On the Feynman path centroid density as a phase space distribution in quantum statistical mechanics

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The phase space formulation of quantum statistical mechanics using the Feynman path centroid density offers an alternative perspective to the standard Wigner prescription for the classical-like evaluation of equilibrium and/or dynamical quantities of statistical systems. The use of this formulation has been implicit in recent work on quantum rate theories, for example, in which the centroid density distribution replaces the classical Boltzmann distribution. In order to further understand the approximations involved in this and similar transcriptions, the present work elaborates and clarifies the issue of operator ordering in a rigorous centroid-based formulation. In particular, through the use of the Weyl correspondence, a precise definition of the centroid symbol of operators and their products is presented. Though we fall short of finding the algebraic structure tantamount to that found in the Weyl symbols—of which the Wigner distribution is an example—the resulting expressions have internal consistency and are amenable to approximate evaluation through cumulant expansions.

I. INTRODUCTION

Quantum effects play a significant role in the dynamics of many complex systems of chemical interest. Unfortunately, these effects are rarely calculated exactly because the construction *and* solution of the full quantum statistical problem is often unmanageable. On the other hand, Monte Carlo and molecular dynamics techniques have proven to be very effective in calculating *classical* quantities within statistical mechanics. The conclusion of this syllogism is that a quantum statistical problem viewed classically—*i.e.,* in terms of some underlying phase space with an associated classical Hamiltonian—would be amenable to calculation. This phase space perspective is particularly needed in obtaining quantum *dynamical* properties as the extensions to equilibrium properties are better understood.[1–16]

As early as the 1930s, Wigner[1,2] proposed a phase space distribution function which is a classical-type-correspondent to the quantum density matrix, and with which one can compute equilibrium averages within a classical framework[3] up to the arbitrary desired order in $\hbar$. Concurrently, Weyl[4] presented a correspondence rule between quantum operators and their corresponding classical *symbols* over the complex numbers. The two methods are intimately related[5] as the Wigner distribution can be defined in terms of the Weyl symbols, but the use of the Weyl correspondence does not necessarily imply the use of the Wigner prescription. Nonetheless, while the use of the Wigner distribution has led to several important successes, its use has been hampered by the classically unphysical negative values it can take, and by the difficulty associated with calculating time-dependent behavior.[6–9] These drawbacks are intimately related since both are manifestations of the fact that the Wigner distribution is not a classical density, and consequently does not satisfy a classical—*i.e.,* linear differential—transport equation, nor the classical Liouville's theorem for density conservation.[9]

Alternatively, the discretization of the Feynman path integral representation[10] of a quantum partition function has been shown to be isomorphic to the classical partition function of a flexible ring polymer.[11–16] The main drawback of this method is that the isomorphic classical phase space is significantly larger than the original phase space of the classical problem. Use of the path centroid variable—as a projection of this enlarged space—avoids this problem in providing a classical symbol which acts on a classical phase space with a dimensionality equal to that of the original problem.[10] Besides being conceptually appealing, the centroid formulation can also provide accurate results as is suggested by recent work[17–25] as well as by the original calculation of Feynman and Hibbs[10] in which they show that the centroid is the classical-like coordinate for which a perturbation theory has no first-order correction. Thus the centroid provides an optimal variational (classical-like) phase space representation for the path integral. A missing element in the original Feynman–Hibbs theory,[10] as well as its generalizations,[17,18,21] was the classical phase space framework in which the centroid density could be used to calculate equilibrium averages or correlations in a general sense. Two independent, but similar, formulations have been proposed recently within the literature, with the differences being found primarily in the approximate scheme chosen to evaluate the centroid path integrals.[23,26]

At the simplest level, one can use a variational approximation[17,18,21,27] to evaluate the centroid constrained path integral or centroid "density." Tognetti and co-workers,[26] have suggested an interesting extension of this theory into the centroid phase space through an approach similar to the self-consistent harmonic approximation (SCHA).[28–31] Alternatively, in previous work,[21,23] two of the present authors have used a second-order cumulant expansion to evaluate operator averages and imaginary-time correlations in the centroid phase space. In principle, evaluation of the second-order cumulant expressions using the exact Hamiltonian can provide a better treatment than the SCHA approach, as it directly includes anharmonic effects in the averaging. In practice, this quantity must be evaluated approximately or numerically; in particular, if a harmonic approximation is employed, the error is on the same order as that of the harmonic estimates.[25] In summary, the cumulant approach has the advantages that, unlike the SCHA estimate, it provides a systematic method for obtaining the phase space centroid representation of equilibrium quantities for a general potential, and it need not involve the SCHA. However, the presentation in Ref. 23 of the phase space centroid formulation did not stress the correspondence between quantum operators and their symbols, or the associated problems resulting from non-commutative operators, and this paper serves to clarify these concepts.

The outline of the paper is as follows: The phase space path centroid density perspective is reviewed in Sec. II. In order to construct the desired averages, one must first stipulate the quantum-classical correspondence. In this work, the Weyl ordering rule[4] is used to specify the canonical ordering for the quantum mechanical operators, and some relevant results are reviewed briefly in Sec. III. (This is a natural choice for the correspondence and it is also the one taken by Tognetti and coworkers.)[26] In Sec. IV, the equilibrium average with respect to the centroid density is rigorously derived using a proof based on the earlier heuristic argument of Ref. 23. The two primary differences between this derivation and the previous one are (a) that care is taken to establish the appropriate classical correspondents—*symbols*—to the quantum operators, and (b) that the non-commutativity of the position and momentum operators is explicitly considered. As a consequence, the final general expressions are actually of a different form, with the earlier *literal* results[23] being related to it by a stationary phase approximation. The centroid-based expression for imaginary-time correlation functions is obtained in Sec. V taking advantage of this earlier analysis. As in previous work,[21,23] the form of these averages lends itself to a second-order cumulant expansion and the revised expressions are presented in Sec. VI. These formulas provide a rigorous justification for the practical algorithm implicit in the earlier work for the inclusion of non-commutative effects. The generalization of these formulas for the construction of real-time correlation functions[22,23] is presented in Sec. VII. Finally, some suggestions for the implementation of this formulation are discussed in the concluding Sec. VIII.

