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On the Validity of Stochastic Rate Equations in Finite Systems with Finite-Strength Interactions

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Starting with the Hamiltonian for a linear harmonic chain of $2N$ particles of mass m and one of mass M, we have carried out numerical calculations for the momentum autocorrelation function of the mass defect particle for chains with finite number N of mass points and for nonzero values of the mass ratio $\mu \equiv m/M$. These results have been compared with the well-known exponential relaxation of the momentum autocorrelation function which is found to be the rigorous result when passing to the thermodynamic and weak-coupling limit. In these limits, the dynamics of the mass defect particle is exactly described by a Fokker–Planck equation, i.e., a stochastic equation of motion. We have shown that, to an excellent approximation, an exponential relaxation of the momentum autocorrelation function is obtained for mass ratios as high as $\mu = 0.1$ and for chains with only 50 particles. Thus, for the harmonic chain considered here, the stochastic equations of motion can be applied to a very good approximation far outside the usually imposed thermodynamic and weak-coupling limits.

KEY WORDS: Stochastic equations; Fokker–Planck equation; thermodynamic limit; weak-coupling limit; momentum autocorrelation function; linear harmonic chain.

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1. INTRODUCTION

In the derivation of the master equation of nonequilibrium statistical mechanics from the Liouville equation, two limiting processes are always invoked.[1] First, one performs calculations in the thermodynamic limit in which the size of the system and the number of particles in the system are allowed to increase without bound in such a way that the concentration (number per volume) of the particles remains finite. The other limit is the weak-coupling limit, where some interaction parameter is allowed to approach zero while the time approaches infinity such that their product is a constant. The passage to these limits is essential in the *rigorous derivation* of the master equation from the Liouville equation.[1]

From a practical point of view, however, all physically realizable systems are finite, the interaction parameter does not go to zero, and it is too time-consuming to make observations as time goes to infinity. The question thus arises as to just what error is involved in applying stochastic equations to finite systems with finite-strength interactions. It is to this question that this paper is addressed.

Our model system for this study is the ubiquitous linear harmonic chain and the specific property to be investigated is the momentum autocorrelation function of a mass defect particle in the chain. We have chosen this model since it is possible to carry out exact dynamic calculations for the autocorrelation function for finite chains with finite interaction forces. These can then be compared with known analytic stochastic results obtained in the thermodynamic (infinite chain) and weak-coupling (infinite mass defect) limits.[2] Since the ultimate aim of any dynamic theory is the calculation of some average time-dependent quantity, the examination of the momentum autocorrelation function is an appropriate test for the validity of the stochastic equations.

It is known[3] that the dynamical behavior of local properties in a finite chain of N oscillators with short-range forces is essentially identical with the $N \to \infty$ results over a range of time which is proportional to the size N of the system and depends on the mass ratio. We present a numerical study of this situation which clearly demonstrates this point. We find that for $N \sim 50$, the computer results on the relaxation of the momentum autocorrelation functions are indistinguishable from the thermodynamic limit results over a range of time in which the autocorrelation function has relaxed essentially to its zero value. This certainly indicates, at least for the model studied here, that the stochastic equations are valid for finite systems far removed from the thermodynamic limit.

We have also examined numerically the weak-coupling limit. It is known[2] that in a one-dimensional harmonic lattice with point masses m

and an impurity of mass M, the heavy particle undergoes Brownian motion in the weak-coupling limit $\mu \equiv m/M \to 0$, $t \to \infty$, $\mu t = c$. This implies that in this limit, the momentum autocorrelation function decays exponentially. Our numerical computer study shows that this exponential decay of the momentum autocorrelation function is also obtained to within a very close apprximation for nonzero values of μ and for finite times. Thus, excellent agreement with exponential relaxation is already found for $\mu = 0.1$, i.e., for $M = 10m$. Clearly, the stochastic results are again in excellent agreement with the exact dynamic results far from the weak-coupling limit.

We have also studied the infinite chain with long-range interactions. We have shown that one obtains an excellent approximation to the exponential relaxation of the autocorrelation function of the heavy impurity M for $\mu > 0$, and $0 < \gamma < 1$, where γ is an interaction parameter such that $\gamma \to 0$ corresponds to nearest-neighbor interactions and $\gamma \to 1$ corresponds to interactions of zero strength and infinite extent.

