A quantum stochastic Fokker–Planck theory for adiabatic processes in condensed phases[a)]

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A maximum entropy approach to time-dependent phenomena is employed to construct a quantum stochastic theory for adiabatic processes in condensed phases. This theory is illustrated by considering the relative motion of a two-particle system interacting with a heat bath. We present a fully quantum mechanical phase space master equation, which is new. In the limit where the length of thermal spatial fluctuations along the relative coordinates is much greater than half the wavelength for thermal momentum fluctuations associated with relative motion, our master equation reduces to a simpler form, and the principle of detailed balance emerges. This limit is shown to be equivalent to fulfilling a "thermal Heisenberg uncertainty" relation: $\Delta\bar{p}\Delta\bar{q} >> \hbar/2$. The simpler master equation is utilized in the development of a quantum mechanical nonlinear Fokker–Planck equation. For cases in which correlations involving spatial and momentum fluxes are short ranged, the nonlinear Fokker–Planck equation reduces to the usual linear form, with "collision" and "streaming" terms that contain quantum corrections to all orders in $\hbar$. The relationship between the classical limit of the present theory and Brownian motion theory based on the Chapman–Kolmogorov equation is established.

I. INTRODUCTION

Numerous relaxation processes involving the fragmentation of two-particle systems and/or the collision of two particles in condensed phases have been described in terms of the Fokker–Planck equation,[1] the Smoluchowski equation,[1,2] and the stochastic Liouville equation.[3] These equations treat the relative motion of the two particles classically and characterize this motion in terms of a classical phase space distribution function. This distribution function is also a quantum density operator for a quantum subsystem, e.g., the electron spins, in the stochastic Liouville equation.[3]

Of particular interest is the importance of quantum corrections to the above-mentioned classical descriptions of nuclear motion. We expect quantum corrections to be important when the two-particle system is located in bounded regions of the potential energy surfaces for relative motion and in spatial regions where there is surface crossing. It is the purpose of this paper to present some preliminary results of a quantum stochastic theory that will allow us to introduce these quantum corrections and examine the importance of quantum effects in chemical reactions and motional dynamics in condensed phases.

The present theory is illustrated by considering the relative motion of a two-particle system along a single potential energy surface. The generalization of these results to include nonadiabatic motion will be reported in a companion paper.[4]

The quantum stochastic theory developed in this paper is in the spirit of previous quantum Fokker–Planck theories[5,6] based on the Wigner distribution function.[7,8] However, the present approach does not assume simplifications such as spatially independent distribution functions,[5(a),5(b),6] weak coupling[5(a)] between the relevant particles and bath, and the heavy mass limit.[5,6,9] Unlike other quantum Fokker–Planck theories,[5,6] the "streaming" and "collision" terms in the present work are fully quantum mechanical and not limited to correction terms of order $\hbar^2$.

The present results are based on a maximum entropy approach for treating time dependent phenomena. The approach adopted by us has been referred to as the quantum statistical mechanical (QSM) approach,[10] which has been well described in past applications to radiationless decay processes.[10(b)–10(g)] In the following, we briefly review the fundamental postulates of the QSM approach and give the results for the linear domain ("near thermal equilibrium") with the appropriate modifications.

We construct a quantum phase space master equation, which has not previously been reported. In the limit where the length of thermal spatial fluctuations along the relative coordinates is much greater than half the wavelength for thermal momentum fluctuations for relative motion, our master equation reduces to a simpler form and the principle of detailed balance[11] emerges. This limit is shown to be equivalent to fulfilling a "thermal" Heisenberg uncertainty relation: $\Delta\bar{p}\Delta\bar{q} \gg \hbar/2$.

It is shown that the state-to-state rate constants appearing in the simpler quantum phase space master equation may be evaluated by employing Wigner equivalence methods or by working in the energy representation. Although the quantum phase space representation and Wigner equivalence methods provide a convenient scheme for carrying out our theoretical development and allows us to make direct contact with classical Fokker–Planck theories,[1(b),12] we show that actual computations can be more readily carried out in energy space. The rate constant associated with transitions in quantum phase space is related to processes involving transitions between the energy states for relative motion and the interruption of coherence in energy space.

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The methods adopted by us allow us to go beyond the usual class of linear Fokker–Planck equations. We convert our simpler quantum phase space master equation into a nonlinear Fokker–Planck equation that is consistent with the relaxation of the system to thermal equilibrium. Microscopic expressions for the nonlinear transport coefficients are given. When correlations involving spatial and momentum fluxes are short ranged our nonlinear Fokker–Planck equation reduces to a quantum analog of the usual linear form with quantum corrections to all orders in $\hbar$.

The present theory allows us to examine the fundamental assumptions required to develop classical Brownian motion theory by comparison with the Chapman–Kolmogorov–Langevin scheme,[1(b),12] which is usually used to generate it. In other words, our development "maps" into the Chapman–Kolmogorov–Langevin scheme in such a manner as to delineate the quantum stochastic assumptions inherent in this approach.

In Sec. II, we employ Weyl correspondence[13] to construct quantum phase space number operators that are the quantum analog of the classical density function for a phase point in classical phase space. The transformation between the number operators in energy space and the number operators in quantum phase space is given. Also, we present some theorems concerning Wigner equivalence that will be employed in the theoretical development presented in Secs. III and IV.

The linear domain of QSM theory is employed to construct a quantum phase space master equation in Sec. III. We obtain a simpler form of the quantum phase space master equation with state-to-state rate constants satisfying the principle of detailed balance. The classical limit of this equation is established. In Appendix B, we present quantum correction terms of order $\hbar^2$ to the classical state-to-state rate constants.

Section IV is devoted to the construction of a quantum mechanical nonlinear Fokker–Planck equation. For cases in which correlations involving momentum and spatial fluxes are short ranged, we obtain a linear Fokker–Planck equation with "streaming" and "collision" terms that contain quantum corrections to all orders in $\hbar$. In Appendix C, we present quantum corrections of order $\hbar^2$ to the classical friction tensor.

The relationship between the classical limit of the present theory and classical Brownian motion theory based on the Chapman–Kolmogorov equation[1(b),12] is established in Sec. V.

Finally, we present some concluding remarks in Sec. VI.

II. WEYL CORRESPONDENCE AND WIGNER EQUIVALENCE METHODS

In this section we discuss some pertinent results concerning Weyl correspondence[13] and Wigner equivalence methods.[7,8] First, we construct a quantum phase space number operator that is a quantum analog of the classical density function for a phase point in classical phase space. Then, we present some Wigner equivalence theorems that will be utilized in Secs. III and IV to manipulate correlation functions involving these operators.

A. Quantum phase space number operators

The ensemble average of any observable can be written as[8]

$$\langle \hat{B}(t)\rangle = \mathrm{Tr}\,\hat{B}\hat{\rho}(t) = \int d\Gamma\, \hat{B}^{\omega}(\Gamma)\hat{\rho}^{\omega}(\Gamma, t)\ , \tag{1}$$

where $\hat{B}^{\omega}(\Gamma)$ and $\hat{\rho}^{\omega}(\Gamma, t)$ are the Wigner equivalents of the quantum mechanical operators $\hat{B}$ and $\hat{\rho}(t)$, the time dependent statistical density operator. Here, Γ denotes the phase point specified by $(\mathbf{q}, \mathbf{p})$.

We wish to introduce a quantum phase space number operator $\hat{N}(\Gamma)$ that satisfies the relation

$$\hat{\rho}^{\omega}(\Gamma, t) = \langle \hat{N}(\Gamma, t)\rangle = \mathrm{Tr}\,\hat{\rho}(t)\hat{N}(\Gamma) = \int d\Gamma_D \hat{\rho}^{\omega}(\Gamma_D, t)\hat{N}^{\omega}(\Gamma_D, \Gamma)\ . \tag{2}$$

The last line of Eq. (2) implies that $\hat{N}^{\omega}(\Gamma_D, \Gamma)$ is the classical density function $n_D(\Gamma) = \delta(\Gamma - \Gamma_D)$. For the relative motion of the two-particle system, we write

$$n_D(\Gamma) \equiv \delta(\mathbf{q} - \mathbf{q}_D)\delta(\mathbf{p} - \mathbf{p}_D) = \prod_{i=1}^{3} \delta(q_i - q_{D,i})\delta(p_i - p_{D,i})\ , \tag{3}$$

where $q_{D,i}$ and $p_{D,i}$ are the Cartesian components of the dynamical position and momentum vectors $\mathbf{q}_D$ and $\mathbf{p}_D$ for relative motion. Now, $\hat{N}(\Gamma)$ in Eq. (2) must be the Weyl operator[13] corresponding to the classical density function given by Eq. (3).

According to Weyl's rule,[8,13] we write

$$\hat{N}(\Gamma) = (2\pi\hbar)^{-6}\int d\sigma \int d\tau \times \exp[+i(\sigma\cdot\hat{\mathbf{Q}} + \tau\cdot\hat{\mathbf{P}})/\hbar]\alpha(\sigma, \tau; \Gamma)\ , \tag{4}$$

where

$$\alpha(\sigma, \tau; \Gamma) = \int d\mathbf{q}_D \int d\mathbf{p}_D \times \exp[-i(\sigma\cdot\mathbf{q}_D + \tau\cdot\mathbf{p}_D)/\hbar]n_D(\Gamma) \tag{5}$$

is the Fourier transform of the classical density function. In Eq. (4), $\hat{Q}_i$ and $\hat{P}_i$ correspond to position and momentum operators.

Employing Eqs. (3)–(5), we obtain

$$\hat{N}(\Gamma) = (2\pi\hbar)^{-6}\int d\sigma \int d\tau\, \exp\{+i[\sigma\cdot(\hat{\mathbf{Q}} - \mathbf{q}) + \tau\cdot(\hat{\mathbf{P}} - \mathbf{p})/\hbar]\} = (2\pi\hbar)^{-6}\int d\sigma \int d\tau\, \exp[+i\sigma\cdot(\hat{\mathbf{Q}} - \mathbf{q})/\hbar]\exp[+i\tau\cdot(\hat{\mathbf{P}} - \mathbf{p})/\hbar]\exp(+i\sigma\cdot\tau/2\hbar)\ . \tag{6}$$

We arrived at the latter form by making use of the identity

$$\exp(\hat{A}+\hat{B})=\exp(\hat{A})\exp(\hat{B})\exp(\tfrac{1}{2}[\hat{B},\hat{A}]) , \tag{7}$$

where the operators $\hat{A}$ and $\hat{B}$ commute with the commutator $[\hat{A},\hat{B}]$.

Expanding the last exponential factor in Eq. (6), we write

$$\hat{N}(\Gamma)=(2\pi\hbar)^{-6}\sum_{n=0}^{\infty}\frac{(i/2\hbar)^n}{n!}\int d\sigma\int d\tau(\sigma\cdot\tau)^n\exp[+i\sigma\cdot(\hat{\mathbf{Q}}-\mathbf{q})/\hbar]\exp[+i\tau\cdot(\hat{\mathbf{P}}-\mathbf{p})/\hbar]$$

$$=(2\pi\hbar)^{-6}\sum_{n=0}^{\infty}\frac{1}{n!}\left[-\left(\frac{i\hbar}{2}\right)\nabla_q\cdot\nabla_p\right]^n\int d\sigma\int d\tau\exp[+i\sigma\cdot(\hat{\mathbf{Q}}-\mathbf{q})/\hbar]\exp[+i\tau\cdot(\hat{\mathbf{P}}-\mathbf{p})/\hbar] . \tag{8}$$

Now, we introduce the δ-function *operators*, defined by

$$\delta(\mathbf{q}-\hat{\mathbf{Q}})\equiv(2\pi\hbar)^{-3}\int d\sigma\exp[+i\sigma\cdot(\hat{\mathbf{Q}}-\mathbf{q})/\hbar] \tag{9a}$$

and

$$\delta(\mathbf{p}-\hat{\mathbf{P}})\equiv(2\pi\hbar)^{-3}\int d\tau\exp[+i\tau\cdot(\hat{\mathbf{P}}-\mathbf{p})/\hbar] , \tag{9b}$$

so that $\delta(\mathbf{q}-\hat{\mathbf{Q}})|\mathbf{q}'\rangle=\delta(\mathbf{q}-\mathbf{q}')|\mathbf{q}'\rangle$. Hence, $\delta(\mathbf{q}-\hat{\mathbf{Q}})=|\mathbf{q}\rangle\langle\mathbf{q}|$.

Upon substitution of Eqs. (9a) and (9b) into Eq. (8), we obtain the desired form for the quantum phase space number operator:

$$\hat{N}(\Gamma)=\exp(-i\hbar\nabla_q\cdot\nabla_p/2)\delta(\mathbf{q}-\hat{\mathbf{Q}})\delta(\mathbf{p}-\hat{\mathbf{P}}) \tag{10a}$$

$$=\delta(\mathbf{q}-\hat{\mathbf{Q}})\exp(-i\hbar\overleftarrow{\nabla}_{\hat{Q}}\cdot\overrightarrow{\nabla}_{\hat{P}}/2)\delta(\mathbf{p}-\hat{\mathbf{P}}) , \tag{10b}$$

where $\nabla_{\hat{Q}}$ and $\nabla_{\hat{P}}$ are the vector operators

$$\nabla_{\hat{Q}}=\sum_{i=1}^{3}\mathbf{e}_i\frac{\partial}{\partial\hat{Q}_i} \tag{11a}$$

and

$$\nabla_{\hat{P}}=\sum_{i=1}^{3}\mathbf{e}_i\frac{\partial}{\partial\hat{P}_i} . \tag{11b}$$

In Eq. (10b), the arrows over the ∇ operators indicate the direction of operation. If arrows over these operators are absent, as in Eq. (10a), the direction of operation is to the right. It is readily established that the number operators $\hat{N}(\Gamma)$ satisfy the relations

$$\int d\mathbf{p}\,\hat{N}(\Gamma)=\delta(\mathbf{q}-\hat{\mathbf{Q}}) , \tag{12a}$$

$$\int d\mathbf{q}\,\hat{N}(\Gamma)=\delta(\mathbf{p}-\hat{\mathbf{P}}) , \tag{12b}$$

and

$$\int d\Gamma\,N(\hat{\Gamma})=\hat{I} , \tag{12c}$$

where $\hat{I}$ is the identity operator.