For simplicity, the following conventions have been adopted in the notation throughout the paper. Vectors and matrices are not explicitly identified through the notation. The phase space is assumed to be $2N$-dimensional and contains the element $z=(p,q)$ with position q and momentum p. In general, position (momentum) components of a phase space variable are referred to through a q (p) subscript. An operator $\hat{O}$ is specifically identified as such by an overhat.

II. PHASE SPACE FEYNMAN PATH CENTROID DENSITY

The phase space centroid density is defined through the constrained path integral[23,26]

$$\rho_c(\zeta_c)=\int \mathfrak{D}\zeta\,\delta(\zeta_c-\zeta_0)e^{-S[\zeta(\cdot)]/\hbar}, \tag{2.1}$$

where ζ_c is a phase space vector, and ζ_0 is a functional of the Feynman path $\zeta(\cdot)$ defined through the centroid formula,[10]

$$\zeta_0=(\hbar\beta)^{-1}\int_0^{\hbar\beta} d\tau\,\zeta(\tau). \tag{2.2}$$

[Note that the center dot in the notation "$\zeta(\cdot)$" is used to emphasize that ζ is a path—i.e., a function of the imaginary time—and not the value $\zeta(\tau)$ specified by the dummy index τ. The notation which this would otherwise afford is not desirable here—though standard in the literature—as the path *and* the value it can take at a particular imaginary time slice will often appear within the same formula.] The action functional for the imaginary-time phase space path integral is the usual action over the path $\zeta(\cdot)$,

$$S[\zeta(\cdot)]=\int_0^{\hbar\beta} d\tau\,\mathfrak{L}[\zeta(\tau)], \tag{2.3}$$

but with the imaginary-time Lagrangian,[32]

$$\mathfrak{L}(\zeta)=\tfrac{1}{2}\zeta_p\cdot m^{-1}\cdot\zeta_p-i\zeta_p\cdot\dot{\zeta}_q+V(\zeta). \tag{2.4}$$

The ultimate goal of the centroid formulation of quantum statistical mechanics is to obtain expressions in which the final statistical quantities are obtained by averaging over the distribution of the effective classical-like phase space variable ζ_c—i.e., the centroid.[21,23,26] This is tantamount to requiring that averages be computed through the classical-like partition expression,

$$\langle\hat{A}\rangle=\frac{\int d\zeta\,a_c(\zeta)\rho_c(\zeta)}{\int d\zeta\,\rho_c(\zeta)}, \tag{2.5}$$

where the *centroid symbol* a_c corresponds to the operator $\hat{A}$. Either because the algebraic structure of this symbol is intrinsically interesting, or because of the importance of correlation functions in statistical mechanics, it is also useful to derive a *centroid* $\star$-product rule,

$$(\hat{A}\hat{B})_c=a_c\star b_c, \tag{2.6}$$

in analogy to the Weyl $*$-product to be reviewed in the next section. Given the centroid symbols of operators one can proceed to calculate exact quantum statistical mechanical averages through Eq. (2.5) within a calculation which has a classical structure. In this work, we fall short of obtaining the general rule [Eq. (2.6)] and present a result only for centroid symbols within a trace. This, however, is sufficient to evaluate thermodynamic quantities. Moreover, the formalism to be presented can be used to guide the approximate derivations of these quantities using the cumulant expansion[23] or the SCHA[26] for the centroid symbol, or using analogous techniques to those employed for the Wigner distribution.[3,7,8,33]

III. WEYL CORRESPONDENCE RULE

The first step in obtaining the centroid symbol requires an identification between an operator and its classical symbol. The Weyl correspondence provides a natural identification in which the position and momentum operators are treated on an equal footing, and as such is an ideal choice for the centroid phase space objects we wish to construct.[4,34]

The canonical ordering of the position and momentum operators is fixed through the parametric family of Heisenberg operators:[4,34]

$$\hat{T}(p,q) \equiv e^{i(p\hat{q}-q\hat{p})/\hbar}, \tag{3.1}$$

where the hats denote operators. Alternatively, one can use a $\hat{q}$-before-$\hat{p}$ or $\hat{p}$-before-$\hat{q}$ ordering, for example, as was done implicitly in the centroid phase space formulation of Ref. 23. Though these are simpler, they do not place momentum and position on the same footing, nor do they manifestly provide a Fourier structure to the representation. It is these two features of the Heisenberg operators which are exploited in the construction of the centroid symbols in the remainder of this work.

The Weyl correspondence rule between an operator and its *symbol* can be defined implicitly through the Heisenberg operators.[34] The alternate symbol ϕ_a, corresponding to the operator $\hat{A}$, is defined through either of the equations:

$$\hat{A} = (2\pi\hbar)^{-N} \int dz\, \phi_a(z) \hat{T}(z), \tag{3.2a}$$

$$\phi_a(z) = \mathrm{Tr}[\hat{T}(z)^\dagger \hat{A}]. \tag{3.2b}$$

The symbol a corresponding to the operator $\hat{A}$ is implicitly defined through the alternate symbol,

$$(\hat{A})_s \equiv a(z) = (2\pi\hbar)^{-N} \int dz'\, \phi_a(z') e^{i(p'q-q'p)/\hbar}, \tag{3.2c}$$

or

$$\phi_a(z) = (2\pi\hbar)^{-N} \int dz'\, a(z') e^{i(p'q-q'p)/\hbar}. \tag{3.2d}$$

Intuitively, the one-to-one correspondence between an operator and its symbol can be seen from the fact that each can be uniquely represented by the Fourier-like components ϕ_a. The uniqueness of the projection from the operator onto its symbol can also be seen through the more standard—but equivalent—definition of the Weyl symbol,[3]

$$a(z) = \int dx'\, e^{ipx'/\hbar} \langle x - \tfrac{1}{2}x' | \hat{A} | x + \tfrac{1}{2}x' \rangle. \tag{3.3}$$

In this work, Eq. (3.2) is preferred because its structure is symmetric in the position and momentum variables as well as being reminiscent of the Fourier transformations used in the earlier heuristic arguments of the phase space centroid formalism.[23]

The symbol of a product of operators is related through the $*$-product, defined by

$$a * b \equiv (\hat{A}\hat{B})_s = a e^{i\overleftrightarrow{\Lambda}/2\hbar} b, \tag{3.4}$$

where $\overleftrightarrow{\Lambda}$ is the Janus operator which acts as a differential on both sides,[5,35,36]

$$\overleftrightarrow{\Lambda} \equiv \sum_i \frac{\overleftarrow{\partial}}{\partial q_i} \frac{\overrightarrow{\partial}}{\partial p_i} - \frac{\overleftarrow{\partial}}{\partial p_i} \frac{\overrightarrow{\partial}}{\partial q_i}, \tag{3.5}$$

where the overarrows indicate the directionality of the operator. However, it turns out that within a trace the $*$-product reduces to a simple product, and thus traces can be obtained easily through the relation,

$$\mathrm{Tr}\hat{A}\hat{B} = (2\pi\hbar)^{-N} \int dz\, a(z) b(z), \tag{3.6}$$

where it should be emphasized that there is no approximation involved in this relation.[34] The approximations involved in using the Weyl correspondence will in general arise either because the symbol is obtained approximately, or because it is time-evolved through the classical equations of motion rather than through the correspondence of the time-evolved quantum operator.

