The values of the degree of ion binding, Fig. 5, calculated according to any of the three definitions show almost the same dependence on $\bar{N}_1$. In the whole interval of $\bar{N}_1$ the divalent counterions are more bound than the monovalent counterions. Further, the degree of ion binding of the less bound monovalent ionic species increases and that of the more bound divalent ionic species decreases with increasing of the corresponding equivalent fractions. This finding reminds us of a similar rule about the dependence of the selectivity coefficient of ion exchange on the fraction of ionic species within the resin phase.

It is necessary to emphasize that the calculations presented in this paper are exclusively based on electrostatic interaction and therefore may be only compared with experimental results obtained with polyelectrolyte solutions exhibiting no specific interactions.

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Quantum Corrections to the Momentum Relaxation Time of a Brownian Particle*

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The long-time, heavy-mass limit of the quantum-mechanical momentum autocorrelation function of a massive particle immersed in a bath of light particles is considered. An expression for the momentum relaxation time is obtained. It is found that the symmetrized and canonical correlation functions yield identical results in this limit. The momentum relaxation time, which is the inverse of the friction constant of the quantum Fokker–Planck equation, is expanded in powers of Planck's constant to obtain the first quantum correction to the classical result. Quantum corrections for canonical correlation functions are discussed.

I. INTRODUCTION

In recent years, the availability of time correlation function expressions for transport coefficients has prompted considerable interest in these functions.[1] In the present article, we investigate the long-time behavior of the quantum-mechanical momentum autocorrelation function of a Brownian (B) particle of mass M immersed in a bath of particles of mass m in the limit that $M \gg m$. For long times, the correlation function decays exponentially and we obtain a quantum-mechanical expression for the relaxation time. The first quantum correction to the classical relaxation time is then obtained by an expansion of this expression in powers of Planck's constant.

Our starting point in Sec. II is the definition of the canonical and symmetrized correlation functions.[2] With the aid of Mori's generalized theory of Brownian motion,[3] we show that both these correlation functions satisfy an integro-differential equation of the now familiar form.[4] In Sec. III, these equations are recast by the use of the Wigner equivalent technique[5,6] in a form which facilitates the development of Sec. IV, where by employing a heavy-mass limiting procedure, we obtain an explicit expression for the momentum relaxation time for each of the two correlation function definitions. The identity of these two expressions is demonstrated and the relationship of our results to the friction constant expressions obtained in several studies[7–9] of the quantum Fokker–Planck equation is discussed.

In Sec. V, we find an explicit expression for the first quantum correction to the classical momentum

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relaxation time. Finally, in the appendix, we discuss quantum corrections for general canonical correlation functions.

II. BROWNIAN PARTICLE MOMENTUM CORRELATION FUNCTIONS

The Hamiltonian operator of the quantum-mechanical system composed of the B particle and N bath particles is

$$H=\frac{\mathbf{P}\cdot\mathbf{P}}{2M}+\sum_{i=1}^{N}\frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m}+\sum_{i=1}^{N}u_i(|\mathbf{r}_i-\mathbf{R}|)+\sum_{i<j}^{N}\phi_{ij}(|\mathbf{r}_i-\mathbf{r}_j|), \quad (2.1)$$

or in condensed notation,

$$H=(\mathbf{P}\cdot\mathbf{P}/2M)+(\mathbf{p}\cdot\mathbf{p}/2m)+U(\mathbf{R},\mathbf{r})+\Phi(\mathbf{r}), \quad (2.2)$$

where $\mathbf{P}$, $\mathbf{R}$ and $\mathbf{p}_i$, $\mathbf{r}_i$ denote the momentum and position operators of the B particle and bath particle i, Φ is the interaction of the bath particles, and U is the interaction of the B particle with the bath.[10] We assume that the entire equilibrium system is enclosed in a large volume V and that Boltzmann statistics are obeyed.

We define a time autocorrelation function of the B particle momentum operator by

$$g(t)=(P_\mu(t),P_\mu)=(P_\mu,P_\mu(t)), \quad (2.3)$$

where

$$P_\mu(t)=\exp[(i/\hbar)Ht]P_\mu\exp[-(i/\hbar)Ht]\equiv\exp(iLt)P_\mu, \quad (2.4)$$

with the quantum Liouville operator defined by the commutator

$$iL(\cdots)=(i/\hbar)[H,(\cdots)]. \quad (2.5)$$

In Eq. (2.3), $\mu=x,y,z$ and we have used the convention of summation over repeated Greek indices.

Following Mori,[3] we shall consider two possible definitions for the bracket (A_μ, B_ν) of two Hermitian operators $\mathbf{A}$ and $\mathbf{B}$. The canonical bracket is characterized by the presence of a Kubo transform,[2]

$$(A_\mu,B_\nu)_c=\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho[\exp(\lambda\hbar L)A_\mu]B_\nu\}, \quad (2.6)$$

while the symmetrized bracket is defined as

$$(A_\mu,B_\nu)_s=\tfrac{1}{2}\,\mathrm{Tr}\{\rho[A_\mu,B_\nu]_+\}, \quad (2.7)$$

where the + subscript denotes the anticommutator. In Eqs. (2.6) and (2.7), $\beta=(kT)^{-1}$ and ρ is the normalized canonical ensemble density operator:

$$\rho=\{\mathrm{Tr}[\exp(-\beta H)]\}^{-1}\exp(-\beta H). \quad (2.8)$$

[10] In our notation, we do not explicitly distinguish between a quantum-mechanical operator and the corresponding variable or function, i.e., $\mathbf{P}_{\mathrm{op}}$ is denoted $\mathbf{P}$. It should be apparent from the context, however, which meaning is intended.

Depending upon the choice of bracket, there are two alternatives for the definition of the correlation function $g(t)$. The Fourier transforms of these two correlation functions are related by[2]

$$\int_{-\infty}^{\infty}dt\exp(-i\omega t)g_c(t)=\frac{2}{\beta\hbar\omega}\tanh\tfrac{1}{2}(\beta\hbar\omega)\times\int_{-\infty}^{\infty}dt\exp(-i\omega t)g_s(t). \quad (2.9)$$

As correlations of the form Eq. (2.6) are obtained in linear response theory,[2] we accept $g_c(t)$ as the appropriate definition. We shall find in Sec. IV, however, that $g_c(t)=g_s(t)$ in the heavy-mass limit. Since in the remainder of this section we obtain an equation for $g(t)$ which is valid for either definition, we omit the bracket subscripts.

