

Momentum Autocorrelation Function of a Particle in a One-Dimensional Box*

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The momentum autocorrelation function of a particle in a one-dimensional box is calculated both classically and quantum mechanically. The classical function is found by using the eigenfunctions of the Liouville operator for the system. The quantum-mechanical function is calculated and shown to be a non-analytic function of \hbar .

I. INTRODUCTION

There are very few dynamical systems for which exact calculations of time correlation functions¹ are possible. In this article we investigate a simple example—the momentum autocorrelation function $\pi(t)$ of a single particle of mass m in a one-dimensional box of length L . Our calculation has two points. First, it illustrates that the choice of a *a priori* distribution function determines the decay of the classical autocorrelation function. Second, a comparison of the classical and quantum-mechanical correlation functions shows that, even when the classical function decays, the corresponding quantum-mechanical function is periodic. We show how the eigenfunctions of the Liouville operator may be used to compute the classical momentum autocorrelation function

$$\pi_{cl}(t) = \int_0^L dx \int_{-\infty}^{+\infty} d\rho \rho_{eq}(p) \dot{p} \dot{p}(t). \quad (1)$$

Here $\dot{p}(t)$ is the momentum of the particle at time t , given that the particle had momentum p at position x at $t=0$. The quantity $\dot{p}(t)$ may be expressed as

$$\dot{p}(t) = \exp(i\mathcal{L}t) \dot{p}, \quad (2)$$

where \mathcal{L} is the classical Liouville operator² of the system; $\rho_{eq}(p)$ is the *a priori* probability density of finding the particle in the neighborhood of x and p at $t=0$. We shall assume conditions appropriate to a canonical distribution,

$$\rho_{eq}(p) = L^{-1} (2\pi m k_B T)^{-1/2} \exp(-\beta p^2/2m). \quad (3)$$

For this choice one finds that $\pi_{cl}(t)$ asymptotically decays to zero and is neither a periodic or almost-periodic function of the time.³

The quantum-mechanical symmetrized momentum autocorrelation function for the particle in a box is

$$\pi(t) = \frac{1}{2} \text{Tr} \{ \hat{\rho}_{eq} [\dot{p}(t) \dot{p} + \dot{p} \dot{p}(t)] \}. \quad (4)$$

Here $\hat{\rho}_{eq}$ is the equilibrium density matrix appropriate to a canonical ensemble,

$$\hat{\rho}_{eq} = Z^{-1} \exp(-\beta H); \quad Z = \text{Tr} \exp(-\beta H), \quad (5)$$

H being the Hamiltonian and \dot{p} the momentum operator for the particle. We find that the quantum-mechanical autocorrelation function is a *periodic* function of the

time, which raises the question of how to take the classical limit and obtain quantum “corrections” to the classical autocorrelation function.

II. EVALUATION OF THE CLASSICAL AUTOCORRELATION FUNCTION

An expression for the classical momentum autocorrelation function for a particle in a one-dimensional box was obtained some time ago by Nossal.³ His analysis was based on a direct calculation of the dynamical motion of the particle. In this section we present an instructive alternative analysis based on determining the eigenfunctions of the Liouville equation⁴ appropriate to this problem.

Within the walls the particle satisfies the Liouville equation for a free particle,

$$\frac{\partial \rho(x, p; t)}{\partial t} = \frac{-p}{m} \frac{\partial \rho(x, p; t)}{\partial x} = -i\mathcal{L} \rho(x, p; t), \quad (6)$$

where $\rho(x, p; t)$ is the probability density of finding the particle at position x with momentum p at time t . Since collisions with the walls at $x=0$ and $x=L$ occur with specular reflection, the appropriate boundary conditions are

$$\rho(L, p; t) = \rho(L, -p; t), \quad (7)$$

$$\rho(0, p; t) = \rho(0, -p; t). \quad (8)$$

In order to determine the eigenfunctions of Eq. (6) we look for solutions of the form

$$\rho(x, p; t) = e^{-i\mu t} \psi(x, p), \quad (9)$$

which leads to the equation

$$(i\mathcal{L} - i\mu) \psi(x, p) = -[i\mu + (p/m)(\partial/\partial x)] \psi(x, p) = 0, \quad (10)$$