The following equivalent forms of Eq. (10a) are useful:

$$\hat{N}(\Gamma)=\exp(-i\hbar\nabla_q\cdot\nabla_p/2)\delta(\mathbf{q}-\hat{\mathbf{Q}})\delta(\mathbf{p}-\hat{\mathbf{P}}) \tag{13a}$$

$$=\exp(-i\hbar\nabla_q\cdot\nabla_p/2)|\mathbf{q}\rangle\langle\mathbf{q}|\mathbf{p}\rangle\langle\mathbf{p}| \tag{13b}$$

$$=\sum_{i,j}a_{ij}(\Gamma)\hat{N}_{ij} , \tag{13c}$$

where

$$a_{ij}(\Gamma)=\exp(-i\hbar\nabla_q\cdot\nabla_p/2)\phi_i^*(\mathbf{q})\langle\mathbf{q}|\mathbf{p}\rangle\phi_j(\mathbf{p}) . \tag{14}$$

Here, $\phi_i(\mathbf{q})=\langle\mathbf{q}|i\rangle$ $(\phi_j(\mathbf{p})=\langle\mathbf{p}|j\rangle)$ is the wave function in the coordinate (momentum) representation for relative motion in the state $i(j)$.

The form given by Eq. (13c) establishes the transformation between number operators in the energy representation $\{\hat{N}_{ij}=|i\rangle\langle j|\}$ and the quantum phase space number operators. This transformation enables one to convert a theory in terms of $\langle\hat{N}_{ij}(t)\rangle$ to a theory in terms of $\langle\hat{N}(\Gamma,t)\rangle$.

B. Wigner equivalence theorems

Now that we have established the properties of our quantum phase space number operators, we move on to some theorems that will be employed in the remaining sections of this paper. The theorems are as follows[8]:

$$\text{(i)}\quad (\hat{A}\hat{B})^{\omega}=\hat{A}^{\omega}(\Gamma_D)\exp(-i\hbar T_D/2)\hat{B}^{\omega}(\Gamma_D) , \tag{15}$$

where

$$T_D=\overleftarrow{\nabla}_{p_D}\cdot\overrightarrow{\nabla}_{q_D}-\overleftarrow{\nabla}_{q_D}\cdot\overrightarrow{\nabla}_{p_D} , \tag{16}$$

with the arrows over the ∇ operators indicating the direction of operation;

$$\text{(ii)}\quad \mathrm{Tr}\,\hat{A}\hat{B}=(2\pi\hbar)^{-3}\int d\Gamma_D\hat{A}^{\omega}(\Gamma_D)\hat{B}^{\omega}(\Gamma_D) ; \tag{17}$$

and

$$\text{(iii)}\quad \dot{\hat{A}}^{\omega}(t)=i\hat{\mathfrak{L}}^{\omega}\hat{A}^{\omega}(t) ; \tag{18}$$

where

$$i\hat{\mathfrak{L}}^{\omega}=(2/\hbar)\hat{H}^{\omega}(\Gamma_D)\sin(\hbar T_D/2) , \tag{19}$$

with $\hat{\mathfrak{L}}^{\omega}$ and $\hat{H}^{\omega}$ denoting the Wigner equivalent of the Liouville operator $\hat{\mathfrak{L}}$ and the Hamiltonian operator $\hat{H}$, respectively.

III. QUANTUM PHASE SPACE MASTER EQUATION

In this section, the linear domain ("near thermal equilibrium") of the QSM approach to molecular relaxation phenomena[10] is used to construct a quantum phase space master equation for the relative motion of a two-particle system. For simplicity, we take the center of mass motion to be at thermal equilibrium. The relative motion of the two-particle system is confined to a single potential energy surface, which is assumed to possess both bounded and unbounded regions.

A. Review of QSM methodology

Here, we briefly review the basic methodology employed in the QSM approach to molecular relaxation processes.[10] The maximum entropy principle[14] is used to construct a generalized canonical density operator $\hat{\rho}(t)$ of maximum Gibbs entropy subject to constraints at a given time t. The constraints are chosen to be the energy conservation constraint for the system plus surroundings and the relevant time dependent "observables" $\langle \hat{O}_i(t)\rangle = \mathrm{Tr}\,\hat{\rho}(t)\hat{O}_i$.[10(e)–10(g)] The density operator obtained by this prescription describes a microscopic state having maximum Gibbs entropy consistent with the given information at time t.

The maximum entropy density operator is used to compute the "observed" response of the system to displacements from equilibrium. We take the "observed" response to be given by the phenomenological currents $\langle \dot{\hat{O}}_i(t;\Delta t)\rangle = \langle \hat{J}_i(t;\Delta t)\rangle = \mathrm{Tr}\,\hat{\rho}(t)\hat{J}_i(\Delta t)$, where $\hat{J}_i(\Delta t)$ is a coarse-grained current operator defined by $\hat{J}_i(\Delta t) \equiv [\hat{O}_i(\Delta t) - \hat{O}_i(0)]/\Delta t$, with Δt denoting the time resolution of the macroscopic observer. The introduction of coarse-grained current operators corresponds to time smoothing of microscopic currents over the time scale of macroscopic measurements. By averaging the phenomenological current operators $\hat{J}_i(\Delta t)$ over the maximum entropy density operator $\hat{\rho}(t)$, we are making use of the macroscopic information at time t to predict the macroscopic currents $\langle \dot{\hat{O}}_i(t;\Delta t)\rangle$. This method of approach to time dependent processes is equivalent to asserting that the system of interest is Markovian on the time scale of macroscopic measurements.

In our past applications of the above-described methodology,[10(c)–10(g)] the system of interest was characterized in terms of energy space. For this case, the relevant time dependent "observables" are $\{\langle \hat{N}_{ij}(t)\rangle\}$,[10(e)–10(g)] where $\{\hat{N}_{ij} = |i\rangle\langle j|\}$ are number operators for the system in the energy representation. Rather than adopting an energy space description, one could employ a quantum phase space description that provides the same information [see Eq. (13c)]. If the quantum phase space description is adopted, the relevant "observables" are $\{\langle \hat{N}(\Gamma, t)\rangle\}$, where $\hat{N}(\Gamma)$ is the quantum phase space number operator discussed in the previous section. Implicit in this choice of "observables" is the assumption that we are considering the motion of the two-particle system on the coarse-grained time domain $\tau_R \ll \Delta t \ll \tau_s$, where τ_s is the time scale required for the onset of the relaxation of the relevant "observables" and τ_R is the time scale required for the bath to respond to the motion of the two-particle system and re-equilibrate. Assuming this to be the case, it follows that the only change required in passing from our previous work in the energy representation[10(e)–10(g)] to the quantum phase space representation is to replace the number operators $\{\hat{N}_{ij}\}$ with the number operators $\{\hat{N}(\Gamma)\}$. In part B, we present the results for the linear domain, "near thermal equilibrium," obtained by making this replacement.

B. Generalized phase space master equation

In the linear domain of the QSM approach, the equations of motion for the quantum phase space distribution are given by

$$\langle \Delta\dot{\hat{N}}(\Gamma, t;\Delta t)\rangle = \int d\Gamma'\, L(\Gamma,\Gamma')\Lambda(\Gamma', t) \tag{20}$$

and

$$\langle \Delta\hat{N}(\Gamma, t)\rangle = -\int d\Gamma'\, \sigma(\Gamma,\Gamma')\Lambda(\Gamma', t) , \tag{21}$$

where $L(\Gamma,\Gamma')$ is a first-order Onsager coefficient, $\sigma(\Gamma,\Gamma')$ is an element of the covariance matrix σ, and $\{\Lambda(\Gamma', t)\}$ are the thermodynamic driving forces, which provide a measure of the displacements from thermal equilibrium $\{\langle \Delta\hat{N}(\Gamma, t)\rangle = \langle \hat{N}(\Gamma, t)\rangle - \langle \hat{N}(\Gamma, \infty)\rangle\}$. The thermal equilibrium distribution is given by

$$\langle \hat{N}(\Gamma, \infty)\rangle = \mathrm{Tr}\,\hat{\rho}_{EQ}\hat{N}(\Gamma) , \tag{22}$$

where $\hat{\rho}_{EQ}$ is the equilibrium density operator for the system plus bath.

The first-order Onsager coefficient $L(\Gamma,\Gamma')$ is comprised of two parts:

$$L(\Gamma,\Gamma') = L_s(\Gamma,\Gamma') + L_c(\Gamma,\Gamma') , \tag{23}$$

where

$$L_s(\Gamma,\Gamma') = -\beta^{-1}\int_0^\beta d\lambda\, \langle \hat{N}(\Gamma', -i\hbar\lambda)\dot{\hat{N}}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}} \tag{24}$$

is a "streaming" coefficient due to instantaneous interactions and

$$L_c(\Gamma,\Gamma') = \beta^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^\beta d\lambda \times \langle \dot{\hat{N}}(\Gamma', -t-i\hbar\lambda)\dot{\hat{N}}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}} \tag{25}$$

is a "collision" coefficient arising from interactions occurring on the time scale of interest, denoted by Δt. In Eqs. (24) and (25),

$$\dot{\hat{N}}(\Gamma, 0) = i\hat{\mathfrak{L}}\hat{N}(\Gamma, 0) = (i/\hbar)[\hat{H}, \hat{N}(\Gamma, 0)] \tag{26}$$

and

$$\dot{\hat{N}}(\Gamma, -t-i\hbar\lambda) = \exp[-i\hat{\mathfrak{L}}(t+i\hbar\lambda)/\hbar]\dot{\hat{N}}(\Gamma, 0) = \exp[-i\hat{H}(t+i\hbar\lambda)/\hbar] \times \dot{\hat{N}}(\Gamma, 0)\exp[+i\hat{H}(t+i\hbar\lambda)/\hbar] , \tag{27}$$

where $\hat{H}$ is the total Hamiltonian of the system plus bath, $\hat{\mathfrak{L}}$ is the corresponding quantum Liouville operator, and $\hat{N}(\Gamma, 0) = \hat{N}(\Gamma)$.

The elements of the covariance matrix σ are given by

$$\sigma(\Gamma,\Gamma') = \chi(\Gamma,\Gamma') - \langle \hat{N}(\Gamma,\infty)\rangle\langle \hat{N}(\Gamma',\infty)\rangle , \tag{28}$$

where

$$\chi(\Gamma,\Gamma') = \beta^{-1}\int_0^\beta d\lambda\, \langle \hat{N}(\Gamma', -i\hbar\lambda)\hat{N}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}} . \tag{29}$$

The correlation function given by $\chi(\Gamma,\Gamma')$ provides a measure of the correlation between the probability densities at the phase points Γ and Γ' in quantum phase space.

Solving Eq. (21) for $\Lambda(\Gamma', t)$ by inverting the matrix σ, we obtain

$$\langle \Delta\dot{\hat{N}}(\Gamma, t;\Delta t)\rangle = i\int d\Gamma'\omega(\Gamma,\Gamma')\langle \Delta\hat{N}(\Gamma', t)\rangle - \int d\Gamma'\Gamma_R(\Gamma,\Gamma')\langle \Delta\hat{N}(\Gamma', t)\rangle , \tag{30}$$

where the kinetic coefficients $\omega(\Gamma, \Gamma')$ and $\boldsymbol{\Gamma}_R(\Gamma, \Gamma')$ are given by

$$i\omega(\Gamma, \Gamma') = -\int d\Gamma'' \, L_S(\Gamma, \Gamma'')\sigma^{-1}(\Gamma'', \Gamma') \tag{31}$$

and

$$\boldsymbol{\Gamma}_R(\Gamma, \Gamma') = \int d\Gamma'' \, L_C(\Gamma, \Gamma'')\sigma^{-1}(\Gamma'', \Gamma') \ . \tag{32}$$

The elements $\sigma^{-1}(\Gamma, \Gamma')$ of the inverse matrix σ^{-1} are defined by $\int d\Gamma' \sigma^{-1}(\Gamma, \Gamma')\sigma(\Gamma', \Gamma'') = \delta(\Gamma - \Gamma'')$. Hereafter, we shall refer to Eq. (30) as the generalized linear quantum phase space master equation.

It should be noted that Eq. (30) is of the form of a Markovian version of the generalized Langevin equations.[15] The kinetic coefficients defined by ω and $\boldsymbol{\Gamma}_R$ are the quantum statistical mechanical analogs of the frequency and relaxation matrices, respectively. The covariance matrix σ is the analog of the susceptibility matrix.

One might argue against the use of Eqs. (30)–(32) because this system of equations is Markovian. Since the construction of generalized Langevin equations requires one to make an intuitive selection of an appropriate set of slowly relaxing variables, whose relaxation time is much slower than the relaxation time of other variables, a coarse-grained time scale is implicitly built into the theory. In the application of generalized Langevin equations to real problems, one usually introduces a Markovian approximation at some point in the analysis. Rather than introduce Markovian behavior as a mathematical approximation at the later stages of a theoretical development, we assume this at the beginning of our analysis.

C. Simplified phase space master equation

Although the generalized linear phase space master equation given by Eq. (30) possesses a simple form, it is by no means a simple task to determine the kinetic coefficients $\omega(\Gamma, \Gamma')$ and $\boldsymbol{\Gamma}_R(\Gamma, \Gamma')$. A major difficulty arises from the problem of determining the inverse of the covariance matrix σ. For classical systems this problem is trivial. Below, we shall discuss simplifying assumptions that will bring Eq. (30) into a more manageable form.

