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Poincaré Cycles and Ergodic Behavior of a Linear Diatomic Chain

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The ergodic behavior of a linear diatomic chain is shown to be analogous to that of a linear monatomic chain. Starting with the expressions for the time-relaxed correlation functions between any two particles in the chain, we show that the existence of Poincaré cycles is not inconsistent with the development of an equilibrium state. Also, we show that those dynamical variables that are ergodic for the linear monoatomic chain remain ergodic in the diatomic chain. It is shown that the autocorrelation functions for particles with equal or different masses decay in time as $t^{-1/2}$.

KEY WORDS: Poincaré cycles; ergodic behavior; momentum autocorrelation functions; diatomic chain.

1. INTRODUCTION

In several recent papers the problems of irreversibility and the existence of recurrence times for dynamical systems have been examined in great detail for the case of linear chains[1,2] and for systems of coupled harmonic oscillators in one, two, and three dimensions.[3] In this paper we wish to extend the calculations of Mazur and Montroll[3] to a diatomic linear chain in which

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we have a two-component ordered system consisting of $2N$ oscillators coupled in a periodic array. We shall limit ourselves to a discussion of the different time-dependent correlation functions and to a study of their relation with the existence of Poincaré cycles for a large number of degrees of freedom and with the ergodic behavior of some dynamical variables of the system. This discussion will be carried out in the realm of classical mechanics. leaving the quantum mechanical treatment for a further discussion.

In Section 1 of this paper we briefly review the dynamics of a linear diatomic chain. In Section 2 we study the classical statistics of such a system; in particular, we show how the existence of Poincaré cycles is not inconsistent with passage of the system to its equilibrium state. Also, we indicate which are some of the dynamical variables that are ergodic. Finally, in Section 3 a detailed calculation of the momentum autocorrelation functions will show that they decay in time as $t^{-1/2}$.

2. DYNAMICS OF A LINEAR DIATOMIC CHAIN

Consider a linear chain consisting of $2N$ mass points N of which have a mass M and N a mass m. We shall assume that $M > m$ and also impose a periodic boundary condition of the Born–von Kármán type. Fixing the particles with mass m at the even-numbered lattice points $2n$, $2n + 2$,... and the particles with mass M at the odd-numbered lattice points $2n - 1$, $2n + 1$,..., the Hamiltonian for the system is given by

$$H = \sum_{n=0}^{N-1} (\tfrac{1}{2}m\dot{q}_{2n}^2 + \tfrac{1}{2}M\dot{q}_{2n+1}^2) + \tfrac{1}{2}\gamma \sum_{n=0}^{N-1} [(q_{2n+1} - q_{2n})^2 + (q_{2n-1} - q_{2n})^2] \tag{1}$$

where the q's represent the displacements of the particles from their equilibrium position and γ is the force constant between any two masses. The imposition of periodic boundary conditions implies that

$$q_{k+2N} = q_k \tag{2}$$

for any k.

It is convenient for our purposes to express (1) in terms of the normal coordinates of the system. These coordinates are defined[4] by the following relations:

$$\begin{aligned} q_{2n} &= \frac{1}{\sqrt{N}} \sum_{k=1}^{N} e^{2\pi ikn/N} \left(\xi_k \frac{\cos \alpha_k}{\sqrt{m}} + \eta_k \frac{\sin \alpha_k}{\sqrt{m}}\right) \\ q_{2n+1} &= \frac{1}{\sqrt{N}} \sum_{k=1}^{N} e^{\pi ik(2n+1)/N} \left(-\xi_k \frac{\sin \alpha_k}{\sqrt{M}} + \eta_k \frac{\cos \alpha_k}{\sqrt{M}}\right) \end{aligned} \tag{3}$$

where ξ_k and η_k satisfy the reality conditions

$$\xi_k^* = \xi_{-k}, \qquad \eta_k^* = \eta_{-k} \tag{4}$$

and α_k is defined through the relation

$$\tan 2\alpha_k = [2(mM)^{1/2}/(M-m)] \cos(\pi k/N) \tag{5}$$

Substituting Eq. (3) into Eq. (1) and using Eq. (4), we find that in terms of the normal coordinates ξ_k and η_k the Hamiltonian reads

$$H = \sum_{k=1}^{N} \tfrac{1}{2}[|\dot{\xi}_k|^2 + |\dot{\eta}_k|^2 + (\omega_k^{(1)})^2 |\xi_k|^2 + (\omega_k^{(2)})^2 |\eta_k|^2] \tag{6}$$

where

$$\begin{aligned} (\omega_k^{(1)})^2 &= (\gamma/Mm)[M + m + (M^2 + m^2 + 2Mm \cos \varphi_k)^{1/2}] \\ (\omega_k^{(2)})^2 &= (\gamma/Mm)[M + m - (M^2 + m^2 + 2Mm \cos \varphi_k)^{1/2}] \end{aligned} \tag{7}$$

and $\varphi_k = 2\pi k/N$. Here $\omega_k^{(1)}$ and $\omega_k^{(2)}$ are the well-known dispersion relations defining the optical and acoustical branches, respectively.

