$

and where all averages and dynamics are computed for the uncoupled system (i.e., for $\lambda=0$).

When the separable form of $H_{S,B}$ [cf. Eq. (2.22)] is used, it follows that $\dot{\mathsf{A}}^{\ddagger}(t',t)=\dot{\mathsf{A}}_0^{\ddagger}(t')$ [cf. Eq. (3.20)], which, together with Eqs. (A6) and (A7), allows the quadratic terms, Eq. (A5), to be rewritten as

$$\int_0^\beta \frac{ds}{\beta}\int_s^\beta \frac{ds'}{\beta}\langle \dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}(i\hbar s)\mathsf{A}(i\hbar s')\rangle$$
$$\sim \frac{\lambda^2}{i\hbar}\sum_{\alpha,\alpha'}\Bigg\{\Bigg[\Bigg(-\int_0^\beta ds\langle\hat{\mathcal{B}}^{(\alpha)}(t-i\hbar s)\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[\dot{\mathsf{A}},\mathcal{S}^{(\alpha)}](t)\mathsf{A}e^{-sH_0}\mathcal{S}^{(\alpha')}e^{sH_0}\rangle$$
$$+\frac{1}{i\hbar}\int_0^t dt'\langle\hat{\mathcal{B}}^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[[\mathsf{A},\mathcal{S}^{(\alpha)}](t'),\mathcal{S}^{(\alpha')}]\mathsf{A}(t'-t)\rangle\Bigg)*[\mathbb{1}-\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\langle\mathsf{A}(t)\mathsf{A}\rangle]$$
$$+\int_0^\beta\frac{ds}{\beta}\int_0^s ds'\langle\hat{\mathcal{B}}^{(\alpha)}(t-i\hbar s')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle[[\mathsf{A}(t-i\hbar s',t),\mathcal{S}^{(\alpha)}],\mathcal{S}^{(\alpha')}]\mathsf{A}(i\hbar(s-s'))\rangle*\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\langle\mathsf{A}(t)\mathsf{A}\rangle\Bigg]_{\mathsf{x}_1,\mathsf{x}_2;\mathsf{x}_5,\mathsf{x}_4}$$
$$\times\delta(\mathsf{x}_3-\mathsf{x}_6)\overset{*}{*}\int_0^\beta\frac{ds'}{\beta}\mathsf{G}^T(i\hbar s';0)\int_0^s\frac{ds}{\beta}\mathsf{G}^T(i\hbar s;0)$$
$$+\int_0^\beta\frac{ds}{\beta}\int_s^\beta\frac{ds'}{\beta}\Bigg[\Bigg(\int_0^s ds''\langle\hat{\mathcal{B}}^{(\alpha)}(t-i\hbar s'')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle([\mathsf{A},\mathcal{S}^{(\alpha)}])(t)([\mathsf{A},\mathcal{S}^{(\alpha')}])(i\hbar s'')\mathsf{A}\rangle\overset{*}{*}\mathsf{G}^T(i\hbar s';0)\mathsf{G}^T(i\hbar s;i\hbar s'')$$
$$+\int_0^{s'} ds''\langle\hat{\mathcal{B}}^{(\alpha)}(t-i\hbar s'')\hat{\mathcal{B}}^{(\alpha')}\rangle\langle([\mathsf{A},\mathcal{S}^{(\alpha)}])(t)\mathsf{A}([\mathsf{A},\mathcal{S}^{(\alpha')}])(i\hbar s'')\rangle\overset{*}{*}\mathsf{G}^T(i\hbar s';i\hbar s'')\mathsf{G}^T(i\hbar s;0)\Bigg)\Bigg]\Bigg\}+O(\lambda^3). \tag{A9}$$

This expression simplifies where there is a separation of time scales between bath and subsystem degrees of freedom—i.e., when the $\hat{\mathcal{B}}^{(\alpha)}$ correlations decorrelate on a time scale $\tau_B \ll \tau_S$. In this case (assuming the integrations in complex time do not change the correlation times significantly), all but one of the terms in Eq. (A9) will vanish on the τ_B time scale. What remains can be written as

$$\int_0^\beta\frac{ds}{\beta}\int_s^\beta\frac{ds'}{\beta}\langle\dot{\mathsf{A}}^{\ddagger}(t)\mathsf{A}(i\hbar s)\mathsf{A}(i\hbar s')\rangle\sim\left(\frac{\lambda}{i\hbar}\right)^2\sum_{\alpha,\alpha'}\int_0^\infty dt'\langle\hat{\mathcal{B}}^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle(\langle[[\mathsf{A},\mathcal{S}^{(\alpha)}],\mathcal{S}^{(\alpha')}]\mathsf{A}(-t)\rangle*[\mathbb{1}$$
$$-\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\langle\mathsf{A}(t)\mathsf{A}\rangle])_{\mathsf{x}_1,\mathsf{x}_2;\mathsf{x}_5,\mathsf{x}_4}\delta(\mathsf{x}_3-\mathsf{x}_6)\overset{*}{*}\int_0^\beta\frac{ds'}{\beta}\mathsf{G}^T(i\hbar s';0)\int_0^{s'}\frac{ds}{\beta}\mathsf{G}^T(i\hbar s;0). \tag{A10}$$