As a first step towards simplifying Eq. (30), we make use of the identity

$$\hat{N}(\Gamma, -i\hbar\lambda) = \exp(\hbar\lambda\hat{\mathfrak{L}})\hat{N}(\Gamma, 0) \tag{33a}$$

$$= \sum_{n=0}^{\infty}\left[\frac{(-i\hbar\lambda)^n}{n!}\right]\hat{N}^{(n)}(\Gamma, 0) \ , \tag{33b}$$

where

$$\hat{N}^{(n)}(\Gamma, 0) = (i\hat{\mathfrak{L}})^n\hat{N}(\Gamma, 0) \ . \tag{34}$$

The above identity allows us to recast Eq. (29) into the form

$$\chi(\Gamma, \Gamma') = \sum_{n=0}^{\infty}\left[\frac{\beta^n(-i\hbar)^n}{(n+1)!}\right]C_n(\Gamma, \Gamma') \ , \tag{35}$$

where

$$C_n(\Gamma, \Gamma') = \langle \hat{N}^{(n)}(\Gamma', 0)\hat{N}(\Gamma, 0)\rangle_{\hat{\rho}_{\rm EQ}} \ . \tag{36}$$

$C_n(\Gamma, \Gamma')$ provides a measure of the correlation between the nth order current of the probability density at Γ' and the probability density at Γ.

The Wigner equivalent form of Eq. (36) is given by

$$C_n(\Gamma, \Gamma') = \int d\Gamma_D \int d\Gamma_D^B \, \rho_{\rm EQ}^{\omega}(\Gamma_D, \Gamma_D^B) \times \{[(i\hat{\mathfrak{L}}^{\omega})^n n_D(\Gamma')]\exp(-i\hbar T_D/2)n_D(\Gamma)\} \ , \tag{37}$$

where $\rho_{\rm EQ}^{\omega}$ is the Wigner equivalent of the equilibrium density operator for the system plus bath. Here, we have denoted the dynamical variables of the bath by $\boldsymbol{\Gamma}_D^B = (\mathbf{q}_D^B, \mathbf{p}_D^B)$. In writing Eq. (37), we have used theorems (i)–(iii) of Sec. II. It should be noted that $\hat{\mathfrak{L}}^{\omega}$ and T_D, defined by Eqs. (16) and (19), now include the momenta and coordinates of the bath as well as the relative coordinates and momenta of the two-particle system. As stated earlier, the center of mass motion is considered as part of the bath.

Making use of Eq. (37), we rewrite Eq. (35) as follows:

$$\chi(\Gamma, \Gamma') = \left(\frac{\lambda\!\!\!^{-}_M}{\hbar L_M}\right)^6 \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\left[\frac{(-2)^n(i)^m}{(n+1)!\,m!}\right] \times (\lambda\!\!\!^{-}_M/2L_M)^{m+n}\bar{\chi}_{n,m}(\Gamma, \Gamma') \ , \tag{38}$$

where $\bar{\chi}_{n,m}(\Gamma, \Gamma')$ is a dimensionless correlation function given by

$$\bar{\chi}_{n,m}(\Gamma, \Gamma') = \langle \dot{\tilde{n}}_D^{(n)}(\Gamma')\tilde{T}_D^m \tilde{n}_D(\Gamma)\rangle_{\tilde{\rho}_{\rm EQ}^{\omega}} \ , \tag{39}$$

with

$$\dot{\tilde{n}}_D^{(n)}(\Gamma') = (i\tilde{\mathfrak{L}}^{\omega})^n \prod_{i=1}^{3}\delta[\tilde{q}_i - \tilde{q}_{D,i}(0)]\delta[\tilde{p}_i - \tilde{p}_{D,i}(0)] \tag{40}$$

and

$$\tilde{T}_D^m = \left[\tilde{T}_{D,M} + \left(\frac{\lambda\!\!\!^{-}_B}{\lambda\!\!\!^{-}_M}\right)\left(\frac{L_M}{L_B}\right)\tilde{T}_{D,B}\right]^m \ . \tag{41}$$

Here,

$$\tilde{T}_{D,M} = \overleftarrow{\nabla}_{\tilde{p}_D}\cdot\overrightarrow{\nabla}_{\tilde{q}_D} - \overleftarrow{\nabla}_{\tilde{q}_D}\cdot\overrightarrow{\nabla}_{\tilde{p}_D} \tag{42}$$

and

$$\tilde{T}_{D,B} = \sum_{\alpha}[\overleftarrow{\nabla}_{\tilde{p}_D^{\alpha}}\cdot\overrightarrow{\nabla}_{\tilde{q}_D^{\alpha}} - \overleftarrow{\nabla}_{\tilde{q}_D^{\alpha}}\cdot\overrightarrow{\nabla}_{\tilde{p}_D^{\alpha}}] \ , \tag{43}$$

where the summation index α runs over the bath particles. In Eq. (40),

$$i\tilde{\mathfrak{L}}^{\omega} = \left(\frac{2L_M\tilde{H}^{\omega}}{\lambda\!\!\!^{-}_M}\right)\sin\left[\left(\frac{\lambda\!\!\!^{-}_M}{2L_M}\right)\tilde{T}_D\right] \ . \tag{44}$$

In writing Eqs. (38)–(44), we have introduced the length parameters $L_M = [\langle\hat{Q}_i^2(\infty)\rangle - \langle\hat{Q}_i(\infty)\rangle^2]^{1/2}$, the length of thermal spatial fluctuations along the relative coordinates, and $\lambda\!\!\!^{-}_M = \hbar/P_M$, the wavelength for thermal momentum fluctuations for relative motion, where $P_M = [\langle\hat{P}_i^2(\infty)\rangle - \langle\hat{P}_i(\infty)\rangle^2]^{1/2}$. The length parameters $\lambda\!\!\!^{-}_B$ and L_B for the bath are similarly defined. We have scaled the momenta, coordinates, and Hamiltonian as follows: $\tilde{p} = p/P_M$, $\tilde{q} = q/L_M$, and $\tilde{H}^{\omega} = \beta\hat{H}^{\omega}$.

The ratio $(\lambda\!\!\!^{-}_M/2L_M) = (\hbar/2P_ML_M)$ has a close connection with Heisenberg's uncertainty principle. The parameters P_M and L_M are thermal uncertainties $\Delta\bar{p}$ and $\Delta\bar{q}$ in the momenta and coordinates, respectively. Thus, we write $(\lambda_M/2L_M)=(\hbar/2\Delta\bar{p}\Delta\bar{q})$.

At this point, we wish to consider Eq. (38) in the limit $(\lambda_M/2L_M)\ll 1$, which is equivalent to assuming that the thermal uncertainties in the momenta and coordinates satisfy the relation $\Delta\bar{p}\Delta\bar{q}\gg\hbar/2$. (Heisenberg's uncertainty relation requires that $\Delta p\Delta q\geq\hbar/2$.) For $(\lambda_M/2L_M)\ll 1$, the dominant contribution to Eq. (38) is expected to be given by

$$\chi(\Gamma,\Gamma')\simeq\left(\frac{\lambda_M}{\hbar L_M}\right)^6\bar{\chi}_{0,0}(\Gamma,\Gamma') = \langle\hat{N}(\Gamma,\infty)\rangle\delta(\Gamma-\Gamma') . \quad (45)$$

The physical basis for this result is as follows. Quantum phase space is characterized by an internal coherence due to the coupling between the position $\hat{Q}_i$ and momentum $\hat{P}_i$ operators as expressed in Heisenberg's uncertainty relation $i\hbar=[\hat{Q}_i,\hat{P}_i]$. When the length of thermal spatial fluctuations is much greater than half the wavelength for thermal momentum fluctuations, the internal coherence of quantum phase space is "blurred." As a result, the internal coherence of quantum phase space appears to be of infinitesimal length. This is reflected by the presence of the δ function in Eq. (45).

Equation (45) is identical in form to the classical limit of Eq. (38):

$$\lim_{\hbar\to 0}\chi(\Gamma,\Gamma')=\lim_{\hbar\to 0}\left(\frac{\lambda_M}{\hbar L_M}\right)^6\bar{\chi}_{0,0}(\Gamma,\Gamma') = \langle\hat{N}(\Gamma,\infty)\rangle^{CL}\delta(\Gamma-\Gamma') , \quad (46)$$

where $\langle\hat{N}(\Gamma,\infty)\rangle^{CL}$ is the classical limit of $\langle\hat{N}(\Gamma,\infty)\rangle = \hat{\rho}^{\omega}_{EQ}(\Gamma)$, which is given by

$$\langle\hat{N}(\Gamma,\infty)\rangle^{CL}=P^{CL}_{EQ}(\Gamma) = \int d\Gamma^B P^{CL}_{EQ}(\Gamma,\Gamma^B) . \quad (47)$$

Here, $P^{CL}_{EQ}(\Gamma)$ is the classical equilibrium distribution function for the two-particle system and $P^{CL}_{EQ}(\Gamma,\Gamma^B)$ is the joint two-particle system-bath classical equilibrium distribution function:

$$P^{CL}_{EQ}(\Gamma,\Gamma^B)=Z^{-1}\exp\{-\beta[H^{CL}_S(\Gamma) + H^{CL}_B(\Gamma^B)+U^{CL}(\Gamma,\Gamma^B)]\} , \quad (48)$$

where $H^{CL}_S(\Gamma)$ and $H^{CL}_B(\Gamma^B)$ are the classical Hamiltonians for the two-particle system and bath, respectively, $U^{CL}(\Gamma,\Gamma^B)$ is the two-particle system-bath interaction, and Z is the total partition function.

Hereafter, we shall assume $(\lambda_M/2L_M)\ll 1$. Assuming this to be the case, the elements of the matrix χ are approximated by Eq. (45). This approximation leads to the following approximate solution for the thermodynamic driving forces:

$$\Lambda(\Gamma,t)=-\int d\Gamma'\sigma^{-1}(\Gamma,\Gamma')\langle\Delta\hat{N}(\Gamma',t)\rangle \simeq -\langle\Delta\hat{N}(\Gamma,t)\rangle/\langle\hat{N}(\Gamma,\infty)\rangle . \quad (49)$$

Substituting Eq. (49) into Eq. (20), we obtain a simpler form of the phase space master equation:

$$\langle\dot{\hat{N}}(\Gamma,t;\Delta t)\rangle=-[\Gamma_S(\Gamma)+\Gamma_C(\Gamma)]\langle\hat{N}(\Gamma,t)\rangle , \quad (50)$$

where the "streaming" and "collision" operators $\Gamma_S(\Gamma)$ and $\Gamma_C(\Gamma)$, respectively, are defined as follows:

$$-\Gamma_S(\Gamma)\langle\hat{N}(\Gamma,t)\rangle=\int d\Gamma'\,\Omega(\Gamma,\Gamma')\langle\hat{N}(\Gamma',t)\rangle \quad (51)$$

and

$$-\Gamma_C(\Gamma)\langle\hat{N}(\Gamma,t)\rangle=\int d\Gamma' K(\Gamma'\to\Gamma)\langle\hat{N}(\Gamma',t)\rangle , \quad (52)$$

with

$$\Omega(\Gamma,\Gamma')=-L_S(\Gamma,\Gamma')/\langle\hat{N}(\Gamma',\infty)\rangle \quad (53)$$

and

$$K(\Gamma'\to\Gamma)=-L_C(\Gamma,\Gamma')/\langle\hat{N}(\Gamma',\infty)\rangle . \quad (54)$$

The above expression for the streaming operator can be drastically simplified by taking advantage of the assumption $(\lambda_M/2L_M)\ll 1$. Employing Eqs. (24) and (33), we can recast $L_S(\Gamma,\Gamma')$ into the following form:

$$L_S(\Gamma,\Gamma')=\left(\frac{\lambda_M}{\hbar L_M}\right)^6\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\left[\frac{(-2)^n(i)^m}{(n+1)!\,m!}\right] \times\left(\frac{\lambda_M}{2L_M}\right)^{m+n}\bar{\chi}_{n+1,m}(\Gamma,\Gamma') , \quad (55)$$

where the dimensionless correlation function $\bar{\chi}_{n+1,m}$ is given by Eq. (39) with n replaced by $n+1$. Assuming $(\lambda_M/2L_M)\ll 1$, the dominant contribution to Eq. (55) is expected to be given by

$$L_S(\Gamma,\Gamma')\simeq\left(\frac{\lambda_M}{\hbar L_M}\right)^6\bar{\chi}_{1,0}(\Gamma,\Gamma') = -\int d\Gamma_D\int d\Gamma^B_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D,\Gamma^B_D)n_D(\Gamma')[i\hat{\mathcal{L}}^{\omega}n_D(\Gamma)] . \quad (56)$$

This result is identical in form to the classical limit of Eq. (55):

$$\lim_{\hbar\to 0}L_S(\Gamma,\Gamma')=\lim_{\hbar\to 0}\left(\frac{\lambda_M}{\hbar L_M}\right)^6\bar{\chi}_{1,0}(\Gamma,\Gamma') = -\int d\Gamma_D\int d\Gamma^B_D\,P^{CL}_{EQ}(\Gamma_D,\Gamma^B_D)n_D(\Gamma')[i\mathcal{L}^{CL}n_D(\Gamma)], \quad (57)$$

where $\mathcal{L}^{CL}$ is the classical Liouville operator.

In Appendix A, we show that the approximation given by Eq. (56) allows us to write the streaming operator as

$$\Gamma_S(\Gamma)\simeq i\bar{\mathcal{L}}^{\omega}=(2/\hbar)\bar{H}^{CL}\sin(\hbar T_M/2) , \quad (58)$$

where $T_M=\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q-\overleftarrow{\nabla}_q\cdot\overrightarrow{\nabla}_p$. Here, $\bar{H}^{CL}$ is the mean classical Hamiltonian for the two-particle system, i.e., the classical Hamiltonian for the two-particle system plus bath averaged over the quantum equilibrium distribution of the bath.