with boundary conditions

$$\psi(0, p) = \psi(0, -p) \quad (11)$$

and

$$\psi(L, p) = \psi(L, -p). \quad (12)$$

The function

$$\psi(x, p | p_0) = e^{ikx} \delta(p - p_0) + e^{-ikx} \delta(p + p_0) \quad (13)$$

satisfies Eq. (10) provided that

$$\mu = (p_0/m)k. \quad (14)$$

In order to satisfy the boundary conditions e^{ikL} must equal plus or minus unity, which implies that k is some multiple of (π/L) . Thus the eigenfunctions are of the form

$$\psi_n(x, p | p_0) = a_n(p_0)$$

$$\times [\exp(ik_n x) \delta(p-p_0) + \exp(-ik_n x) \delta(p+p_0)], \quad (15)$$

with corresponding eigenvalues

$$\mu_n(p_0) = p_0 k_n / m = (p_0 / m) (n\pi / L). \quad (16)$$

Note that since

$$\psi_{-n}(x, p | -p_0) \equiv \psi_n(x, p | p_0), \quad (17)$$

we have a choice in how to specify the set of integers n and p_0 . A suitable choice is to take $p_0 > 0$ for $n=0$ and $-\infty < p_0 < +\infty$ for all positive integers $n=1, \dots, \infty$. With $a_n(p_0) = [1/(2L)^{1/2}]$ the set of functions can easily be shown to be orthonormal and to form a complete set. Any function $\chi(x, p)$, defined in the region $0 < x < L$, $-\infty < p < +\infty$, may be expanded in this set according to the prescription

$$\chi(x, p) = \int_0^\infty dp_0 \langle 0, p_0 | \chi \rangle \psi_0(x, p | p_0) + \sum_{n \geq 1} \int_{-\infty}^{+\infty} dp_0 \langle n, p_0 | \chi \rangle \psi_n(x, p | p_0), \quad (18)$$

where

$$\langle n, p_0 | \chi \rangle = \int_0^L dx \int_{-\infty}^{+\infty} \psi_n^*(x, p | p_0) \chi(x, p). \quad (19)$$

In order to evaluate $\pi_{\text{cl}}(t)$ in terms of these eigenfunctions we must determine the expansion coefficients for $\chi = p$ and $\chi = \rho_{\text{eq}}(p)p$. An elementary calculation shows that the nonvanishing coefficients are

$$\langle 2n+1, p_0 | p \rangle = 2p_0(2L)^{1/2}/i\pi(2n+1) \quad (20)$$

and

$$\langle 2n+1, p_0 | p \rho_{\text{eq}}(p) \rangle = 2p_0 \rho_{\text{eq}}(p_0) (2L)^{1/2}/i\pi(2n+1). \quad (21)$$

Substitution of the expansions into the expression for $\pi(t)$ followed by use of the orthonormality property of the eigenfunctions leads to

$$\pi_{\text{cl}}(t) = \sum_{n=0}^{\infty} \int_{-\infty}^{+\infty} dp_0 \exp[i\mu_{2n+1}(p_0)t] \times \langle 2n+1, p_0 | p \rho_{\text{eq}}(p) \rangle^* \langle 2n+1, p_0 | p \rangle; \quad (22)$$

the final integration may easily be accomplished to obtain

$$\pi_{\text{cl}}(t) = \left(\frac{2m}{\pi^2\beta}\right) \sum_{k=0}^{\infty} \exp\left(-\frac{(k+\frac{1}{2})^2 2\pi^2 \ell^2}{mL^2\beta}\right) \times \left(\frac{1}{(k+\frac{1}{2})^2} - \frac{4\pi^2 \ell^2}{m\beta L^2}\right), \quad (23)$$

which is precisely the expression obtained by Nossal.³ Clearly $\pi_{\text{cl}}(t)$ asymptotically approaches zero; numerical calculation (see Fig. 1) shows that π_{cl} passes through zero at a value of the reduced time $T = (2\pi^2/m\beta L^2)^{1/2}t$ of about unity (a better estimate is $T \approx \sqrt{2}$).

