Exact time evolution of a classical harmonic-oscillator chain

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We investigate the dynamical behavior of a classical harmonic-oscillator chain with periodic and fixed-end boundary conditions. The displacement and velocity autocorrelation functions are obtained by a recurrence relations method. We show that the finite diffusion constant and the divergence in the mean-square displacement of a tagged oscillator arise from the zero-frequency mode present in the chain with periodic boundary conditions. For the chain with fixed-end boundary conditions, the diffusion constant vanishes and there is no divergence in the mean-square displacement. These results should hold for the harmonic-oscillator model in higher dimensions.

I. INTRODUCTION

Coupled-harmonic-oscillator models have long been used in the study of lattice vibrations. These models can be studied in one or more dimensions and in the three-dimensional case can be thought of as the simplest idealization of a crystal lattice. The static properties of these models have been the main object of investigation and exact results for dispersion relations, density and normal modes, and thermodynamical quantities are available in the literature.[1–4]

The dynamical properties of these models, however, have not been studied much. To our knowledge, there are just a few papers on the time evolution of these systems, notably by Ford *et al.*,[2] and by Fox.[3] These authors investigate the dynamics of classical linearly-coupled harmonic-oscillator chains obeying periodic boundary conditions. Fox finds that the velocity autocorrelation function $\langle v(t)v \rangle$ is given by

$$\langle v(t)v \rangle = \frac{k_B T}{m} J_0(2\omega t)$$

in the thermodynamic limit. This result yields a nonvanishing diffusion constant for a tagged oscillator. This is unexpected for there should be, as he notes, no diffusion in such systems. In addition, as we shall see, the mean-square displacement of an oscillator as calculated from the solution due to Ford *et al.* is found to diverge. On the other hand, Montroll[4] obtained a finite value for the mean-square displacement by using fixed-end boundary conditions.

Our aim is to investigate the role of both periodic and fixed-end boundary conditions in this model. We are particularly interested in clarifying the physical meaning of the finite diffusion constant obtained by Fox, as well as in the divergence of the mean-square displacement.

A major feature of the present work is the introduction of the method of recurrence relations due to Lee[5] in the treatment of the dynamics of a classical system. The original formulation of the method of recurrence relations was established for quantum systems. The method has been applied to the dynamic response in an electron gas and in a spin system.[6] We develop a classical version of this method to obtain exact results for both the velocity and displacement autocorrelation functions in coupled harmonic chains.

Our paper is organized as follows. In Sec. II the recurrence relations method for a classical system is presented. In Sec. III this method is used to investigate the dynamical behavior of a classical harmonic-oscillator chain constrained to periodic boundary conditions. Both the velocity and displacement correlation functions are obtained. It is shown that the finite diffusion constant obtained by Fox[3] is due to the zero-frequency mode of this system. This zero-frequency mode is also responsible for the divergence in the mean-square displacement of a tagged oscillator. In Sec. IV the case of a harmonic-oscillator chain whose end points are kept fixed to rigid walls is examined. Analytic expressions for the correlation functions of this system is derived. It is shown that the diffusion constant vanishes, and that the mean-square displacement of an oscillator is finite. In Sec. V our results are discussed.

II. METHOD OF RECURRENCE RELATIONS

Let G represent a dynamical quantity of a classical many-body system governed by a Hamiltonian H. The time evolution of G can be expressed formally as

$$G(t) \doteq e^{tL} G(0) , \tag{2.1}$$

while L is the Liouville operator defined by

$$Lf = \{f, H\} = \sum_i \left[\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial f}{\partial p_i} \right] , \tag{2.2}$$

where q_i and p_i are, respectively, the canonical coordinate and momentum of the ith particle in the system. The expression (2.1) can be given as an expansion in terms of a complete orthogonal set $\{f_\nu\}$, spanning a properly defined Hilbert space S of dimension $d+1$, as follows:

$$G(t) = \sum_{\nu=0}^{d} A_\nu(t) f_\nu . \tag{2.3}$$

The scalar product in S is defined as

$$(A,B)=\frac{1}{Z}\int d^N x\, e^{-\beta H}A^*B \ , \tag{2.4}$$

where β is the inverse temperature, $Z\equiv\int d^N x\, e^{-\beta H}$ is the classical partition function, and

$$d^N x=\prod_{i=1}^{N} dq_i\, dp_i \ .$$

Clearly, this scalar product is positive definite.