The equations of motion for the normal modes are easily derived from Eq. (6), the result being

$$\ddot{\xi}_k + (\omega_k^{(1)})^2 \xi_k = 0, \qquad \ddot{\eta}_k + (\omega_k^{(2)})^2 \eta_k = 0 \tag{8}$$

whose solution is

$$\begin{aligned} \xi_k(t) &= \xi_k(0) \cos(\omega_k^{(1)} t) + (1/\omega_k^{(1)}) \dot{\xi}_k(0) \sin(\omega_k^{(1)} t) \\ \eta_k(t) &= \eta_k(0) \cos(\omega_k^{(2)} t) + (1/\omega_k^{(2)}) \dot{\eta}_k(0) \sin(\omega_k^{(2)} t) \end{aligned} \tag{9}$$

It will be useful for future calculations to express the momentum p_j of any particle at time t in terms of the values of the momenta for all particles at time $t = 0$ and the normal coordinates ξ_k and η_k also at time $t = 0$.

From Eqs. (3) and (9) we have that

$$\begin{aligned} p_{2n}(t) = \sqrt{m} \sum_{k=1}^{N} C_{k,2n}\{&[-\omega_k^{(1)}\xi_k(0) \sin \omega_k^{(1)}t + \dot{\xi}_k(0) \cos \omega_k^{(1)}t] \cos \alpha_k \\ &+ [-\omega_k^{(2)}\eta_k(0) \sin \omega_k^{(2)}t + \dot{\eta}_k(0) \cos \omega_k^{(2)}t] \sin \alpha_k\} \end{aligned} \tag{10}$$

$$\begin{aligned} p_{2n+1}(t) = \sqrt{M} \sum_{k=1}^{N} C_{k,2n+1}\{&[\omega_k^{(1)}\xi_k(0) \sin \omega_k^{(1)}t - \dot{\xi}_k(0) \cos \omega_k^{(1)}t] \sin \alpha_k \\ &+ (-\omega_k^{(2)}\eta_k(0) \sin \omega_k^{(2)}t + \dot{\eta}_k(0) \cos \omega_k^{(2)}t] \cos \alpha_k\} \end{aligned} \tag{10'}$$

where

$$C_{k,2n} = (1/\sqrt{N})\, e^{\pi ik2n/N}; \qquad C_{k,2n+1} = (1/\sqrt{N})\, e^{\pi ik(2n+1)/N} \tag{11}$$

These coefficients satisfy the relations

$$\sum_{j=1}^{N} C_{j,2k}C^{*}_{j,2l} = \sum_{j=1}^{N} C_{j,2k+1}C^{*}_{j,2l+1} = \delta_{kl} \tag{12}$$

If we multiply Eq. (3) by $C^{*}_{j,2n}$ and $C^{*}_{j,2n+1}$, respectively, and sum over the n's, we find, with the use of Eq. (12), that

$$\begin{aligned} \eta_j &= \sum_{n=1}^{N} (\sqrt{m}\; C^{*}_{j,2n}q_{2n} \sin \alpha_j + \sqrt{M}\, C^{*}_{j,2n+1}q_{2n+1} \cos \alpha_j) \\ \xi_j &= \sum_{n=1}^{N} (\sqrt{m}\; C^{*}_{j,2n}q_{2n} \cos \alpha_j - \sqrt{M}\, C^{*}_{j,2n+1}q_{2n+1} \sin \alpha_j) \end{aligned} \tag{13}$$

From Eqs. (13) we can evaluate $\dot{\eta}_j(0)$ and $\dot{\xi}_j(0)$, which are thereafter substituted back in Eqs. (10) to yield:

$$\begin{aligned} p_{2n}(t) &= \sum_{j=1}^{N} [a_{jn}p_{2j}(0) + b_{jn}p_{2j+1}(0) + l_{jn}\xi_j(0) + h_{jn}\eta_j(0)] \\ p_{2n+1}(t) &= \sum_{j=1}^{N} [r_{jn}p_{2j+1}(0) + s_{jn}p_{2j}(0) + f_{jn}\xi_j(0) + g_{jn}\eta_j(0)] \end{aligned} \tag{14}$$

where

$$\begin{aligned} a_{jn} &= (1/N) \sum_{k=1}^{N} e^{2\pi ik(n-j)/N}(\cos \omega_k^{(1)}t \cos^2 \alpha_k + \cos \omega_k^{(2)}t \sin^2 \alpha_k) \\ b_{jn} &= (1/N)(m/M)^{1/2} \sum_{k=1}^{N} e^{2\pi ik(n-j-1/2)/N}(\cos \alpha_k \sin \alpha_k)(\cos \omega_k^{(2)}t - \cos \omega_k^{(1)}t) \end{aligned} \tag{15}$$

$$l_{jn} = -\sqrt{m}\; C_{j,2n}\omega_j^{(1)} \cos \alpha_j \sin \omega_j^{(1)}t, \qquad h_{jn} = -\sqrt{m}\; C_{j,2n}\omega_j^{(2)} \sin \alpha_j \sin \omega_j^{(2)}t$$

and

$$\begin{aligned} r_{jn} &= (1/N) \sum_{k=1}^{N} e^{2\pi ik(n-j)/N}(\sin^2 \alpha_k \cos \omega_k^{(1)}t + \cos^2 \alpha_k \cos \omega_k^{(2)}t) \\ s_{jn} &= (1/N)(m/M)^{1/2} \sum_{k=1}^{N} e^{2\pi ik(n-j-1/2)/N}(\cos \alpha_k \sin \alpha_k)(\cos \omega_k^{(2)}t - \cos \omega_k^{(1)}t) \end{aligned} \tag{16}$$

$$f_{jn} = \sqrt{M}\, C_{j,2n+1}\omega_j^{(1)} \sin \alpha_j \sin \omega_j^{(1)}t, \quad g_{jn} = -\sqrt{M}\, C_{j,2n+1}\omega_j^{(2)} \cos \alpha_j \sin \omega_j^{(2)}t$$

Equations (14)–(16) are the analogs of Eq. (14)–and (16) Ref. 3, Section 3.