We now wish to obtain an operator equation of motion for the B particle momentum. By the use of projection operator techniques,[4] Mori has derived a generalized operator Langevin equation which may be employed for this purpose. If a projection operator $\mathcal{P}$ is defined by

$$\mathcal{P}\mathbf{A}=(\mathbf{A},P_\nu)(P_\nu,P_\nu)^{-1}P_\nu, \quad (2.10)$$

then Mori's analysis yields

$$\frac{dP_\mu(t)}{dt}=E_\mu(t)-\int_0^t ds(E_\mu(s),E_\nu(0))\times(P_\nu,P_\nu)^{-1}P_\nu(t-s), \quad (2.11)$$

where in this generalized Langevin equation the "random force" is given by

$$\mathbf{E}(t)=\exp[(1-\mathcal{P})iLt]iL\mathbf{P}, \quad (2.12)$$

with the property

$$(\mathbf{E}(t),\mathbf{P})=0. \quad (2.13)$$

It follows from Eqs. (2.3), (2.11), and (2.12) that the correlation function $g(t)$ satisfies

$$\frac{dg(t)}{dt}=-\gamma^2\int_0^t ds\,g(t-s)K(s);\qquad g(0)=(P_\mu,P_\mu), \quad (2.14)$$

where $\gamma^2=(m/M)$ and

$$K(s)=[\gamma^2(P_\nu,P_\nu)]^{-1}(E_\mu(s),E_\mu(0)). \quad (2.15)$$

In obtaining this result, we have noted that the tensor $(\mathbf{P}(t),\mathbf{P})$ is diagonal for an isotropic fluid.

III. REFORMULATION OF THE CORRELATION FUNCTION EQUATIONS

We now employ the Wigner equivalent formalism to express Eq. (2.14) in a form which facilitates our subsequent analysis. As the properties and utilization of Wigner equivalents are discussed elsewhere,[5,6] we simply quote here the relationships we require.

For the system of interest, the Wigner equivalent $\hat{A}$ of an operator A is defined as the function

$$\hat{A}(\mathbf{R},\mathbf{P};\mathbf{r},\mathbf{p})=\left[\frac{V}{(2\pi\hbar)^3}\right]^{N+1}\int d\mathbf{Q}d\mathbf{q}\exp\left[-\frac{i}{\hbar}(\mathbf{R}\cdot\mathbf{Q}+\mathbf{r}\cdot\mathbf{q})\right]\langle\mathbf{P}-\tfrac{1}{2}\mathbf{Q},\mathbf{p}-\tfrac{1}{2}\mathbf{q}\mid A\mid\mathbf{P}+\tfrac{1}{2}\mathbf{Q},\mathbf{p}+\tfrac{1}{2}\mathbf{q}\rangle, \quad (3.1)$$

where the kets $|\mathbf{P},\mathbf{p}\rangle$ in coordinate representation are normalized plane waves:

$$\Psi_{\mathbf{P},\mathbf{p}}=(V)^{-(N+1)1/2}\exp[(i/\hbar)(\mathbf{R}\cdot\mathbf{P}+\mathbf{r}\cdot\mathbf{p})]. \quad (3.2)$$

It will prove convenient to redefine the Wigner equivalent in terms of the scaled momentum variable $\mathbf{P}'=\gamma\mathbf{P}$:

$$\hat{A}'(\mathbf{R},\mathbf{P}';\mathbf{r},\mathbf{p})=\left[\frac{V}{(2\pi\hbar)^3}\right]^{N+1}\gamma^{-3}\int d\mathbf{Q}d\mathbf{q}\exp\left[-\frac{i}{\hbar}(\gamma^{-1}\mathbf{R}\cdot\mathbf{Q}+\mathbf{r}\cdot\mathbf{q})\right]$$
$$\times\langle\gamma^{-1}\mathbf{P}'-\tfrac{1}{2}\gamma^{-1}\mathbf{Q},\mathbf{p}-\tfrac{1}{2}\mathbf{q}\mid A\mid\gamma^{-1}\mathbf{P}'+\tfrac{1}{2}\gamma^{-1}\mathbf{Q},\mathbf{p}+\tfrac{1}{2}\mathbf{q}\rangle. \quad (3.3)$$

As our analysis will proceed in terms of the variable $\mathbf{P}'$, we suppress the prime for ease of notation.

With the aid of definition Eq. (3.3), a canonical ensemble average of an operator A may be written as

$$\mathrm{Tr}(\rho A)=\int d\mathbf{R}d\mathbf{P}d\mathbf{r}d\mathbf{p}f(\mathbf{R},\mathbf{P};\mathbf{r},\mathbf{p};\beta)\hat{A}(\mathbf{R},\mathbf{P};\mathbf{r},\mathbf{p})\equiv\int d\mathbf{x}d\mathbf{y}f(\mathbf{x},\mathbf{y};\beta)\hat{A}(\mathbf{x},\mathbf{y}), \quad (3.4)$$

where f is the system Wigner distribution function[11] [see Eq. (3.11) below]. Commutator and anticommutator Wigner equivalents have the form

$$(\widehat{AB})-(\widehat{BA})=2i[\hat{B}\sin(\hbar T/2)\hat{A}], \quad (3.5)$$

$$(\widehat{AB})+(\widehat{BA})=2[\hat{A}\cos(\hbar T/2)\hat{B}]. \quad (3.6)$$

The operator T is

$$T(x,y)=\nabla_{\mathbf{p}}^{\leftarrow}\cdot\nabla_{\mathbf{r}}^{\rightarrow}-\nabla_{\mathbf{r}}^{\leftarrow}\cdot\nabla_{\mathbf{p}}^{\rightarrow}+\gamma\nabla_{\mathbf{P}}^{\leftarrow}\cdot\nabla_{\mathbf{R}}^{\rightarrow}-\gamma\nabla_{\mathbf{R}}^{\leftarrow}\cdot\nabla_{\mathbf{P}}^{\rightarrow}, \quad (3.7)$$

where the arrows indicate in which direction the gradients are to be applied.