By choosing $f_0=G(0)$, it follows from the above-defined scalar product that the set $\{f_\nu\}$ can be generated by the recurrence relation (RR I):

$$f_{\nu+1}=Lf_\nu+\Delta_\nu f_{\nu-1}, \quad \nu\geq 0 \tag{2.5}$$

where

$$\Delta_\nu=\frac{(f_\nu,f_\nu)}{(f_{\nu-1},f_{\nu-1})} \ , \tag{2.6}$$

and

$$f_{-1}\equiv 0, \quad \Delta_0\equiv 1 \ . \tag{2.7}$$

It also follows that the coefficients $A_\nu(t)$ obey a second recurrence relation (RR II):

$$\Delta_{\nu+1}A_{\nu+1}(t)=-\dot{A}_\nu(t)+A_{\nu-1}(t), \quad \nu\geq 0 \tag{2.8}$$

where

$$\dot{A}_\nu(t)\equiv\frac{dA_\nu(t)}{dt}, \quad A_{-1}\equiv 0 \ . \tag{2.9}$$

Thus the recurrence relations RR I and RR II enable one to obtain the complete time behavior of the dynamical quantity $G(t)$. These recurrence relations are a classical version of Lee's recurrence relations.[5]

In the following sections we use this method to obtain the velocity autocorrelation function as well as the displacement autocorrelation function of a classical harmonic-oscillator chain subject to periodic and fixed-end boundary conditions.

III. CLASSICAL HARMONIC-OSCILLATOR CHAIN WITH PERIODIC BOUNDARY CONDITIONS

Consider a linear chain of N identical classical harmonic oscillators of mass m coupled to each other. With no loss of generality we take N to be an even number. The Hamiltonian is given by

$$H=\sum_{j=-N/2}^{N/2-1} p_j^2/2m+\sum_{j=-N/2}^{N/2-1}(k/2)(q_j-q_{j+1})^2 \ , \tag{3.1}$$

where only nearest-neighbor couplings are taken into account, and $k=m\omega^2$ is the coupling constant. Let us impose periodic boundary conditions such that

$$q_{j+N}=q_j \tag{3.2a}$$

and

$$p_{j+N}=p_j \ . \tag{3.2b}$$

This is the system studied by Ford *et al.*[2] and by Fox.[3] The Hamiltonian (3.1) can be diagonalized by the introduction of normal-mode coordinates Q_α and P_α through the transformations

$$q_j=\frac{1}{\sqrt{Nm}}\sum_{\alpha=-N/2}^{N/2-1} e^{i(2\pi j/N)\alpha}Q_\alpha \tag{3.3a}$$

and

$$p_j=\left[\frac{m}{N}\right]^{1/2}\sum_{\alpha=-N/2}^{N/2-1} e^{i(2\pi j/N)\alpha}P_\alpha \ . \tag{3.3b}$$

Notice that the boundary conditions (3.2) are indeed satisfied and the set $\{(1/\sqrt{N})e^{i(2\pi j/N)\alpha}\}$ is orthogonal and complete in a periodic domain of the oscillator labels j. It follows that since q_j and p_j are real,

$$Q_\alpha^*=Q_{-\alpha} \ , \tag{3.4a}$$

$$P_\alpha^*=P_{-\alpha} \ . \tag{3.4b}$$

In terms of the normal-mode coordinates, the Hamiltonian (3.1) now reads

$$H=\tfrac{1}{2}\sum_{\alpha=-N/2}^{N/2-1}(P_\alpha^*P_\alpha+\Omega_\alpha^2 Q_\alpha^* Q_\alpha) \ , \tag{3.5}$$

where

$$\Omega_\alpha^2=4\omega^2\sin^2\left[\frac{\pi\alpha}{N}\right] , \tag{3.6}$$

and Ω_α are the normal-mode frequencies.