The Wigner distribution is the symbol corresponding to the density matrix.[3,34] As such all of the properties described thus far for general operators apply to calculations using the Wigner distribution. However, the use of the Weyl correspondence rule does not require that this be the distribution, and in the remaining sections the centroid density will emerge as an alternative phase space distribution, with the Weyl symbols providing the underlying form for the classical analogues of the quantum operators.

IV. EQUILIBRIUM AVERAGES

The equilibrium average of a quantity can be written in terms of the averages of the Heisenberg operators using the alternate symbols, as

$$\langle \hat{A} \rangle = (2\pi\hbar)^{-N} \int dz_0\, \phi_a(z_0) \langle \hat{T}(z_0) \rangle. \tag{4.1}$$

Each of the equilibrium averages of the Heisenberg operators may in turn be calculated through the Feynman path integral,

$$\langle \hat{A} \rangle = Z^{-1} (2\pi\hbar)^{-N} \int dz_0\, \phi_a(z_0) \times \int \mathfrak{D}\zeta\, T[\zeta(\cdot); z_0] e^{-S[\zeta(\cdot)]/\hbar}, \tag{4.2}$$

where each $\zeta(\cdot)$ is a continuous phase-space path indexed by an imaginary time between 0 and $\hbar\beta$; and T is an expectation value of the Heisenberg operator taken between a particular set of time slices of the path integral,

$$T[\zeta(\cdot); z_0] \equiv \frac{\langle \zeta_q(\tau+\epsilon) | \hat{T}(z_0) | \zeta_p(\tau) \rangle}{\langle \zeta_q(\tau+\epsilon) | \zeta_p(\tau) \rangle}, \tag{4.3}$$

where the time ϵ in $\tau+\epsilon$ denotes the subsequent time slice in the discretized representation of the path, and represents an "infinitesimal" time in the continuum limit. Note that because of the invariance of the trace, Eq. (4.2) is independent of τ, and thus τ has not been included within the argument of T.

The centroid variable ζ_c, and the fluctuation of the Feynman path about it through the relation,

$$\tilde{\zeta}(\tau) \equiv \zeta(\tau) - \zeta_c, \tag{4.4}$$

provides a change-of-variables in the path integral [Eq. (4.2)] which converts it to the suggestive form,

$$\langle\hat{A}\rangle = Z^{-1}\int d\zeta_c a_c(\zeta_c)\rho_c(\zeta_c), \tag{4.5}$$

where

$$a_c(\zeta_c) \equiv \rho_c(\zeta_c)^{-1}(2\pi\hbar)^{-N}\int \mathfrak{D}\tilde{\zeta}\int dz_0\phi_a(z_0)T \times[\zeta_c+\tilde{\zeta}(\cdot);z_0]e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}. \tag{4.6}$$

Equation (4.5) is precisely of the form in Eq. (2.5) since the partition function Z is just the integral over the centroid density. What remains is to simplify the form of the centroid symbol a_c.

The matrix element T provides the first departure from the derivation in the earlier work.[23] If the operator $\hat{A}$ consisted exclusively of commuting position and momentum operators, i.e.,

$$\hat{A} = A(\hat{x}_\parallel,\hat{p}_\perp), \tag{4.7}$$

where $x_\parallel$ and $x_\perp$ represent orthogonal Cartesian subspaces of the configuration space, then the matrix elements $\hat{T}$ depend only on $\zeta(\tau)$ through the expression,

$$T[\zeta(\cdot);z_0] = e^{i[p_0\cdot x_\parallel(\tau)-q_0\cdot p_\perp(\tau)]/\hbar}, \tag{4.8}$$

where the invariance of the trace has been used. Up to a trivial sign, Eq. (4.8) provides the Fourier expansion which led to the configuration representation or momentum representation results for the centroid formula obtained earlier.[21,23] However for an arbitrary operator, all of the matrix elements,

$$T[\zeta(\cdot);z_0] = e^{i[p_0\cdot\zeta_q(\tau+\epsilon)-q_0\cdot\zeta_p(\tau)]/\hbar}e^{-ip_0\cdot q_0/2\hbar}, \tag{4.9}$$

contribute. The presence of the ϵ infinitesimal time is thus a manifestation of the non-commutation between position and momentum, as is the presence of the second term on the right-hand side of the equality in Eq. (4.9). In the continuum limit of the Feynman path integrals, non-continuous paths are significant, and the ϵ term can play a non-trivial role in the calculation.

Upon combining equations (4.6) and (4.9), a Fourier expansion of the alternate symbol into the Weyl symbol of $\hat{A}$ and some standard manipulation leads to

$$a_c(\zeta_c) = \rho_c(\zeta_c)^{-1}(\pi\hbar)^{-N}\int dz_1 a(z_1)\int \mathfrak{D}\tilde{\zeta} \times \Upsilon_1[z_1,\zeta_c;\tau,\tilde{\zeta}(\cdot)]e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}, \tag{4.10a}$$

where

$$\Upsilon_1[z_1,\zeta_c;\tau,\tilde{\zeta}(\cdot)] \equiv e^{-2i[q_1-\zeta_{c,q}-\tilde{\zeta}_q(\tau+\epsilon)][p_1-\zeta_{c,p}-\tilde{\zeta}_p(\tau)]/\hbar}, \tag{4.10b}$$

and τ is explicitly referenced for later convenience though the trace is invariant to it. Other than for a trivial sign in the Fourier components, Eq. (4.10) reduces essentially to Eq. (2.9) in Ref. 23,