Introducing Eq. (58), we rewrite Eq. (50) as

$$\langle\dot{\hat{N}}(\Gamma,t;\Delta t)\rangle=-(2/\hbar)\bar{H}^{CL}\sin(\hbar T_M/2)\langle\hat{N}(\Gamma,t)\rangle + \int d\Gamma' K(\Gamma'\to\Gamma)\langle\hat{N}(\Gamma',t)\rangle . \quad (59)$$

This simplified form of the quantum phase space master equation is applicable in the limit $(\lambda_M/2L_M)\ll 1$.

The state-to-state rate constants appearing in Eq. (59) satisfy the principle of detailed balance[11]

$$\langle \hat{N}(\Gamma', \infty)\rangle K(\Gamma' \to \Gamma) = \langle \hat{N}(\tilde{\Gamma}, \infty)\rangle K(\tilde{\Gamma} \to \tilde{\Gamma}') \ , \quad (60)$$

which follows from the reciprocity relation

$$L_C(\Gamma, \Gamma') = L_C(\tilde{\Gamma}', \tilde{\Gamma}) \ , \quad (61)$$

where $\tilde{\Gamma} = (-\mathbf{p}, \mathbf{q})$ denotes the time reversal of $\Gamma = (\mathbf{p}, \mathbf{q})$. This relationship is easily derived from Eq. (25). The kinetic coefficients $\Gamma_R(\Gamma, \Gamma')$ in Eq. (30) do not satisfy the principle of detailed balance. It appears that a quantum version of the principle of detailed balance can be established only in the limit $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$.

The results given by Eqs. (59)–(61) are based on the assumption that half the wavelength $\lambda\!\!\!^{-}_M$ for thermal momentum fluctuations is much shorter than the length L_M for thermal spatial fluctuations. Since this assumption has played a central role in our development, it deserves some additional comment.

To further clarify the physical meaning of the inequality $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$, we first consider a simple one-dimensional ($1D$) harmonic oscillator. For a quantum oscillator of frequency ω, we obtain $\lambda\!\!\!^{-}_M = [\hbar/\mu\omega(\bar{n}+1/2)]$, $L_M = [\hbar(\bar{n}+1/2)/\mu\omega]$, and $(\lambda\!\!\!^{-}_M/2L_M) = [1/(2\bar{n}+1)]$, where $\bar{n}$ is the mean vibrational quantum number at temperature T. It is readily established that $(\lambda\!\!\!^{-}_M/2L_M)$ satisfies the following relations: (a) $\lim_{T\to 0}(\lambda\!\!\!^{-}_M/2L_M) = 1$, (b) $(\lambda\!\!\!^{-}_M/2L_M) \leq 1/2$ for $\ln(\hbar\omega/2kT) \leq 3$ or $(\hbar\omega/kT) \lesssim 1.1$, and (c) $(\lambda\!\!\!^{-}_M/2L_M) = (\hbar\omega/2kT) \ll 1$ for $kT \gg \hbar\omega/2$. [The result for (c) is identical to that for a classical harmonic oscillator.] The result given by (a) follows from the zero temperature result $\lim_{T\to 0}\Delta\bar{p}\Delta\bar{q} = \hbar/2$, so it represents the maximum possible value of $\lambda\!\!\!^{-}_M/2L_M$. The above relationships indicate that our results would be applicable to a $1D$ harmonic oscillator provided kT is greater than or comparable to the energy level spacing $\hbar\omega$. If we wish to provide an adequate description of quantum effects in the bounded region of a potential energy surface for systems in which the inequality $kT \gtrsim \hbar\omega$ is not satisfied, use of the $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$ results may appear to be troublesome.

The condition $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$ should be less restrictive for realistic $3D$ systems with a potential energy minimum as compared to the $1D$ harmonic oscillator. Our reasoning is as follows. Let us consider a simple diatomic molecule. The relative motion of its atoms is given by its one degree of vibrational and two degrees of rotational motion. Under normal experimental conditions there will be significant thermal population of the rotational energy levels in the bounded region of the potential energy surface. In fact, we expect these levels to form an effective continuum on the energy scale kT. As the thermal rotational energy increases, the root mean square linear momentum along the Cartesian coordinates will increase, leading to a decrease in the wavelength $\lambda\!\!\!^{-}_M$ for thermal momentum fluctuations. Also, the centrifugal force due to rotational motion will tend to increase the root mean square separation between the two particles, leading to the increase in L_M. Thus, we expect the ratio $(\lambda\!\!\!^{-}_M/2L_M)$ to decrease as the thermal population of the rotational levels increases. Anharmonicities should also contribute to the reduction of $(\lambda\!\!\!^{-}_M/2L_M)$.

At a given temperature, the combined effect of rotational motion and anharmonicities should lead to a smaller value for $(\lambda\!\!\!^{-}_M/2L_M)$ in $3D$ systems as compared to the $1D$ harmonic oscillator. Hence, we expect the $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$ results to be applicable to cases in which kT may be less than the energy of the first excited "vibrational" state provided there is significant thermal population of the rotational levels. Nonetheless, we do expect the results based on the $(\lambda\!\!\!^{-}_M/2L_M) \ll 1$ assumption to provide a better description of quantum effects in the spatial regions located above the zero point level of a potential energy minimum than for the spatial region located below this level.

D. Comments on the state-to-state rate constants

If one wishes to study the influence of microscopic interactions on the rate coefficients $K(\Gamma' \to \Gamma)$, one needs to cast the formal expression given by Eq. (54) into a more manageable form. We could use Wigner equivalence methods and work in phase space. Alternatively, we could introduce the energy representation and work in energy space.

If Wigner equivalence methods are employed, we must evaluate the following expressions:

$$L_C(\Gamma, \Gamma') = \beta^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma_D^B \Big(\hat{\rho}^{\omega}_{EQ}(\Gamma_D, \Gamma_D^B) \times \exp\left(-\frac{i\hbar T_D}{2}\right)\{\exp[-i\hat{\mathfrak{L}}^{\omega}(t+i\hbar\lambda)](i\hat{\mathfrak{L}}^{\omega})n_D(\Gamma')\}\Big) \times [(i\hat{\mathfrak{L}}^{\omega})n_D(\Gamma)] \quad (62)$$

and

$$\langle \hat{N}(\Gamma', \infty)\rangle = \int d\Gamma_D^B\, \hat{\rho}^{\omega}_{EQ}(\Gamma', \Gamma_D^B) \ . \quad (63)$$

There appears to be no straightforward method for evaluating Eqs. (62) and (63). One method of approach is to expand the Wigner equivalent forms given by Eqs. (62) and (63) in a power series in $\hbar$.[16] This approach will lead to classical results with quantum correction terms involving classical correlation functions. [In Appendix B, we present the classical forms of Eqs. (62) and (63) with quantum corrections of order $\hbar^2$.] Although a power series expansion in $\hbar$ may be justified in the near classical limit, it is unclear whether such an approach will pick out the most important contributions to $L_C(\Gamma, \Gamma')$ and $\langle \hat{N}(\Gamma', \infty)\rangle$. In addition, the expansion of $L_C(\Gamma, \Gamma')$ in terms of $\hbar$ leads to very complicated forms with quantum correction terms that are difficult to evaluate. (See Appendix B.)

If we introduce the energy representation by employing Eq. (13c), the computation of the rate coefficients $K(\Gamma' \to \Gamma)$ requires us to evaluate the following expressions:

$$\langle \hat{N}(\Gamma', \infty)\rangle = \sum_{i,j} a_{ij}(\Gamma')\langle \hat{N}_{ij}(\infty)\rangle \quad (64)$$

and

$$L_C(\Gamma,\Gamma')=\sum_{i,j,k,l} a_{ij}(\Gamma)a_{kl}(\Gamma')L_{ij,kl} , \tag{65}$$

where

$$L_{ij,kl}=\beta^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)] \times\int_0^{\beta} d\lambda\langle\hat{\dot{N}}_{kl}(-t-i\hbar\lambda)\hat{\dot{N}}_{ij}(0)\rangle_{\hat{\rho}_{EQ}} . \tag{66}$$

Here, $L_{ij,kl}$ is a first-order Onsager coefficient in the energy representation. We have discussed Onsager coefficients of this type in past applications of QSM theory to radiationless decay processes.[10(e)–10(g)]

For cases in which quantum effects may be significant, it is expected that computations based on the forms given by Eqs. (64) and (65) will be much easier to carry out than computations employing Eqs. (62) and (63). For a given microscopic model, one could utilize results obtained by using Eqs. (64) and (65) to check the validity of a simple power series expansion of Eqs. (62) and (63) in terms of $\hbar$.

The form given by Eq. (65) provides us with some physical insight into the various contributions to $L_C(\Gamma, \Gamma')$. To clarify this point, we consider the contribution given by

$$a_{ii}(\Gamma)a_{jj}(\Gamma')L_{ii,jj}=-a_{jj}(\Gamma')\langle\hat{N}_{jj}(\infty)\rangle K(j\to i)a_{ii}(\Gamma) , \tag{67}$$

where

$$\langle\hat{N}_{jj}(\infty)\rangle=\mathrm{Tr}\,\hat{\rho}_{EQ}\hat{N}_{jj} \tag{68}$$

is the equilibrium population of the state j and[10(e)–10(g)]

$$K(j\to i)=-L_{ii,jj}/\langle\hat{N}_{jj}(\infty)\rangle \tag{69}$$

is the state-to-state rate constant associated with a transition in energy space from the state j to the state i. The diagonal matrix element $a_{ii}(\Gamma)$ of the phase space number operator $\hat{N}(\Gamma)$ can be interpreted as the probability of finding the two-particle system at the phase point Γ given that the system is in the quantum state i. It follows that the term given by Eq. (67) represents the rate at which the system passes from the phase point Γ' to the phase point Γ via a transition from the thermally populated state j to the state i. In other words, terms of this form describe the influence of energy exchange between the two-particle system and the bath on the propagation of the two-particle system through quantum phase space. Similar terms can be written down to describe the influence of the interruption of coherence in energy space on the passage of the system from Γ' to Γ.

E. Classical phase space master equation

The classical limit of Eq. (59) is obtained by allowing $\hbar\to 0$ in Eqs. (62) and (63). Taking this limit, we obtain the classical form of Eq. (59):

$$\langle\dot{N}(\Gamma,t;\Delta t)\rangle=-\left[\frac{p}{\mu}\cdot\nabla_q-\nabla_q\bar{U}\cdot\nabla_p\right]\langle\hat{N}(\Gamma,t)\rangle +\int d\Gamma' K^{\mathrm{CL}}(\Gamma'\to\Gamma)\langle\hat{N}(\Gamma',t)\rangle , \tag{70}$$

where $\bar{U}$ is the mean potential of interaction between the two particles and $K^{\mathrm{CL}}(\Gamma'\to\Gamma)$ is the classical state-to-state rate constant:

$$K^{\mathrm{CL}}(\Gamma'\to\Gamma)=-L_C^{\mathrm{CL}}(\Gamma,\Gamma')/\langle\hat{N}(\Gamma',\infty)\rangle^{\mathrm{CL}} , \tag{71}$$

with

$$L_C^{\mathrm{CL}}(\Gamma,\Gamma')=\int_0^{\Delta t} dt\,[1-(t/\Delta t)] \times\langle\dot{n}_D(\Gamma',-t)\dot{n}_D(\Gamma,0)\rangle_{P_{EQ}^{CL}} . \tag{72}$$

Here, the averages are over the classical equilibrium distribution function given by Eq. (48) and $\dot{n}_D(\Gamma)$ is the classical current defined by

$$\dot{n}_D(\Gamma)=i\mathfrak{L}^{\mathrm{CL}}n_D(\Gamma) , \tag{73}$$

where $\mathfrak{L}^{\mathrm{CL}}$ is the classical Liouville operator. In Appendix B, we obtain quantum corrections of order $\hbar^2$ to the classical state-to-state rate constant given by Eq. (71).

Phase space master equations of the form given by Eq. (70) have served as a useful starting point for stochastic modeling of chemical reactions in liquids.[17] Usually, some phenomenological form is assumed for the rate constants.

Unlike previous work, the result presented in this paper may be employed to study the influence of microscopic interactions on the state-to-state rate constants $K(\Gamma'\to\Gamma)$ in terms of classical as well as quantum mechanical models. For computations based on quantum mechanical models, the relevant results are given by Eqs. (54) and (64)–(66). Computations involving classical models can be based on Eqs. (71) and (72). For the latter case, the appropriate quantum correction terms are given by Eqs. (B10)–(B18) and (B21) of Appendix B.

IV. FOKKER–PLANCK EQUATIONS

In this section, we employ the linear master equation given by Eq. (59) to construct a nonlinear quantum phase space Fokker–Planck equation.

Consider the collision term given by Eq. (52). It should be noted that $\mathbf{\Gamma}_C$ satisfies the relation

$$\mathbf{\Gamma}_C(\Gamma)\langle\hat{N}(\Gamma,\infty)\rangle=0 , \tag{74}$$

which follows from Eqs. (12c), (25), (52), and (54). This relationship is necessary in order for Eq. (59) to give rise to thermal equilibrium.

Now, we wish to recast the collision operator into the following differential form:

$$\mathbf{\Gamma}_C(\Gamma)=\sum_{k,l=1}^{6}\sum_{s_1,s_2,s_3=0}^{\infty}\sum_{r_1,r_2,r_3=0}^{\infty}\mathbf{\Gamma}_C(k,l,s_1,s_2,s_3,r_1,r_2,r_3;\Gamma) , \tag{75}$$

where each differential operator appearing in the sum satisfies the relation

$$\mathbf{\Gamma}_C(k,l,s_1,s_2,s_3,r_1,r_2,r_3;\Gamma)\langle\hat{N}(\Gamma,\infty)\rangle=0 . \tag{76}$$

Writing the collision operator in this form allows any approximate form for $\mathbf{\Gamma}_C$, obtained by truncating the sum in Eq. (75), to satisfy the important relation given by Eq. (74). This will allow the system to relax to thermal equilibrium.