We are interested in correlation functions of the form

$$\langle A(t)A(0)\rangle=\frac{1}{Z}\int d^N x\, A(t)A(0)e^{-\beta H} \ , \tag{3.7}$$

where A can be either the velocity of the jth oscillator $v_j=p_j/m$ or its displacement q_j. The correlation functions $\langle v_j(t)v_j(0)\rangle$ and $\langle q_j(t)q_j(0)\rangle$ can be cast in the following forms:

$$\langle v_j(t)v_j(0)\rangle=\frac{1}{Nm}\sum_{\alpha,\alpha'} e^{-i(2\pi/N)(\alpha-\alpha')}(P_\alpha(t),P_{\alpha'}) \tag{3.8}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{1}{Nm}\sum_{\alpha,\alpha'} e^{-i(2\pi/N)(\alpha-\alpha')}(Q_\alpha(t),Q_{\alpha'}) \ . \tag{3.9}$$

Consider the dynamical quantity $P_\alpha(t)$. By using the first recurrence relation (RR I) and making the following choice for the basis vector f_0:

$$f_0=P_\alpha(0)\equiv P_\alpha \ , \tag{3.10a}$$

we obtain the next basis vector

$$f_1=LP_\alpha=-\Omega_\alpha^2 Q_{-\alpha} \ . \tag{3.10b}$$

Here the Liouville operator is given by

$$L=\sum_{\alpha=-N/2}^{N/2-1}\left[P_{-\alpha}\frac{\partial}{\partial Q_\alpha}-\Omega_\alpha^2 Q_{-\alpha}\frac{\partial}{\partial P_\alpha}\right] . \tag{3.11}$$

It can be readily seen that $(f_0,f_0)=1/\beta$, and $(f_1,f_1)=\Omega_\alpha^2/\beta$. Then $\Delta_1=(f_1,f_1)/(f_0,f_0)=\Omega_\alpha^2$. By taking these results into RR I, we obtain $f_2=0$, which leads to $\Delta_2=0$. Moreover, we find that $f_\nu=0$ for $\nu\geq 2$. Thus, the Hilbert space for $P_\alpha(t)$ is two dimensional, with basis vectors f_0 and f_1 given by Eqs. (3.10).

The above results together with the second recurrence relation (RR II) yield the equations for $A_\nu(t)$,

$$\Omega_\alpha^2 A_1(t)=-\dot{A}_0(t)\ , \tag{3.12a}$$

and

$$0=-\dot{A}_1(t)+A_0(t)\ , \tag{3.12b}$$

with initial conditions $A_0(0)=1$ and $A_1(0)=0$. The solutions of these equations are

$$A_0(t)=\cos(\Omega_\alpha t) \tag{3.13a}$$

and

$$A_1(t)=\frac{1}{\Omega_\alpha}\sin(\Omega_\alpha t)\ . \tag{3.13b}$$

Thus the time evolution of $P_\alpha(t)$ is determined to be

$$P_\alpha(t)=\cos(\Omega_\alpha t)P_\alpha-\Omega_\alpha\sin(\Omega_\alpha t)Q_{-\alpha}\ . \tag{3.14}$$

We then obtain the following scalar products:

$$(P_\alpha(t),P_{\alpha'})=\frac{\delta_{\alpha,\alpha'}}{\beta}\cos(\Omega_\alpha t) \tag{3.15a}$$

and

$$(P_\alpha(t),Q_{\alpha'})=0\ . \tag{3.15b}$$

By using the above results in Eq. (3.8), we obtain the velocity autocorrelation function,

$$\langle v_j(t)v_j(0)\rangle=\frac{k_BT}{Nm}\sum_{\alpha=-N/2}^{N/2-1}\cos(\Omega_\alpha t)\ . \tag{3.16}$$

