

Symmetries and detailed balance in forward–backward semiclassical dynamics

Jian Liu, Nancy Makri *

Department of Chemistry, University of Illinois, 601 S. Goodwin Avenue, Urbana, IL 61801, United States

Received 10 June 2005; accepted 12 August 2005

Available online 23 September 2005

Abstract

Symmetry properties of time correlation functions within the forward–backward semiclassical dynamics (FBSD) approximation are considered. It is shown that FBSD autocorrelation functions of momentum and position-dependent operators satisfy rigorously the time symmetry relation of the quantum mechanical expression. The detailed balance condition follows from this symmetry in the special case where the density is given by the Boltzmann operator. The derived properties are illustrated with numerical simulations on liquid neon. © 2005 Elsevier B.V. All rights reserved.

Keywords: Semiclassical; Dynamics; Correlation functions

1. Introduction

Time correlation functions encode important dynamical information. For example, dipole moment correlation functions are related to absorption spectra, flux correlation functions yield reaction rates, and velocity correlation functions can be used to calculate diffusion coefficients. One of the practical advantages of the time correlation function approach is that the observable of interest often can be obtained from relatively short time information. While most theoretical efforts have been devoted to the calculation of two-time correlation functions that correspond to linear experiments, multi-time correlation functions have also received attention as a tool for analyzing nonlinear spectroscopic data.

This paper deals with time correlation functions of the form

$$C_{AB}(t) \equiv \text{Tr}(\hat{\rho}_0 \hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}). \quad (1.1)$$

Here, a (hermitian) operator \hat{A} is multiplied by a time-evolved (hermitian) operator

$$\hat{B}(t) \equiv e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \quad (1.2)$$

and the product is ensemble-averaged with respect to an equilibrium density operator $\hat{\rho}_0$. Most relevant to condensed phase processes are finite temperature correlation functions, in which the density is given by the Boltzmann operator $\hat{\rho}_0 = e^{-\beta\hat{H}}/Z$, where $Z = \text{Tr} e^{-\beta\hat{H}}$ ($\beta = 1/k_{\text{B}}T$).

Time-dependent semiclassical theory [1] offers a rigorous and sufficiently accurate approximation [2] to the quantum mechanical propagator in the $\hbar \rightarrow 0$ limit. However, its application to polyatomic systems is hindered by the oscillatory character of the semiclassical phase, which impairs dramatically the efficiency of Monte-Carlo methods. The forward–backward semiclassical dynamics (FBSD) approximation [3–6] reduces the oscillatory behavior of the integrand by combining the actions of the forward and backward propagators into a single semiclassical step, which amounts to the stationary phase limit of the quantum mechanical expression. Thus, it provides a rigorous and practically useful methodology for simulating the dynamics of condensed phase systems that exhibit quantum mechanical effects and thus are not treatable by classical molecular dynamics. Its practicality lies in the extraction of dynamical properties

* Corresponding author. Tel.: +1 217 333 6589; fax: +1 217 244 3186.
E-mail address: nancy@makri.scs.uiuc.edu (N. Makri).

from classical trajectories. Unlike ordinary molecular dynamics methods, FBSD trajectories are sampled from a properly quantized phase space distribution and thus capture important quantum mechanical effects. A number of calculations in our group have shown that FBSD can reliably reproduce the imaginary part of time correlation functions [5,7–9], account for frequency shifts associated with high-frequency vibrations [5], yield nearly quantitative results for the diffusion constant of liquid p -H₂ in a temperature range where molecular dynamics treatments lead to a qualitatively incorrect description of the system's thermodynamic phase [8], and accurately incorporate identical particle exchange effects [10]. Recently, Nakayama and Makri [11] reported the first successful simulation of superfluid helium, where FBSD reproduced remarkably well the measured incoherent structure factor in the intermediate to high neutron momentum regime.

In this paper, we derive various symmetry properties of time correlation functions in the FBSD approximation [4,5]. Restricting our presentation to one-dimensional systems for simplicity, the FBSD approximation to the Heisenberg time-evolved operator defined in Eq. (1.2) takes the form [6,12]

$$\hat{B}^{\text{FBSD}}(t) = (2\pi\hbar)^{-1} \int dx_0 \int dp_0 \left\{ \frac{3}{2} |g_{x_0 p_0}\rangle \langle g_{x_0 p_0}| - 2\gamma(\hat{x} - x_0) |g_{x_0 p_0}\rangle \langle g_{x_0 p_0}| (\hat{x} - x_0) \right\} B(x_t, p_t). \quad (1.3)$$

Here, $g_{x_0 p_0}$ are coherent states with wavefunctions given by the relation

$$\langle x | g_{x_0 p_0} \rangle = \left(\frac{2\gamma}{\pi} \right)^{\frac{1}{4}} \exp \left(-\gamma(x - x_0)^2 + \frac{i}{\hbar} p_0(x - x_0) \right) \quad (1.4)$$

and x_t, p_t are the phase space coordinates reached at the time t by a classical trajectory originating at x_0, p_0 . Eq. (1.3) is derived by expressing the operator \hat{B} in an exponential derivative form and applying the time-dependent semiclassical approximation in the coherent state representation [13] to the resulting product of exponential operators. Thus, the FBSD approximation is the stationary phase limit of the Heisenberg-evolved operator.