The Liouville operator for this system is Hermitian; consequently all the eigenvalues $\mu_n(p_0)$ are real and the time factors occurring in Eq. (22) are all oscillating. Our calculation clearly indicates how the superposition of these oscillating terms may still lead to a decaying correlation function. The eigenvalues of the propagator need not have a positive imaginary part in order for the correlation function to decay. Mathematically speaking the correlation function may decay if the eigenvalue spectrum of the Hermitian propagator is continuous (or has a continuous part). Furthermore our example illustrates that one need not take the thermodynamic limit in order to arrive at a continuous eigenvalue spectrum for the classical Liouville operator.

What feature is responsible for the temporal relaxation? As pointed out by Nossal the controlling feature in this model is the nature of the initial distribution $\rho_{\text{eq}}(p)$. Initial distributions other than the canonical distribution Eq. (3) need not lead to relaxation. For example, we may examine an initial distribution appropriate to a microcanonical ensemble at energy E ,

$$\rho_{\text{eq}}(p) = \Gamma_{\text{eq}}(p) = (2L)^{-1} \{ \delta[p - (2mE)^{1/2}] + \delta[p + (2mE)^{1/2}] \}. \quad (24)$$

The nonvanishing coefficients of $p\Gamma_{\text{eq}}(p)$ in the Liouville eigenfunction expansion are

$$\langle 2n+1, p_0 | \Gamma_{\text{eq}}(p) \rangle = 2p_0 \Gamma_{\text{eq}}(p_0) (2L)^{1/2}/i\pi(2n+1). \quad (25)$$

From Eq. (22) we may compute the momentum correlation function appropriate to this initial condition $\pi_{\text{cl}}^E(t)$; the result is

$$\pi_{\text{cl}}^E(t) = \frac{16mE}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cos\left[\left(\frac{2E}{m}\right)^{1/2} \left(\frac{n\pi}{L}\right) t\right]. \quad (26)$$

Clearly this correlation function does not decay; indeed it is a periodic function of the time with a recurrence time $t_r = (2m/E)^{1/2}L$.

The difference in the effect of the two initial conditions may be understood on a physical basis. The imposition of an initial Maxwell-Boltzmann distribution for the single particle in the box implies the weak coupling of the particle to some sort of infinite heat bath that maintains a temperature. In this circumstance we might alternatively describe the particle in the box as a subsystem of a global microcanonical system of particle plus bath. In the limit of an infinite bath and very weak coupling we may expect relaxation. If one uses an initial canonical distribution, the motion of the particle in the box may usefully be regarded as a special

limiting case of Brownian motion in a system of finite size.⁵

Our results for the classical correlation function lead us in the next section to inquire into the behavior of the quantum-mechanical momentum correlation function. We wish to note, in passing, that our qualitative considerations apply equally well to eigenfunctions and time correlation functions of a classical free rotor; this system has recently been studied in detail by St. Pierre and Steele.⁶

III. EVALUATION OF THE QUANTUM-MECHANICAL AUTOCORRELATION FUNCTION

For a quantum-mechanical particle in a box the orthonormal eigenfunctions are

$$|n\rangle = (2/L)^{1/2} \sin(n\pi x/L), \quad n=1, 2, \dots, \infty, \quad (27)$$

with corresponding energy eigenvalues

$$E_n = \hbar^2 n^2 \pi^2 / 2mL^2. \quad (28)$$

The correlation function $\pi(t)$, Eq. (4), may be expressed as

$$\pi(t) = \frac{2}{Z} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \exp(-\beta E_n) \times |\langle n | p | m \rangle|^2 \cos\left(\frac{(E_n - E_m)t}{\hbar}\right). \quad (29)$$

The matrix element $\langle n | p | m \rangle$ is

$$\langle n | p | m \rangle = (4m\hbar/iL) [n/(n^2 - m^2)] \Delta(n, m), \quad (30)$$

where $\Delta(n, m)$ is equal to unity if n is even and m odd or if n is odd and m even; otherwise $\Delta(n, m)$ is zero.