$$a_c^{\rm SPA}(\zeta_c) = \rho_c(\zeta_c)^{-1}(2\pi\hbar)^{-N}\int dz\phi_a(z)e^{-i(q\zeta_{c,p}-p\zeta_{c,q})/\hbar} \times\int \mathfrak{D}\tilde{\zeta}e^{-i[q\tilde{\zeta}_p(\tau)-p\tilde{\zeta}_q(\tau+\epsilon)]/\hbar}e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}, \tag{4.11}$$

upon integration over z_1 through the stationary phase approximation (SPA). This should not be surprising as the SPA ignores the higher order terms which manifest the noncommutativity of the position and momentum operators, and this is precisely what was not explicitly addressed in the earlier analysis. Equation (4.10), however, contains no approximation and is the central result of this section. Alternatively, the approximate evaluation of Eq. (4.10) using a cumulant expansion—see Sec. VI—does retain terms arising from the non-commutativity.

We note, in passing, that the equilibrium average of an operator can be written with respect to the Wigner distribution as

$$\langle\hat{A}\rangle = Z^{-1}(2\pi\hbar)^{-N}\int dz a(z)(e^{-\beta\hat{H}})_s, \tag{4.12}$$

where here the Wigner distribution has been explicitly written as the Weyl symbol of the Boltzmann density. Since the operator $\hat{A}$ is arbitrary, comparison with Eq. (4.10) suggests the following path integral form for the Wigner distribution:

$$(e^{-\beta\hat{H}})_s(z) = 2^N\int \mathfrak{D}\zeta e^{-2i[q-\zeta_q(\tau+\epsilon)][p-\zeta_p(\tau)]/\hbar}e^{-S[\zeta(\cdot)]/\hbar}, \tag{4.13}$$

which is equivalent to the path integral evaluation of the definition in Eq. (3.2).

V. IMAGINARY-TIME CORRELATION FUNCTIONS

In the $\tau\to 0$ limit, the imaginary-time correlation function, $\langle\hat{A}(\tau)\hat{B}(0)\rangle$, reduces to the equilibrium average of the operator product, $\hat{A}\hat{B}$. To illustrate that this is indeed the case, both of these expressions are explicitly presented in this section. This comparison further illustrates the necessary role played by the infinitesimal ϵ in representing noncommutativity in the continuum limit.

A. Zero imaginary-time case

As before, the equilibrium average of a product of operators, $\hat{A}$ and $\hat{B}$, may be written in terms of their corresponding alternate Weyl symbols,

$$\langle\hat{A}\hat{B}\rangle = (2\pi\hbar)^{-2N}\int dz_a\int dz_b\phi_a(z_a)\phi_b(z_b) \times\langle\hat{T}(z_a)\hat{T}(z_b)\rangle. \tag{5.1}$$

This may be evaluated most directly by taking advantage of the product rule of Heisenberg operators,[34] which may be written as

$$\hat{T}(z_a)\hat{T}(z_b) = \hat{T}(z_a+z_b)e^{i(p_aq_b-q_ap_b)/2\hbar}. \tag{5.2}$$

With this substitution, the derivation is now analogous to that employed in the previous section for the equilibrium average, and the result follows similarly, providing

$$\langle \hat{A}\hat{B}\rangle = Z^{-1}\int d\zeta_c (\hat{A}\hat{B})_c \rho_c(\zeta_c), \tag{5.3}$$

where

$$(\hat{A}\hat{B})_c = \rho_c(\zeta_c)^{-1}(\pi\hbar)^{-2N}\int dz_a \int dz_b a(z_a) b(z_b) \times \int \mathfrak{D}\tilde{\zeta}\Upsilon_2[z_a, z_b, \zeta_c; \tau, \tilde{\zeta}(\cdot)] e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}, \tag{5.4a}$$

and

$$\Upsilon_2[z_a, z_b, \zeta_c; \tau, \tilde{\zeta}(\cdot)] \equiv e^{-2i[(q_b-q_a)\zeta_{c,p}-(p_b-p_a)\zeta_{c,q}+q_a p_a + q_b p_b - 2q_b p_a]/\hbar} \times e^{-2i[(q_b-q_a)\tilde{\zeta}_p(\tau)-(p_b-p_a)\tilde{\zeta}_q(\tau+\epsilon)]/\hbar}. \tag{5.4b}$$

Noting that the Weyl symbol for the identity operator is 1, $(\hat{A})_c$ and $(\hat{B})_c$ as calculated through Eq. (5.4) reduce respectively to a_c and b_c as calculated through Eq. (4.10). Alternatively, this expression could also have been obtained through the use of the equilibrium result in Eq. (4.10) with the Weyl product $a*b$ representing the operator $\hat{A}\hat{B}$.

Though the result in Eq. (5.4) may seem somewhat complicated, it is actually simpler than that for the equilibrium average in light of the cumulant approximation used earlier to evaluate the centroid-path integral.[23] Namely Eq. (5.4) is amenable to a cumulant expansion because the exponent of the integrand is linear in the fluctuation variable $\tilde{\zeta}$ whereas the corresponding exponent in Eq. (4.10) is not. However, the two are equivalent as the latter can be obtained from the former as noted above, and the former may be obtained from the latter through the introduction of an auxiliary variable. The results for both equilibrium averages and correlation functions using this "trick" and the cumulant expansion are described in Sec. VI.

B. General case

The imaginary-time correlation function may be written in analogy to the equilibrium average in Eq. (4.2) as

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle = Z^{-1}(2\pi\hbar)^{-2N}\int dz_a \int dz_b \phi_a(z_a)\phi_b(z_b) \times \int \mathfrak{D}\zeta T[\zeta(\cdot); z_a, (\tau+\epsilon)] \times T[\zeta(\cdot); z_b, 0] e^{-S[\zeta(\cdot)]/\hbar}, \tag{5.5}$$

where now the imaginary-time dependence is explicitly included in the argument list of T in Eq. (4.3). Note that the infinitesimal imaginary time ϵ in this expression is necessary; for example, if ϵ is set trivially to 0, the zero-time limit result (5.4) is not recovered. A series of manipulations similar to that in Sec. IV leads to the result,

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle = Z^{-1}\int d\zeta_c \Big(\hat{A}(\tau)\hat{B}(0)\Big)_c \rho_c(\zeta_c), \tag{5.6a}$$

where

$$(\hat{A}(\tau)\hat{B}(0))_c \equiv \rho_c(\zeta_c)^{-1}(\pi\hbar)^{-2N}\int dz_a \int dz_b a(z_a) b(z_b) \times \int \mathfrak{D}\tilde{\zeta}\Upsilon_1[z_a, \zeta_c; (\tau+\epsilon), \tilde{\zeta}(\cdot)] \times \Upsilon_1[z_b, \zeta_c; 0, \tilde{\zeta}(\cdot)] e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}, \tag{5.6b}$$

with Υ_1 defined as in Eq. (4.10b).