Use of Eq. (1.3) in Eq. (1.1) leads directly to the FBSD approximation for time correlation functions,

$$C_{AB}^{\text{FBSD}}(t) = (2\pi\hbar)^{-1} \int dx_0 \int dp_0 \left\{ \frac{3}{2} \langle g_{x_0 p_0} | \hat{\rho}_0 \hat{A} | g_{x_0 p_0} \rangle - 2\gamma \langle g_{x_0 p_0} | (\hat{x} - x_0) \hat{\rho}_0 \hat{A} (\hat{x} - x_0) | g_{x_0 p_0} \rangle \right\} B(x_t, p_t). \quad (1.5)$$

To implement the approximation, classical trajectories are sampled from a phase space distribution proportional to the exponential part of

$$P_A(x_0, p_0) = \langle g_{x_0 p_0} | \left[\frac{3}{2} \hat{\rho}_0 \hat{A} - 2\gamma(\hat{x} - x_0) \hat{\rho}_0 \hat{A} (\hat{x} - x_0) \right] | g_{x_0 p_0} \rangle. \quad (1.6)$$

Because this operator involves only the equilibrium density, it can be fully quantized (e.g., by expressing the Boltzmann operator as an imaginary time path integral [14]). The accurate representation of the phase space distribution that determines the weights of the classical trajectories ensures a correct description of important quantum mechanical effects associated with zero-point energy, frequency shifts, and imaginary components that are responsible for spectral asymmetries. At the same time, the combination of a quantum mechanical treatment of the initial density with a subsequent classical propagation leads to various inconsistencies. Among the most significant questions that arise are (i) whether FBSD satisfies the detailed balance condition and (ii) how the quantized distribution evolves at long times. The present paper focuses on the first of these questions. The characteristics of the long-time evolution of the quantized phase space density will be the subject of another paper [15].

In a recent paper, Wright and Makri [16] performed numerical calculations for the evolution of the phase space density in model one-dimensional systems and demonstrated that the FBSD correlation function satisfies the detailed balance condition within the statistical precision of the calculations. Detailed balance is a manifestation of symmetries in the correlation function, and we revisit this issue in the present paper by investigating under what conditions certain time-domain symmetries hold *rigorously* for the FBSD correlation function. We find that *auto* correlation functions of interest satisfy these desirable symmetries, and thus obey the detailed balance principle. Because the static and dynamical operators in the FBSD expression are treated at different levels, correlation functions of different operators (and thus expectation values) do not in general display these features and can exhibit spurious temporal fluctuations. A practical conclusion of this study is that the FBSD results for time autocorrelation functions can be expected to be more reliable than considered in the past, and that accuracy tests based on the performance of expectation values tend to over-estimate significantly the error in the autocorrelation function.

For use in the following section, we review here the path integral representation of the FBSD correlation function derived in [5]. For a system of d atoms described by the $3d$ coordinates x_{sj} , $s = 1, 2, 3$, $j = 1, \dots, d$, the inner product correlation function of two vector operators \hat{A} and \hat{B} takes the form

$$\begin{aligned} C_{A \cdot B}(t) &\equiv Z^{-1} \text{Tr} \left(e^{-\beta \hat{H}} \hat{A} \cdot e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right) \\ &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \\ &\quad \times \Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \Lambda_{A \cdot B}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N). \end{aligned} \quad (1.7)$$

Here,

$$\begin{aligned}
\Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) &= \langle \mathbf{g}_{\mathbf{x}_0, \mathbf{p}_0} | e^{-\Delta\beta\hat{H}_0/2} | \mathbf{x}_1 \rangle e^{-\Delta\beta V(\mathbf{x}_1)} \langle \mathbf{x}_1 | e^{-\Delta\beta\hat{H}_0} | \mathbf{x}_2 \rangle \\
&\quad \dots e^{-\Delta\beta V(\mathbf{x}_N)} \langle \mathbf{x}_N | e^{-\Delta\beta\hat{H}_0/2} | \mathbf{g}_{\mathbf{x}_0, \mathbf{p}_0} \rangle \dots \\
&= \prod_{s=1}^d \prod_{j=1}^3 \left(\frac{2\gamma_{sj}}{\pi} \right)^{\frac{1}{2}} \frac{m_s}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} \left(\frac{m_s}{2\pi\hbar^2 \Delta\beta} \right)^{\frac{N-1}{2}} \\
&\quad \times \exp \left\{ -\frac{m_s}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} \left(\gamma_{sj} (x_{sj,1} - x_{sj,0})^2 \right. \right. \\
&\quad \left. \left. + \gamma_{sj} (x_{sj,N} - x_{sj,0})^2 + \frac{\Delta\beta}{2m} p_{sj,0}^2 + \frac{i}{\hbar} p_{sj,0} (x_{sj,1} - x_{sj,N}) \right) \right. \\
&\quad \left. - \frac{m_s}{2\hbar^2 \Delta\beta} \sum_{k=2}^N (x_{sj,k} - x_{sj,k-1})^2 - \Delta\beta \sum_{k=1}^N V(x_{sj,k}) \right\} \quad (1.8)
\end{aligned}$$

is the path integral discretization of the coherent state transform of the Boltzmann operator alone, and the other factor depends on the operators under consideration. The function $\Lambda_{A \cdot B}$ depends on the specific form of the operators; the explicit form of that function is given in the following section for some operators of interest.