The $\Delta(n, m)$ factor leads to sums restricted to odd and to even values in Eq. (28). Unrestricted sums will prove more convenient so we change the sums to the indices p and k where $n = p - k$ and $m = p + k + 1$. After considerable algebra we find that $\Pi(t)$ may be expressed in the form

$$\begin{aligned} \Pi(t) = & \left(\frac{\hbar^2}{ZL^2}\right) \text{Re} \sum_{p=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \left(\exp\left\{-\frac{1}{4}(\alpha\beta)[(2p+1)^2 - (2k+1)^2]\right\} \exp\left(i(2k+1)(2p+1)\frac{\alpha t}{\hbar}\right) \right. \\ & \left. \times \left(\frac{(2p+1)^2}{(2k+1)^2} - 1\right) \right), \quad (31) \end{aligned}$$

where

$$\alpha = \hbar^2 \pi^2 / 2mL^2. \quad (32)$$

In contrast to the classical case $\pi(t)$ is completely periodic with period $T_Q = (2\pi\hbar/\alpha)$. Furthermore for all times which are odd multiples of $(\pi\hbar/2\alpha)$, $\pi(t)$ is identically zero. For times that are odd multiples of $(\pi\hbar/\alpha)$, $\pi(t)$ is equal to the negative of the initial

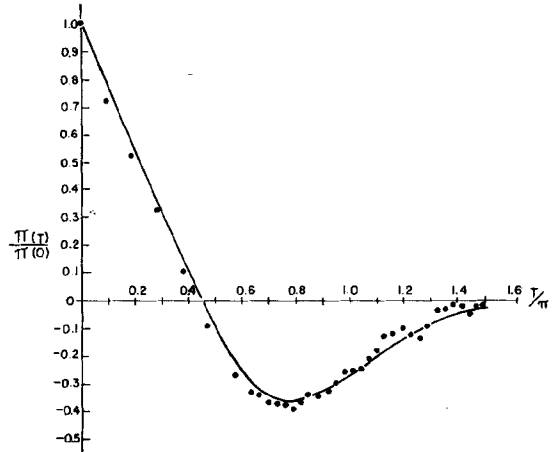


FIG. 1. The momentum autocorrelation function as a function of time. The curve is the classical result; the points are the quantum-mechanical result.

value $\pi(0)$. The question arises as to how one can take the classical limit $\hbar \rightarrow 0$ of this expression to recover the classical result and how one should express quantum corrections to the classical limit.

It is clear that Eq. (3) is a poor representation of $\pi(t)$ for small $\alpha\beta$. In order to address the question of quantum corrections, we shall convert the sum over p into an integral in the following way:

$$\sum_{p=-\infty}^{+\infty} f(p) = \int_{-\infty}^{+\infty} dz \sum_{p=-\infty}^{+\infty} \delta(z-p) f(z). \quad (33)$$

But⁷

$$\sum_{p=-\infty}^{+\infty} \delta(z-p) = \sum_{p=-\infty}^{+\infty} \exp(i2\pi pz) = 1 + 2 \sum_{p=1}^{\infty} \cos 2\pi pz. \quad (34)$$

Thus,

$$\sum_{p=-\infty}^{+\infty} f(p) = \int_{-\infty}^{+\infty} dz f(z) \left(1 + 2 \sum_{p=1}^{\infty} \cos 2\pi pz\right); \quad (35)$$

$\pi(t)$ can now be written

$$\begin{aligned} \pi(t) = & \frac{\hbar^2}{ZL^2} \text{Re} \sum_{k=-\infty}^{+\infty} \int_{-\infty}^{+\infty} dz \left(1 + 2 \sum_{p=1}^{\infty} \cos 2\pi pz\right) \\ & \times \left\{ \exp\left[-\frac{1}{4}(\alpha\beta)((2z+1)^2 - (2k+1)^2)\right] \right\} \\ & \times \left[\exp\left(i(2k+1)(2p+1)\frac{\alpha t}{\hbar}\right) \left(\frac{(2z+1)^2}{(2k+1)^2} - 1\right) \right]. \quad (36) \end{aligned}$$