In order to write Γ_C in the differential form given by Eq. (75), we make use of the relation

$$L_C(\Gamma,\Gamma')=\sum_{k,l=1}^{6}\nabla_{\Gamma_k}\nabla_{\Gamma'_l}M_{\Gamma_k\Gamma'_l}(\Gamma,\Gamma')\ , \tag{77}$$

where

$$M_{\Gamma_k\Gamma'_l}(\Gamma,\Gamma')=\beta^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^{\beta}d\lambda \times\langle\hat{J}_{\Gamma'_l}(\Gamma';-t-i\hbar\lambda)\hat{J}_{\Gamma_k}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}}\ , \tag{78}$$

with the quantum flux operators $\hat{J}_{\Gamma_k}$ defined by

$$\hat{J}_{q_k}(\Gamma,0)\equiv\hat{\hat{Q}}_k\hat{N}(\Gamma,0) \tag{79a}$$

and

$$\hat{J}_{p_k}(\Gamma,0)\equiv\hat{N}(\Gamma,0)\hat{\hat{P}}_k\ . \tag{79b}$$

Here, we have introduced the six-dimensional vector $\nabla_\Gamma=\nabla_p\mathbf{1}_p+\nabla_q\mathbf{1}_q$. Equations (77)–(79) are obtained by making use of Eqs. (9), (10), and (25).

Introducing Eq. (77) into Eq. (54) and performing a moment expansion of $M_{\Gamma_l\Gamma'_j}$, we cast the "collision" term defined by Eq. (52) into the following form:

$$-\Gamma_C(\Gamma)\langle\hat{N}(\Gamma,t)\rangle=+\Gamma_{GFP}(\Gamma)\langle\hat{N}(\Gamma,t)\rangle=\sum_{k,l=1}^{6}\sum_{s_1=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{s_3=0}^{\infty}\sum_{r_1=0}^{\infty}\sum_{r_2=0}^{\infty}\sum_{r_3=0}^{\infty}\frac{(-1)^{(s_1+s_2+s_3+r_1+r_2+r_3)}}{s_1!\,s_2!\,s_3!\,r_1!\,r_2!\,r_3!}$$
$$\times\nabla_{q_1}^{s_1}\nabla_{q_2}^{s_2}\nabla_{q_3}^{s_3}\nabla_{p_1}^{r_1}\nabla_{p_2}^{r_2}\nabla_{p_3}^{r_3}\nabla_{\Gamma_k}\left\{\left[\frac{m'_{\Gamma_k\Gamma_l}(s_1s_2s_3,r_1r_2r_3;\Gamma)}{\hat{N}(\Gamma,\infty)}\right][\nabla_{\Gamma_l}-\nabla_{\Gamma_l}\ln\langle\hat{N}(\Gamma,\infty)\rangle]\langle\hat{N}(\Gamma,t)\rangle\right\}\ , \tag{80}$$

where the moments $m'_{\Gamma_k\Gamma_l}$ are given by

$$m'_{\Gamma_k\Gamma_l}(s_1s_2s_3,r_1r_2r_3;\Gamma)=\int d\Gamma'\,M_{\Gamma_k\Gamma_l}(\Gamma',\Gamma)(q'_1-q_1)^{s_1}(q'_2-q_2)^{s_2}(q'_3-q_3)^{s_3}(p'_1-p_1)^{r_1}(p'_2-p_2)^{r_2}(p'_3-p_3)^{r_3}\ . \tag{81}$$

The explicit expressions for the moments are quite complicated, so we present only the results for $m'_{p_kp_l}$:

$$m'_{p_kp_l}(s_1s_2s_3,r_1r_2r_3;\Gamma)=\beta^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^{\beta}d\lambda\,C_{p_kp_l}(s_1,s_2,s_3,r_1,r_2,r_3;-t-i\hbar\lambda)\ , \tag{82}$$

where

$$C_{p_kp_l}(-t-i\hbar\lambda)=\sum_{k_1=0}^{s_1}\sum_{k_2=0}^{s_2}\sum_{k_3=0}^{s_3}\sum_{l_1=0}^{r_1}\sum_{l_2=0}^{r_2}\sum_{l_3=0}^{r_3}(-1)^{(k_1+k_2+k_3+l_1+l_2+l_3)}\binom{s_1}{k_1}\binom{s_2}{k_2}\binom{s_3}{k_3}\binom{r_1}{l_1}\binom{r_2}{l_2}\binom{r_3}{l_3}q_1^{k_1}q_2^{k_2}q_3^{k_3}p_1^{l_1}p_2^{l_2}p_3^{l_3}$$
$$\times\langle\hat{J}_{p_l}(\Gamma,-t-i\hbar\lambda)[\hat{Q}_1(0)^{(s_1-k_1)}\hat{Q}_3(0)^{(s_2-k_2)}\hat{Q}_3(0)^{(s_3-k_3)}\exp(-i\hbar\overleftarrow{\nabla}_{\hat{Q}}\cdot\overrightarrow{\nabla}_{\hat{P}}/2)$$
$$\times\hat{P}_1(0)^{(r_1-l_1)}\hat{P}_2(0)^{(r_2-l_2)}\hat{P}_3(0)^{(r_3-l_3)}]\hat{\hat{P}}_k(0)\rangle_{\hat{\rho}_{EQ}}\ . \tag{83}$$

We see that the formal structure of the differential operator Γ_{GFP}, defined by Eq. (80), is of the desired form given by Eq. (75). Each differential term in Eq. (80) satisfies Eq. (76). This follows from

$$[\nabla_{\Gamma_l}-\nabla_{\Gamma_l}\ln\langle\hat{N}(\Gamma,\infty)\rangle]\langle\hat{N}(\Gamma,\infty)\rangle=0\ . \tag{84}$$

In view of the above results, we can recast our quantum phase space master equation given by Eq. (59) into the form of a quantum mechanical nonlinear Fokker–Planck equation:

$$\langle\hat{\dot{N}}(\Gamma,t;\Delta t)\rangle=\left[-\frac{2}{\hbar}\overline{H}^{CL}\sin\!\left(\frac{\hbar T_\mu}{2}\right)+\Gamma_{GFP}(\Gamma)\right]\langle\hat{N}(\Gamma,t)\rangle\ , \tag{85}$$

where $\Gamma_{GFP}(\Gamma)$ is the generalized Fokker–Planck (GFP) operator defined by Eq. (80).

If we assume that the correlation between the quantum fluxes described by Eq. (78) is short ranged, the dominant contribution to Eq. (80) will come from the zero-order moments $m'(\{s_i=0,r_j=0\};\Gamma)$ [see Eq. (81)]. For this case, we write

$$\Gamma_{GFP}(\Gamma)\simeq\nabla_\Gamma\cdot\mathbf{m}(\Gamma)\cdot[\nabla_\Gamma-\nabla_\Gamma\ln\langle\hat{N}(\Gamma,\infty)\rangle]\ , \tag{86}$$

where the components of $\mathbf{m}$ are given by

$$m_{\Gamma_k\Gamma_l}(\Gamma)=[\beta\langle\hat{N}(\Gamma,\infty)\rangle]^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^{\beta}d\lambda\langle\hat{J}_{\Gamma_l}(\Gamma,-i\hbar\lambda)\hat{\dot{\Gamma}}_k(t)\rangle_{\hat{\rho}_{EQ}}\ . \tag{87}$$

For the two-particle system, Eq. (86) can be written in the explicit form

$$\Gamma_{GFP}(\Gamma)\simeq\{\nabla_q\cdot\mathbf{m}_{qq}\cdot[\nabla_q-\beta\mathbf{F}_R]+\nabla_p\cdot\mathbf{m}_{pq}\cdot[\nabla_q-\beta\mathbf{F}_R]+\nabla_q\cdot\mathbf{m}_{qp}\cdot[\nabla_p+(\beta/\mu)\mathbf{p}_R]+\nabla_p\cdot\mathbf{m}_{pp}\cdot[\nabla_p+(\beta/\mu)\mathbf{p}_R]\ , \tag{88}$$

where $\mathbf{F}_R$ and $\mathbf{p}_R$ are "renormalized" mean force and momentum vectors, respectively, defined by

$$\mathbf{F}_R=-\beta^{-1}\nabla_q\ln\langle\hat{N}(\Gamma,\infty)\rangle \tag{89}$$

and

$$\mathbf{p}_R=-(\mu/\beta)\nabla_p\ln\langle\hat{N}(\Gamma,\infty)\rangle\ . \tag{90}$$

Now, we consider Eq. (88) in the classical limit. For this case, the "renormalized" force and momentum vectors are the usual classical momentum and mean force vectors **p** and **F**. To obtain the classical components of the tensor **m**, we must recast Eq. (87) into its Wigner equivalent form and allow $\hbar \to 0$.

Employing Eqs. (15)–(19), we write the following Wigner equivalent form of Eq. (87):

$$m_{\Gamma_k\Gamma_l}(\Gamma) = [\beta\langle\hat{N}(\Gamma,\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma_D^{\beta}\left\{\hat{\rho}^{\omega}_{EQ}(\Gamma_D,\Gamma_D^{\beta})\exp\left(-\frac{i\hbar T_D}{2}\right)[\exp(\hbar\lambda\hat{\mathcal{L}}^{\omega})\hat{J}^{\omega}_{\Gamma_l}(\Gamma)]\right\}[\exp(+i\hat{\mathcal{L}}^{\omega}t)\hat{\dot{\Gamma}}^{\omega}_k] \ . \tag{91}$$

Allowing $\hbar \to 0$, we obtain the classical components of **m** (see Appendix C):

$$m_{q_kq_l} = \int_0^{\Delta t} dt\ [1-(t/\Delta t)]\langle \mathring{q}_l(0)\mathring{q}_k(t)\rangle_B \ , \tag{92}$$

$$m_{p_kq_l} = \int_0^{\Delta t} dt[1-(t/\Delta t)]\langle \mathring{q}_l(0)\mathring{p}_k(t)\rangle_B \ , \tag{93}$$

$$m_{q_lp_k} = \int_0^{\Delta t} dt[1-(t/\Delta t)]\langle \mathring{p}_k(0)\mathring{q}_l(t)\rangle_B \ , \tag{94}$$

and

$$m_{p_kp_l} = \int_0^{\Delta t} dt[1-(t/\Delta t)]\langle \mathring{p}_l(0)\mathring{p}_k(t)\rangle_B \ , \tag{95}$$

where the averages denoted by $\langle\ \rangle_B$ are over the classical equilibrium distribution for the bath with the two-particle system held fixed in space.

Recall that Δt is restricted to the time domain $\tau_R \ll \Delta t \ll \tau_s$, where τ_R is the time scale for the bath to respond to the motion of the two-particle system and re-equilibrate and τ_s is the time scale for the onset of thermal equilibrium in the two-particle system. The time scale τ_s can be identified with the time scale for momentum relaxation. For this time domain, we expect the contributions to Eq. (88) due to Eqs. (92)–(94) to be negligible. This is equivalent to assuming that the correlations involving spatial and momentum fluxes as described by $M_{q_kq'_l}$, $M_{q_kp'_l}$, and $M_{p_kq'_l}$ can be neglected. [See Eq. (78). Also, see the discussion in the next section.]

Neglecting Eqs. (92)–(94), the classical limit of Eq. (88) reduces to the usual linear FP operator

$$\mathbf{\Gamma}_{\rm GFP}(\Gamma) \simeq \nabla_p \cdot \mathcal{E}\cdot[\nabla_p + (\beta/\mu)\mathbf{p}] \ , \tag{96}$$

where the classical friction tensor is given by[18]

$$\mathcal{E} = \int_0^{\Delta t} dt[1-(t/\Delta t)]\langle \mathring{\mathbf{p}}(0)\mathring{\mathbf{p}}(t)\rangle_B \tag{97}$$

with **p** denoting the momentum vector for relative motion in the two-particle system.

If we carry the arguments leading to Eq. (96) for the classical case over to the quantum domain, we are led to the following quantum analog of the linear Fokker–Planck equation:

$$\langle\hat{\dot{N}}(\Gamma,t;\Delta t)\rangle = \{-(\mathbf{p}/\mu)\cdot\nabla_q - (2/\hbar)\overline{U}\sin(\hbar T_M/2) + \nabla_p\cdot\mathcal{E}\cdot[\nabla_p + (\beta/\mu)\mathbf{p}_R]\}\langle\hat{N}(\Gamma,t)\rangle \ , \tag{98}$$

where $\overline{U}$ is the mean potential of interaction between the two particles and the components of the quantum friction tensor ϵ are given by

$$\epsilon_{p_kp_l}(\Gamma) = [\beta\langle\hat{N}(\Gamma,\infty)\rangle]^{-1}\int_0^{\Delta t} dt\ [1-(t/\Delta t)]\int_0^{\beta} d\lambda \times\langle\hat{N}(\Gamma,-i\hbar\lambda)\hat{\dot{P}}_l(-i\hbar\lambda)\hat{\dot{P}}_k(t)\rangle_{\hat{\rho}_{EQ}} \ . \tag{99}$$

The above expression for the components of the quantum friction tensor can be evaluated by using Wigner equivalence methods or working in energy space. (See the discussion in Sec. III D on the use of these methods to compute state-to-state rate constants.) In Appendix C, we use Wigner equivalence methods to obtain quantum corrections of order $\hbar^2$ to the classical friction tensor given by Eq. (97).

It should be noted that our derivation of Eq. (98) is based on the following assumptions.

(i) Half the wavelength for thermal momentum fluctuations for relative motion is much shorter than the length of thermal spatial fluctuations along the relative coordinates for the two-particle system.