In the following section, we investigate various time symmetries of time correlation functions within the FBSD approximation. One of these symmetries is used to prove rigorously the validity of the detailed balance property for force or velocity autocorrelation functions obtained through FBSD calculations. In Section 3, we present a simulation on liquid neon and show that the detailed balance condition is obeyed accurately. Finally, Section 4 summarizes the findings of this work.

2. Time symmetries and detailed balance in FBSD

As is well known, at finite temperature the quantum mechanical time correlation function defined by Eq. (1.1) satisfies the symmetry relation

$$C_{AB}(t) = C_{BA}^*(-t). \quad (2.1)$$

This relation holds for equilibrium correlation functions because the density operator $\hat{\rho}_0 = e^{-\beta\hat{H}}$ commutes with the Hamiltonian that generates the time evolution.

For $\hat{A} \neq \hat{B}$, the FBSD correlation function generally does not satisfy the above condition. Expectation values offer a clear illustration of this symmetry violation: Setting $\hat{B} = 1$, the FBSD expression reduces to the exact quantum mechanical expectation value of the operator \hat{A} , thus $C_{A1}^{\text{FBSD}}(t) = \text{Tr} \hat{\rho}_0 \hat{A}$. With the choice $\hat{A} = 1$ and $\hat{B} \neq 1$ the FBSD expression $C_{1B}^{\text{FBSD}}(t)$ generally yields expectation values that exhibit a mild time dependence, in contrast to the exact quantum mechanical result that remains stationary [15]. The spurious time dependence of FBSD is a consequence of the lack of commutation between the density, which is treated fully quantum mechanically, and its time evolution, which is based on classical mechanics.

It is encouraging, however, that essentially all time *auto* correlation functions of practical interest rigorously satisfy

the symmetry relation (2.1). This is shown first from the explicit form of the path integral-discretized expression, Eq. (1.7), for position or momentum autocorrelation functions ($\hat{A} = \hat{B} = \hat{x}$ or \hat{p}), for which the integrand factor becomes [5]

$$\begin{aligned}
\Lambda_{\mathbf{x}, \mathbf{x}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) &= \left(1 + \frac{3}{2}d \right) \xi - 2 \sum_{s=1}^d \sum_{j=1}^3 \gamma_{sj} f_{sj}^{\beta*}(x_{sj,0}, p_{sj,0}, x_{sj,1}) \\
&\quad \times \left(\frac{\hbar^2 \Delta\beta/2}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} x_{sj}(t) + \xi f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,N}) \right) \quad (2.2)
\end{aligned}$$

or

$$\begin{aligned}
\Lambda_{\mathbf{p}, \mathbf{p}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; t) &= \left(1 + \frac{3}{2}d \right) i\theta(\mathbf{x}_0, \mathbf{p}_0; t) - 2i \sum_{s=1}^d \sum_{j=1}^3 \gamma_{sj} f_{sj}^{\beta*}(x_{sj,0}, p_{sj,0}, x_{sj,1}) \\
&\quad \times \left(-\hbar \frac{m_s}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} p_{sj}(t) + \theta(\mathbf{x}_0, \mathbf{p}_0; t) f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,N}) \right). \quad (2.3)
\end{aligned}$$

In these equations

$$\begin{aligned}
f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,k}) &= \frac{\langle x_{sj,k} | e^{-\Delta\beta\hat{H}_0/2} (\hat{x}_{sj} - x_{sj,0}) | \mathbf{g}_{x_{sj,0}, p_{sj,0}} \rangle}{\langle x_{sj,k} | e^{-\Delta\beta\hat{H}_0/2} | \mathbf{g}_{x_{sj,0}, p_{sj,0}} \rangle} \\
&= \frac{m_s}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} \left(x_{sj,k} - x_{sj,0} + i\hbar \frac{\Delta\beta}{2m} p_{sj,0} \right), \quad (2.4)
\end{aligned}$$

$$\xi(\mathbf{x}_0, \mathbf{p}_0; t) = \sum_{s=1}^d \sum_{j=1}^3 (f_{sj}(x_{sj,0}, p_{sj,0}, x_{sj,N}) + x_{sj,0}) x_{sj}(t), \quad (2.5)$$

and

$$\theta(\mathbf{x}_0, \mathbf{p}_0; t) = \sum_{s=1}^d \sum_{j=1}^3 w_{sj}(x_{sj,0}, p_{sj,0}, x_{sj,N}) p_{sj}(t), \quad (2.6)$$

where

$$\begin{aligned}
w_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_k) &= -i \frac{\langle x_{sj,k} | e^{-\Delta\beta\hat{H}_0/2} \hat{p}_{sj} | \mathbf{g}_{x_{sj,0}, p_{sj,0}} \rangle}{\langle x_{sj,k} | e^{-\Delta\beta\hat{H}_0/2} | \mathbf{g}_{x_{sj,0}, p_{sj,0}} \rangle} \\
&= \frac{m_s}{m_s + \hbar^2 \Delta\beta \gamma_{sj}} [-ip_{sj,0} + 2\hbar\gamma(x_{sj,k} - x_{sj,0})]. \quad (2.7)
\end{aligned}$$