Keeping the leading term, we find

$$\begin{aligned} \pi^{(0)}(T) = & \frac{2\hbar^2}{\alpha\beta L^2} (2Z)^{-1} \left(\frac{\pi}{\alpha\beta}\right)^{1/2} \sum_{k=-\infty}^{+\infty} \exp\left(-(2k+1)^2 \frac{1}{4} T^2\right) \\ & \times \left[\left(\frac{2}{(2k+1)^2} - T^2\right) \cos(2k+1)^2 \frac{1}{2} T \right. \\ & \left. - 2\zeta T \sin(2k+1)^2 \frac{1}{2} T \right], \quad (37) \end{aligned}$$

TABLE I. The momentum autocorrelation function $\hat{\pi}(T) = \pi(T)/\pi(0)$.

A.	T	$\hat{\pi}_{cl}$	$\hat{\pi}^{(0)}(\zeta=0.1)$	$\hat{\pi}(\zeta=0.1)$
	0	1.000	1.000	1.000
	0.1 π	0.774	0.764	0.764
	0.2 π	0.549	0.543	0.543
	0.3 π	0.323	0.319	0.319
	0.4 π	0.099	0.095	0.096
	0.5 π	-0.106	-0.110	-0.111
	0.6 π	-0.259	-0.263	-0.264
	0.7 π	-0.343	-0.345	-0.345
	0.8 π	-0.361	-0.364	-0.365
	0.9 π	-0.329	-0.330	-0.330
	1.0 π	-0.270	-0.272	-0.273
	1.1 π	-0.204	-0.203	-0.203
	1.2 π	-0.142	-0.137	-0.139
	1.3 π	-0.092	-0.087	-0.089
	1.4 π	-0.056	-0.055	-0.055
	1.5 π	-0.032	-0.026	-0.028
B.	T	$\hat{\pi}_{cl}$	$\hat{\pi}^{(0)}[\zeta=(0.1)^{1/2}]$	$\hat{\pi}[\zeta=(0.1)^{1/2}]$
	0	1.000	1.000	1.000
	0.09 π	0.810	0.723	0.723
	0.18 π	0.573	0.525	0.525
	0.28 π	0.368	0.323	0.323
	0.38 π	0.143	0.107	0.106
	0.47 π	-0.048	-0.096	-0.096
	0.57 π	-0.220	-0.269	-0.268
	0.66 π	-0.318	-0.343	-0.345
	0.76 π	-0.361	-0.380	-0.390
	0.85 π	-0.350	-0.337	-0.342
	0.95 π	-0.302	-0.286	-0.300
	1.04 π	-0.244	-0.250	-0.247
	1.14 π	-0.178	-0.133	-0.132
	1.23 π	-0.125	-0.130	-0.128
	1.33 π	-0.080	-0.053	-0.046
	1.42 π	-0.050	-0.023	-0.023

where

$$T = t(2\pi^2/m\beta L^2)^{1/2}. \tag{38}$$

and

$$\zeta = (\alpha\beta)^{1/2} \sim \theta(\hbar). \tag{39}$$

The resemblance of Eq. (36) to the classical result [Eq. (23)] is obvious. In fact, for $\zeta=0$, Eq. (36) reduces to Eq. (23). However, it should be noted that $\pi^{(0)}(T)$ is *not* periodic in time. The neglect of the higher terms has removed the recurrences.

Before discussing the behavior of $\pi^{(0)}(T)$, we discuss the partition function, Z , which also has some interesting analytic properties as a function of ζ (which is the ratio of the mean de Broglie wavelength to the length of the box). Evaluating the partition function

as above, or by the Poisson sum formula,⁷ we find

$$Z = \sum_{n=1}^{\infty} \exp(-n^2\zeta^2) = \frac{1}{2} \frac{\pi^{1/2}}{\zeta} \sum_{m=-\infty}^{+\infty} \exp\left(-\frac{\pi^2 m^2}{\zeta^2}\right) - \frac{1}{2} = \frac{1}{2} \left[\left(\frac{\pi^{1/2}}{\zeta}\right) - 1 \right] + \frac{\pi^{1/2}}{\zeta} \sum_{m=1}^{\infty} \exp\left(-\frac{m^2\pi^2}{\zeta^2}\right). \tag{40}$$

Since ζ is proportional to \hbar , it is clear that the partition function is *not* an analytic function of \hbar . However for small ζ , it will be of order unity plus corrections of order \hbar and of order $\exp(-1/\hbar^2)$.