3. CLASSICAL STATISTICS OF A DIATOMIC CHAIN

We start this section by calculating the time-relaxed correlation function between two particles of the chain separated by a lattice vector **r**. It is quite clear that we shall have three such correlation functions, namely two corresponding to correlations between two particles of equal mass and the joint correlation function between two particles of different mass.

If we denote by $\rho_N^{(m)}(t)$ and $\rho_N^{(M)}(t)$ the correlation functions between particles of masses m and M, respectively, and by $\rho_N^{(J)}(t)$ the same function for particles of different mass, then, choosing the proper normalization factor so that $\rho_N(t, r) \to 1$ when t, r approach zero, we have that

$$\rho_N^{(m,M)}(t, r) = F_N^{(m,M)}(t, r)/F_N^{(m,M)}(0, 0) \tag{17}$$

and

$$\rho_N^{(J)}(t, r) = F_N^{(J)}(t, r)/[F_N^{(m)}(0, 0)\, F_M^{(M)}(0, 0)]^{1/2} \tag{17'}$$

where

$$F_N^{(m,M)} = \tfrac{1}{2}E\{p_{s+r}(t)\, p_s^*(0) + p_s(t)\, p_{s+r}^*(0)\} \tag{18}$$

s being an even- or odd-numbered lattice point,

$$F_N^{(J)} = \tfrac{1}{2}E\{p_{2s+1}(t)\, p_{2s+r}^*(0) + p_{2s+r}(t)\, p_{2s+1}^*(0)\} \tag{18'}$$

and E indicates an average over a microcanonical ensemble.

If we assume that initially there exists equipartition, i.e., that

$$\begin{gathered} E\{\dot{\xi}_k(0)\, \dot{\xi}_l(0)\} = kT\delta_{kl}\,, \qquad E\{\dot{\eta}_k(0)\, \dot{\eta}_l(0)\} = kT\delta_{kl} \\ E\{\dot{\xi}_k(0)\, \eta_l^*(0)\} = E\{\dot{\xi}_k(0)\, \xi_l^*(0)\} = E\{\dot{\eta}_k(0), \eta_l^*(0)\} = 0 \end{gathered} \tag{19}$$

then substituting Eqs. (10) and (10′) into Eqs. (18) and (18′) yields, after some manipulations, with the aid of Eqs. (19), the following results:

$$\begin{aligned} F_N^{(m)}(r, t) &= \frac{mkT}{N} \sum_k \cos \frac{2\pi kr}{N} (\cos \omega_k^{(1)} t \cos^2 \alpha_k + \cos \omega_k^{(2)} t \sin^2 \alpha_k) \\ F_N^{(M)}(r, t) &= \frac{MkT}{N} \sum_k \cos \frac{2\pi kr}{N} (\cos \omega_k^{(1)} t \sin^2 \alpha_k + \cos \omega_k^{(2)} t \cos^2 \alpha_k) \end{aligned} \tag{20}$$

where in these expressions r is an even multiple of the unit lattice vector since the unit vector is the distance between two particles with different mass. We also have

$$F_N^{(J)}(r', t) = (Mm)^{1/2} \frac{kT}{N} \sum_k \cos \frac{\pi kr'}{N} (\sin \alpha_k \cos \alpha_k)(\cos \omega_k^{(2)} t - \cos \omega_k^{(1)} t) \tag{21}$$

In this expression r' is obviously an odd multiple of the unit lattice vector. It is easy to show that all these expressions reduce to the corresponding F function for a monatomic lattice with $2N$ particles when we let the masses of the two particles coincide.

Finally, substituting these results into Eqs. (17) and (17′), we obtain the desired time-relaxed correlation functions,

$$\rho_N^{(m)}(r, t) = (1/N) \sum_k [\cos(2\pi kr/N)](\cos \omega_k^{(1)}t \cos^2 \alpha_k + \cos \omega_k^{(2)}t \sin^2 \alpha_k) \tag{22}$$

$$\rho_N^{(M)}(r, t) = (1/N) \sum_k [\cos(2\pi kr/N)](\cos \omega_k^{(1)}t \sin^2 \alpha_k + \cos \omega_k^{(2)}t \cos^2 \alpha_k) \tag{22'}$$

$$\rho_N^{(J)}(r', t) = (1/N) \sum_k [\cos(\pi kr'/N)](\sin \alpha_k \cos \alpha_k)(\cos \omega_k^{(2)}t - \cos \omega_k^{(1)}t) \tag{22''}$$

and the autocorrelation functions are just obtained from Eqs. (22) and (22′) by setting $r = 0$.