In order to evaluate the displacement autocorrelation function, Eq. (3.9), we follow a similar procedure. Again, by using RR I, we find that the dynamical Hilbert space of $Q_\alpha(t)$ has just two dimensions, with basis vectors,

$$f_0=Q_\alpha \tag{3.17a}$$

and

$$f_1=P_{-\alpha}\ . \tag{3.17b}$$

The nontrivial Δ_ν is given by $\Delta_1=\Omega_\alpha^2$. This leads to a system of equations for $A_\nu(t)$, which is identical to (3.12). We finally obtain

$$Q_\alpha(t)=\cos(\Omega_\alpha t)Q_\alpha+\frac{1}{\Omega_\alpha}\sin(\Omega_\alpha t)P_{-\alpha}\ . \tag{3.18}$$

We then obtain the following scalar product

$$(Q_\alpha(t),Q_{\alpha'})=\frac{\delta_{\alpha,\alpha'}}{\beta\Omega_\alpha^2}\cos(\Omega_\alpha t)\ , \tag{3.19}$$

which when used together with Eq. (3.19) yields the displacement autocorrelation function,

$$\langle q_j(t)q_j(0)\rangle=\frac{k_BT}{Nm}\sum_{\alpha=-N/2}^{N/2-1}\frac{\cos(\Omega_\alpha t)}{\Omega_\alpha^2}\ . \tag{3.20}$$

Equations (3.16) and (3.20) were first obtained by Ford *et al.*[2] by using another method.

In the thermodynamic limit, $N\to\infty$, Eqs. (3.16) and (3.20) read

$$\langle v_j(t)v_j(0)\rangle=\frac{k_BT}{m}\int_{-1/2}^{1/2}dx\cos[\Omega(x)t] \tag{3.21}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{k_BT}{m}\int_{-1/2}^{1/2}dx\frac{\cos[\Omega(x)t]}{\Omega^2(x)}\ , \tag{3.22}$$

where

$$\Omega^2(x)=4\omega^2\sin^2(\pi x)\ . \tag{3.23}$$

Notice that these correlation functions do not depend on the oscillator label j, reflecting the translational invariance of the system.

Equation (3.21) can also be put into the form

$$\langle v_j(t)v_j\rangle=\frac{k_BT}{m}\frac{2}{\pi}\int_0^{(1/2)\pi}dy\cos(2\omega t\sin y)=\frac{k_BT}{m}J_0(2\omega t)\ , \tag{3.24}$$

where J_0 is the Bessel function of order zero. This expression was first derived by Fox.[3] He noted that it leads to a finite value for the diffusion constant given by the Green-Kubo formula[7,8]

$$D=\int_0^\infty dt\ \langle v_j(t)v_j(0)\rangle=\frac{k_BT}{2m\omega}\ . \tag{3.25}$$

This is contrary to the expectation that a system of oscillators should not diffuse.

In order to clarify the meaning of this result, we consider the more fundamental definition of the diffusion constant[7]

$$D=\lim_{t\to\infty}\left[\frac{1}{2t}\langle[q_j(t)-q_j(0)]^2\rangle\right]\ . \tag{3.26}$$

By using Eq. (3.20) in the above expression we obtain

$$D=\lim_{t\to\infty}\left[\frac{1}{t}\frac{2k_BT}{Nm}\sum_{\alpha=-N/2}^{N/2-1}\frac{\sin^2(\Omega_\alpha t/2)}{\Omega_\alpha^2}\right]\ . \tag{3.27}$$