For small ζ , we expect from Eq. (36) that $\pi^{(0)}(T)$ will be very similar to $\pi_{cl}(T)$. However, when ζT is of order unity, we expect to see oscillations [at frequencies equal to $(2k+1)^{2\frac{1}{2}}\zeta$ for all k]. Indeed, numerical calculations have shown this to be the case. These oscillations are completely quantum mechanical in character and are absent from the classical approximations.

Let us now go back to Eq. (35) and calculate the remaining terms in $\pi(T)$. Using the techniques of the theta function transformations,⁸ we find, after much algebra,

$$\begin{aligned} \pi(T) &= \left(\frac{2\hbar^2}{\zeta^2 L^2}\right) \left(\frac{\pi^{1/2}}{2\zeta Z}\right) \sum_{k=-\infty}^{+\infty} \sum_{n=-\infty}^{+\infty} \\ &\times \exp - \left((2k+1)\frac{1}{2}T - \frac{n\pi}{\zeta} \right)^2 \\ &\times \left[\frac{2}{(2k+1)^2} - \frac{4}{(2k+1)^2} \left(\frac{1}{2}(2k+1)T - \frac{n\pi}{\zeta} \right)^2 \right] \\ &\times \cos(2k+1)^{2\frac{1}{2}}\zeta T - \frac{4\zeta}{(2k+1)} \left(\frac{1}{2}(2k+1)T - \frac{n\pi}{\zeta} \right) \\ &\times \sin(2k+1)^{2\frac{1}{2}}\zeta T \}. \tag{41} \end{aligned}$$

Thus, the approximate function, $\pi^{(0)}(T)$ is equivalent to the neglect of all terms for which $n \neq 0$ in Eq. (40).

For small ζ , we expect that $\pi(t)$ will consist of a repeating alternating series of peaks: for t which are close to multiples of $(2\pi\hbar/\alpha)$ the peak will closely resemble π_{cl} , while for t which are close to odd multiples of $\pi\hbar/\alpha$ the peaks will closely resemble $-\pi_{cl}$. As ζ becomes progressively smaller, the peaks become better separated and the recurrence time gets larger. Notice that from Eq. (40), $\pi(t)$ is a nonanalytic function of ζ (and hence of \hbar), in contradiction to the usual assumption made, but not proven, for interacting many-particle systems.⁹

In order to compare the various forms of the correlation function, we have calculated $\pi_{cl}(t)$, $\pi^{(0)}(t)$, and $\pi(t)$ in the manner described below. We have calculated

$\pi^{(0)}(t)$ and $\pi(t)$ for $\zeta^2=0.001$, $\zeta^2=0.01$, and $\zeta^2=0.1$ for $0 \leq T \leq 1.5\pi$.

For each value of T , we performed the sums in Eqs. (23) and (36) for $0 < k < 50\,000$. For each value of T and each value of k (up to $k=50\,000$), we have summed the two largest terms of the n series in Eq. (40). The largest term of the series is that for which $n \approx \zeta T/2\pi(2k+1)$. For each value of k and ζT , we picked the two values of n which bracketed $\zeta T(2k+1)/2\pi$. In this way, for these values of k , we have neglected terms of order $\exp(-\pi^2/\zeta^2)$ [$\sim \exp(-100)$]. Table I lists the values obtained for $\pi(T)$, $\pi^{(0)}(T)$, and $\pi_{cl}(T)$ in terms of their values at $T=0$. It is clear that for $\zeta \leq 0.1$, and for $T \leq 1.5\pi$, the quantum-mechanical correlation function is very similar to the classical function. However, one should notice that the $n \neq 0$ terms do contribute to $\pi(t)$; hence there is no simple way to write the quantum corrections to $\pi(t)$. For $\zeta^2=0.1$, we find pronounced oscillations of $\pi(t)$ [and $\pi^{(0)}(t)$] about the classical value. As pointed out above, these arise from the sinusoidal terms in $\pi(t)$. We present the calculated $\pi(t)$ for $\zeta^2=0.1$ as a set of points in Fig. 1. The solid curve is the classical correlation function. In order to check our numerical results, we have also calculated $\pi(t)$ from Eq. (30) for $\zeta^2=0.1$; the results agree with those presented in Table I.