(ii) We are observing the two-particle system on the coarse-grained time scale $\tau_R \ll \Delta t \ll \tau_S$.

(iii) The correlations involving the spatial and momentum fluxes described by $M_{q_kq'_l}$, $M_{q_kp'_l}$, and $M_{p_kq'_l}$ are negligible in the time domain given in (ii).

(iv) The correlations involving the momentum fluxes described by $M_{p_lp'_k}$ are short ranged for the time scale given in (ii).

Assumptions (ii)–(iv) are very similar to assumptions that are introduced in classical Brownian motion theory based on the Chapman–Kolmogorov–Langevin scheme.[1(b),12] The connection between this scheme and the classical limit of the present work will be established in the next section.

The present work enables us to consider quantum effects on both the "streaming" and "diffusional" aspects of the relative motion of a two-particle system confined to a single potential energy surface. Unlike previous quantum Fokker–Planck theories,[5,6] both the "streaming" and Fokker–Planck terms in Eq. (98) contain quantum corrections to all orders in $\hbar$. In addition, the present results are not based on such simplifications as spatially independent distribution functions,[5(a),5(b),6] weak coupling[5(a)] between the relevant particles and the bath, and the heavy mass limit[5,6,9] of the relevant particles.

Note that our quantum friction tensor, Eq. (99), involves the correlation between the components of the quantum momentum fluxes and the components of the quantum forces. The quantum forces involve both the force between the two particles and the force due to the coupling of the relative motion to the bath particle motion. The ensemble average in the correlation function is over the joint equilibrium density operator for the system plus bath. Also, note that the correlation function is divided by the equilibrium probability density at the phase point Γ. The time development of the operators in Eq. (99) is generated by the full quantum Liouville operator for the system plus bath. In general, our friction tensor will depend on both the relative coordinates and momenta.

For small spatial separations, the force between the two particles is significant, leading to the acceleration (or deceleration) of particle motion. The accelerated motion of the particles will perturb the bath particle motion, resulting in a rearrangement of the local structure of the bath. This rearrangement process plays an important role in the dissipation of the relative momentum of the two particles. In other words, when the spatial separation between the particles is small, the relative motion of the two particles and the bath particle motion will become highly correlated. This correlated motion is reflected in our expression for the quantum friction tensor. [See Eq. (99).]

Expressions for single particle quantum friction tensors have been given in the literature.[5,6,9] The quantum friction tensor obtained by us is for the relative motion of a two-particle system. The following conditions allow us to connect the present results with the previous single particle results.

(i′) The contribution to the time development operator due to the relative motion of the two particles is neglected. (Heavy mass limit.)

(ii′) The force between the two particles is neglected.

(iii′) The quantum momentum flux is replaced with the quantum force.

(iv′) We replace the joint equilibrium density operator with that of the bath for the two-particle system held fixed in space.

(v′) We set $\langle \hat{N}(\Gamma, \infty)\rangle = 1$.

V. RELATIONSHIP TO THE CHAPMAN-KOLMOGOROV SCHEME

Classical Brownian motion theory is usually based on the Chapman–Kolmogorov equation[1(b),12]

$$P(\Gamma, t+\Delta t) = \int d\Gamma' P(\Gamma \mid \Gamma'; \Delta t) P(\Gamma', t) , \tag{100}$$

where $P(\Gamma \mid \Gamma'; \Delta t)$ is the conditional transition probability for making a transition from the phase point Γ' to the phase point Γ during the time interval Δt. It is assumed that the transition probabilities satisfy the principle of detailed balance. The time interval Δt is taken to be short compared to the intervals in which the physical parameters change, but sufficiently long for the system to experience a number of collisions with the bath particles. This assumption is analogous to assumption (ii) for the derivation of the Fokker–Planck equation given by Eq. (98).

If we introduce the rate coefficients $W(\Gamma' \to \Gamma)$ defined by

$$P(\Gamma \mid \Gamma'; \Delta t) \equiv \delta(\Gamma' - \Gamma) + \Delta t W(\Gamma' \to \Gamma) \tag{101}$$

into Eq. (100), we obtain the master equation

$$\dot{P}(\Gamma, t; \Delta t) = \int d\Gamma' W(\Gamma' \to \Gamma) P(\Gamma', t) . \tag{102}$$

There are two basic approaches for converting Eqs. (100) and (102), which are formally equivalent, into a Fokker–Planck equation. One approach relies on the following *ad hoc* factorization of the transition probabilities[1(b),12(a)]:

$$P(\Gamma \mid \Gamma'; \Delta t) = P(\mathbf{q}', \mathbf{p}'; \Delta \mathbf{p}) \delta(\Delta \mathbf{q} - \mathbf{p}' \Delta t/\mu) , \tag{103}$$

where $\Delta \mathbf{p}$ and $\Delta \mathbf{q}$ are the changes in momenta and coordinates during the time interval Δt. Once this assumption is introduced, the left-hand side and right-hand side of Eq. (100) are expanded in a Taylor series. Another approach relies on a multidimensional Kramers–Moyal (KM) expansion[12,19] of Eq. (102). Since the connection between the classical limit of our theory and the latter approach is more obvious, we shall consider this connection first. Once we have established this relationship, we shall comment on the former approach.

A Kramers–Moyal expansion of Eq. (102) leads to the generalized Fokker–Planck equation[12,19]:

$$\dot{P}(\Gamma, t; \Delta t) = \sum_{s_1=0}^{\infty} \cdots \sum_{s_N=0}^{\infty} \left[\frac{(-1)^{(s_1+\cdots+s_N)}}{s_1! \cdots s_N!}\right] \times \nabla_{\Gamma_1}^{s_1} \cdots \nabla_{\Gamma_N}^{s_N} [\mathbf{K}_{\Gamma_1 \cdots \Gamma_N}^{(s_1+\cdots+s_N)}(\Gamma) P(\Gamma, t)] , \tag{104}$$

where $\mathbf{K}_{\Gamma_1 \cdots \Gamma_N}^{(s_1+\cdots+s_N)}$ are the moments of $W(\Gamma \to \Gamma')$:

$$\mathbf{K}_{\Gamma_1 \cdots \Gamma_N}^{(s_1+\cdots+s_N)}(\Gamma) \equiv \int d\Gamma' (\Gamma_1' - \Gamma_1)^{s_1} \cdots (\Gamma_N' - \Gamma_N)^{s_N} W(\Gamma \to \Gamma') , \tag{105}$$

with $\Gamma_1 \cdots \Gamma_N$ denoting the values of the classical variables at the phase point Γ.

If moments higher than second order are neglected, Eq. (104) reduces to the linear Fokker–Planck equation:

$$\dot{P}(\Gamma, t; \Delta t) = -\nabla_\Gamma \cdot [\mathbf{K}^{(1)}(\Gamma) P(\Gamma, t)] + \tfrac{1}{2} \nabla_\Gamma : [\mathbf{K}^{(2)}(\Gamma) P(\Gamma, t)] , \tag{106}$$

where

$$\mathbf{K}_{\Gamma_i}^{(1)} = \int d\Gamma' (\Gamma_i' - \Gamma_i) W(\Gamma \to \Gamma') = \int d\Gamma' (\Gamma_i' - \Gamma_i) \left[\frac{P(\Gamma' \mid \Gamma; \Delta t)}{\Delta t}\right] \tag{107}$$

and

$$\mathbf{K}_{\Gamma_i \Gamma_j}^{(2)} = \int d\Gamma' (\Gamma_i' - \Gamma_i)(\Gamma_j' - \Gamma_j) W(\Gamma \to \Gamma') = \int d\Gamma' (\Gamma_i' - \Gamma_i)(\Gamma_j' - \Gamma_j) \left[\frac{P(\Gamma' \mid \Gamma; \Delta t)}{\Delta t}\right] . \tag{108}$$

At this point, it is usually assumed that the average of the classical variables over the conditional transition probabilities, so-called "stochastic averaging," is equivalent to taking the ensemble average of classical equations of motion over the equilibrium distribution of the bath.[1(b),12] More specifically, Eqs. (107) and (108) are assumed to be of the form

$$\mathbf{K}_{\Gamma_i}^{(1)} = \frac{\langle[\Gamma_i(\Delta t) - \Gamma_i(0)]\rangle_B}{\Delta t} \tag{109}$$

and

$$\mathbf{K}_{\Gamma_i\Gamma_j}^{(2)} = \frac{\langle[\Gamma_i(\Delta t) - \Gamma_i(0)][\Gamma_j(\Delta t) - \Gamma_j(0)]\rangle_B}{\Delta t} , \tag{110}$$

where $\langle\ \rangle_B$ denotes ensemble averaging over the equilibrium distribution of the bath.

To make a connection between our work and the above-described procedure, we introduce the "renormalized" rate coefficients [see Eqs. (50)–(54)]:

$$W(\Gamma' \to \Gamma) \equiv \Omega(\Gamma, \Gamma') + K(\Gamma' \to \Gamma) . \tag{111}$$

Introducing Eq. (111), we can cast the classical limit of our phase space master equation into the form given by Eq. (102). A subsequent Kramers–Moyal expansion of this equation leads to the following expressions for the first and second moments:

$$\mathbf{K}_{\Gamma_i}^{(1)} = [\langle \hat{N}(\Gamma, \infty)\rangle^{\mathrm{CL}}]^{-1}\Big[\langle n_D(\Gamma, 0)\dot{\Gamma}_{D,i}(0)\rangle_{\rho_{\mathrm{EQ}}^{\mathrm{CL}}} - \int_0^{\Delta t} dt\, [1 - (t/\Delta t)]\, \langle \dot{n}_D(\Gamma, 0)\dot{\Gamma}_{D,i}(t)\rangle_{\rho_{\mathrm{EQ}}^{\mathrm{CL}}}\Big] \tag{112}$$

and

$$\mathbf{K}_{\Gamma_i\Gamma_j}^{(2)} = (\langle \hat{N}(\Gamma, \infty)\rangle^{\mathrm{CL}})^{-1}\Big\{\langle n_D(\Gamma, 0)\, [\overline{\Gamma_{D,j}(0)\Gamma_{D,i}(0)}^{\,\boldsymbol{\cdot}} - \Gamma_j\dot{\Gamma}_{D,i}(0) - \Gamma_i\dot{\Gamma}_{D,j}(0)]\rangle_{\rho_{\mathrm{EQ}}^{\mathrm{CL}}} - \int_0^{\Delta t} dt\, [1 - (t/\Delta t)] \times \langle \dot{n}_D(\Gamma, 0)\, [\overline{\Gamma_{D,j}(t)\Gamma_{D,i}(t)}^{\,\boldsymbol{\cdot}} - \Gamma_j\dot{\Gamma}_{D,i}(t) - \Gamma_i\dot{\Gamma}_{D,j}(t)]\rangle_{\rho_{\mathrm{EQ}}^{\mathrm{CL}}}\Big\} , \tag{113}$$

where the average are over the classical joint equilibrium distribution for the system plus bath.

Rearrangement of Eqs. (112) and (113) lead to the moment expressions given by Eqs. (109) and (110). In view of these results, we see that the formal equivalence between "stochastic averaging" and ensemble averaging over the bath follows from the basic methodology adopted by us. This result is a consequence of the averaging of the coarse-grained current operators over the statistical density operator $\hat{\rho}(t)$ for the "near equilibrium" case.

In the application of Eqs. (106), (109), and (110) to the construction of Fokker–Planck equations, one usually introduces Langevin equations[1b,12] to compute the moments and assumes that $\mathbf{K}_{p_iq_j}^{(2)}$ and $\mathbf{K}_{q_iq_j}^{(2)}$ can be neglected. The *ad hoc* factorization of the transition probabilities, as expressed by Eq. (103), appears to be justified provided we neglect $\mathbf{K}_{p_iq_j}^{(2)}$ and $\mathbf{K}_{q_iq_j}^{(2)}$. Within the framework of the Chapman–Kolmogorov–Langevin scheme, the neglect of these terms is valid for Δt much shorter than the momentum relaxation time. This assumption is similar to the assumption made in passing from Eq. (88) to Eq. (96).

We have shown that the basic theoretical framework for classical Brownian motion theory is derivable from the classical limit of the results presented in Sec. III. Both approaches assume Markovian behavior on the time scale of macroscopic measurements. Nonetheless, there are essential differences between the approach adopted by us and the Chapman–Kolmogorov–Langevin scheme. In contrast to the latter approach, we have provided quantum and classical expressions for the rate constants associated with transitions in phase space. These rate constants may, in principle, be calculated in terms of microscopic interactions. In addition, we have introduced an alternative expansion for the rate constants so that any approximate form of the generalizee Fokker–Planck operator will lead to thermal equilibrium. Truncation of the Kramers–Moyal expansion in Eq. (104) does not guarantee this important requirement. The Chapman–Kolmogorov–Langevin scheme overcomes this deficiency by the introduction of stochastic Langevin dynamics.

VI. CONCLUDING REMARKS

We have constructed a quantum phase space theory for adiabatic relaxation processes based on the QSM approach. The theory was illustrated by considering the relative motion of a two-particle system interacting with a heat bath.

A fully quantum mechanical phase space master equation [Eq. (30)] was presented. In the limit where half the wavelength for thermal momentum fluctuations for relative motion is much shorter than the length of thermal spatial fluctuations along the relative coordinates, we found that our master equation reduces to a simpler form [Eq. (59)] with state-to-state rate constants satisfying the principle of detailed balance. (This limit is equivalent to fulfilling a "thermal Heisenberg uncertainty relation": $\Delta\bar{p}\,\Delta\bar{q} \gg \hbar/2$.) It was shown that the rate constants could be evaluated by employing Wigner equivalence methods or by working in the energy representation. The classical limit of our phase space master equation [Eq. (70)] was established. The resulting form is similar to that used in stochastic modeling of chemical reactions.[17]

We employed the simpler form of the phase space master equation [Eq. (59)] to construct a quantum nonlinear Fokker–Planck equation [Eq. (85)]. Microscopic expressions [Eqs. (81)–(83)] were given for the nonlinear transport coefficients. It was shown that any truncated form of our nonlinear Fokker–Planck equation leads to thermal equilibrium.