In the $\tau\to 0$ limit, the imaginary-time correlation function in Eq. (5.6b) reduces to the zero imaginary-time expression in Eq. (5.4). In this limit, the correlation function in Eq. (5.6b) contains discrete terms dependent on the three times, τ, $\tau+\epsilon$, and $\tau+2\epsilon$, while only two of these appear in Eq. (5.4). As before, these infinitesimal imaginary times arise from the the non-commutation between position and momentum operators. Equation (5.4) contains only two of these imaginary times because the operators were explicitly reordered by way of Eq. (5.2), thereby eliminating the need for one of the imaginary time slices in the path integral.

VI. CUMULANT EXPANSIONS

Though results (4.10) and (5.6b) are formally the correct quantum-mechanical centroid-based expressions, they may offer little or no computational advantages compared to the original path integrals. The perspective gained in these constructions, however, suggests that the path fluctuations should provide a small perturbation to the mostly classical behavior of the path centroid. This motivates the approximate path integration over the fluctuating paths $\tilde{\zeta}(\cdot)$. Following earlier work,[23] the averages will be expanded here in terms of their cumulants and truncated at second order. The reader is referred to Ref. 26 for an alternative treatment involving the SCHA.

It is useful to begin by defining the centroid-constrained average of a possibly imaginary-time dependent quantity, $\mathcal{Q}$, in phase space as

$$\langle \mathcal{Q}\rangle_c \equiv \rho_c(\zeta_c)^{-1}\int \mathfrak{D}\tilde{\zeta}\mathcal{Q} e^{-S[\zeta_c+\tilde{\zeta}(\cdot)]/\hbar}, \tag{6.1}$$

where the dependence on the centroid variable ζ_c is implicit, and the subscript "c" denotes a centroid-constrained average. With respect to this average, the cumulant expansion[37] truncated to second order may be written as

$$\langle e^{\sum_i a_i \mathcal{Q}_i}\rangle_c \approx \exp\left[\sum_i a_i \langle\langle \mathcal{Q}_i\rangle\rangle_c + \frac{1}{2}\sum_{i,j} a_i a_j \langle\langle \mathcal{Q}_i \mathcal{Q}_j\rangle\rangle_c\right], \tag{6.2}$$

where the double brackets $\langle\langle\cdot\rangle\rangle$ are used to denote a cumulant average, and $\langle\langle\cdot\rangle\rangle_c$ denotes a centroid-constrained cumulant average.

The first-order cumulant for the centroid fluctuation is trivial, i.e.,

$$\langle\langle \tilde{\zeta}(\tau)\rangle\rangle_c = 0, \tag{6.3}$$

which follows from the fact that averages are independent of the imaginary time, and that the centroid-constrained average requires that the integral of the fluctuation over the path is zero. The construction of the cumulant average to second order thus depends only on the second-order cumulant matrix $C_c(\tau,\zeta_c)$ defined by the matrix elements,

$$C_c(\tau,\zeta_c)_{i,j}\equiv\langle\langle\tilde{\zeta}_i'(\tau)\tilde{\zeta}_j'(0)\rangle\rangle_c=\langle\tilde{\zeta}_i'(\tau)\tilde{\zeta}_j'(0)\rangle_c, \tag{6.4}$$

where

$$\tilde{\zeta}'(\tau)\equiv\begin{pmatrix}\tilde{\zeta}_p(\tau)\\ \tilde{\zeta}_q(\tau+\epsilon)\end{pmatrix}, \tag{6.5}$$

and the second equality results because the first-order averages in the fluctuations are zero according to Eq. (6.3). Note that the definition of $C_c(\tau,\zeta_c)$ differs from that in Ref. 23 in that the momentum and position terms are now evaluated at infinitesimally different time slices.

A. Equilibrium averages

The equilibrium average in Eq. (4.10) may be written using the zero time product formula in Eq. (5.4) by taking one of the operators to be the identity operator. (The corresponding Weyl symbol of the latter is 1.) The equilibrium average may be equivalently written as

$$a_c(\zeta_c)=(\pi\hbar)^{-2N}\int dz_a a(z_a)\times\int dz_b\langle\Upsilon_2[z_a,z_b,\zeta_c;\tau,\tilde{\zeta}(\cdot)]\rangle_c. \tag{6.6}$$

Taking advantage of the tensor algebra of the full phase space, the inner integrand of this equation takes the form,

$$\langle\Upsilon_2[z_a,z_b,\zeta_c;\tau,\tilde{\zeta}(\cdot)]\rangle_c=e^{-2i[(z_a-z_b)J(z_a-\zeta_c)+1/2(z_a-z_b)|J|(z_a-z_b)]/\hbar}\times\langle e^{2i(z_a-z_b)J\tilde{\zeta}'(\tau)/\hbar}\rangle_c, \tag{6.7}$$

where use is made of the symplectic matrix,

$$J\equiv\begin{pmatrix}0 & -I\\ I & 0\end{pmatrix}, \tag{6.8}$$

in which I is the N by N identity matrix. Note that the symplectic matrix is anti-Hermitian ($J^\dagger=-J$) and unitary ($J^\dagger J=1$).