In the remainder of this section we shall discuss, first, the time behavior of the autocorrelation functions and its relation to the existence of Poincaré cycles, and second, how one obtains the ergodic properties for dynamical quantities following an analysis similar to that given by Mazur and Montroll.[3]

Since Eqs. (22) and (22′) have the same structure, it suffices to consider in detail only one of them. Let then $r = 0$ in (22), so that

$$\rho_N^{(m)}(0, t) = (1/N) \sum_k (\cos^2 \alpha_k \cos \omega_k^{(1)}t + \sin^2 \alpha_k \cos \omega_k^{(2)}t) \tag{23}$$

Here the first summation extends over all the normal mode frequencies of the optical branch and the second one over all frequencies of the acoustical branch. Thus, Eq. (23) is simply the sum of two "almost periodic functions" of the type

$$f_N(t) = (1/N) \sum_{j=0}^{N-1} a_j \cos \omega_j t \tag{24}$$

and to find the average frequency with which any value of $f_N(t)$ is achieved, a slight generalization of Kaç's theorem[3,5] is needed.

Let $N_{\Delta T}(h)$ be the number of zeros of $f_N(t) - h$ in the interval ΔT. Then the mean frequency for the achievement of h by $f_N(t)$ is given by

$$L(h) = \lim_{\Delta T \to \infty} [N_{\Delta T}(h)/\Delta T] \tag{25}$$

For almost periodic functions $L(h)$ is equal to the phase average of f over any interval $\Delta T^{(5)}$ and as it is shown in Appendix A by an extension of Kaç's theorem that one finds

$$L(bn^{1/2}) = (\omega_0/\pi a_0)\exp(-b^2/a_0{}^2) \tag{26}$$

where

$$\omega_0{}^2 = (1/n)\sum_{j=1}^{n} a_j{}^2\omega_j{}^2; \qquad a_0{}^2 = (1/n)\sum_{j=1}^{n} a_j{}^2 \tag{26'}$$

The conditions under which Eq. (26) is valid are

$$\lim_{n\to\infty}(1/n^2)\sum_{j=1}^{n} a_j{}^4 \to 0, \qquad \lim_{n\to\infty}(1/n^2)\sum_{j=1}^{n}\omega_j{}^2 a_j{}^4 \to 0, \qquad \lim_{n\to\infty}(1/n^2)\sum_{j=1}^{N}\omega_j{}^4 a_j{}^4 \to 0 \tag{27}$$

Since

$$\rho_N^{(m)}(t) = f_N^{(1)}(t) + f_N^{(2)}(t) \tag{28}$$

using Eqs. (25)–(27), we see that the mean frequency for the achievement of a value h by $\rho_N^{(m)}(t)$ is given by

$$L(bN^{1/2}) = (\omega_m^{(1)}/\pi a_0^{(1)})\exp[-(b/a_0^{(1)})^2] + (\omega_m^{(2)}/\pi a_0^{(2)})\exp[-(b/a_0^{(2)})^2] \tag{29}$$

where

$$\begin{aligned}(\omega_m^{(1)})^2 &= (1/N)\sum_{j=1}^{N}(\cos^4\alpha_j)(\omega_j^{(1)})^2, \qquad a_0^{(1)} = (1/N)\sum_{j=1}^{N}\cos^4\alpha_j\\ (\omega_m^{(2)})^2 &= (1/N)\sum_{j=1}^{N}(\sin^4\alpha_j)(\omega_j^{(2)})^2, \qquad a_0^{(2)} = (1/N)\sum_{j=1}^{N}\sin^4\alpha_j\end{aligned} \tag{30}$$

Also, for $\rho_N^{(M)}(t)$ we obtain

$$L(cN^{1/2}) = (\omega_M^{(1)}/\pi a_0^{(2)})\exp[-(c/a_0^{(2)})^2] + (\omega_M^{(2)}/\pi a_0^{(1)})\exp[-(c/a_0^{(1)})^2] \tag{31}$$

where $a_0^{(1)}$ and $a_0^{(2)}$ are defined in Eq. (30) and

$$(\omega_M^{(1)})^2 = (1/N)\sum_{j=1}^{N}(\sin^4\alpha_j)(\omega_j^{(1)})^2; \qquad (\omega_M^{(2)})^2 = (1/N)\sum_{j=1}^{N}(\cos^4\alpha_j)(\omega_j^{(2)})^2 \tag{32}$$

On the other hand, one can also find the value for $L(h)$ defined in (25) when h is near $a = \sum_i^n a_i$. This calculation has been done by Slater[5,6], the result being

$$L(h) = \frac{1}{\Gamma(\frac{1}{2}N + \frac{1}{2})} \left\{ \left[\frac{(\omega_m^{(1)})^2}{\prod_{j=1}^N \cos^2 \alpha_j} \right]^{1/2} \left[\frac{a^{(1)} - h}{2\pi} \right]^{(N-1)/2} + \left[\frac{(\omega_m^{(2)})^2}{\prod_{j=1}^N \sin^2 \alpha_j} \right]^{1/2} \left(\frac{a^{(2)} - h}{2\pi} \right)^{(N-1)/2} \right\} \tag{33}$$

and

$$L(h) = \frac{1}{\Gamma(\frac{1}{2}N + \frac{1}{2})} \left\{ \left[\frac{(\omega_M^{(1)})^2}{\prod_{j=1}^N \sin^2 \alpha_j} \right]^{1/2} \left(\frac{a^{(2)} - h}{2\pi} \right)^{(N-1)/2} + \left[\frac{(\omega_M^{(2)})^2}{\prod_{j=1}^N \cos^2 \alpha_j} \right] \left(\frac{a^{(1)} - h}{2\pi} \right)^{(N-1)/2} \right\} \tag{33'}$$

for particles with mass m and M, respectively. In this equation $a^{(1)}$ and $a^{(2)}$ are given by

$$a^{(1)} = \sum_{j=1}^N \cos^2 \alpha_j; \qquad a^{(2)} = \sum_{j=1}^N \sin^2 \alpha_j$$

If we compare our results with those obtained in Ref. 3 for the monatomic chain, we see that both for the light and heavy masses the behavior of $\rho_N(t)$ for each frequency branch is the same as in the monatomic chain when $t \to \infty$, and therefore we may conclude that the existence of an equilibrium state is not inconsistent with the existence of Poincaré cycles for a diatomic chain.