In Section 2, we introduce the model Hamiltonian and indicate the various representations from which one can compute the momentum autocorrelation function of the impurity. In Section 3, we discuss the autocorrelation function for finite systems and for finite interaction strength for chains with nearest-neighbor interactions. In Section 4, we introduce the chain with long-range interactions and discuss the new features which occur in this system. In Section 5, we present a summary and discussion of our results.

2. HAMILTONIAN AND REPRESENTATION OF AUTOCORRELATION FUNCTION

The Hamiltonian appropriate to a chain of $2N$ particles of mass m and one of mass M bound by harmonic nearest-neighbor forces with cyclic boundary conditions is

$$H = (1/2M)\,\hat{P}^2 + (1/2m)\sum_{k=1}^{2N} \hat{p}_k{}^2 + \tfrac{1}{2}\alpha \sum_{k=1}^{2N-1} (\hat{q}_k - \hat{q}_{k+1})^2$$
$$= +\tfrac{1}{2}\alpha[(\hat{Q} - \hat{q}_1)^2 - (\hat{Q} - \hat{q}_{2N})^2] \qquad (1)$$

Here, the $\{\hat{p}_k, \hat{q}_k\}$ are the momenta and positions of the $2N$ equal mass particles, $\hat{P}$ and $\hat{Q}$ are the momentum and position of the impurity particle, and α is the force constant. If one partially diagonalizes this Hamiltonian according to the transformations

$$m^{-1/2}\hat{p}_k = p_k{}', \qquad M^{-1/2}\hat{P} = P$$
$$m^{1/2}\hat{q}_k = q_k{}', \qquad M^{1/2}\hat{Q} = Q \qquad (2)$$

and

$$\hat{p}_k = \sum_{l=1}^{2N} T_{kl} p_l', \qquad \hat{q}_k = \sum_{l=1}^{2N} T_{kl} q_l' \tag{3}$$

with

$$T_{kl} = [2/(2N+1)]^{1/2} \sin[kl\pi/(2N+1)] \tag{4}$$

one obtains

$$H = \tfrac{1}{2}(P^2 + \Omega^2 Q^2) + \tfrac{1}{2} \sum_{k=1}^{2N} [(p_k')^2 + \omega_k^2 (q_k')^2] + \mu^{1/2} \sum_{k=1}^{2N} \epsilon_k q_k' Q \tag{5}$$

with

$$\omega_k^2 = \omega_0^2 \sin^2[k\pi/2(2N+1)], \qquad \omega_0^2 = 4\alpha/m, \qquad \Omega^2 = \tfrac{1}{2}\mu\omega_0^2 \tag{6}$$

where ω_0 is the maximum frequency of the chain,

$$\begin{aligned} \epsilon_k &= -\tfrac{1}{2}\omega_0^2 [2/(2N+1)]^{1/2} \sin[k\pi/(2N+1)], && k = 1, 3, \dots, 2N-1 \\ \epsilon_k &= 0, && k = 2, 4, \dots, 2N \end{aligned} \tag{7}$$

and

$$\mu = m/M \tag{8}$$

In this form, the Hamiltonian exhibits an explicit dependence on the mass ratio μ, which is a convenient form for our discussion of the weak-coupling limit. We now transform to the fully diagonal form with

$$\begin{aligned} Q &= \sum_j{}' X_{0j}\eta_j, \qquad P = \sum_j{}' X_{0j}\Pi_j \\ q_k' &= \sum_j{}' X_{kj}\eta_j, \qquad p_k' = \sum_j{}' X_{kj}\Pi_j, \qquad k = 1, 3, \dots, 2N-1 \\ q_{2k}' &= \eta_{2k}, \qquad p_{2k}' = \Pi_{2k}, \qquad k = 1, 2, \dots, N \end{aligned} \tag{9}$$

where the prime on the sums indicates $j = 0, 1, 3, \dots, 2N-1$.

By direct substitution, one then finds that the secular equation may be written in the form[4]

$$G(z) = 0 = z - \Omega^2 - T_N(z) \tag{10}$$

with

$$T_N(z) = \sum_{i=1}^{2N} [\epsilon_i^2/(z - \omega_i^2)] \tag{11}$$

The solutions $\{z = s_i^2\}$ of this secular equation are the eigenfrequencies $\{s_i\}$ of the fully diagonalized Hamiltonian. In addition, one finds that

$$X_{0k}^2 = 1/[1 + S_N(k)] \tag{12}$$

with

$$S_N(k) = \sum_{i=1}^{2N} [\epsilon_i^2/(s_k^2 - \omega_i^2)^2] \tag{13}$$

As indicated in the introduction, we shall focus on the momentum autocorrelation function ρ of the impunity. The normalized correlation function is given by

$$\rho(t) = \langle PP(t)\rangle/\langle P^2\rangle \tag{14}$$

where the brackets denote the canonical average

$$\langle A(P, Q, p^N, q^N)\rangle = \frac{\int dP\, dQ\, dp^N\, dq^N\, e^{-\beta H} A(P, Q, p^N, q^N)}{\int dP\, dQ\, dp^N\, dq^N\, e^{-\beta H}} \tag{15}$$