Consider a trajectory with initial conditions $(\mathbf{x}_0, \mathbf{p}_0)$ which at the time t reaches the phase space point $(\mathbf{x}_t, \mathbf{p}_t)$. The classical equations of motion

$$\frac{d\mathbf{x}_t}{dt} = \mathbf{m}^{-1} \cdot \mathbf{p}_t, \quad \frac{d\mathbf{p}_t}{dt} = -\frac{\partial V(\mathbf{x}_t)}{\partial \mathbf{x}_t}$$

imply that, upon integration in the negative time direction to the final time $-t$, a trajectory with initial conditions $(\mathbf{x}_0, -\mathbf{p}_0)$ will reach the phase space point $(\mathbf{x}_t, -\mathbf{p}_t)$. It

follows that the same initial condition $(\mathbf{x}_0, -\mathbf{p}_0)$ will reach the phase space coordinates $(\mathbf{x}_{-t}, -\mathbf{p}_{-t})$ at the time t , thus

$$\mathbf{x}_t(\mathbf{x}_0, -\mathbf{p}_0) = \mathbf{x}_{-t}, \quad \mathbf{p}_t(\mathbf{x}_0, -\mathbf{p}_0) = -\mathbf{p}_{-t}. \quad (2.8)$$

We now examine the effect of reversing the direction of the initial momentum on the FBSD expressions given above. Eq. (1.8) implies

$$\Theta(\mathbf{x}_0, -\mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) = \Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N)^*.$$

Next, from Eqs. (2.4)–(2.7) we obtain

$$f_{sj}^\beta(x_{sj,0}, -p_{sj,0}, x_{sj,k}) = f_{sj}^\beta(x_{sj,0}, p_{sj,0}, x_{sj,k})^*,$$

$$w_{sj}^\beta(x_{sj,0}, -p_{sj,0}, x_k) = w_{sj}^\beta(x_{sj,0}, p_{sj,0}, x_k)^*,$$

from which it follows that

$$\theta(\mathbf{x}_0, -\mathbf{p}_0; t) = -\theta(\mathbf{x}_0, \mathbf{p}_0; -t)^*$$

and

$$\zeta(\mathbf{x}_0, -\mathbf{p}_0; t) = \zeta(\mathbf{x}_0, \mathbf{p}_0; -t)^*.$$

Using these relations one concludes that

$$A_{\mathbf{p}\mathbf{p}}(\mathbf{x}_0, -\mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; t) = A_{\mathbf{p}\mathbf{p}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; -t)^* \quad (2.9)$$

and

$$A_{\mathbf{x}\mathbf{x}}(\mathbf{x}_0, -\mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; t) = A_{\mathbf{x}\mathbf{x}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; -t)^*. \quad (2.10)$$

It is straightforward to prove the symmetry relation (2.1) using Eqs. (2.9) and (2.10). From Eq. (1.7) one finds

$$\begin{aligned} C_{\mathbf{p}\mathbf{p}}(t) &= (2\pi\hbar)^{-3d} \int_{-\infty}^{\infty} d\mathbf{x}_0 \int_{-\infty}^{\infty} d\mathbf{p}_0 \int_{-\infty}^{\infty} d\mathbf{x}_1 \cdots \int_{-\infty}^{\infty} d\mathbf{x}_N \\ &\quad \times \Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) A_{\mathbf{p}\mathbf{p}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; t) \\ &= (2\pi\hbar)^{-3d} \int_{-\infty}^{\infty} d\mathbf{x}_0 \int_{-\infty}^{\infty} d\mathbf{p}_0 \int_{-\infty}^{\infty} d\mathbf{x}_1 \cdots \int_{-\infty}^{\infty} d\mathbf{x}_N \\ &\quad \times \Theta(\mathbf{x}_0, -\mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N)^* A_{\mathbf{p}\mathbf{p}}(\mathbf{x}_0, -\mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N; -t)^* \\ &= C_{\mathbf{p}\mathbf{p}}(-t)^* \end{aligned}$$

and similarly,

$$C_{\mathbf{x}\mathbf{x}}(t) = C_{\mathbf{x}\mathbf{x}}(-t)^*.$$

Interestingly, this symmetry property can also be proven for a general density that is not necessarily given by the Boltzmann factor and for essentially all autocorrelation functions of interest. We show this below by manipulating the coherent state matrix elements of the density operator in Eq. (1.5). For simplicity the derivation is presented in one-dimensional notation.

Consider first autocorrelation functions of position operators, where $\hat{B} = \hat{A} = A(\hat{x})$. Of much practical importance is the case where correlation functions of the dipole moment operator ($\hat{A} = \mu(\hat{x})$), force autocorrelation functions ($\hat{A} = \mu(\hat{x})$), and the reactant–product form of the flux operator [17] ($\hat{A} = h(\hat{x}), \hat{B} = h(-\hat{x})$, where h is a step function) which is useful in the calculation of rate constants. The matrix elements of the density with position-dependent operators satisfy the properties

$$\begin{aligned} &\langle g_{x_0, p_0} | \hat{\rho}_0 A(\hat{x}) | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | x' \rangle \langle x' | \hat{\rho}_0 | x'' \rangle A(x'') \langle x'' | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, -p_0} | x' \rangle^* \langle x' | \hat{\rho}_0 | x'' \rangle A(x'') \langle x'' | g_{x_0, -p_0} \rangle^* \\ &= \langle g_{x_0, -p_0} | \hat{\rho}_0 A(\hat{x}) | g_{x_0, -p_0} \rangle^* \end{aligned}$$

and

$$\begin{aligned} &\langle g_{x_0, p_0} | (\hat{x} - x_0) \hat{\rho}_0 A(\hat{x}) (\hat{x} - x_0) | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | x' \rangle (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle \\ &\quad \times A(x'') (x'' - x_0) \langle x'' | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, -p_0} | x' \rangle^* (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle \\ &\quad \times A(x'') (x'' - x_0) \langle x'' | g_{x_0, -p_0} \rangle^* \\ &= \langle g_{x_0, -p_0} | (\hat{x} - x_0) \hat{\rho}_0 A(\hat{x}) (\hat{x} - x_0) | g_{x_0, -p_0} \rangle^*. \end{aligned}$$