As a consequence of the fact that the asymptotic value, with respect to N, of the transition probability from $p_j(0)$ to $p_j(t)$ for a linear monatomic chain has a Gaussian character and the fact that $\rho_N(t) \to 0$ when N and t simultaneously tend to infinity, the following results are shown in Ref. 3 to be true:

(1) The expectation value of kinetic energy approaches the equipartition value kT when $t \to \infty$, while it approaches its initial value at $t = 0$.

(2) $p_j(t)$, the momentum of the jth particle at time t, is an ergodic quantity.

(3) $p_j^2(t)$ is also ergodic.

(4) Any function depending only on p_j and whose phase average exists is ergodic.

We shall now show that these results also hold for a diatomic chain; to do so one must prove that $P_N(p_j(t) \mid p_j(0))$, the transition probability from $p_j(0)$ to $p_j(t)$, has an asymptotic Gaussian character with respect to N both for $j = 2n$ and $j = 2n + 1$. Also $\rho_N^{(m)}(t)$ and $\rho_N^{(M)}(t)$ must approach zero when $N, t \to \infty$, but this is quite obvious since for the monatomic case $\rho_N(t)$ is a sum of cosines which satisfies the property (3) and in our case each term of the sum is multiplied by a constant a_j such that $| a_j | < 1$.

Let us then calculate $P_N(p_{2n}(t) | p_{2n}(0))$ by assuming that at time $t = 0$ the particle has momentum $p_{2n}(0)$ while the remaining $4N - 1$ variables are distributed initially according to a microcanonical distribution such that the total energy of the assembly is E. Then

$$\sum_{j\neq n} (1/2m)\, p_{2j}^2(0) + \sum_j \tfrac{1}{2}[(1/M)\, p_{2j+1}^2(0) + (\omega_j^{(1)})^2\, \xi_j{}^2(0) + (\omega_j^{(2)})^2\, \eta_j{}^2(0)] = R^2 \tag{34}$$

and from Eq. (14) we can write

$$\begin{aligned} Y(t) &= p_{2n}(t) - \rho_N^{(m)}(t)\, p_{2n}(0) \\ &= \sum_{j\neq n} a_{jn} p_{2j}(0) + \sum_j [b_{jn} p_{2j+1}(0) + l_{jn}\xi_j(0) + h_{jn}\eta_j(0)] \end{aligned} \tag{35}$$

Following the procedure described in Ref. 3 we must find the distribution function of (35) over the energy ellipsoid defined by Eq. (34). One then finds that the distribution function of $Y(t)$ when $N \to \infty$ is given by

$$F(Y) = [1/\sigma R(2\pi/N)^{1/2}] \exp(-NY^2/2\sigma^2R^2)$$

where

$$\sigma^2 = \sum_k \{2m\gamma_{jk}^2 + 2M\eta_{jk}^2 + [2/(\omega_k^{(1)})^2]\, l_{jk}^2 + [2/(\omega_k^{(2)})^2]\, h_{jk}^2 - 2m(\rho_N^{(m)})^2(t)$$

Evaluating σ^2, and since $R^2 = NkT$ as $N \to \infty$, we finally find that

$$\begin{aligned} P_N(p_{2n}(t) \mid p_{2n}(0)) &= \{2\pi mkT[1 - (\rho_N^{(m)})^2(t)]\} \\ &\quad \times \exp\{-[p_{2n}(t) - p_{2n}(0)\, \rho_N^{(m)}(t)]^2/2mkT[1 - (\rho_N^{(m)})^2(t)]\} \end{aligned} \tag{36}$$

and similarly

$$\begin{aligned} &P_N(p_{2n+1}(t) \mid p_{2n+1}(0)) \\ &\quad = \{2\pi MkT[1 - (\rho_N^{(M)})^2(t)]\} \\ &\qquad \times \exp\{-[p_{2n+1}(t) - p_{2n+1}(0)\, \rho_N^{(M)}(t)]^2/2MkT[1 - (\rho_N^{(M)})^2(t)]\} \end{aligned} \tag{36'}$$

which are the desired relations.

4. CALCULATION OF MOMENTUM CORRELATION FUNCTIONS

We wish to consider in this final section the dependence in time of the momentum autocorrelation functions obtained from Eqs. (22) and (22′) when $r = 0$ and $N \to \infty$ and of the correlation function between two neighboring particles, i.e., when $r' = 1$ in Eq. (22″) under the same condition for N. In particular, we shall show that, as in the case of the monatomic chain, the envelope of all these three functions goes to zero as $t^{-1/2}$ when $t \to \infty$.