A cumulant expansion over the centroid average of the "fluctuation" $\tilde{\zeta}'(\tau)$ truncated at second-order results in

$$\langle\Upsilon_2[z_a,z_b,\zeta_c;\tau,\tilde{\zeta}(\cdot)]\rangle_c\approx\exp\{-(2/\hbar^2)(z_a-z_b)J[C_c(0,\zeta_c)-(i\hbar/2)|J|]\times J^\dagger(z_a-z_b)-(2i/\hbar)(z_a-z_b)J(z_a-\zeta_c)\}, \tag{6.9}$$

where

$$|J|\equiv\begin{pmatrix}0 & I\\ I & 0\end{pmatrix}. \tag{6.10}$$

Gaussian integration over the vector variable $(z_a-z_b)J$ provides the final result,

$$a_c(\zeta_c)\approx\det{}^{-1/2}\{2\pi[C_c(0,\zeta_c)-(i\hbar/2)|J|]\}\times\int d\tilde{\zeta}a(\zeta_c+\tilde{\zeta})\times\exp\{-\tfrac{1}{2}\tilde{\zeta}[C_c(0,\zeta_c)-(i\hbar/2)|J|]^{-1}\tilde{\zeta}\}, \tag{6.11}$$

where the Gaussian fluctuation $\tilde{\zeta}$ is now a $2N$-dimensional phase space vector and not a path.

The result in Eq. (6.11) has the same structure as that obtained in Ref. 23, except for modification of the Gaussian coupling matrix. In addition to the subtle imaginary-time modification in Eq. (6.5) found in the cumulant matrix $C_c(0,\zeta_c)$, there is now an additional term, $-i\hbar|J|/2$, which affects only those fluctuations involving $\hat{q}_i$ and $\hat{p}_i$ with the same index. This is consistent with the approximation of the previous work in which the non-commutation of position and momentum was not explicitly discussed.

B. Correlation functions

Though the evaluation of the equilibrium average in Eq. (6.6) in the previous section was motivated by using the zero time centroid product formula, the result can also be derived directly. Briefly, the form of the equilibrium average amenable to the cumulant expansion may also be derived directly from Eq. (4.10) by the introduction of an auxiliary variable through the following steps: (a) multiplication by the identity operator expressed as an integral over a delta function whose argument is either of the terms in the exponent in Υ_1[in Eq. (4.10b)], (b) subsequent Fourier representation of the delta function, and (c) Gaussian integration over a transformed variable. Similarly, the product centroid symbol (5.6b) may be rewritten with respect to not one but two auxiliary variables as,

$$(\hat{A}(\tau)\hat{B}(0))_c\equiv(\pi\hbar)^{-4N}\int dz_a\int dz_b a(z_a)b(z_b)\int dz_a'\times\int dz_b'\langle\Upsilon_2[z_a,z_a',\zeta_c;(\tau+\epsilon),\tilde{\zeta}(\cdot)]\times\Upsilon_2[z_b,z_a',\zeta_c;0,\tilde{\zeta}(\cdot)]\rangle_c. \tag{6.12}$$

Evaluating the integrand of Eq. (6.12) provides

$$\langle\Upsilon_2[z_a,z_a',\zeta_c;(\tau+\epsilon),\tilde{\zeta}(\cdot)]\Upsilon_2[z_b,z_a',\zeta_c;0,\tilde{\zeta}(\cdot)]\rangle_c=e^{-2i[(z_a-z_a')J(z_a-\zeta_c)+(1/2)(z_a-z_a')|J|(z_a-z_a')]/\hbar}\times e^{-2i[(z_b-z_b')J(z_b-\zeta_c)+(1/2)(z_b-z_b')|J|(z_b-z_b')]/\hbar}\times\langle e^{2i\{(z_a-z_a')J\tilde{\zeta}'(\tau+\epsilon)+(z_b-z_b')J\tilde{\zeta}'(0)\}/\hbar}\rangle_c. \tag{6.13}$$

Once again, a cumulant expansion of the centroid-constrained average, transformation of the integration variables by a simplifying unitary transformation and Gaussian integration—all of which are analogous to the less tedious manipulations performed in the derivation of the equilibrium average—leads to the result,

$$(\hat{A}(\tau)\hat{B}(0))_c \approx \det{}^{-1/2}\{4\pi^2 C_c^+(\tau,\zeta_c) C_c^-(\tau,\zeta_c)\} \times \int d\tilde{\zeta}_+ \int d\tilde{\zeta}_- a(\zeta_c+\tilde{\zeta}_a) b(\zeta_c+\tilde{\zeta}_b) \times e^{-(1/2)\tilde{\zeta}_+[C_c^+(\tau,\zeta_c)]^{-1}\tilde{\zeta}_+ -(1/2)\tilde{\zeta}_-[C_c^-(\tau,\zeta_c)]^{-1}\tilde{\zeta}_-}, \tag{6.14}$$

where the effective Gaussian path fluctuations,

$$\tilde{\zeta}_a \equiv \frac{\tilde{\zeta}_+ + \tilde{\zeta}_-}{\sqrt{2}}, \tag{6.15a}$$

$$\tilde{\zeta}_b \equiv \frac{\tilde{\zeta}_+ - \tilde{\zeta}_-}{\sqrt{2}}, \tag{6.15b}$$

correspond to fluctuations about the centroid ζ_c in the symbols a and b, respectively. The fluctuations $\tilde{\zeta}_\pm$ are phase space vectors obeying Gaussian statistics through the Gaussian coupling matrix,

$$C_c^\pm(\tau,\zeta_c) \equiv [C_c(0,\zeta_c) - (i\hbar/2)|J|] \pm [C_c(\tau+\epsilon,\zeta_c) - (i\hbar/2)|J|], \tag{6.16}$$

which once again differs slightly from that in Ref. 23. As in the previous subsection, the term $i\hbar|J|/2$ would be zero if terms of order $\hbar$ are ignored, as was effectively done in previous work wherein the operators were replaced with the zeroth-order classical—*vis-a-vis* principal—symbols. Since the cumulant expansion does retain terms of order $\hbar$, the final results (6.11) and (6.14) do retain an order $\hbar$ correction. Close inspection of Eq. (6.16) in the $\tau \to 0$ limit reveals that C_c^- would be zero if one did not take proper care of the infinitesimal times included in this expression. The presence of the infinitesimals, however, ensures that the zero-time result of the previous subsection is recovered in this limit.