It follows that the phase space density defined in Eq. (1.6) obeys the relation

$$P_{A(x)}(x_0, p_0) = P_{A(x)}(x_0, -p_0)^*.$$

This, along with the first of the relations in Eq. (2.8), proves the desired symmetry relation for the force autocorrelation function (or that of any position-dependent operator).

The symmetry of the momentum autocorrelation function can be shown in a similar fashion: the first matrix element in Eq. (1.6) becomes

$$\begin{aligned} &\langle g_{x_0, p_0} | \hat{\rho}_0 \hat{p} | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | x' \rangle \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{p} | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | x' \rangle \langle x' | \hat{\rho}_0 | x'' \rangle i\hbar \frac{\partial}{\partial x_0} \langle x'' | g_{x_0, p_0} \rangle \\ &= - \int dx' \int dx'' \langle g_{x_0, -p_0} | x' \rangle^* \langle x' | \hat{\rho}_0 | x'' \rangle \left(i\hbar \frac{\partial}{\partial x_0} \langle x'' | g_{x_0, -p_0} \rangle \right)^* \\ &= - \int dx' \int dx'' \langle g_{x_0, -p_0} | x' \rangle^* \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{p} | g_{x_0, -p_0} \rangle^* \\ &= - \langle g_{x_0, -p_0} | \hat{\rho}_0 \hat{p} | g_{x_0, -p_0} \rangle^*, \end{aligned} \quad (2.11)$$

while the second term is rewritten as

$$\begin{aligned} &\langle g_{x_0, p_0} | (\hat{x} - x_0) \hat{\rho}_0 \hat{p} (\hat{x} - x_0) | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | \hat{x} - x_0 | x' \rangle \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{p} (\hat{x} - x_0) | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \langle g_{x_0, p_0} | x' \rangle (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle i\hbar \frac{\partial}{\partial x_0} (x'' - x_0) \langle x'' | g_{x_0, p_0} \rangle \\ &= - \int dx' \int dx'' \langle g_{x_0, -p_0} | x' \rangle^* (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle \\ &\quad \times \left(i\hbar \frac{\partial}{\partial x_0} (x'' - x_0) \langle x'' | g_{x_0, -p_0} \rangle \right)^* \\ &= - \int dx' \int dx'' \langle g_{x_0, -p_0} | \hat{x} - x_0 | x' \rangle^* \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{p} (\hat{x} - x_0) | g_{x_0, -p_0} \rangle^* \\ &= - \langle g_{x_0, -p_0} | (\hat{x} - x_0) \hat{\rho}_0 \hat{p} (\hat{x} - x_0) | g_{x_0, -p_0} \rangle^*. \end{aligned}$$

It follows that the phase space density defined in Eq. (1.6) obeys the relation

$$P_p(x_0, p_0) = -P_p(x_0, -p_0)^*.$$

Together with the second of the relations in Eq. (2.8), the last equation proves the desired symmetry relation for the momentum autocorrelation function.

Finally, we consider the flux–flux autocorrelation function [17], whose integral yields the rate constant for a barrier crossing process. The relevant operator

$$\hat{A} \equiv \hat{F} = \frac{1}{2m} (\delta(\hat{x})\hat{p} + \hat{p}\delta(\hat{x}))$$

has position matrix elements given by the expression

$$\begin{aligned} \langle x' | \hat{F} | x'' \rangle &= -\frac{i\hbar}{2m} (\delta'(x')\delta(x'') - \delta(x')\delta'(x'')), \\ \langle x' | \hat{F} | x'' \rangle^* &= -\langle x' | \hat{F} | x'' \rangle. \end{aligned}$$

The coherent state matrix elements become

$$\begin{aligned} &\langle g_{x_0, p_0} | \hat{\rho}_0 \hat{F} | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \int dx''' \langle g_{x_0, p_0} | x' \rangle \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{F} | x''' \rangle \langle x''' | g_{x_0, p_0} \rangle \\ &= - \int dx' \int dx'' \int dx''' \langle g_{x_0, -p_0} | x' \rangle^* \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{F} | x''' \rangle^* \langle x''' | g_{x_0, -p_0} \rangle^* \\ &= -\langle g_{x_0, -p_0} | \hat{\rho}_0 \hat{F} | g_{x_0, -p_0} \rangle^* \end{aligned}$$