We may now reformulate Eq. (2.14) for the canonical correlation function $g_c(t)=(P_\mu,P_\mu(t))_c$:

$$\frac{dg_c(t)}{dt}=-\gamma^2\int_0^t ds g_c(t-s)K_c(s);$$
$$g_c(0)=(P_\mu,P_\mu)_c. \quad (3.8)$$

Application of Eqs. (3.3)–(3.7) enables us to write $g_c(t)$ as

$$g_c(t)=(P_\mu,P_\mu(t))_c$$
$$=\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho[\exp(\lambda\hbar L)\mathbf{P}]\cdot\exp(iLt)\mathbf{P}\}$$
$$=(\beta\gamma^2)^{-1}\int_0^\beta d\lambda\int d\mathbf{x}d\mathbf{y}\left\{f\exp\left(\frac{\hbar T}{2i}\right)[\exp(\lambda\hbar\hat{L})\mathbf{P}]\right\}\cdot\exp(i\hat{L}t)\mathbf{P}, \quad (3.9)$$

where the operator $i\hat{L}$ is

$$i\hat{L}(\mathbf{x},\mathbf{y})=(\mathbf{p}/m)\cdot\nabla_{\mathbf{r}}+\gamma(\mathbf{P}/m)\cdot\nabla_{\mathbf{R}}-(2/\hbar)\sin(\tfrac{1}{2}\hbar\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}})\Phi(\mathbf{r})-(2/\hbar)\sin[\tfrac{1}{2}\hbar(\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}+\gamma\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{P}})]U(\mathbf{R},\mathbf{r}), \quad (3.10)$$

and the Wigner distribution function (wdf) f is the normalized solution to

$$\frac{\partial f'}{\partial\beta}(\mathbf{x},\mathbf{y};\beta)=-\left\{-\frac{\hbar^2\gamma^2}{8m}\nabla_{\mathbf{R}}^2-\frac{\hbar^2}{8m}\nabla_{\mathbf{r}}^2+\frac{\mathbf{P}\cdot\mathbf{P}}{2m}+\frac{\mathbf{p}\cdot\mathbf{p}}{2m}+\cos(\tfrac{1}{2}\hbar\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}})\Phi(\mathbf{r})\right.$$
$$\left.+\cos[\tfrac{1}{2}\hbar(\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}+\gamma\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{P}})]U(\mathbf{R},\mathbf{r})\right\}f'(\mathbf{x},\mathbf{y};\beta), \quad (3.11)$$

with $f'(\mathbf{x},\mathbf{y};0)=[(\pi\hbar)^{3N+3}\gamma^3]^{-1}$. In Eqs. (3.10) and (3.11), the position gradients in the arguments of the sine and cosine operators are understood to act only upon the potentials. In the appendix, we outline how the above procedure may be used to obtain quantum corrections for time correlation functions of the form Eq. (2.6).

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While the initial value $g_c(0)$ may be obtained from the Wigner form in Eq. (3.9), the calculation is most readily effected with the aid of the following identity due to Kubo[2]:

$$\frac{i}{\hbar}[A,\rho]=\int_0^\beta d\lambda\{\rho[\exp(\lambda\hbar L)iLA]\}. \tag{3.12}$$

With the use of this relation and the commutation properties of $\mathbf{R}$ and $\mathbf{P}$, we find

$$\begin{aligned}g_c(0)&=\beta^{-1}\int_0^\beta d\lambda\ \mathrm{Tr}\{\rho[\exp(\lambda\hbar L)\mathbf{P}]\cdot\mathbf{P}\}\\&=(im/\beta\hbar\gamma^2)\ \mathrm{Tr}\{[\mathbf{R},\rho]\cdot\mathbf{P}\}=3m/\beta\gamma^2.\end{aligned} \tag{3.13}$$

We now cast the kernel $K_c(s)$ in terms of Wigner equivalents. Using Eqs. (2.15), (2.6), and (3.13), we have after some manipulation

$$K_c(s)=(3m)^{-1}\int_0^\beta d\lambda\ \mathrm{Tr}\{\rho[\exp(\lambda\hbar L)\mathbf{E}_c]\cdot\mathbf{E}_c(s)\}. \tag{3.14}$$

Application of Eqs. (3.3)–(3.7) enables us to write this in the Wigner formalism as

$$K_c(s)=(3m)^{-1}\int_0^\beta d\lambda\int d\mathbf{x}d\mathbf{y}\left\{f\exp\left(\frac{\hbar T}{2i}\right)[\exp(\lambda\hbar\hat{L})\hat{\mathbf{E}}_c]\right\}\cdot\hat{\mathbf{E}}_c(s), \tag{3.15}$$

where $\hat{\mathbf{E}}_c(s)=\hat{\mathbf{E}}_c(\mathbf{x},\mathbf{y};s)$ is the Wigner equivalent of $\mathbf{E}_c(s)$. The function $\hat{\mathbf{E}}_c(s)$ is obtained by consideration of the operator equation satisfied by $\mathbf{E}_c(s)$. Differentiation of Eq. (2.12) and use of the definitions Eqs. (2.10) and (2.6) yield

$$\begin{aligned}(d/ds)\mathbf{E}_c(s)&=(1-\mathcal{P}_c)iL\mathbf{E}_c(s)\\&=iL\mathbf{E}_c(s)+\frac{\gamma^2\mathbf{P}}{m}\cdot\left(\int_0^\beta d\lambda\ \mathrm{Tr}\{\rho[\exp(\lambda\hbar L)\mathbf{E}_c]\mathbf{E}_c(s)\}\right),\end{aligned} \tag{3.16}$$

with $\mathbf{E}_c(0)=iL\mathbf{P}$. Forming the Wigner equivalent of both sides of Eq. (3.16), we find

$$\begin{aligned}\frac{\partial}{\partial s}\hat{\mathbf{E}}_c(\mathbf{x},\mathbf{y};s)=i\hat{L}(\mathbf{x},\mathbf{y})\hat{\mathbf{E}}_c(\mathbf{x},\mathbf{y};s)+\frac{\gamma\mathbf{P}}{m}\cdot\int_0^\beta d\lambda\int d\mathbf{x}'d\mathbf{y}'\Bigg(f(\mathbf{x}',\mathbf{y}';\beta)\\\times\exp\left(\frac{\hbar T}{2i}\right)\{\exp[\lambda\hbar\hat{L}(\mathbf{x}',\mathbf{y}')]\hat{\mathbf{E}}_c(\mathbf{x}',\mathbf{y}')\}\Bigg)\hat{\mathbf{E}}_c(\mathbf{x}',\mathbf{y}';s),\end{aligned} \tag{3.17}$$

with

$$\hat{\mathbf{E}}_c(\mathbf{x},\mathbf{y};0)=-\nabla_{\mathbf{R}}U(\mathbf{R},\mathbf{r})=\sum_{i=1}^N\nabla_{\mathbf{r}_i}u_i(|\mathbf{r}_i-\mathbf{R}|)\equiv\mathbf{F}(\mathbf{R},\mathbf{r}), \tag{3.18}$$

where $\mathbf{F}$ is the force exerted on the B particle by the N bath particles.