Since, once more, the details of the calculations are similar in the three cases, we shall give the details for only one of them and write down the results for the remaining two.

Let us, then, consider the autocorrelation function for a particle having a mass m. We have

$$N\rho_N^{(m)}(t) = \sum_{k=0}^{N-1} (\cos^2 \alpha_k \cos \omega_k^{(1)} t + \sin^2 \alpha_k \cos \omega_k^{(2)} t) \tag{37}$$

Letting $N \to \infty$, we may replace k by a continuous variable, so, using Eqs. (5) and (7) and writing

$$\varphi_k \equiv 2\pi k/N = \theta$$

we get

$$\rho^{(m)}(t) = I_1 + I_2 \tag{38}$$

where

$$I_1 = \frac{1}{4\pi} \int_0^{2\pi} \left[1 + \frac{M - m}{(M^2 + m^2 + 2Mm \cos \theta)^{1/2}}\right] \times \cos \left\{t \left(\frac{\gamma}{Mm}\right)^{1/2} [M + m + (M^2 + m^2 + 2Mm \cos \theta)^{1/2}]^{1/2}\right\} d\theta$$

and

$$I_2 = \frac{1}{4\pi} \int_0^{2\pi} \left[1 - \frac{M - m}{(M^2 + m^2 + 2Mm \cos \theta)^{1/2}}\right] \times \cos \left\{t \left(\frac{\gamma}{Mm}\right)^{1/2} [M + m - (M^2 + m^2 + 2Mm \cos \theta)^{1/2}]^{1/2}\right\} d\theta$$

In each one of these integrals we split the interval of integration into two parts, from 0 to π and from π to 2π. In the integration over the latter one we make $\theta \to \theta' + \pi$, so that each one of these integrals breaks up into two parts.

For I_1 we have

$$4\pi I_1 = \int_0^\pi \left[1 + \frac{M-m}{(M^2+m^2+2Mm\cos\theta)^{1/2}}\right]$$
$$\times \cos\left\{t\left(\frac{\gamma}{Mm}\right)^{1/2}[M+m+(m^2+M^2+2Mm\cos\theta)^{1/2}]^{1/2}\right\} d\theta$$
$$+ \int_0^\pi \left[1 + \frac{M-m}{(M^2+m^2-2mM\cos\theta)^{1/2}}\right]$$
$$\times \cos\left\{t\left(\frac{\gamma}{Mm}\right)^{1/2}[M+m+(m^2+M^2-2Mm\cos\theta)^{1/2}]^{1/2}\right\} d\theta$$

and we have a similar expression for I_2.

In this expression for I_1 we now make the change of variable

$$M + m + (M^2 + m^2 \pm 2Mm\cos\theta)^{1/2} = (Mm/\gamma)\, x^2$$

and write

$$\omega_1^2 = 2\gamma/m; \qquad \omega_2^2 = 2\gamma/M; \qquad \omega_L^2 = \omega_1^2 + \omega_2^2 \tag{39}$$

We thus obtain

$$I_1 = (2/\pi)\int_{\omega_1}^{\omega_L} [(x^2-\omega_2^2)/(x^2-\omega_1^2)(\omega_L^2-x^2)]^{1/2}\cos xt\, dx \tag{40}$$

and by a similar analysis, one can show that

$$I_2 = (2/\pi)\int_0^{\omega_2} [(x^2-\omega_2^2)/(x^2-\omega_1^2)(\omega_L^2-x^2)]^{1/2}\cos xt\, dx \tag{41}$$

Hence,

$$\rho^{(m)}(t) = (2/\pi)\left\{\int_0^{\omega_2} [(x^2-\omega_2^2)/(x^2-\omega_1^2)(\omega_L^2-x^2)]^{1/2}\cos xt\, dx\right.$$
$$\left. + \int_{\omega_1}^{\omega_L} [(x^2-\omega_2^2)/(x^2-\omega_1^2)(\omega_L^2-x^2)]\cos xt\, dx\right\} \tag{42}$$

The results for the other two cases are

$$\rho^{(M)}(t) = (2/\pi)\left\{\int_0^{\omega_2} [(x^2-\omega_1^2)/(x^2-\omega_2^2)(\omega_L^2-x^2)]^{1/2}\cos xt\, dx\right.$$
$$\left. + \int_{\omega_1}^{\omega_L} [(x^2-\omega_1^2)/(x^2-\omega_2^2)(\omega_L^2-x^2)]^{1/2}\cos xt\, dx\right\} \tag{43}$$

and

$$\rho^{(J)}(1, t) = [(Mm)^{1/2}/\pi\gamma] \left\{ \int_0^{\omega_2} [(x^2 - \omega_1^2)(x^2 - \omega_2^2)/(\omega_L^2 - x^2)]^{1/2} \cos xt \, dx \right.$$

$$\left. + \int_{\omega_1}^{\omega_L} [(x^2 - \omega_1^2)(x^2 - \omega_L^2)/(\omega_L^2 - x^2)]^{1/2} \cos xt \, dx \right\} \qquad (44)$$

In Eqs. (42)–(44) if we let $m \to M$, noting that from Eq. (39) $\omega_1 \to \omega_2$ and $\omega_L \to 2(\gamma/M)^{1/2} = \omega_m$, we get

$$\rho(t) = \frac{2}{\pi} \int_0^{\omega_m} \frac{\cos xt \, dx}{[\omega_m^2 - x^2]^{1/2}}$$

which is the well known result for the monatomic case.