and

$$\begin{aligned} &\langle g_{x_0, p_0} | (\hat{x} - x_0) \hat{\rho}_0 \hat{F} (\hat{x} - x_0) | g_{x_0, p_0} \rangle \\ &= \int dx' \int dx'' \int dx''' \langle g_{x_0, p_0} | x' \rangle (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle \langle x'' | \hat{F} | x''' \rangle \\ &\quad \times (x''' - x_0) \langle x''' | g_{x_0, p_0} \rangle \\ &= - \int dx' \int dx'' \int dx''' \langle g_{x_0, -p_0} | x' \rangle^* (x' - x_0) \langle x' | \hat{\rho}_0 | x'' \rangle \\ &\quad \times \langle x'' | \hat{F} | x''' \rangle^* (x''' - x_0) \langle x''' | g_{x_0, -p_0} \rangle^* \\ &= -\langle g_{x_0, -p_0} | (\hat{x} - x_0) \hat{\rho}_0 \hat{F} (\hat{x} - x_0) | g_{x_0, -p_0} \rangle^*. \end{aligned}$$

From these it follows that

$$P_F(x_0, p_0) = -P_F(x_0, -p_0)^*.$$

Further, Eq. (2.8) implies

$$F(x_t, -p_t) = -\frac{1}{2} \left(\delta(x_t) \frac{p_t}{m} + \frac{p_t}{m} \delta(x_t) \right) = -F(x_t, p_t).$$

The last two relations lead to the result

$$C_{FF}(t) = C_{FF}(-t)^*.$$

The validity of Eq. (2.1) implies that momentum and position (or force) FBSD autocorrelation functions have an even real part and an odd imaginary part. As a consequence, the spectral function

$$G_{AA}(\omega) = \int_{-\infty}^{\infty} C_{AA}(t) e^{-i\omega t} dt \quad (2.12)$$

is real-valued for these autocorrelation functions.

It is possible to show that the FBSD autocorrelation function for a system at thermal equilibrium satisfies another time symmetry, which is closely related to the detailed balance condition. Consider the correlation function for a complex time argument,

$$C_{AB}(t + i\hbar\beta) \equiv \text{Tr}(\hat{\rho}_0 \hat{A} e^{-\beta\hat{H}} e^{i\hbar t/\hbar} B e^{-i\hbar t/\hbar} e^{\beta\hat{H}}). \quad (2.13)$$

In the special case where $\hat{\rho}_0 = e^{-\beta\hat{H}}/Z$, the FBSD approximation to Eq. (2.13) is

$$\begin{aligned} C_{AB}^{\text{FBSD}}(t + i\hbar\beta) &= \text{Tr}(\hat{\rho}_0 \hat{A} e^{-\beta\hat{H}} \hat{B}^{\text{FBSD}}(t) e^{\beta\hat{H}}) \\ &= \text{Tr}(e^{\beta\hat{H}} \hat{\rho}_0 \hat{A} e^{-\beta\hat{H}} \hat{B}^{\text{FBSD}}(t)) \\ &= \text{Tr}(\hat{A} \hat{\rho}_0 \hat{B}^{\text{FBSD}}(t)). \end{aligned}$$

Substituting the FBSD expression of Eq. (1.5), this becomes

$$\begin{aligned} C_{AB}^{\text{FBSD}}(t + i\hbar\beta) &= \int dx_0 dp_0 \left(\frac{3}{2} \langle g_{x_0 p_0} | \hat{A} \hat{\rho}_0 | g_{x_0 p_0} \rangle \right. \\ &\quad \left. - 2\gamma \langle g_{x_0 p_0} | (\hat{x} - x_0) \hat{A} \hat{\rho}_0 (\hat{x} - x_0) | g_{x_0 p_0} \rangle \right) B(x_t, p_t) \\ &= \int dx_0 dp_0 \left(\frac{3}{2} \langle g_{x_0 p_0} | \hat{\rho}_0 \hat{A} | g_{x_0 p_0} \rangle \right. \\ &\quad \left. - 2\gamma \langle g_{x_0 p_0} | (\hat{x} - x_0) \hat{A} (\hat{x} - x_0) | g_{x_0 p_0} \rangle \right)^* B(x_t, p_t) \\ &= C_{AB}^{\text{FBSD}*}(t). \end{aligned} \quad (2.14)$$

Further, by virtue of Eq. (2.1), canonical FBSD autocorrelation functions must satisfy the relation

$$C_{AA}^{\text{FBSD}}(t + i\hbar\beta) = C_{AA}^{\text{FBSD}}(-t).$$

Next, we focus on the spectral function defined in Eq. (2.12). Changing the integration variable,

$$G_{AA}^{\text{FBSD}}(-\omega) = \int_{-\infty}^{\infty} C_{AA}^{\text{FBSD}}(-t) e^{-i\omega t} dt.$$

Substituting the complex time form derived in Eq. (2.14), making a new change of integration variables and shifting the contour of integration, we obtain

$$\begin{aligned} G_{AA}^{\text{FBSD}}(-\omega) &= \int_{-\infty}^{\infty} G_{AA}^{\text{FBSD}}(t + i\hbar\beta) e^{-i\omega t} dt \\ &= e^{-\hbar\omega\beta} \int_{-\infty}^{\infty} G_{AA}^{\text{FBSD}}(t) e^{-i\omega t} dt = e^{-\hbar\omega\beta} G_{AA}^{\text{FBSD}}(\omega). \end{aligned}$$