VII. REAL-TIME CORRELATION FUNCTIONS

As was pointed out in previous work,[22,23] the exact real-time centroid-based correlation function may be obtained through the inverse Wick rotation[16,38]—i.e., the analytic continuation, $\tau \to it$—of the imaginary-time correlation function in Eq. (5.6). However, the analytic continuation of the centroid-based correlation functions approximated by the cumulant expansion—see, e.g., Eq. (6.14) or Ref. 23— or the SCHA may lead to inaccuracies at intermediate to long times. A better approach[22,23] may be to express the general imaginary-time correlation functions in terms of a centroid-*un*constrained cumulant expansion. This expression, in turn, may be formally continued analytically to real time and evaluated using the centroid molecular dynamics (CMD) approach.[22–24] This prescription has been developed previously for configuration space operators,[22] and in phase space using the arguments of Ref. 23. In this section we rigorously derive the formulas using the arguments employed in the preceding sections.

The general imaginary-time correlation function corresponding to the centroid-based formula in Eq. (5.5) can be written with respect to the Weyl alternate symbols and the Heisenberg operator matrix elements as

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle = (2\pi\hbar)^{-2N} \int dz_a \int dz_b \phi_a(z_a)\phi_b(z_b) \times \langle T[\zeta(\cdot); z_a, (\tau'+\tau+\epsilon)] \times T[\zeta(\cdot); z_b, \tau']\rangle, \tag{7.1}$$

where the general path-integral average is over all paths, i.e.,

$$\langle \cdots \rangle \equiv \frac{\int \mathfrak{D}\zeta[\cdots] e^{-S[\zeta(\cdot)]/\hbar}}{\int \mathfrak{D}\zeta e^{-S[\zeta(\cdot)]/\hbar}}, \tag{7.2}$$

instead of the centroid-constrained average $\langle \cdots \rangle_c$ defined by Eq. (6.1). As in Sec. V B, the general imaginary-time correlation function may be written directly with respect to the Weyl symbols as

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle = (\pi\hbar)^{-2N} \int dz_a \int dz_b a(z_a) b(z_b) \times \langle \Upsilon_1[z_a,\zeta_c;(\tau+\epsilon),\tilde{\zeta}(\cdot)] \times \Upsilon_1[z_b,\zeta_c;0,\tilde{\zeta}(\cdot)]\rangle, \tag{7.3}$$

where the Υ_1 function defined in Eq. (4.10b) depends on the path $\zeta(\cdot)$ through its components ζ_c and $\tilde{\zeta}(\cdot)$. As before, this expression is not amenable to cumulant expansion because the exponent is non-linear with respect to the path $\zeta(\cdot)$. Introduction of auxiliary variables as in Sec. VI B provides the desired form,

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle = (\pi\hbar)^{-4N} \int dz_a \int dz_b a(z_a) b(z_b) \int dz_a' \int dz_b' \times e^{(1/2)(z_a-z_a')|J|(z_a-z_a'+z_b-z_b')/\hbar} \times \langle e^{2i\{(z_a-z_a')J\zeta'(\tau+\epsilon)+(z_b-z_b')J\zeta'(0)\}/\hbar}\rangle, \tag{7.4}$$

which is analogous to Eqs. (6.12) and (6.13), but with the centroid-based average $\langle \cdots \rangle_c$ replaced by the general path-integral average $\langle \cdots \rangle$.

The cumulant approximation may now be taken as in Sec. VI providing the result

$$\langle \hat{A}(\tau)\hat{B}(0)\rangle \approx \det{}^{-1/2}\{4\pi^2 C_\delta^+(\tau) C_\delta^-(\tau)\} \times \int d\zeta_+ \int d\zeta_- a(\langle\zeta\rangle+\zeta_a) b(\langle\zeta\rangle+\zeta_b) \times e^{-(1/2)\zeta_+[C_\delta^+(\tau)]^{-1}\zeta_+ -(1/2)\zeta_-[C_\delta^-(\tau)]^{-1}\zeta_-}, \tag{7.5}$$

where $\{\zeta_a, \zeta_b\}$ are related to $\zeta_\pm$ by the transformation in Eq. (6.15). The average $\langle\zeta\rangle$ in the argument of the symbols originates from the first-order cumulant term which was zero in the earlier derivation. The generalized coupling matrices are here defined as,

$$C_\delta^\pm(\tau) \equiv [C_\delta(0) - (i\hbar/2)|J|] \pm [C_\delta(\tau+\epsilon) - (i\hbar/2)|J|], \tag{7.6a}$$

where the second-order cumulant matrix $C_\delta(\tau)$ is defined by its matrix elements,

$$C_\delta(\tau)_{i,j} = \langle \zeta_i'(\tau)\zeta_j'(0)\rangle - \langle \zeta_i'(\tau)\rangle\langle \zeta_j'(0)\rangle, \tag{7.6b}$$

in which the ζ' are related to ζ by the transformation in Eq. (6.5). Note that these formulas do reduce to the centroid formulas in the earlier sections upon replacement of the general path-integral average with the centroid-based average.

The real-time correlation function may now be obtained by analytic continuation of Eq. (7.5). Since the only time dependence is to be found in the cumulant matrices, this can be performed formally by the change of variables, $\tau \rightarrow it$. Thus an arbitrary correlation function may be obtained after one calculates the second order correlation function $C_\delta(t)$. In practice, the elements of this correlation function matrix are obtained using the CMD method.[22–24,39] Note also, that this algorithm is not unrelated to the previous sections as the CMD method implicitly assumes that an average may be written as in Eq. (2.5).

VIII. CONCLUDING REMARKS

In light of the present work, the previous development[23] of the phase space centroid formalism may be interpreted either as (a) a ''rigorous'' derivation of the formulation in which operator non-commutativity is not explicitly addressed, or (b) a heuristic derivation of the cumulant formulas which implicitly includes the non-commutativity of the position and momentum operators through a q-before-p or p-before-q symbol. The first interpretation (a) suggested the use of the Weyl analysis used in this work to generalize the rigorous formulation of the phase space theory. As such it is the interpretation which has been generally adopted throughout this work.

Under the second interpretation (b), it was heretofore necessary to interpret the cumulant-based formulas in a prescribed way in order to include the non-commutativity. Upon using the cumulant approximation, the centroid symbols which result are all simply Gaussian averages. Since the Gaussian average of an arbitrary product of operators can be written as a sum of terms, all of which involve only products of pairs of operators, then the final result can be written explicitly in terms of matrix elements of the cumulant matrix C_c defined by Eq. (6.4). If one takes care in retaining the order of the operators when this is performed, then the final results will inherit the correct non-commutative structure found in C_c. Thus this intuitive approach will provide the results of this paper under the cumulant approximation for those operators which can be written as polynomials in position and momentum. However, the present work provides a formally correct expression which can be evaluated explicitly as written, and which can be used for operators of arbitrary structure.