The values of these expressions are straightforward but lengthy to compute. The computation may be done either using some well-known theorems for asymptotic Fourier integrals[7] or using methods of the generalized Fourier analysis[8]. In Appendix B we work out one of them (since the method is the same for all) but only the results will be given here. These are the following:

$$\rho^{(m)}(t) = \left(\frac{2}{\pi t}\right)^{1/2} \left[\left(\frac{\omega_1^2 - \omega_2^2}{\omega_1 \omega_2^2}\right)^{1/2} \cos\left(\omega_1 t + \frac{\pi}{4}\right) \right.$$

$$\left. + \frac{\omega_1}{\omega_2 \sqrt{\omega_L}} \cos\left(\omega_L t - \frac{\pi}{4}\right) \right] + O(t^{-3/2}) \qquad (45)$$

$$\rho^{(M)}(t) = \left(\frac{2}{\pi t}\right)^{1/2} \left[\left(\frac{\omega_1^2 - \omega_2^2}{\omega_1^2 \omega_2}\right)^{1/2} \cos\left(\omega_2 t - \frac{\pi}{4}\right) \right.$$

$$\left. + \frac{\omega_2}{\omega_1 \sqrt{\omega_L}} \cos\left(\omega_L t - \frac{\pi}{4}\right) \right] + O(t^{-3/2}) \qquad (46)$$

$$\rho^{(J)}(1, t) = \left(\frac{Mm}{2\pi\omega_L t}\right)^{1/2} \frac{\omega_1 \omega_2}{\gamma} \cos\left(\omega_L t - \frac{\pi}{4}\right) + O(t^{-3/2}) \qquad (47)$$

thus showing that these functions tend to zero as $t^{-1/2}$ when $t \to \infty$. It is also worthwhile pointing out that if in these equations we let $M \to m$, they all yield the result for the monatomic chain, namely

$$\rho(t) = (2/\pi\omega_L t)^{1/2} \cos(\omega_L t - \tfrac{1}{4}\pi)$$

APPENDIX A

It has been shown by Kaç[3,5] that the number of zeros of an "almost periodic function" is given by

$$L(h) = \frac{1}{2\pi^2} \iint_{-\infty}^{+\infty} \frac{1}{\eta^2} \cos(h\alpha) \left\{ \prod_{k=1}^{n} J_0(| a_k | \alpha) - \prod_{k=1}^{n} J_0(| a_k | [\alpha^2 + \eta^2 \omega_k^2]^{1/2}) \right\} d\alpha \, d\eta \tag{A.1}$$

Starting from this expression, we want to find the order of magnitude of $L(h)$ for large values of n, i.e., we want to obtain Eq. (26). To do this, let us rewrite Eq. (A.1) in the form

$$L(h) = (1/2\pi^2) \iint_{-\infty}^{+\infty} (1/\eta^2)[U(\alpha, 0) - \tfrac{1}{2} U(\alpha, \eta) - \tfrac{1}{2} U(\alpha, -\eta)] \, d\alpha \, d\eta \tag{A.2}$$

where

$$U(\alpha, \beta) = e^{i\alpha h} \prod_{j=1}^{n} J_0[a_j(\alpha^2 + \beta^2 \omega_j^2)] \tag{A.3}$$

Using for $J_0(x)$ the approximation:

$$J_0(x) \approx \exp(-x^2/4)[1 - (x^4/64)] \tag{A.4}$$

one finds that

$$U(\alpha, \beta) = \exp\left[i\alpha h - \frac{\alpha^2}{4} \sum_{j=1}^{n} a_j^2 - \frac{\beta^2}{4} \sum_{j=1}^{n} \omega_j^2\right] \left[1 - \frac{1}{64} \sum_{j=1}^{n} a_j^4 (\alpha^2 + \beta^2 \omega_j^2)^2\right] \tag{A.5}$$

Substituting (A.5) into (A.2) and introducing the new variables

$$h = bn^{1/2}; \qquad \alpha n^{1/2} = x; \qquad \eta n^{1/2} = y \tag{A.6}$$

one gets

$$L(bn^{1/2}) = \frac{1}{2\pi^2} \iint_{-\infty}^{\infty} \frac{1}{y^2} \left\{ \exp\left[ibx - \frac{x^2}{4} a_0^2\right] \left[1 - \frac{1}{64} \frac{x^2}{n^2} \sum_{j=1}^{n} a_j^4\right] - \exp\left[ibx - \frac{x^2}{4} a_0^2 - \frac{y^2}{4} \omega_0^2\right] \times \left[1 - \frac{1}{64n^2} \sum_{j=1}^{n} a_j^4 (x^4 + 2x^2 y^2 \omega_j^2 + y^4 \omega_j^4)\right] \right\} dx \, dy \tag{A.7}$$

where

$$a_0^2 = (1/n) \sum_{j=1}^{n} a_j^2, \qquad \omega_0^2 = (1/n) \sum_{j=1}^{n} a_j^2\omega_j^2 \tag{A.8}$$

If we now take the limit as $n \to \infty$ and assume that the conditions expressed by Eq. (27) hold true, we get

$$L(bn^{1/2}) = \frac{1}{(2\pi^2)} \int_{-\infty}^{+\infty} \frac{1 - \exp(-\frac{1}{4}y^2\omega_0^2)}{y^2}\, dy \int_{-\infty}^{+\infty} \exp\left[ibx - \left(\frac{x}{2}\, a_0\right)^2\right] dx \tag{A.9}$$

The integration of Eq. (A.9) is straightforward, the result being

$$L(bn^{1/2}) = (\omega_0/\pi a_0) \exp(-b^2/a_0^2)$$

which is Eq. (26).