Combining Eqs. (3.8), (3.13), and (3.15), we find that the canonical correlation function satisfies

$$\begin{aligned}\frac{dg_c(t)}{dt}&=-\frac{\gamma^2}{3m}\int_0^t dsg_c(t-s)\int_0^\beta d\lambda\int d\mathbf{x}d\mathbf{y}\left\{f\exp\left(\frac{\hbar T}{2i}\right)[\exp(\lambda\hbar\hat{L})\hat{\mathbf{E}}_c]\right\}\cdot\hat{\mathbf{E}}_c(s);\\g_c(0)&=(3m/\beta\gamma^2).\end{aligned} \tag{3.19}$$

One may show in an analogous fashion that the symmetrized correlation function may be written in the form[6]

$$g_s(t)=\gamma^{-2}\int d\mathbf{x}d\mathbf{y}f\mathbf{P}\cdot[\exp(i\hat{L}t)\mathbf{P}] \tag{3.20}$$

and satisfies

$$\begin{aligned}\frac{dg_s(t)}{dt}&=-\gamma^2\langle\mathbf{P}\cdot\mathbf{P}\rangle^{-1}\int_0^t dsg_s(t-s)\int d\mathbf{x}d\mathbf{y}[f\cos(\tfrac{1}{2}\hbar T)\hat{\mathbf{E}}_s]\cdot\hat{\mathbf{E}}_s(s);\\g_s(0)&=\gamma^{-2}\langle\mathbf{P}\cdot\mathbf{P}\rangle\equiv\gamma^{-2}\int d\mathbf{x}d\mathbf{y}f\mathbf{P}\cdot\mathbf{P},\end{aligned} \tag{3.21}$$

where $\hat{\mathbf{E}}_s(s)$ is the solution to

$$\frac{\partial}{\partial s}\hat{\mathbf{E}}_s(\mathbf{x},\mathbf{y};s)=i\hat{L}(\mathbf{x},\mathbf{y})\hat{\mathbf{E}}_s(\mathbf{x},\mathbf{y};s)+3\gamma\langle\mathbf{P}\cdot\mathbf{P}\rangle^{-1}\mathbf{P}\cdot\int d\mathbf{x}'d\mathbf{y}'[f(\mathbf{x}',\mathbf{y}';\beta)\cos(\tfrac{1}{2}\hbar T)\hat{\mathbf{E}}_s(\mathbf{x}',\mathbf{y}')]\hat{\mathbf{E}}_s(\mathbf{x}',\mathbf{y}';s);$$

$$\hat{\mathbf{E}}_s(\mathbf{x},\mathbf{y};0)=\mathbf{F}(\mathbf{R},\mathbf{r}). \tag{3.22}$$

In the next section, we shall find that in the limit $\gamma\rightarrow0$ (if the temperature is not too low), Eqs. (3.17) and (3.22) are identical. In this limit, these equations may be integrated to yield an expression for the force on the B particle whose time dependence is calculated with the B particle fixed at $\mathbf{R}$.

IV. HEAVY-MASS LIMIT

In this section, we apply the heavy-mass limit[4,12,13]

$$\gamma\rightarrow0,\qquad t\rightarrow\infty;\qquad \gamma^2t=\tau=\text{constant} \tag{4.1}$$

to Eqs. (3.19) and (3.21) to extract the long-time exponential behavior of the correlation functions. Before proceeding with the formal analysis, we briefly consider the basis for the application of this limit and its interpretation.

In a *classical* dense fluid, the ratio of the magnitude of the B particle momentum to that of a bath particle is of order γ^{-1} and we expect that P changes very slowly compared to p as a result of collisions. In order of magnitude, the relative change of P during the B-particle–bath-particle time of collision $\tau_B\sim R_0(m\beta)^{1/2}$ is

$$\Delta P/P\sim(u_0/R_0)R_0(m\beta)^{1/2}(\beta/M)^{1/2}\sim\gamma, \tag{4.2}$$

where we have taken the potential u to have strength $u_0\sim kT$ and a characteristic length R_0. During this same interval, the relative change of the momentum of a bath particle is approximately $\Delta p/p\sim1$.

We recall from Eq. (2.14) that the momentum correlation functions satisfy

$$\frac{dg(t)}{dt}=-\gamma^2\int_0^t dsg(t-s)K(s), \tag{4.3}$$

where $K(s)$ is the correlation function of a modified force acting on the B particle. As the change of $g(t)$ is extremely slow ($\sim\gamma^2$) on the time scale t for $\gamma\ll1$, introduction of the time scale $\tau=\gamma^2t$ will enable us to follow significant changes of $g(t)$. Roughly speaking, we may interpret the limit $\gamma\rightarrow0$ as expressing the condition that the mass ratio be small enough to insure that the relaxation time of $g(t)$ ($\sim\gamma^{-2}$) be widely separated from the relevant microscopic times. In our problem, the relevant time will be the relaxation time of the modified force correlation function, which we assume to be several units of τ_B. In the same spirit, we may view the limit $t\rightarrow\infty$ as indicating that times are to be considered which are much greater than this microscopic time. With this orientation, we proceed with the formal limiting argument.

We first consider the canonical correlation function. With the change of variables $\tau=\gamma^2t$ and the definition $\gamma^2g_c(t)=\bar{g}_c(\tau)$, Eq. (3.19) becomes

$$\frac{d\bar{g}_c(\tau)}{d\tau}=-\int_0^{\tau/\gamma^2}ds\bar{g}_c(\tau-\gamma^2s)\left[(3m)^{-1}\int_0^\beta d\lambda\int d\mathbf{x}d\mathbf{y}\left\{f\exp\left(\frac{\hbar T}{2i}\right)[\exp(\lambda\hbar\hat{L})\hat{\mathbf{E}}_c]\right\}\cdot\hat{\mathbf{E}}_c(s)\right], \tag{4.4}$$

with $\bar{g}_c(0)=(3m/\beta)$. Executing the limit Eq. (4.1) and reverting to our original variables, we find

$$g_c(t)=(3M/\beta)\exp(-t/\tau_c);\qquad t>0, \tag{4.5}$$

where the momentum relaxation time τ_c is

$$\tau_c^{-1}=\frac{\gamma^2}{3m}\int_0^\infty ds\lim_{\gamma\to0}\left(\int_0^\beta d\lambda\int d\mathbf{x}d\mathbf{y}\left\{f\exp\left(\frac{\hbar T}{2i}\right)[\exp(\lambda\hbar\hat{L})\hat{\mathbf{E}}_c]\right\}\cdot\hat{\mathbf{E}}_c(s)\right). \tag{4.6}$$