For the case in which correlations involving spatial and momentum fluxes are short ranged, the nonlinear Fokker–Planck equation reduces to a quantum analog [Eq. (98)] of the usual linear form. Unlike previously reported results,[5,6,9] both the "collision" and "streaming" terms of the linear Fokker–Planck equation contain quantum corrections to all orders in $\hbar$. The quantum friction tensor [Eq. (99)] obtained by us was shown to contain important information concerning the correlated motion between the bath particles and the two-particle system when the two particles are in close proximity.

In the future, we plan to examine these correlations in order to develop a more complete picture of the role of bath particle motion in reactive events.

The relationship between the classical version of our theory and Brownian motion theory based on the Chapman–Kolmogorov–Langevin scheme[1b,12] was established. It was shown that the basic theoretical structure of the latter theory was derivable from the classical limit of the theory presented in this paper.

In summary, we have presented a quantum stochastic phase space theory for adiabatic processes involving two particles interacting with a heat bath. The present results provide us with a formal theoretical framework that will enable us to investigate the role of quantum effects in adiabatic chemical reactions as well as motional dynamics in condensed phases.

APPENDIX A: EVALUATION OF QUANTUM STREAMING TERM

Here, we consider the evaluation of the quantum streaming term [see Eq. (51) of the text]:

$$-\Gamma_s(\Gamma)\langle\hat{N}(\Gamma,t)\rangle = \int d\Gamma'\,\Omega(\Gamma,\Gamma')\langle\hat{N}(\Gamma',t)\rangle = -\int d\Gamma'\left[\frac{L_s(\Gamma,\Gamma')}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\langle\hat{N}(\Gamma',t)\rangle\ , \tag{A1}$$

where $L_s(\Gamma,\Gamma')$ is defined by Eq. (24).

Introducing the approximate form of $L_s(\Gamma,\Gamma')$ given by Eq. (56), we write Eq. (A1) as

$$\begin{aligned}
-\Gamma_s(\Gamma)\langle\hat{N}(\Gamma,t)\rangle &\simeq \int d\Gamma'\int d\Gamma_D\int d\Gamma_D^B\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D,\Gamma_D^B)\,n_D(\Gamma')\,[i\hat{\mathcal{L}}^{\omega}\,n_D(\Gamma)]\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\\
&= \int d\Gamma'\int d\Gamma_D\int d\Gamma_D^B\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D,\Gamma_D^B)\,n_D(\Gamma')\left[\frac{2}{\hbar}\,H^{\mathrm{CL}}(\Gamma_D,\Gamma_D^B)\sin\left(\frac{\hbar T_D}{2}\right)n_D(\Gamma)\right]\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\\
&= \int d\Gamma'\int d\Gamma_D\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D)\,n_D(\Gamma')\left[\left(\frac{2}{\hbar}\right)\bar{H}^{\mathrm{CL}}(\Gamma_D)\sin\left(\frac{\hbar T_D}{2}\right)n_D(\Gamma)\right]\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\ ,
\end{aligned} \tag{A2}$$

where

$$\bar{H}^{\mathrm{CL}}(\Gamma_D) \equiv \int d\Gamma_D^B\,\hat{\rho}^{\omega;B}_{\mathrm{EQ}}(\Gamma_D^B\,|\,\Gamma_D)\,H(\Gamma_D,\Gamma_D^B) \tag{A3}$$

is the mean classical Hamiltonian of the two-particle system.

Here, $\hat{\rho}^{\omega;B}_{\mathrm{EQ}}(\Gamma_D^B\,|\,\Gamma_D)$ is the conditional Wigner equilibrium distribution for the bath, which has been introduced by making the definition

$$\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D)\,\hat{\rho}^{\omega;B}_{\mathrm{EQ}}(\Gamma_D^B\,|\,\Gamma_D) \equiv \hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D,\Gamma_D^B)\ , \tag{A4}$$

where

$$\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D) \equiv \int d\Gamma_D^B\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D,\Gamma_D^B)\ . \tag{A5}$$

Since $n_D(\Gamma)$ is constructed from δ functions involving $(\mathbf{q}-\mathbf{q}_D)$ and $(\mathbf{p}-\mathbf{p}_D)$, we may replace the differential operators $\vec{\nabla}_{q_D}$ and $\vec{\nabla}_{p_D}$ acting on $n_D(\Gamma)$ in Eq. (A2) by $\vec{\nabla}_q$ and $\vec{\nabla}_p$ at the same time replacing the dynamical variables $\mathbf{q}_D$ and $\mathbf{p}_D$ involved in the derivatives of $\bar{H}^{\mathrm{CL}}$ by the parameters $\mathbf{q}$ and $\mathbf{p}$. Hence, we rewrite the last line of Eq. (A2) as follows:

$$\begin{aligned}
-\Gamma_s(\Gamma)\langle\hat{N}(\Gamma,t)\rangle &= -\int d\Gamma'\int d\Gamma_D\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D)\,n_D(\Gamma')\left[\left(\frac{2}{\hbar}\right)\bar{H}^{\mathrm{CL}}(\Gamma)\sin\left(\frac{\hbar T_M}{2}\right)n_D(\Gamma)\right]\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\\
&= -\left(\frac{2}{\hbar}\right)\bar{H}^{\mathrm{CL}}(\Gamma)\sin\left(\frac{\hbar T_M}{2}\right)\left\{\int d\Gamma'\int d\Gamma_D\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D)\,n_D(\Gamma')\,n_D(\Gamma)\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle N(\Gamma',\infty)\rangle}\right]\right\}\\
&= -\left(\frac{2}{\hbar}\right)\bar{H}^{\mathrm{CL}}(\Gamma)\sin\left(\frac{\hbar T_M}{2}\right)\left\{\int d\Gamma'\,\langle\hat{N}(\Gamma',\infty)\rangle\,\delta(\Gamma-\Gamma')\left[\frac{\langle\hat{N}(\Gamma',t)\rangle}{\langle\hat{N}(\Gamma',\infty)\rangle}\right]\right\}\ ,
\end{aligned} \tag{A6}$$

where $T_M = \overleftarrow{\nabla}_p\cdot\vec{\nabla}_q - \overleftarrow{\nabla}_q\cdot\vec{\nabla}_p$.

Performing the integration in the last line of Eq. (A6), we obtain the result given by Eq. (58) of the text.

APPENDIX B: QUANTUM CORRECTIONS TO THE RATE CONSTANTS

Here, we obtain quantum corrections to the classical state-to-state rate constants given by Eq. (71) of the text. This will be accomplished by using the Wigner equivalent form of Eq. (54), which is given by Eqs. (62) and (63). We shall take the bath to be a classical system and consider only quantum corrections due to the relative motion of the two-particle system and the coupling of this system to the bath. These corrections will be limited to terms of order $\hbar^2$.

First, we consider the lowest order quantum corrections to the classical equilibrium distribution $P^{\mathrm{CL}}_{\mathrm{EQ}}(\Gamma_D,\Gamma_D^B)$, [see Eq. (48)]. To obtain these corrections, it is necessary to determine the Wigner equivalent of the equilibrium density operator $\hat{\rho}^{\omega}_{EQ}(\Gamma_D, \Gamma^B_D)$, which is given by the normalized solution of the following equation[7b,8]:

$$\frac{\partial \hat{\Omega}^{\omega}(\beta)}{\partial \beta} = -\hat{H}^{\omega} \cos\left(\frac{\hbar T_D}{2}\right) \hat{\Omega}^{\omega}(\beta) , \tag{B1}$$

where $\hat{H}^{\omega} = H^{CL}$ and $\hat{\Omega}^{\omega}(\beta)$ is the Wigner equivalent of the exponential operator $\exp(-\beta \hat{H})$. Expanding the right-hand side of Eq. (B1) to second order in $\hbar$, we obtain

$$\frac{\partial \hat{\Omega}^{\omega}(\beta)}{\partial \beta} = -\left[H^{CL} - \left(\frac{\hbar^2}{8}\right) H^{CL}\, T_D^2\right] \hat{\Omega}^{\omega}(\beta) . \tag{B2}$$

Treating the quantum correction term as a small perturbation, we obtain

$$\Omega^{\omega}(\beta) \simeq \exp(-\beta H^{CL}) \left[1 + \tfrac{1}{8}\hbar^2 \chi(\Gamma_D, \Gamma^B_D)\right] , \tag{B3}$$

where

$$\chi(\Gamma_D, \Gamma^B_D) = \left[-\left(\frac{\beta^2}{\mu}\right)\nabla^2_{q_D} H^{CL} + \left(\frac{\beta^3}{3\mu}\right)(\vec{\nabla}_{q_D} H^{CL} \cdot \vec{\nabla}_{q_D} H^{CL}) + \left(\frac{\beta^3}{3\mu^2}\right)\vec{\nabla}^{(2)}_{q_D} H^{CL} \cdot \vec{p}^{(2)}_D\right] . \tag{B4}$$

Normalizing Eq. (B3), we find the second-order Wigner equivalent of the equilibrium density operator:

$$\hat{\rho}^{\omega}_{EQ}(\Gamma_D, \Gamma^B_D) = P^{CL}_{EQ}(\Gamma_D, \Gamma^B_D)\{[1 + \tfrac{1}{8}\hbar^2 \chi(\Gamma_D, \Gamma^B_D)]/[1 + \tfrac{1}{8}\hbar^2 \langle \chi(\Gamma_D, \Gamma^B_D)\rangle_{S,B}]\} \tag{B5}$$

where the brackets $\langle\ \rangle_{S,B}$ indicate the average of Eq. (B4) over the classical equilibrium distribution function $P^{CL}_{EQ}(\Gamma_D, \Gamma^B_D)$ for the two-particle system plus bath.

It follows from Eq. (B5) that the equilibrium distribution function for the two-particle system to second order in $\hbar$ is given by [see Eq. (63)]:

$$\langle \hat{N}(\Gamma', \infty)\rangle = \int d\Gamma^B_D\, \hat{\rho}^{\omega}_{EQ}(\Gamma', \Gamma^B_D) = \int d\Gamma^B_D\, P^{CL}_{EQ}(\Gamma', \Gamma^B_D)\{[1 + \tfrac{1}{8}\hbar^2 \chi(\Gamma', \Gamma^B_D)]/[1 + \tfrac{1}{8}\hbar^2 \langle \chi(\Gamma', \Gamma^B_D)\rangle_{S,B}]\} . \tag{B6}$$

Treating the bath classically, the Wigner equivalent of the Liouville operator to second order in $\hbar$ is written [see Eq. (19)]

$$+i\hat{\mathcal{L}}^{\omega} \simeq i\mathcal{L}^{CL} - \left(\frac{\hbar^2}{24}\right) H^{CL}\, T_D^3 = i\mathcal{L}^{CL} + \left(\frac{\hbar^2}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D} , \tag{B7}$$

where $\mathcal{L}^{CL}$ is the classical Liouville operator for the two-particle system plus bath.

Employing Eqs. (B5), (B7), and (62), we obtain the following expression for the "collision" Onsager coefficient:

$$\begin{aligned} L_c(\Gamma, \Gamma') = \beta^{-1}\int_0^{\Delta t} dt\,[1 - (t/\Delta t)] \int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma^B_D \Bigg[\Bigg\{\Bigg(P^{CL}_{EQ}(\Gamma_D, \Gamma^B_D)\,[1 + \tfrac{1}{8}\hbar^2 \chi(\Gamma_D, \Gamma^B_D)]/[1 + \tfrac{1}{8}\hbar^2 \langle \chi(\Gamma_D, \Gamma^B_D)\rangle_{S,B}]\Bigg)\Bigg\} \\ \times \exp\left(-\frac{i\hbar T_D}{2}\right)\Bigg(\exp\left\{-i\left[\mathcal{L}^{CL} - \left(\frac{i\hbar^2}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\right](t + i\hbar\lambda)\right\}\left\{i\left[\mathcal{L}^{CL} - \left(\frac{i\hbar^2}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\right] n_D(\Gamma')\right\}\Bigg)\Bigg] \\ \times \left\{i\left[\mathcal{L}^{CL} - \left(\frac{i\hbar^2}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\right] n_D(\Gamma)\right\} . \end{aligned} \tag{B8}$$

Treating the terms of order $\hbar$ and higher as small perturbations, we approximate Eq. (B8) as

$$\begin{aligned} L_c(\Gamma, \Gamma') = \beta^{-1}\int_0^{\Delta t} dt\,[1 - (t/\Delta t)] \int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma^B_D \left[\{P^{CL}_{EQ}(\Gamma_D, \Gamma^B_D)\,[1 + \tfrac{1}{8}\hbar^2 \Delta\chi(\Gamma_D, \Gamma^B_D)]\}\right]\left[1 - \frac{i\hbar T_D}{2} - \frac{\hbar^2 T_D^2}{8}\right] \\ \times\Bigg(\Bigg[1 + \lambda\hbar\mathcal{L}^{CL} - \lambda\left(\frac{i\hbar^3}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\Bigg]\Bigg[\exp(-i\mathcal{L}^{CL} t) - \left(\frac{\hbar^2}{24}\right)\exp(-i\mathcal{L}^{CL} t)\int_0^t ds\, \exp(+i\mathcal{L}^{CL} s) \\ \times \vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D} \exp(-i\mathcal{L}^{CL}_s)\Bigg]\left\{i\left[\mathcal{L}^{CL} - \left(\frac{i\hbar^2}{24}\right)\vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\right] n_D(\Gamma')\right\}\Bigg)\Bigg]\left\{i\left[\mathcal{L}^{CL}\left(-\frac{i\hbar^2}{24}\right) \quad \vec{\nabla}^{(3)}_{q_D} H^{CL} \cdot \vec{\nabla}^{(3)}_{p_D}\right] n_D(\Gamma)\right\} , \end{aligned} \tag{B9}$$

where $\Delta\chi(\Gamma_D, \Gamma^B_D) = \chi(\Gamma_D, \Gamma^B_D) - \langle \chi(\Gamma_D, \Gamma^B_D)\rangle_{S,B}$.