APPENDIX B

In this appendix we shall illustrate how one obtains Eqs. (44)–(46) from their corresponding integral expressions using the methods of Ref. 8. It will be sufficient to evaluate one expression, for instance, $\rho^{(J)}(t)$. Let us write it as follows:

$$\rho^{(J)}(t) = [(Mm)^{1/2}/\pi\gamma](I_1 + I_2) \tag{B.1}$$

where

$$I_1 = \mathrm{Re}(2\pi)^2 \int_{-\infty}^{+\infty} \left\{\frac{[x^2 - (\omega_1')^2][x^2 - (\omega_0')^2]}{(\omega_L')^2 - x^2}\right\}^{1/2} \times H(x)\, H(\omega_2' - x)\, e^{2\pi ixt}\, dx$$

$$I_2 = \mathrm{Re}(2\pi)^2 \int_{-\infty}^{+\infty} \left\{\frac{[x^2 - (\omega_1')^2][x^2 - (\omega_2')^2]}{(\omega_L')^2 - x^2}\right\}^{1/2} \times H(x - \omega_1')\, H(\omega_L' - x)\, e^{2\pi ixt}\, dx$$

where $\omega_i' = \omega_i/2\pi$ for $i = 1, 2, L$ and $H(x)$ is Heaviside's step function.

We now use the following theorem [(8)]: If the generalized function $f(x)$ has a finite number of singularities and at each one of them $f(x) - F_i(x)$ has absolutely integrable Nth derivative in an interval including the singularity x_i, where $F_i(x)$ is a linear combination of functions of the type

$$|x - x_i|^\beta; \qquad |x - x_i|^\beta \operatorname{sgn}(x - x_i); \qquad |x - x_i|^\beta \log|x - x_i|$$

$$|x - x_i|^\beta \log|x - x_i| \operatorname{sgn}(x - x_i)$$

and $\delta^{(p)}(x - x_i)$ for different values of β and p, and if $f^N(x)$ is well behaved at infinity, then $g(y)$, Fourier transform of $f(x)$, satisfies

$$g(y) = \sum_i G_i(y) + O(|y|^{-N}) \qquad \text{as} \quad N \to \infty \tag{B.2}$$

$G_i(y)$ is the Fourier transform of $F_i(x)$.

I_1 and I_2 are Fourier transforms of their corresponding integrands so we may apply the theorem to them. Since we shall only need $\rho^{(J)}(t)$ to lowest order in t, it will only be required that at each singularity of the integrands, which we shall denote by $f(x)$, $f(x) - F_i(x)$ has absolutely integrable first derivative. Let us consider I_1 and write

$$f(x) = \left\{ \frac{[x^2 - (\omega_1')^2][x^2 - (\omega_2')^2]}{(\omega_L')^2 - x^2} \right\}^{1/2} H(x)\, H(\omega_2' - x)$$

which has singularities at $x = 0$ and $x = \omega_2'$. [Notice that at $x = \omega_L'$, $f(x) = 0$.]

At $x = 0$

$$f(x) - (\omega_1'\omega_2'/\omega_L')\, H(x) \cong O(|x|^2)$$

Thus

$$F_1(x) = (\omega_1'\omega_2'/\omega_L')\, H(x)$$

and

$$G_1(t) = (\omega_1'\omega_2'/\omega_L')(2\pi i t)^{-1}$$

which has no real part and hence gives no contribution to $\rho^{(J)}(t)$.

At $x = \omega_2'$ we easily find that

$$F_2(x) = \text{const} \times |\omega_2' - x|^{1/2} H(\omega_2' - x)$$

which has a Fourier transform proportional to $t^{-3/2}$, and we therefore neglect it.

Similarly, the integrand of I_2 has two singularities, at $x = \omega_1'$ and $x = \omega_L'$. The first one gives terms of the order $t^{-3/2}$ and higher, so we drop it. For the second one we have

$$f(x) - [\omega_1'\omega_2'/(2\omega_L')^{1/2}]\, |\omega_L' - x|^{-1/2} H(\omega_L' - x) = O(|\omega_L' - x|^{1/2})$$

and writing

$$F(x) = [\omega_1'\omega_2'/(2\omega_L')^{1/2}]\, |\omega_L' - x|^{-1/2} H(\omega_L' - x)$$

we find that

$$G(t) = [\omega_1'\omega_2'/(2\omega_L')^{1/2}]\{\exp[-i(2\pi i\omega_L' t - \tfrac{1}{4}\pi)\}(2t)^{-1/2} \tag{B.3}$$

so that collecting these results and substituting back in Eq. (B.1), we find that

$$\rho^{(J)}(t) = \left(\frac{Mm}{2\pi}\right)^{1/2} \frac{1}{\gamma} \frac{\omega_1\omega_2}{(\omega_L t)^{1/2}} \cos\left(\omega_L t - \frac{\pi}{4}\right) + O(t^{-3/2})$$

which is Eq. (47).

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