To obtain the limiting form of the phase integral in Eq. (4.6), we expand the operators and functions appearing there in powers of γ. With the aid of Eqs. (3.10), (3.11), (3.17), and (3.18), we find

$$\begin{aligned}i\hat{L}(\mathbf{x},\mathbf{y})&=i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})+O(\gamma)\\&=(\mathbf{p}/m)\cdot\nabla_r-(2/\hbar)\sin[\tfrac{1}{2}\hbar(\nabla_r\cdot\nabla_p)][U(\mathbf{R},\mathbf{r})+\Phi(\mathbf{r})]+O(\gamma),\end{aligned} \tag{4.7}$$

and

$$\hat{\mathbf{E}}_c(\mathbf{x},\mathbf{y};s)=\exp[i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})s]\mathbf{F}(\mathbf{R},\mathbf{r})+O(\gamma). \tag{4.8}$$

From Eq. (3.11), we obtain $f=f_0+O(\gamma)$, where

$$f_0(\mathbf{x},\mathbf{y};\beta)=(\beta/2\pi m)^{3/2}[\exp(-\beta\mathbf{P}\cdot\mathbf{P}/2m)]f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta), \tag{4.9}$$

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with f_b, the bath wdf, the solution to

$$(\partial f_b'/\partial\beta) = -\{-(\hbar^2/8m)\nabla_r^2 + (\mathbf{p}\cdot\mathbf{p}/2m) + \cos[\tfrac{1}{2}\hbar(\nabla_r\cdot\nabla_p)][U(\mathbf{R},\mathbf{r})+\Phi(\mathbf{r})]\}f_b' \tag{4.10}$$

normalized with respect to $\mathbf{R}$, $\mathbf{r}$, and $\mathbf{p}$. Both f_b and $\hat{L}_b$ are appropriate to a system of interacting bath particles in the field of the B particle fixed at $\mathbf{R}$.

To complete the calculation, we note from Eq. (3.7) that

$$T(\mathbf{x},\mathbf{y}) = T_0(\mathbf{r},\mathbf{p}) + 0(\gamma) \equiv \overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_r - \overleftarrow{\nabla}_r\cdot\overrightarrow{\nabla}_p + O(\gamma). \tag{4.11}$$

In consequence of Eqs. (4.6)–(4.9) and Eq. (4.11), the relaxation time for $g_c(t)$ is

$$\tau_c^{-1} = (3M)^{-1}\int_0^\infty ds\int_0^\beta d\lambda\int d\mathbf{R}d\mathbf{r}d\mathbf{p}\left(f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta)\exp\left(\frac{\hbar T_0}{2i}\right)\{\exp[\lambda\hbar\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})]\mathbf{F}(\mathbf{R},\mathbf{r})\}\right)\cdot\{\exp[i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})s]\mathbf{F}(\mathbf{R},\mathbf{r})\}, \tag{4.12}$$

where [see Eq. (4.10)]

$$f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta) = \left[\int d\mathbf{R}d\mathbf{r}d\mathbf{p}f_b'(\mathbf{R};\mathbf{r},\mathbf{p};\beta)\right]^{-1} f_b'(\mathbf{R};\mathbf{r},\mathbf{p};\beta). \tag{4.13}$$

Noting that the integrations in Eq. (4.12) over the bath variables $\mathbf{r}$ and $\mathbf{p}$ yield quantities independent of $\mathbf{R}$ (as may be seen by letting $\mathbf{R}\to\mathbf{R}'$, $\mathbf{r}_i\to\mathbf{r}_i'+\mathbf{R}'$), we may perform the $\mathbf{R}$ integrations to obtain

$$\tau_c^{-1} = (3M)^{-1}\int_0^\infty ds\int_0^\beta d\lambda\int d\mathbf{r}d\mathbf{p}\left(f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta)\exp\left(\frac{\hbar T_0}{2i}\right)\times\{\exp[\lambda\hbar\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})]\mathbf{F}(\mathbf{R},\mathbf{r})\}\right)\cdot\{\exp[i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})s]\mathbf{F}(\mathbf{R},\mathbf{r})\}, \tag{4.14}$$

where we have retained the same notation for the bath wdf f_b, now redefined as the solution to Eq. (4.10) normalized with respect to $\mathbf{r}$ and $\mathbf{p}$.

In order to obtain an expression for the symmetrized correlation function in the heavy-mass limit, we shall require the $\gamma=0$ limits of the quantities appearing in the kernel of Eq. (3.21). From Eq. (4.9) we find

$$\langle\mathbf{P}\cdot\mathbf{P}\rangle = \int d\mathbf{x}d\mathbf{y}f(\mathbf{x},\mathbf{y};\beta)\mathbf{P}\cdot\mathbf{P} = (3m/\beta) + O(\gamma). \tag{4.15}$$

[Note that this average also appears in the initial condition of Eq. (3.21).] From Eqs. (3.22), (4.7), (4.9), (4.11), and (4.15), we obtain

$$\hat{\mathbf{E}}_s(\mathbf{x},\mathbf{y};s) = \exp[i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})s]\mathbf{F}(\mathbf{R},\mathbf{r}) + O(\gamma). \tag{4.16}$$

Finally, we have from Eq. (4.11),

$$\cos[\tfrac{1}{2}\hbar T(\mathbf{x},\mathbf{y})] = \cos[\tfrac{1}{2}\hbar T_0(\mathbf{r},\mathbf{p})] + O(\gamma). \tag{4.17}$$

With these results and Eqs. (4.7) and (4.9), we may apply the limit Eq. (4.1) in the same manner as above to Eq. (3.21) to find for the symmetrized correlation function

$$g_s(t) = (3M/\beta)\exp(-t/\tau_s);\qquad t>0, \tag{4.18}$$

where the relaxation time is

$$\tau_s^{-1} = \frac{\beta}{3M}\int_0^\infty ds\int d\mathbf{r}d\mathbf{p}\times[f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta)\cos(\tfrac{1}{2}\hbar\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_r)\mathbf{F}(\mathbf{R},\mathbf{r})]\cdot\{\exp[i\hat{L}_b(\mathbf{R};\mathbf{r},\mathbf{p})s]\mathbf{F}(\mathbf{R},\mathbf{r})\}. \tag{4.19}$$

In obtaining Eq. (4.19), we have again formally integrated over $\mathbf{R}$ and redefined f_b to be normalized with respect to $\mathbf{r}$ and $\mathbf{p}$.