If we take the thermodynamic limit first, we find

$$\begin{aligned}D&=\lim_{t\to\infty}\left[\frac{1}{t}\frac{2k_BT}{m}\int_{-1/2}^{1/2}dx\frac{\sin^2[\Omega(x)t/2]}{\Omega^2(x)}\right]\\&=\frac{\pi k_BT}{2m}\int_{-1/2}^{1/2}dx\left[\lim_{t\to\infty}\frac{\sin^2[\Omega(x)t/2]}{\pi t[\Omega(x)/2]^2}\right]\\&=\frac{\pi k_BT}{2m}\int_{-1/2}^{1/2}dx\ \delta\left[\frac{\Omega(x)}{2}\right]\ ,\end{aligned} \tag{3.28}$$

where δ is the Dirac δ function. The above expression can be written as

$$D=\frac{k_B T}{m}\sum_i \int_{-1/2}^{1/2} dx \frac{\delta(x-x_i)}{\left|\frac{d\Omega(x)}{dx}\right|_{x=x_i}}, \tag{3.29}$$

where x_i are the zeros of $\Omega(x)$. In this case,

$x_i=0,\pm 1,\pm 2,\ldots$.

Notice that only $x_i=0$ contributes to the integral. This corresponds to the mode with zero frequency, which is the mode with full translational symmetry. This contribution from the zero-frequency mode yields the finite diffusion constant,

$$D=\frac{\pi k_B T}{m}\int_{-1/2}^{1/2} dx \frac{\delta(x)}{2\pi\omega} = \frac{k_B T}{2m\omega},$$

which is the same as Eq. (3.25). The existence of the zero-frequency mode, resulting in a finite diffusion constant, is evidently due to the periodic boundary conditions used. Presumably if we use fixed boundary conditions, that is, the end points of the harmonic-oscillator chain fixed to rigid walls, the diffusion constant would vanish. This will be shown in Sec. IV.

We shall now give the final expression for the displacement autocorrelation function after the integral in Eq. (3.26) is done. The result is

$$\langle q_j(t)q_j(0)\rangle-\langle q_j^2(0)\rangle = -\frac{k_B T}{2m\omega}t\sum_{n=0}^{\infty}[J_{2n+1}(2\omega t)+J_{2n+3}(2\omega t)], \tag{3.30}$$

where J_n are the Bessel functions of order n. The mean-square displacement of the jth oscillator $\sigma_j^2 \equiv \langle q_j^2\rangle - \langle q_j\rangle^2 = \langle q_j^2\rangle$ diverges as

$$\langle q_j^2\rangle = \lim_{\Gamma\to\infty}\left[\frac{k_B T}{2\pi m\omega^2}\Gamma\right]. \tag{3.31}$$

This divergence is a result of the translational invariance of the system imposed by the periodic boundary conditions.

We conclude this section by presenting the asymptotic forms of the autocorrelation functions. The velocity and the displacement autocorrelation functions for large times are given, respectively, by

$$\langle v_j(t)v_j(0)\rangle \sim \frac{k_B T}{(\pi m^2\omega)^{1/2}}\frac{\cos(2\omega t-\pi/4)}{t^{1/2}} \quad \text{as } t\to\infty \tag{3.32}$$

and

$$\langle q_j(t)q_j(0)\rangle-\langle q_j^2(0)\rangle \sim \frac{-k_B T}{2m\omega}t\left[1-\frac{1}{(4\pi\omega^3)^{1/2}}\frac{\cos(2\omega t-\pi/4)}{t^{3/2}}\right] \quad \text{as } t\to\infty . \tag{3.33}$$

Notice that by using Eq. (3.33) in Eq. (3.26), we see that the diffusion constant approaches its finite value (3.25) as

$$D=\lim_{t\to\infty}\left[\frac{k_B T}{2m\omega}\left[1-\frac{1}{(4\pi\omega^3)^{1/2}}\frac{\cos(2\omega t-\pi/4)}{t^{3/2}}\right]\right]. \tag{3.34}$$

The autocorrelation functions at short times are given by

$$\langle v_j(t)v_j(0)\rangle \cong \frac{k_B T}{m}(1-\omega^2 t^2), \tag{3.35}$$

and

$$\langle q_j(t)q_j(0)\rangle-\langle q_j^2(0)\rangle \cong -\frac{k_B T}{2m}t^2, \tag{3.36}$$

where $\langle q_j^2(0)\rangle$ is given by Eq. (3.31).