This proves that the FBSD autocorrelation function satisfies the detailed balance condition

$$G_{AA}^{\text{FBSD}}(-\omega) = e^{-\hbar\omega\beta} G_{AA}^{\text{FBSD}}(\omega). \quad (2.15)$$

The spectral function may be partitioned into symmetric $G_{AA,\text{sym}}$ and antisymmetric $G_{AA,\text{asym}}$ parts, which correspond to the Fourier transforms of the real and imaginary parts of the correlation function, respectively. Eq. (2.15) implies the following relation between the symmetric and antisymmetric components:

$$G_{AA,\text{asym}}^{\text{FBSD}}(\omega) = \tanh\left(\frac{1}{2}\hbar\omega\beta\right) G_{AA,\text{sym}}^{\text{FBSD}}(\omega). \quad (2.16)$$

3. Detailed balance in liquid neon

We illustrate the validity of the detailed balance condition with a simulation on liquid neon. The system is treated as a Lennard–Jones fluid with parameters $\sigma = 2.749 \text{ \AA}$, $\varepsilon/k_B = 35.6 \text{ K}$ and $m = 3.35 \times 10^{-26} \text{ kg}$, at a reduced density $\rho^* = 0.78$ and temperature $T^* = 0.84$. This state point is at a fairly low temperature, while still in the liquid region of both the Lennard–Jones and experimental phase diagrams [9,18]. Quantum effects are significant under these conditions: the kinetic energy computed by path integral Monte-Carlo methods is about 55.15 K, amounting to a 20% quantum correction to the classical kinetic energy of 44.85 K. These sizable quantum mechanical effects arise from the large zero-point energy of the light neon atoms. The dynamical consequences of these quantum effects are even greater: the momentum correlation function computed by FBSD was found to differ substantially from that obtained by classical molecular dynamics methods, and various quantum correction factor prescriptions give rise to different results, none of which is in good agreement with the FBSD results [9]. Using the pair-product approximation [8] to the coherent state matrix element of the Boltzmann operator, the present simulation converged with a single path integral bead.

Fig. 1 shows the Fourier transforms Eq. (2.12) of the FBSD velocity time correlation functions for this system. As has been argued in previous work [7], the existence of an imaginary component in the FBSD time correlation function leads to the observed asymmetry in frequency space. Fig. 1 shows that the detailed balance relation, Eq. (2.15), is satisfied accurately. (The validity of this relation is demonstrated in the figure by multiplying the positive-frequency part of the function by the Boltzmann factor $e^{-\hbar\omega\beta}$, which generates the left-hand-side of Eq. (2.15); negative-frequency points are not processed this way, as the exponentially growing Boltzmann factor would lead to a large magnification of statistical errors.) The other manifestation of the detailed balance condition, Eq. (2.16), is also shown to hold accurately over the entire frequency domain.

4. Concluding remarks

Thermal quantum mechanical time correlation functions satisfy the detailed balance condition, which is a consequence of a time symmetry given in Eq. (2.1). In turn, the latter is a manifestation of the commutation between the Boltzmann density operator and that quantum evolution operator that generates the dynamics.

Within the FBSD formulation, time correlation functions take a hybrid form, where the density operator is evaluated fully quantum mechanically, and all dynamical effects enter through classical trajectories. An immediate

consequence of mixing quantum and classical mechanics is the breakdown of commutation properties, which leads to an apparent violation of time symmetry and the detailed balance relation.

In the case of autocorrelation functions, the time symmetry of the exact quantum mechanical expression is not related to the form of the density operator, but is purely a manifestation of unitarity for the time-evolution operator generated from a Hermitian Hamiltonian. Interestingly, we have shown in this paper that FBSD autocorrelation functions for momentum or position-dependent operators, and even flux autocorrelation functions, also rigorously satisfy the time symmetry of the quantum mechanical expression and, as a consequence, the detailed balance condition in the special case where the density is given by the Boltzmann operator. This property is a very desirable one, and gives us further confidence in the accuracy of the FBSD approximation to time autocorrelation functions. We emphasize again that expectation values, which can be thought of as a special case of time correlation functions for mixed operators, do not share these features. Indeed, numerical calculations have shown that FBSD expectation values can exhibit a spurious time dependence; it was found that the latter can be minimized through a judicious choice of the coherent state parameter, but cannot be eliminated.

Finally, we point out that the time symmetry used in this paper to prove the validity of the detailed balance condition also holds for the quasiclassical Wigner approximation to correlation functions of select operators. In this approximation the correlation function takes the form

$$C_{AB}^W(t) = \int dx_0 \int dp_0 W_{\rho_0 A}(x_0, p_0) W_B(x_t, p_t), \quad (4.1)$$