Equation (4.19) for τ_s^{-1} may easily be shown to be equivalent to the friction constant expression obtained by Davis *et al.*[7] in a study of the quantum Fokker–Planck equation.[14]

The Wigner equivalent formulations for τ_c and τ_s may be "inverted"[5] to yield the following expressions of the more usual quantum-mechanical form:

$$\tau_c^{-1} = \frac{\beta}{3M}\int_0^\infty ds\beta^{-1}\int_0^\beta d\lambda\times\mathrm{Tr}_b\{\rho_b[\exp(\lambda\hbar L_b)G_\mu][\exp(iL_bs)G_\mu]\}, \tag{4.20}$$

$$\tau_s^{-1} = \frac{\beta}{3M}\int_0^\infty ds\tfrac{1}{2}\,\mathrm{Tr}_b(\rho_b\{G_\mu,[\exp(iL_bs)G_\mu]\}_+), \tag{4.21}$$

[14] In Ref. 7, the factor M^{-1} is not included in the definition of the friction constant. A factor of $\frac{1}{3}$ should appear in the definition Eq. (III-62) of this reference.

where Tr_b indicates a trace over bath variables and

$$\mathbf{G}\equiv(i/\hbar)[U,\mathbf{p}]$$
$$=\left(\frac{i}{\hbar}\right)\sum_{i=1}^{N}[u_i,\mathbf{p}_i] \qquad (4.22)$$

is the quantum mechanical force exerted on the bath particles by the B particle fixed at $\mathbf{R}$. Here ρ_b and L_b are the density and Liouville operators [cf. Eqs. (2.5) and (2.8)] containing the Hamiltonian of the bath including the bath interaction with the fixed B particle. The quantities $\mathbf{G}$, ρ_b, and L_b depend on $\mathbf{R}$, regarded as a parameter which locates the source of a prescribed field in which the bath particle motion occurs. Equation (4.21) is identical in form to the friction constant expression obtained by Dagonnier and Résibois[9] in their treatment of the Fokker–Planck equation for a system composed of a B particle immersed in a Bose fluid.

The equivalence of τ_c and τ_s may be established by noting that an equation of the form Eq. (2.9) holds[2] for the correlation functions in Eqs. (4.20) and (4.21). For $\omega=0$,

$$\int_{-\infty}^{\infty}dt\beta^{-1}\int_0^{\beta}d\lambda\ \mathrm{Tr}_b\{\rho_b[\exp(\lambda\hbar L_b)G_\mu][\exp(iL_bt)G_\mu]\}$$
$$=\int_{-\infty}^{\infty}dt\tfrac{1}{2}\ \mathrm{Tr}_b(\rho_b\{G_\mu,[\exp(iL_bt)G_\mu]\}_+). \qquad (4.23)$$

As both correlation functions are even in t, we see that $\tau_c=\tau_s$.

We note that our results will not be valid for large but finite t and M in all circumstances. Difficulties of this nature were first noted by McKenna and Frisch,[8] who observed that the quantum Fokker–Planck equation was invalid for sufficiently low temperatures. As further discussed by Résibois and Dagonnier,[15] at low temperatures, where quantum effects are dominant, the magnitudes of the momenta of the B particle and the bath particles are determined essentially by their zero-point motion and are independent of mass. Hence, the ratio of the momenta will not be of order γ^{-1} and the basis for the limiting procedure discussed previously is not appropriate. This difficulty is evident if one examines the higher-order terms in the γ expansion of the kernels appearing in Eqs. (3.19) and (3.21). While the exact behavior of these terms is difficult to ascertain, it may be readily verified that the series will contain terms proportional to the factor $(\Lambda/R_0)^n(\lambda/R_0)^m$, where

$$\Lambda=\gamma\hbar/2(mkT)^{1/2}\equiv\gamma\lambda \qquad (4.24)$$

is the mean de Broglie wavelength of the B particle. Thus we see that the large mass of the B particle will not be sufficient to render these higher-order terms negligible in the low-temperature limit.

This interesting low-temperature regime has been discussed in detail from the point of view of the quantum Fokker–Planck equation by Résibois and Dagonnier.[15] The complications arising when Fermi statistics are obeyed by the system have been examined by Davis and Dagonnier.[16]

We restrict our further discussion to intermediate temperatures where quantum effects are so slight that Eqs. (4.5) and (4.18) are valid descriptions of the relaxation. In particular, we assume that the ratios of the mean de Broglie wavelength $\lambda=\hbar/2(mkT)^{1/2}$ of a bath particle to the characteristic lengths R_0 and r_0 of the potentials are small but not negligible compared to unity. In view of Eq. (4.24), this implies that for the B particle de Broglie wavelength,

$$\Lambda/R_0=\gamma\lambda/R_0\ll1 \qquad (4.25)$$

for large M, and therefore the system may be described as a classical B particle immersed in a slightly quantum-mechanical bath. Under these circumstances, the particle momenta will stand in the ratio

$$P/p\sim\gamma^{-1}[1+O(\lambda/R_0)^2+O(\lambda/r_0)^2], \qquad (4.26)$$

and the difficulties associated with the low-temperature regime will not be encountered.

V. QUANTUM CORRECTIONS TO THE RELAXATION TIME

In this section, we obtain the first quantum correction to the classical momentum relaxation time (or, equivalently, the friction constant) by expanding Eq. (4.19) for τ_s^{-1} in powers of $\hbar$. Our result will be appropriate for the temperature regime where the bath quantum effects are slight, i.e., λ/R_0, $\lambda/r_0<1$. As expansions of this type are considered in detail elsewhere,[6] we give only a brief account here.

From Eq. (4.10), we find for the bath wdf:

$$f_b(\mathbf{R};\mathbf{r},\mathbf{p};\beta)=f_b^{\mathrm{cl}}(\mathbf{R};\mathbf{r},\mathbf{p};\beta)$$
$$\times\{1+\hbar^2[\theta(\mathbf{R};\mathbf{r},\mathbf{p};\beta)-\langle\theta\rangle_{\mathrm{cl}}]\}+O(\hbar^4), \qquad (5.1)$$

where $(U_T\equiv U+\Phi)$

$$\theta(\mathbf{R};\mathbf{r},\mathbf{p};\beta)=(\beta^2/8m)$$
$$\times\{-\nabla_r^2U_T+\tfrac{1}{3}\beta[(\nabla_rU_T)^2+\nabla_r\nabla_rU_T:(\mathbf{pp}/m)]\}, \qquad (5.2)$$

and the angle brackets with subscript cl denote an average over the classical bath distribution

$$f_b^{\mathrm{cl}}(\mathbf{R};\mathbf{r},\mathbf{p};\beta)=Z_b^{-1}\exp\{-\beta[(\mathbf{p}\cdot\mathbf{p}/2m)+U_T(\mathbf{R},\mathbf{r})]\};$$
$$Z_b=\int d\mathbf{r}d\mathbf{p}\exp\left\{-\beta\left[\frac{\mathbf{p}\cdot\mathbf{p}}{2m}+U_T(\mathbf{R},\mathbf{r})\right]\right\}. \qquad (5.3)$$

[15] (a) P. Résibois and R. Dagonnier, Phys. Letters **22**, 252 (1966). (b) P. Résibois and R. Dagonnier, Bull. Acad. Sci. Belg. **52**, 1475 (1966).