When Eq. (A10) is used for the quadratic terms in Eq. (3.13), these become

$$\left(\frac{\lambda}{i\hbar}\right)^2\sum_{\alpha,\alpha'}\int_0^\infty dt'\langle\hat{\mathcal{B}}^{(\alpha)}(t')\hat{\mathcal{B}}^{(\alpha')}\rangle\{\langle[[\mathsf{A},\mathcal{S}^{(\alpha)}],\mathcal{S}^{(\alpha')}]\mathsf{A}(-t)\rangle*[\mathbb{1}-\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\langle\mathsf{A}(t)\mathsf{A}\rangle]\}_{\mathsf{x}_1,\mathsf{x}_2;\mathsf{x}_5,\mathsf{x}_4}\overset{*}{*}\int_0^\beta\frac{ds'}{\beta}[\mathsf{G}^T(i\hbar s';0)$$
$$*\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\rho_{NE}(t)]_{\mathsf{x}_5,\mathsf{x}_3}\int_0^{s'}\frac{ds}{\beta}[\mathsf{G}^T(i\hbar s;0)*\langle\mathsf{A}_K(t)\mathsf{A}\rangle^{-1}*\rho_{NE}(t)]_{\mathsf{x}_3,\mathsf{x}_4}, \tag{A11}$$

where the $*$'s imply that all repeated x's are integrated or summed. To proceed, remember that all time correlation functions are for the uncoupled system; as such, it is useful to evaluate Eq. (A11) in the energy representation—i.e., where

$$H_S|\mathsf{x}\rangle=\varepsilon_{\mathsf{x}}|\mathsf{x}\rangle. \tag{A12}$$

In this representation it is easily shown that

$$\langle\mathsf{A}(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle=\delta_{\mathsf{x}_1,\mathsf{x}_4}\delta_{\mathsf{x}_2,\mathsf{x}_3}e^{-i\omega_{\mathsf{x}_1,\mathsf{x}_2}t}\frac{e^{-\beta\varepsilon_{\mathsf{x}_2}}}{q}, \tag{A13a}$$

$$\langle\mathsf{A}_K(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle=\delta_{\mathsf{x}_1,\mathsf{x}_4}\delta_{\mathsf{x}_2,\mathsf{x}_3}e^{-i\omega_{\mathsf{x}_1,\mathsf{x}_2}t}\frac{e^{-\beta\varepsilon_{\mathsf{x}_2}}}{q}\times\left(\frac{1-e^{-\beta\hbar\omega_{\mathsf{x}_1,\mathsf{x}_2}}}{\beta\hbar\omega_{\mathsf{x}_1,\mathsf{x}_2}}\right), \tag{A13b}$$

$$\langle\mathsf{A}_K(\mathsf{x}_1,\mathsf{x}_2;t)\mathsf{A}(\mathsf{x}_3,\mathsf{x}_4)\rangle^{-1}=\delta_{\mathsf{x}_1,\mathsf{x}_4}\delta_{\mathsf{x}_2,\mathsf{x}_3}e^{-i\omega_{\mathsf{x}_1,\mathsf{x}_2}t}e^{\beta\varepsilon_{\mathsf{x}_1}}q\times\left(\frac{\beta\hbar\omega_{\mathsf{x}_2,\mathsf{x}_1}}{1-e^{-\beta\hbar\omega_{\mathsf{x}_2,\mathsf{x}_1}}}\right), \tag{A13c}$$

and

$$\mathsf{G}(t;s)_{\mathsf{x}_1,\mathsf{x}_2;\mathsf{x}_3,\mathsf{x}_4}=\delta_{\mathsf{x}_1,\mathsf{x}_3}\delta_{\mathsf{x}_2,\mathsf{x}_4}e^{-i\omega_{\mathsf{x}_1,\mathsf{x}_2}(t-s)}, \tag{A13d}$$

where $\delta_{i,j}$ is a Kronecker delta (or δ function if the eigenspectrum is continuous), $\omega_{i,j} \equiv (\varepsilon_i - \varepsilon_j)/\hbar$ is the transition frequency between states i and j, and q is the canonical partition function for the isolated subsystem. By using Eqs. (A13a)–(A13d) and (A11) becomes

$$\left(\frac{\lambda}{i\hbar}\right)^2 \sum_{\alpha,\alpha'} \int_0^\infty dt' \langle \hat{\mathcal{B}}^{(\alpha)}(t') \hat{\mathcal{B}}^{(\alpha')} \rangle \langle \mathsf{x}_5 | [[\mathsf{A}(\mathsf{x}_1, \mathsf{x}_2), \mathcal{S}^{(\alpha)}], \mathcal{S}^{(\alpha')}] | \mathsf{x}_4 \rangle e^{\beta \varepsilon_{\mathsf{x}_3}} q$$
$$\times \frac{(e^{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4}} - 1 - \beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4})(\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_3} e^{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4}} - \beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4} e^{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_3}} + \beta\hbar\omega_{\mathsf{x}_3,\mathsf{x}_4})}{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4}(e^{\beta\hbar\omega_{\mathsf{x}_3,\mathsf{x}_4}} - 1)(e^{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_3}} - 1)(e^{\beta\hbar\omega_{\mathsf{x}_5,\mathsf{x}_4}} - 1)} \rho_{NE}(\mathsf{x}_3, \mathsf{x}_5; t) \rho_{NE}(\mathsf{x}_4, \mathsf{x}_3; t), \tag{A14}$$

where repeated indices are summed (or integrated). In the semiclassical limit—i.e., when $\beta\hbar\omega \ll 1$—Eq. (A14) reduces to Eq. (3.29).

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