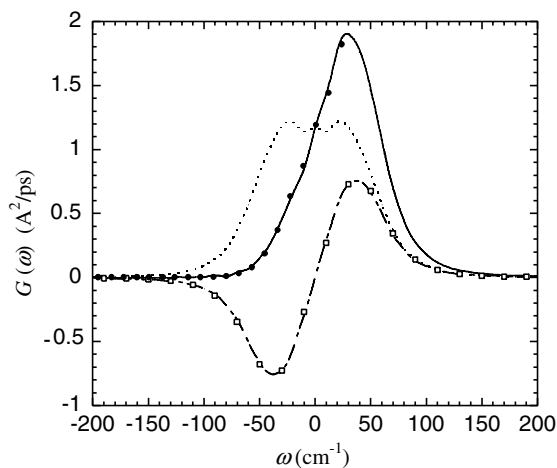


Fig. 1. Fourier transform of the velocity time correlation function for neon at the thermodynamic point specified in Section 3. Solid line: Fourier transform of the total velocity autocorrelation function. Solid circles show the right-hand-side of Eq. (2.15) for $\omega > 0$. Dotted line: the symmetric part of the spectral function. Dot-dashed line: the antisymmetric part of the spectral function. Hollow squares show the right-hand-side of Eq. (2.16). The width parameter of the coherent state is $\gamma = 6 \text{ a.u.}$

where

$$W_A(x_0, p_0) = (2\pi\hbar)^{-1} \int dy \langle x_0 + \frac{1}{2}y | \hat{A} | x_0 - \frac{1}{2}y \rangle e^{-ip_0y/\hbar} \quad (4.2)$$

is the Wigner transform of the operator \hat{A} . Clearly, the Wigner transform of $\hat{\rho}_0 A(\hat{x})$ is real-valued and $W_{A(x)}(x_t, p_t) = A(x_t)$, so following the arguments given in the previous section one concludes

$$W_{A(x)}(x_0, p_0) = W_{A(x)}(x_0, -p_0)^* \quad (4.3)$$

For $\hat{A} = \hat{p}$ one has

$$\left\langle x_0 + \frac{1}{2}y | \hat{\rho}_0 \hat{p} | x_0 - \frac{1}{2}y \right\rangle = \int dx \int dp \left\langle x_0 + \frac{1}{2}y | \hat{\rho}_0 | x \right\rangle p e^{ip(x-x_0+\frac{1}{2}y)/\hbar}, \quad (4.4)$$

which leads to the relation

$$W_p(x_0, p_0) = -W_p(x_0, -p_0)^* \quad (4.5)$$

These relations prove the detailed balance condition within the Wigner quasiclassical approximation.

Apart from providing a deeper theoretical understanding of the FBSD approximation, the above observations will find practical utility in analyzing the results of challenging FBSD simulations on condensed-phase systems.

Acknowledgments

This material is based upon work supported by the US Department of Energy, Division of Materials Sciences under Award No. DEFG02-91ER45439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign. J.L. thanks Dr. Akira Nakayama for his assistance with the simulation of liquid neon.

References

- [1] J.H. Van Vleck, Proc. Natl. Acad. Sci. USA 14 (1928) 178; C. Morette, Phys. Rev. 81 (1952) 848; M.C. Gutzwiller, J. Math. Phys. 8 (1967) 1979.
- [2] W.H. Miller, J. Chem. Phys. 53 (1970) 3578; W.H. Miller, Adv. Chem. Phys. 25 (1974) 69; M.S. Child, Semiclassical Mechanics with Molecular Applications, Clarendon, Oxford, 1991; M.A. Sepulveda, F. Grossmann, Adv. Chem. Phys. XCVI (1996) 191.
- [3] N. Makri, K. Thompson, Chem. Phys. Lett. 291 (1998) 101; K. Thompson, N. Makri, J. Chem. Phys. 110 (1999) 1343; K. Thompson, N. Makri, Phys. Rev. E 59 (1999) R4729.
- [4] J. Shao, N. Makri, J. Phys. Chem. A 103 (1999) 7753; J. Shao, N. Makri, J. Phys. Chem. A 9479 (1999) 103; E. Jezek, N. Makri, J. Phys. Chem. 105 (2001) 2851.
- [5] N. Makri, J. Phys. Chem. B 106 (2002) 8390.
- [6] N. Makri, A. Nakayama, N. Wright, J. Theor. Comp. Chem. 3 (2004) 391.
- [7] N.J. Wright, N. Makri, J. Chem. Phys. 119 (2003) 1634.
- [8] A. Nakayama, N. Makri, J. Chem. Phys. 119 (2003) 8592.
- [9] C.P. Lawrence, A. Nakayama, N. Makri, J.L. Skinner, J. Chem. Phys. 120 (2004) 6621.
- [10] A. Nakayama, N. Makri, Chem. Phys. 304 (2004) 147.
- [11] A. Nakayama, N. Makri, Proc. Natl. Acad. Sci. USA 102 (2005) 4230.
- [12] N. Makri, J. Shao, in: M. Hoffmann (Ed.), Accurate Description of Low-Lying Electronic States and Potential Energy Surfaces, Oxford University Press, 2002.
- [13] M.F. Herman, E. Kluk, Chem. Phys. 91 (1984) 27.
- [14] R.P. Feynman, Statistical Mechanics, Addison-Wesley, Redwood City, 1972.
- [15] J. Liu, N. Makri (submitted).
- [16] N.J. Wright, N. Makri, J. Phys. Chem. B 108 (2004) 6816.
- [17] W.H. Miller, S.D. Schwartz, J.W. Tromp, J. Chem. Phys. 79 (1983) 4889.
- [18] V.A. Rabinovich, A.A. Vasserman, V.I. Nedostup, L.S. Veksler (Eds.), Thermodynamic Properties of Neon, Argon, Krypton, and Xenon, Springer-Verlag, Berlin, 1988; J.K. Johnson, J.A. Zollweg, K.E. Gubbins, Mol. Phys. 78 (3) (1993) 591.