[16] H. T. Davis and R. Dagonnier, J. Chem. Phys. **44**, 4030 (1966).

From Eqs. (4.7) and (4.16), the time-dependent force, correct to $O(\hbar^2)$, is

$$\exp[i\hat{L}_b s]\mathbf{F} = \exp[iL_b^{\text{cl}}s]\mathbf{F} + (\hbar^2/24) \times \int_0^s dz \exp[iL_b^{\text{cl}}z](\nabla_r^* \cdot \nabla_p)\, ^3U_T \times \{\exp[iL_b^{\text{cl}}(s-z)]\mathbf{F}\}, \quad (5.4)$$

where iL_b^{cl} is the classical bath Liouville operator

$$iL_b^{\text{cl}}(\mathbf{R}; \mathbf{r}, \mathbf{p}) = (\mathbf{p}/m)\cdot\nabla_r - \nabla_r U_T(\mathbf{R}, \mathbf{r})\cdot\nabla_p, \quad (5.5)$$

and the asterisk has been placed upon ∇_r to indicate that ∇_r operates only on U_T.

The correction arising from the cosine operator is

$$\cos[\tfrac{1}{2}\hbar(\nabla_p^{\leftarrow}\cdot\nabla_r^{\rightarrow})] = 1 - (\hbar^2/8)(\nabla_p^{\leftarrow}\cdot\nabla_r^{\rightarrow})^2 + O(\hbar^4). \quad (5.6)$$

With these results, it follows that, to $O(\hbar^2)$, Eq. (4.19) is

$$\tau_s^{-1} \equiv \zeta = \zeta_{\text{cl}} + \hbar^2\zeta_1, \quad (5.7)$$

where the classical friction constant is given by[17]

$$\zeta_{\text{cl}} = \frac{\beta}{3M}\int_0^\infty dt \int d\mathbf{r}d\mathbf{p} f_b^{\text{cl}}\mathbf{F}\cdot[\exp(iL_b^{\text{cl}}t)\mathbf{F}], \quad (5.8)$$

and the first quantum correction consists of three terms[18]:

$$\zeta_1 = \zeta_1^{(1)} + \zeta_1^{(2)} + \zeta_1^{(3)}, \quad (5.9)$$

where

$$\zeta_1^{(1)} = \frac{\beta}{3M}\int_0^\infty dt \int d\mathbf{r}d\mathbf{p} f_b^{\text{cl}}[\theta - \langle\theta\rangle_{\text{cl}}]\mathbf{F}\cdot[\exp(iL_b^{\text{cl}}t)\mathbf{F}], \quad (5.10)$$

$$\zeta_1^{(2)} = \frac{\beta}{3M}\int_0^\infty dt \int d\mathbf{r}d\mathbf{p} f_b^{\text{cl}} \times \left\{\left[\frac{\beta}{8m}\nabla_r^2 - \frac{\beta^2}{8m^2}\mathbf{pp}:\nabla_r\nabla_r\right]\mathbf{F}\right\}\cdot[\exp(iL_b^{\text{cl}}t)\mathbf{F}], \quad (5.11)$$

$$\zeta_1^{(3)} = \frac{\beta}{72M}\int_0^\infty dt \int d\mathbf{r}d\mathbf{p} f_b^{\text{cl}}\mathbf{F} \cdot\left(\int_0^t dz \exp(iL_b^{\text{cl}}z)(\nabla_r^*\cdot\nabla_p)\, ^3U_T \times \{\exp[iL_b^{\text{cl}}(t-z)]\mathbf{F}\}\right). \quad (5.12)$$

[17] J. L. Lebowitz and E. Rubin, Phys. Rev. **131**, 2381 (1963).

[18] The analysis of McKenna and Frisch (Ref. 8) utilizes the Husimi transform method to obtain a Fokker–Planck equation. We have been unable to verify the identity of our ζ_1 with the results of these authors. We note, however, that the over-all quantum correction to the friction constant obtained by these authors may be shown to be of order $\hbar^2$ [see Ref. 15(b)]. The advantage of the McKenna–Frisch analysis is the demonstration that the B-particle distribution function satisfies a Fokker–Planck equation. For this purpose, it is advantageous to employ a Husimi transform which is both real and nonnegative (unlike the wdf) and hence may serve as a probability density in phase space.

If Eq. (4.14) is expanded to obtain the first quantum correction to ζ_{cl}, we find, in addition to Eqs. (5.8)–(5.12), the term

$$-\frac{\beta}{3M}\frac{\beta^2\hbar^2}{12}\int_0^\infty dt \frac{d}{dt}\int d\mathbf{r}d\mathbf{p} f_b^{\text{cl}}(iL_b^{\text{cl}}\mathbf{F})\cdot[\exp(iL_b^{\text{cl}}t)\mathbf{F}], \quad (5.13)$$

which vanishes if we assume that $\mathbf{F}(t=\infty)$ is uncorrelated with the initial rate of change of **F**.

VI. CONCLUDING REMARKS

We have shown that, except at low temperatures, both the canonical and the symmetrized B particle momentum correlation functions decay exponentially in the heavy-mass limit with the same relaxation time. The first quantum correction to the inverse of this relaxation time (the friction constant) was then obtained by an expansion in $\hbar$. This expansion may be used to obtain quantum corrections to the diffusion constant of a massive particle immersed in a quantum fluid, as this constant may be expressed as a time integral of the momentum correlation function.[1] As these corrections will involve the mass of the bath particles through the factor $\lambda = \hbar/2(mkT)^{1/2}$, isotope effects for this transport coefficient may be investigated.

The procedure outlined in the appendix for obtaining quantum corrections for canonical correlation functions may be employed to find quantum corrections for a variety of hydrodynamic transport coefficients, which may be expressed as time integrals of these functions.[1]

In a recent, related article[19] McLaughlin, Palyvos, and Davis consider quantum corrections to the friction coefficient in a system where there is *weak coupling* between the particles. As their treatment involves the weak coupling limit as opposed to the heavy-mass limit considered in the present work, no direct comparison between results is appropriate. The virtue of the very interesting article of McLaughlin *et al.*[19] is that approximate *numerical* values for the quantum correction are presented. It is our intent to compute numerical values for the correction term ζ_1 obtained here [Eq. (5.9)] by use of the "linear trajectory approximation."[20] In this way we hope to estimate the quantum effect on diffusion of a heavy particle, e.g., Ne, Kr, in liquid H_2 and D_2.

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[19] I. L. McLaughlin, J. A. Palyvos, and H. Ted Davis, J. Chem. Phys. **49**, 1 (1968).

[20] E. Helfand, Phys. Fluids **4**, 681 (1961).