Though one may be tempted to define the product of centroid symbols using the centroid symbol for the product of the corresponding operators as in Eq. (5.4), e.g.,

$$a_c \star b_c \equiv (\hat{A}\hat{B})_c, \tag{8.1}$$

this would be premature here, because the RHS is not explicitly defined in terms of the centroid symbols, a_c and b_c. Moreover, it is not clear if the RHS product rule is associative. Thus as remarked earlier, Eq. (5.4) provides the $\star$-product rule only when two operators appear within a trace. Nonetheless, we are currently working on this issue, as well as studying the algebraic properties of the centroid symbols under various orders of the cumulant expansion.

Note that the above discussion is not just an ''academic'' exercise, as a well-defined algebraic structure for the centroid symbols is the first step towards understanding the transformation properties of the centroid-based phase space traces. This, in turn, should provide a deeper understanding of the phase space coordinate dependence of such formulas, and provide a means of obtaining general variational formulas. For example, though the use of the centroid density in reaction rate theory has already provided intriguing agreement with exact results,[40–43] its use in quantum variational transition state theories is not on a firm footing because, for example, one is unsure if there rigorously exists a pseudoclassical Hamiltonian corresponding to the centroid quantum dynamics. An understanding of the transformation properties of the centroid density could afford us an implicit understanding of the centroid dynamics—without recourse to the precise form of the pseudo-classical centroid Hamiltonian—and thereby lead to a better understanding of the centroid variational rate theories. Generally, this could also lead to a more complete and satisfying derivation of CMD[39,22,24] with the effective potential, defined as the free energy of the centroid density, acting as a true ''propagator'' for the centroid symbol. Work on this and other issues is in progress.

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[1] E. P. Wigner, Phys. Rev. **40**, 749 (1932).
[2] E. P. Wigner, Z. Phys. Chem. B **19**, 203 (1932).
[3] M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, Phys. Rev. **106**, 121 (1984).
[4] H. Weyl, Z. Phys. **46**, 1 (1927).
[5] J. E. Moyal, Proc. Cambridge Philos. Soc. **45**, 99 (1949).
[6] W. H. Miller, J. Chem. Phys. **61**, 4301 (1974).
[7] S. Chapman, B. C. Garrett, and W. H. Miller, J. Chem. Phys. **63**, 2710 (1975).
[8] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[9] G. Torres-Vega and J. H. Frederick, J. Chem. Phys. **98**, 3103 (1993).
[10] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965), Chaps. 10 and 11.
[11] D. Chandler and P. G. Wolynes, J. Chem. Phys. **74**, 4078 (1981).
[12] B. J. Berne and D. Thirumalai, Ann. Rev. Phys. Chem. **41**, 839 (1990).
[13] D. L. Freeman and J. D. Doll, Adv. Chem. Phys. **70**, 139 (1988).
[14] J. D. Doll and D. L. Freeman, Adv. Chem. Phys. **73**, 289 (1989).
[15] *Quantum Simulations of Condensed Matter Phenomena*, edited by J. D. Doll and J. E. Gubernatis (World Scientific, Singapore, 1990).
[16] D. Chandler, in *Liquides, Cristallisation et Transition Vitreuse, Les Houches*, edited by D. Levesque, J. P. Hansen, and J. Zinn-Justin (Elsevier, New York, 1991).
[17] R. P. Feynman and H. Kleinert, Phys. Rev. A **34**, 5080 (1986).
[18] R. Giachetti and V. Tognetti, Phys. Rev. Lett. **55**, 912 (1985); Phys. Rev. B **33**, 7647 (1986).
[19] W. Janke and H. Kleinert, Chem. Phys. Lett. **137**, 162 (1987).
[20] J. Cao and B. J. Berne, J. Chem. Phys. **95**, 7531 (1990).
[21] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5093 (1994).
[22] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5106 (1994).
[23] J. Cao and G. A. Voth, J. Chem. Phys. **101**, 6157 (1994).
[24] J. Cao and G. A. Voth, J. Chem. Phys. **101**, 6168 (1994).
[25] J. Cao and G. A. Voth, J. Chem. Phys. **101**, 6184 (1994).

[26] A. Cuccoli, V. Tognetti, P. Verrucchi, and R. Vaia, Phys. Rev. A **45**, 8414 (1992).
[27] G. A. Voth, Phys. Rev. A **44**, 5302 (1991).
[28] P. Choquard, *Selected Topics in Lattice Dynamics* (Benjamin, New York, 1966).
[29] T. R. Koehler, Phys. Rev. Lett. **17**, 89 (1966).
[30] K. Maki and H. Takayama, Phys. Rev. B **20**, 3223 (1979), **20**, 5009 (1979).
[31] R. F. Dashen, B. Hasslacher, and A. Neveu, Phys. Rev. D **10**, 4144 (1974).
[32] M. S. Swanson, *Path Integrals and Quantum Processes* (Academic, San Diego, 1992).
[33] W. H. Miller, J. Chem. Phys. **63**, 1166 (1975).
[34] R. G. Littlejohn, Phys. Rev. **138**, 193 (1986).
[35] F. A. Berezin and M. A. Šubin, in *Colloquia Mathematica Societatis János Bolyai*, edited by B. S. Z.-Nagy (North-Holland, Amsterdam, 1972), p. 21.
[36] F. Bayen, M. Flato, C. Fronsdal, A. Lichnerowicz, and D. Sternheimer, Ann. Phys. **111**, 61, (1978).
[37] R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).
[38] G. Baym and N. D. Mermin, J. Math. Phys. **2**, 232 (1961).
[39] J. Cao and G. A. Voth, J. Chem. Phys. **99**, 10700 (1993).
[40] G. A. Voth, D. Chandler, and W. H. Miller, J. Chem. Phys. **91**, 7749 (1989).
[41] G. A. Voth, Chem. Phys. Lett. **170**, 289 (1990).
[42] G. A. Voth, J. Phys. Chem. **97**, 8365 (1993).
[43] M. Messina, G. K. Schenter, and B. C. Garrett, J. Chem. Phys. **99**, 8644 (1993).