Neglecting terms of higher order than $\hbar^2$, we rewrite Eq. (B9) in the following form:

$$L_c(\Gamma, \Gamma') = \int_0^{\Delta t} dt\,[1 - (t/\Delta t)]\, C(\Gamma, \Gamma') , \tag{B10}$$

where

$$C(\Gamma, \Gamma') = \sum_{I=1}^{7} C^{(I)}(\Gamma, \Gamma') , \tag{B11}$$

with

$$C^{(1)}(\Gamma,\Gamma')=\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma,\Gamma_D^B)\{\exp(-i\mathcal{L}^{CL}t)[i\mathcal{L}^{CL}n_D(\Gamma')]\}[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B12}$$

$$C^{(2)}(\Gamma,\Gamma')=\left(\frac{\hbar^2}{8}\right)\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,\Delta\chi(\Gamma_D,\Gamma_D^B)\{\exp(-i\mathcal{L}^{CL}t)[i\mathcal{L}^{CL}n_D(\Gamma')]\}[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B13}$$

$$C^{(3)}(\Gamma,\Gamma')=-\left(\frac{\hbar^2}{8}\right)\int d\Gamma_D\int d\Gamma_D^B\,(P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,T_D^2\{\exp(-i\mathcal{L}^{CL}t)[i\mathcal{L}^{CL}n_D(\Gamma')]\})[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B14}$$

$$C^{(4)}(\Gamma,\Gamma')=-\left(\frac{i\beta\hbar^2}{4}\right)\int d\Gamma_D\int d\Gamma_D^B\,(P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,T_D\{\exp(-i\mathcal{L}^{CL}t)[i\mathcal{L}^{CL}n_D(\Gamma')]\})[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B15}$$

$$C^{(5)}(\Gamma,\Gamma')=-\left(\frac{\hbar^2}{24}\right)\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\Bigg\{\Bigg[\exp(-i\mathcal{L}^{CL}t)$$
$$\times\int_0^t ds\,\exp(+i\mathcal{L}^{CL}s)\,\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}\exp(-i\mathcal{L}^{CL}s)\Bigg][i\mathcal{L}^{CL^2}n_D(\Gamma')]\Bigg\}[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B16}$$

$$C^{(6)}(\Gamma,\Gamma')=+\left(\frac{\hbar^2}{24}\right)\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\{\exp(-i\mathcal{L}^{CL}t)[\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}n_D(\Gamma')]\}[i\mathcal{L}^{CL}n_D(\Gamma)]\,, \tag{B17}$$

and

$$C^{(7)}(\Gamma,\Gamma')=+\left(\frac{\hbar^2}{24}\right)\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\{\exp(-i\mathcal{L}^{CL}t)[i\mathcal{L}^{CL}n_D(\Gamma')]\}[\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}n_D(\Gamma)]\,. \tag{B18}$$

In writing Eq. (B10) we have made use of the identity

$$\int_0^\beta d\lambda\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\left[-\left(\frac{i\hbar}{2}\right)T_D+\hbar\lambda\mathcal{L}^{CL}\right]A=\int_0^\beta d\lambda\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\left[-\left(\frac{\hbar\beta}{2}\right)\mathcal{L}^{CL}+\hbar\lambda\mathcal{L}^{CL}\right]A=0\,. \tag{B19}$$

Hence, the terms of order $\hbar$ vanish in Eq. (B9).

From Eq. (B6) we obtain the following second-order expression for the equilibrium distribution of the two-particle system:

$$\langle\hat{N}(\Gamma',\infty)\rangle\simeq\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma',\Gamma_D^B)[1+\tfrac{1}{8}\hbar^2\Delta\chi(\Gamma',\Gamma_D^B)]=\langle\hat{N}(\Gamma',\infty)\rangle^{CL}[1+\tfrac{1}{8}\hbar^2\langle\Delta\chi(\Gamma',\Gamma_D^B)\rangle_B]\,, \tag{B20}$$

where $\langle\hat{N}(\Gamma',\infty)\rangle^{CL}$ is the classical equilibrium distribution for the two-particle system [see Eq. (47).]

Neglecting terms of order $\hbar^2$, we obtain from Eqs. (B10), (B12), (B20), and Eq. (54) the classical rate constant given by Eq. (71). Quantum corrections of order $\hbar^2$ to the classical rate constants are obtained by using the relation

$$K^{QC}(\Gamma'\to\Gamma)=\tfrac{1}{8}\hbar^2\langle\Delta\chi(\Gamma',\Gamma_D^B)\rangle\int_0^{\Delta t}dt[1-(t/\Delta t)]\,\frac{C^{(1)}(\Gamma,\Gamma')}{\langle\hat{N}(\Gamma',\infty)\rangle^{CL}}-\sum_{I=2}^{7}\int_0^{\Delta t}dt[1-(t/\Delta t)]\left[\frac{C^{(I)}(\Gamma,\Gamma')}{\langle\hat{N}(\Gamma',\infty)\rangle^{CL}}\right]\,, \tag{B21}$$

where $[C^{(I)}(\Gamma,\Gamma'),\ I=2,\ldots,7]$ are given by Eqs. (B13)–(B18). In writing Eq. (B21), we have made use of Eqs. (54), (B10), and (B20), and the approximation

$$\langle\hat{N}(\Gamma',\infty)\rangle^{-1}\simeq[\langle\hat{N}(\Gamma',\infty)\rangle^{CL}(1+\tfrac{1}{8}\hbar^2\langle\Delta\chi(\Gamma',\Gamma_D^B)\rangle_B)]^{-1}\simeq\langle\hat{N}(\Gamma',\infty)\rangle^{CL^{-1}}[1-\tfrac{1}{8}\hbar^2\langle\Delta\chi(\Gamma',\Gamma_D^B)\rangle_B]\,. \tag{B22}$$

APPENDIX C: QUANTUM CORRECTIONS TO THE FRICTION TENSOR

Here, we obtain quantum corrections to the classical friction coefficient given by Eq. (97) of the text. The method adopted here is very similar to that employed in Appendix B. Again, we shall treat the bath as a classical system and consider only quantum correction terms due to the relative motion of the two-particle system and the coupling of this system to the bath. The following results are based on the Wigner equivalent form of Eq. (99), which is given by Eq. (91) for $M_{\Gamma_k\Gamma_l}=\delta_{P_kP_l}$.

The Wigner equivalent of the momentum flux is written

$$\begin{aligned}\hat{J}_{P_l}^{\omega}(\Gamma,0)&=[\hat{N}(\Gamma,0)\,\dot{\hat{P}}_l(0)]^{\omega}\\&=\hat{N}^{\omega}(\Gamma,0)\exp(-i\hbar T_D/2)\,\dot{\hat{P}}_l^{\omega}\\&=n_D(\Gamma,0)\exp(-i\hbar T_D/2)\,\dot{P}_{D,l}(0)\,.\end{aligned} \tag{C1}$$

Substitution of Eq. (C1) into Eq. (91) of the text yields the following Wigner equivalent form for the components of the friction tensor:

$$\mathcal{E}_{P_kP_l} = \beta\langle\hat{N}(\Gamma,\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma_D^B\left(\hat{\rho}_{EQ}^{\omega}(\Gamma_D,\Gamma_D^B)\exp\left(-\frac{i\hbar T_D}{2}\right)\left\{\exp(+i\hbar\lambda\hat{\mathcal{L}}^{\omega})\right.\right.$$
$$\left.\left.\times\left[n_D(\Gamma)\exp\left(-\frac{i\hbar T_D}{2}\right)\dot{p}_{D,l}(0)\right]\right\}\right)[\exp(+i\mathcal{L}^{\omega}t)\,\dot{p}_{D,k}(0)] \ . \tag{C2}$$

Making use of Eqs. (B5)–(B7) of Appendix B and treating terms involving $\hbar$ and higher order as small perturbations, we write the following approximate form of Eq. (C2):

$$\mathcal{E}_{P_kP_l} = \left[\beta\langle\hat{N}(\Gamma,\infty)\rangle^{CL}\left(1+\frac{\hbar^2}{8}\langle\Delta\chi(\Gamma,\Gamma_D^B)\rangle\right)\right]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda \int d\Gamma_D \int d\Gamma_D^B$$
$$\times\left\{P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\left[1+\frac{\hbar^2}{8}\Delta\chi(\Gamma_D,\Gamma_D^B)\right]\right\}\left[1-\frac{i\hbar T_D}{2}-\frac{\hbar^2T_D^2}{8}\right]\left(\left[1+\lambda\hbar\mathcal{L}^{CL}-\lambda\left(\frac{i\hbar^2}{24}\right)\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}\right]\right.$$
$$\left.\times\left\{n_D(\Gamma)\left[1-\frac{i\hbar T_D}{2}-\frac{\hbar^2T_D^2}{8}\right]\dot{p}_{D,l}(0)\right\}\right)\Bigg]\left\{\left[\exp(+i\mathcal{L}^{CL}t)+\left(\frac{\hbar^2}{24}\right)\exp(+i\mathcal{L}^{CL}t)\int_0^t ds\right.\right.$$
$$\left.\left.\times\exp(-i\mathcal{L}^{CL}s)\,\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}\exp(+i\mathcal{L}^{CL}s)\right]\dot{p}_{D,k}(0)\right\} \ . \tag{C3}$$

Neglecting terms of higher order than $\hbar^2$, we rewrite Eq. (C3)

$$\mathcal{E}_{P_kP_l} = \sum_{I=1}^{9}\mathcal{E}_{P_kP_l}^{(I)} \ , \tag{C4}$$

where

$$\mathcal{E}_{P_kP_l}^{(1)} = [\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,n_D(\Gamma)\dot{p}_{D,l}(0)\,[\exp(+i\mathcal{L}^{CL}t)\,\dot{p}_{D,k}(0)] \ , \tag{C5}$$

$$\mathcal{E}_{P_kP_l}^{(2)} = \frac{\hbar^2}{8}[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,\Delta\chi(\Gamma_D,\Gamma_D^B)\,n_D(\Gamma)\,\dot{p}_{D,l}(0)\,[\exp(+i\mathcal{L}^{CL}t)\dot{p}_{D,k}(0)] \ , \tag{C6}$$

$$\mathcal{E}_{P_kP_l}^{(3)} = -\left(\frac{i\beta\hbar^2}{4}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B(P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,T_D\{\mathcal{L}^{CL}[n_D(\Gamma)\,\dot{p}_{D,l}(0)]\})\,[\exp(+i\mathcal{L}^{CL}t)\dot{p}_{D,k}(0)] \ , \tag{C7}$$

$$\mathcal{E}_{P_kP_l}^{(4)} = -\left(\frac{\hbar^2}{4}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\{P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,T_D\,[n_D(\Gamma)T_D\,\dot{p}_{D,l}(0)]\}[\exp(+i\mathcal{L}^{CL}t)\,\dot{p}_{D,k}(0)] \ , \tag{C8}$$

$$\mathcal{E}_{P_kP_l}^{(5)} = -\left(\frac{\hbar^2}{8}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\{P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,T_D^2\,[n_D(\Gamma)\dot{p}_{D,l}(0)]\}[\exp(+i\mathcal{L}^{CL}t)\dot{p}_{D,k}(0)] \ , \tag{C9}$$

$$\mathcal{E}_{P_kP_l}^{(6)} = -\left(\frac{i\beta\hbar^2}{4}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\{P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,\mathcal{L}^{CL}\,[n_D(\Gamma)T_D\,\dot{p}_{D,l}(0)]\}[\exp(+i\mathcal{L}^{CL}t)\,\dot{p}_{D,k}(0)] \ , \tag{C10}$$

$$\mathcal{E}_{P_kP_l}^{(7)} = -\left(\frac{\hbar^2}{8}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,[n_D(\Gamma)T_D^2\,\dot{p}_{D,l}(0)]\,[\exp(+i\mathcal{L}^{CL}t)\dot{p}_{D,k}(0)] \ , \tag{C11}$$

$$\mathcal{E}_{P_kP_l}^{(8)} = \left(\frac{\hbar^2}{24}\right)[\langle\hat{N}(\Gamma,\infty)\rangle^{CL}]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int d\Gamma_D\int d\Gamma_D^B\,P_{EQ}^{CL}(\Gamma_D,\Gamma_D^B)\,n_D(\Gamma)\,\dot{p}_{D,l}(0)$$
$$\times\left\{\left[\exp(+i\mathcal{L}^{CL}t)\int_0^t ds\exp(-i\mathcal{L}^{CL}s)\,\vec{\nabla}_{q_D}^{(3)}H^{CL}\cdot\vec{\nabla}_{p_D}^{(3)}\exp(+i\mathcal{L}^{CL}s)\right]\dot{p}_{D,k}(0)\right\} \ , \tag{C12}$$

and

$$\mathcal{E}_{P_kP_l}^{(9)} = -\frac{\hbar^2}{8}\langle\Delta\chi(\Gamma,\Gamma_D^B)\rangle_B\,\mathcal{E}_{P_kP_l}^{(1)} \ . \tag{C13}$$

In writing Eqs. (C4)–(C13), we have made use of the approximation given by Eq. (B22) of Appendix B.

Performing the integrations over Γ_D and Γ_D^B in Eq. (C5), the components of the classical friction tensor given by Eq. (97) of the text is obtained. Equations (C6)–(C13) are quantum corrections of second order in $\hbar$ to the classical results. The first-order correction terms vanish by virtue of the identity given by Eq. (B19) of Appendix B.

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