APPENDIX

We outline in this appendix how the Wigner technique may be employed to obtain quantum corrections for a canonical correlation function of the form

$$C(t)=\beta^{-1}\int_0^\beta d\lambda\ \mathrm{Tr}\{\rho[\exp(\lambda H)A\exp(-\lambda H)]A(t)\}. \tag{A1}$$

Our procedure is to recast Eq. (A1) in terms of Wigner equivalents and obtain an expansion of the recast expression in powers of Planck's constant. For simplicity we consider an N-particle system with $H=p^2/2m+U(\mathbf{r})$, so that the appropriate form of definition Eq. (3.1) is

$$\hat{A}(\mathbf{r},\mathbf{p})=\left(\frac{V}{(2\pi\hbar)^3}\right)^N\int d\mathbf{q}\exp\left(-\frac{i}{\hbar}\mathbf{r}\cdot\mathbf{q}\right)\times\langle\mathbf{p}-\tfrac{1}{2}\mathbf{q}\,|\,A\,|\,\mathbf{p}+\tfrac{1}{2}\mathbf{q}\rangle. \tag{A2}$$

If the given operator A is an arbitrary function of position and momentum operators, then $\hat{A}$ will in general be $\hbar$ dependent and additional terms in the expansion given below will result. As extension of the expansion procedure to such cases is straightforward, we restrict the discussion to an operator of the form

$$A(\mathbf{r},\mathbf{p})=g(\mathbf{r})+h(\mathbf{p}), \tag{A3}$$

so that $\hat{A}$ has no $\hbar$ dependence and is the same function of position and momentum variables as A is of the corresponding operators.

With the aid of the analogs of Eqs. (3.4)–(3.7), $C(t)$ may be written as

$$C(t)=\beta^{-1}\int_0^\beta d\lambda\int d\mathbf{r}d\mathbf{p}\times\left(f(\mathbf{r},\mathbf{p};\beta)\exp\left[\frac{\hbar}{2i}(\nabla_p^{\leftarrow}\cdot\nabla_r^{\rightarrow}-\nabla_r^{\leftarrow}\cdot\nabla_p^{\rightarrow})\right]\times\{\exp[\lambda\hbar\hat{L}(\mathbf{r},\mathbf{p})]A(\mathbf{r},\mathbf{p})\}\right)\times\{\exp[i\hat{L}(\mathbf{r},\mathbf{p})t]A(\mathbf{r},\mathbf{p})\}, \tag{A4}$$

where

$$i\hat{L}(\mathbf{r},\mathbf{p})=(\mathbf{p}/m)\cdot\nabla_r-(2/\hbar)\sin[\tfrac{1}{2}\hbar(\nabla_r\cdot\nabla_p)]U(\mathbf{r}) \tag{A5}$$

and f is the normalized wdf appropriate to the system.[11] Expansion of Eq. (A4) in powers of $\hbar$ and subsequent integration over λ yields

$$C(t)=\int d\mathbf{r}d\mathbf{p}f_{\mathrm{cl}}(\mathbf{r},\mathbf{p};\beta)A(\mathbf{r},\mathbf{p})A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};t)+\hbar^2C_1(t)+O(\hbar^4), \tag{A6}$$

with

$$A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};t)=\exp[iL_{\mathrm{cl}}(\mathbf{r},\mathbf{p})t]A(\mathbf{r},\mathbf{p}), \tag{A7}$$

where iL_{cl}, the classical Liouville operator, is the $\hbar\to0$ limit of Eq. (A5). The first term in Eq. (A6) is the classical autocorrelation function of A,[1] while the first quantum correction consists of four terms:

$$C_1(t)=C_1^{(1)}(t)+C_1^{(2)}(t)+C_1^{(3)}(t)+C_1^{(4)}(t), \tag{A8}$$

$$C_1^{(1)}(t)=\langle[\theta(\mathbf{r},\mathbf{p};\beta)-\langle\theta\rangle_{\mathrm{cl}}]A(\mathbf{r},\mathbf{p})A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};t)\rangle_{\mathrm{cl}}, \tag{A9}$$

$$C_1^{(2)}(t)=(-1/8)\langle[\Delta_{\mathrm{op}}(\mathbf{r},\mathbf{p};\beta)A(\mathbf{r},\mathbf{p})]A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};t)\rangle_{\mathrm{cl}}, \tag{A10}$$

$$C_1^{(3)}(t)=(1/24)\int_0^t ds\times\langle A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};s-t)[(\nabla_r^*\cdot\nabla_p)^3U(\mathbf{r})]A_{\mathrm{cl}}(\mathbf{r},\mathbf{p};s)\rangle_{\mathrm{cl}}, \tag{A11}$$

$$C_1^{(4)}(t)=(-\beta^2/12)\langle\dot{A}(\mathbf{r},\mathbf{p})\dot{A}_{\mathrm{cl}}(\mathbf{r},\mathbf{p};t)\rangle_{\mathrm{cl}}, \tag{A12}$$

where

$$\theta(\mathbf{r},\mathbf{p};\beta)=\frac{\beta^2}{8m}\left\{-(\nabla_r^2U)+\tfrac{1}{3}\beta\left[(\nabla_rU)^2+\nabla_r\nabla_rU:\frac{\mathbf{pp}}{m}\right]\right\}, \tag{A13}$$

$$\Delta_{\mathrm{op}}(\mathbf{r},\mathbf{p};\beta)=[(\beta/m)^2(\mathbf{p}\cdot\nabla_r)^2-(2\beta^2/m)\mathbf{p}\nabla_rU:\nabla_p\nabla_r+\beta^2(\nabla_rU\cdot\nabla_p)^2-(\beta/m)\nabla_r^2-\beta\nabla_r\nabla_rU:\nabla_p\nabla_p], \tag{A14}$$

and the angular bracket with subscript cl indicates an average over the classical distribution function. We note that, to $O(\hbar^2)$, the canonical correlation function differs from the symmetrized function[6] by the presence of the classical correlation function of the time derivative $\dot{A}$ in Eq. (A12).

An alternate procedure may be employed when the operator A is the time derivative of some operator B:

$$A=(i/\hbar)[H,B]=\dot{B}. \tag{A15}$$

In this event, one may perform the λ integration in Eq. (A1) with the aid of the identity Eq. (3.12) to yield

$$C(t)=(i/\hbar\beta)\ \mathrm{Tr}\{[B,\rho]A(t)\}. \tag{A16}$$

Quantum corrections may then be obtained by application of the Wigner formalism and subsequent expansion in powers of $\hbar$.

Expansions similar to those in this appendix and a discussion of applications of quantum corrections for time correlation functions may be found in Ref. 6.