IV. HARMONIC-OSCILLATOR CHAIN WITH FIXED ENDS

Consider the following harmonic-oscillator chain Hamiltonian

$$H=\sum_{j=0}^{N+1} p_j^2/2m+\sum_{j=0}^{N}(k/2)(q_j-q_{j+1})^2, \tag{4.1}$$

in which the end oscillators are fixed to external rigid walls, such that

$$q_0=q_{N+1}=0 \tag{4.2a}$$

and

$$p_0=p_{N+1}=0. \tag{4.2b}$$

This Hamiltonian can be diagonalized by the linear transformation

$$q_j=\frac{1}{\sqrt{(N+1)m}}\sum_{s=1}^{N}\eta_s \sin\left[\frac{\pi j s}{N+1}\right], \tag{4.3a}$$

$$p_j=\left[\frac{m}{N+1}\right]^{1/2}\sum_{s=1}^{N}\xi_s \sin\left[\frac{\pi j s}{N+1}\right], \tag{4.3b}$$

where η_s and ξ_s are the normal-mode coordinates. In terms of these new coordinates our Hamiltonian becomes

$$H=\sum_{s=1}^{N}\xi_s^2/2+\sum_{s=1}^{N}(\Omega_s^2\xi_s^2)/2, \tag{4.4}$$

where the normal-mode frequencies are given by

$$\Omega_s^2=\frac{4k}{m}\sin^2\left[\frac{\pi s}{2(N+1)}\right],\quad s=1,2,\ldots,N. \tag{4.5}$$

The velocity and displacement autocorrelation functions are given, respectively, by

$$\langle v_j(t)v_j(0)\rangle=\frac{1}{m(N+1)}\sum_{s,s'=1}^{N}\sin\left[\frac{\pi j s}{N+1}\right]\sin\left[\frac{\pi j s'}{N+1}\right]\times(\xi_s(t),\xi_{s'}) \tag{4.6}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{1}{m(N+1)}\sum_{s,s'=1}^{N}\sin\left[\frac{\pi js}{N+1}\right]\sin\left[\frac{\pi js'}{N+1}\right]\times(\eta_s(t),\eta_{s'}) , \tag{4.7}$$

where

$$(\xi_s(t),\xi_{s'})=\frac{1}{Z}\int d^NX\, e^{-\beta H}\xi_s(t)\xi_{s'} , \tag{4.8}$$

$$(\eta_s(t),\eta_{s'})=\frac{1}{Z}\int d^NX\, e^{-\beta H}\eta_s(t)\eta_{s'} , \tag{4.9}$$

$$Z=\int d^NX\, e^{-\beta H} , \tag{4.10}$$

and

$$d^NX=\prod_{s=1}^{N} d\eta_s d\xi_s . \tag{4.11}$$

By applying the recurrence relations method, we determine the time evolution of $\xi_s(t)$ and $\eta_s(t)$. The explicit results for these quantities are, respectively,

$$\xi_s(t)=\xi_s\cos(\Omega_s t)-\eta_s\Omega_s\sin(\Omega_s t) \tag{4.12}$$

and

$$\eta_s(t)=\eta_s\cos(\Omega_s t)+\frac{\xi_s}{\Omega_s}\sin(\Omega_s t) . \tag{4.13}$$

The correlation functions (4.6) and (4.7) can then be evaluated:

$$\langle v_j(t)v_j(0)\rangle=\frac{k_BT}{m(N+1)}\sum_{s=1}^{N}\sin^2\left[\frac{\pi js}{N+1}\right]\cos(\Omega_s t) , \tag{4.14}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{k_BT}{m(N+1)}\sum_{s=1}^{N}\sin^2\left[\frac{\pi js}{N+1}\right]\frac{\cos(\Omega_s t)}{\Omega_s^2} . \tag{4.15}$$