Clearly, one can see from Eq. (40) that $\pi(T)$ will consist of two types of terms: (a) those analytic in \hbar and (b) those nonanalytic in \hbar . The terms for which n is zero [i.e., those making up $\pi^{(0)}(T)$, Eq. (37)] all belong in category (a); the terms for which n is non-zero will, in general, belong in category (b). However, at any value of T such that $T=2n_0\pi/\zeta(2k_0+1)$ where n_0 and k_0 are integers, then there will be many terms (for which $n \neq 0$) which are analytic in \hbar . One can calculate the contribution of these terms to $\pi(T)$. For example, at $T=(2\pi/9\zeta)$ (i.e., at $1/18$ of the recurrence time), those terms for which $n/(2k+1)=\frac{1}{9}$ will be analytic in \hbar [i.e., those for which $n=(2p+1)$ and $(2k+1)=9(2p+1)$, for all p]. The contribution to $\pi(T)$ from these terms alone [$\delta\pi(T)$] is

$$\begin{aligned} \delta\pi(T) &= \left(\frac{2\hbar^2}{\zeta^2 L^2}\right) \left(\frac{\pi^{1/2}}{2\zeta Z}\right) \sum_{p=-\infty}^{+\infty} \frac{2}{9^2(2p+1)^2} \\ &= \frac{2\hbar^2}{\zeta^2 L^2} \frac{\pi^{1/2}}{2\zeta Z} \frac{\pi^2}{2 \times 9^2} \end{aligned} \quad (42)$$

or

$$\frac{\delta\pi(T=2\pi/9\zeta)}{\pi(0)} = \frac{1}{9^2} \approx 0.01. \quad (43)$$

For $\zeta=(0.1)^{1/2}$, this corresponds to $T=0.7\pi$, at which point $\pi^{(0)}(T=0.7\pi) \approx 0.3$; thus, the contribution to

$\pi(T)$ from these terms is approximately 3% of the total. At later times, these terms will contribute even more. Hence the contribution to $\pi(T)$ from these terms is considerable for moderate values of T . In fact, the contribution of these terms is of the same order of magnitude as the difference between $\pi^{(0)}(T)$ and $\pi_{cl}(T)$ (see Table I). At a value of T slightly larger than $2n_0\pi/\zeta(2k_0+1)$ these terms will be nonanalytic in \hbar , but their contribution will still be approximately the same. We conclude that the nonanalytic terms cannot be ignored in calculating corrections to the classical results.

IV. SUMMARY AND CONCLUSIONS

In this article, we have calculated both the classical and quantum-mechanical expressions for the momentum autocorrelation function for a particle in a one-dimensional box.¹⁰ The derivation of the classical expression was based on the eigenfunctions and eigenvalues of the Liouville operator. In the limit that $\hbar=0$, we find that the quantum-mechanical expression becomes identical to the classical; however for nonzero \hbar , we find that the quantal expression cannot be expressed simply as the classical expression plus correction terms in \hbar . The same is true of the partition function, which can be shown to be nonanalytic in the variable \hbar (or ζ , the ratio of the de Broglie wavelength to the length of the box). Our calculation suggests that some care must be taken when discussing quantum corrections to correlation functions.

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¹⁰ The referee has kindly drawn our attention to an article by S. Golden and H. C. Longuet-Higgins on the temporal evolution of dynamical systems [*J. Chem. Phys.* **33**, 1479 (1960)]. The results of our calculation on a specific system are consistent with the results of these authors based on general considerations.