In the thermodynamic limit the above expressions become

$$\langle v_j(t)v_j(0)\rangle=\frac{k_BT}{m}\frac{1}{\pi}\int_0^{\pi}dy\,\sin^2(yj)\times\cos[2\omega t\sin(y/2)] , \tag{4.16}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{k_BT}{m}\frac{1}{\pi}\times\int_0^{\pi}dy\frac{\sin^2(yj)\cos[2\omega t\sin(y/2)]}{4\omega^2\sin^2(y/2)} , \tag{4.17}$$

where $j=1,2,\ldots,$ and $\omega=(k/m)^{1/2}$. The integrals can be expressed in terms of Bessel functions, yielding

$$\langle v_j(t)v_j(0)\rangle=\frac{k_BT}{2m}[J_0(2\omega t)-J_{4j}(2\omega t)] \tag{4.18}$$

and

$$\langle q_j(t)q_j(0)\rangle=\frac{k_BT}{2m\omega^2}\left[j-\frac{\omega t}{2m\omega^2}\sum_{n=0}^{\infty}\left[J_{2n+1}(2\omega t)+J_{2n+3}(2\omega t)-J_{2n+4j+1}(2\omega t)-J_{2n+4j+3}(2\omega t)+\frac{4j}{\omega t}J_{2n+4j+2}(2\omega t)\right]\right] . \tag{4.19}$$

Notice that these correlation functions now depend on the oscillator label j, which gives its location relative to the ends. This reflects the absence of translational symmetry of the system owing to the fixed-end boundary conditions used. As a result, there is no zero-frequency mode, as can also be seen from Eq. (4.5).

When t becomes very large ($t\to\infty$), Eqs. (4.18) and (4.19) assume the following asymptotic forms:

$$\langle v_j(t)v_j(0)\rangle\sim\frac{2k_BTj^2}{m(\pi\omega^3)^{1/2}}\frac{\sin(2\omega t-\pi/4)}{t^{3/2}} \quad \text{as } t\to\infty , \tag{4.20}$$

and

$$\langle q_j(t)q_j(0)\rangle\sim\frac{-k_BTj^2}{2m(\pi\omega^7)^{1/2}}\frac{\cos(2\omega t+\pi/4)}{t^{3/2}} \quad \text{as } t\to\infty . \tag{4.21}$$

On the other hand, for short times ($t\to0$), the correlation functions (4.18) and (4.19) are given by

$$\langle v_j(t)v_j(0)\rangle\cong\frac{k_BT}{2m}(1-\omega^2t^2) , \tag{4.22}$$

and

$$\langle q_j(t)q_j(0)\rangle\cong\frac{k_BT}{2m\omega^2}(j-\omega^2t^2/2) . \tag{4.23}$$

The mean-square displacement of the jth oscillator can be obtained by setting $t=0$ in Eq. (4.19) [or in Eq. (4.23)],

$$\sigma_j^2=\frac{k_BT}{2m\omega^2}j . \tag{4.24}$$

This linear dependence on j was first derived by Montroll[4] in the high-temperature expansion of his quantummechanical calculation.[9]

A straightforward calculation of the diffusion constant by the Green-Kubo formula[7,8] yields

$$D_j = \lim_{t\to\infty} \left[\frac{k_B T}{2\omega^2 t} j \right] = 0 , \tag{4.25}$$

which is physically more reasonable than the previous case of a finite diffusion constant.

V. CONCLUSION

We have examined a classical harmonic-oscillator chain with nearest-neighbor interactions using both periodic and fixed-end boundary conditions. The exact dynamical behavior was determined by the method of recurrence relations. Explicit results for both the velocity and displacement autocorrelation functions were obtained. We find that the finite diffusion constant and the divergent mean-square displacement of a tagged oscillator found in the literature are due to the zero-frequency mode present in periodic boundary condition solutions. By using fixed-end boundary conditions, we have shown that the diffusion is indeed zero and that the mean-square displacement does not diverge. Although these conclusions have been obtained for one-dimensional chains, we expect that they should hold for the harmonic-oscillator model in higher dimensions. We also observe that these autocorrelation functions do *not* decay exponentially.[10]

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