If one now uses the equations of motion of the harmonic lattice and the indicated canonical transformations [Eqs. (1)–(13)], one finds that

$$\rho_N(\mu, t) = \sum_k{}' X_{0k}^2 \cos s_k t, \qquad k = 0, 1,..., 2N - 1 \tag{16}$$

where X_{0k}^2 is given by Eq. (12) and where the $\{s_k\}$ are the normal mode frequencies of the fully diagonalized Hamiltonian. The representation (16) is convenient for discussing the momentum autocorrelation function for the finite-N case if one can sum the functions T_N and S_N of Eqs. (11) and (13). These sums have been evaluated and yield[5] for $G(z)$ and $S_N(\alpha_k)$

$$G(\alpha_k) = 0 = (1 - \mu) - \mu \cot[\pi\alpha k/2(2N + 1)][(\cot \pi\alpha_k - \csc \pi\alpha_k)],$$
$$k = 1, 3,..., 2N - 1 \tag{17}$$

and

$$S_N(\alpha_k) = [\mu/2 \cos^2(\tfrac{1}{2}\pi\alpha_k)]\{2N + \cot[\pi\alpha_k/(2N + 1)] \sin \pi\alpha_k - \cos \pi\alpha_k\},$$
$$k = 1, 3,..., 2N - 1 \tag{18}$$

where the α_k are related to the normalized eigenfrequencies s_k by

$$s_k^2 = \sin^2[\pi\alpha_k/2(2N + 1)], \qquad k = 1, 3,..., 2N - 1 \tag{19}$$

It is easy to see that as $\mu \to 1$, one just recovers the equal-mass nearest-neighbor spectrum

$$s_k^2(\mu = 1) = \sin^2[\pi k/2(2N + 1)] \tag{20}$$

To study the effect of the mass ratio μ in the thermodynamic limit, $N \to \infty$, it is more convenient to represent the momentum autocorrelation function by

$$\rho(t) = (1/2\pi i) \oint \{[\cos(z^{1/2}t)]/G(z)\}\, dz \tag{21}$$

where the contour is chosen as a circle in the complex z-plane enclosing all the zeros of $G(z)$. The representation (21) is equivalent to that in (16). Note that in the limit $N \to \infty$, the zeros of $G(z)$ become dense on the interval $(0, \omega_0^2)$ and one may then contract the above contour to an integral running just above and below the real axis in this interval. If one computes $G(z)$ from Eqs. (10) and (11) in the limit $N \to \infty$, one obtains

$$\rho(\tau) = (\mu/2\pi) \int_{-1}^{+1} \{(1 - x^2)^{1/2}/[(1 - 2\mu)\, x^2 + \mu^2]\} \cos x\tau\, dx \tag{22}$$

where we have introduced the scaled time

$$\tau = \omega_0 t \tag{23}$$

This spectral representation holds for $0 < \mu \leqslant 1$; for $\mu > 1$, a light impurity, one obtains another term corresponding to an isolated frequency which gives rise to a purely periodic component in the correlation function.[6,7]

This completes the summary of the equations for the oscillator chain with nearest-neighbor interactions. In the next section, we discuss the results of computer solutions of Eqs. (16) and (22).

3. CALCULATION OF AUTOCORRELATION FUNCTIONS

We first consider the momentum autocorrelation function of the mass-M particle in the thermodynamic limit with the help of Eq. (22). This integral cannot be evaluated analytically except for $\mu = \frac{1}{2}$ and $\mu = 1$. For $\mu \leqslant 1$, it has an expansion in the form[6,7]

$$\begin{aligned}\rho(\tau) &= \lim_{N\to\infty} \rho_N(\tau) \\ &= J_0(\tau) + [2(1 - \mu)/(1 - 2\mu)] \sum_{l=1}^{\infty} (1 - 2\mu)^l J_{2l}(\tau)\end{aligned} \tag{24}$$

This expressions simplifies for certain mass ratios; for $\mu = 1$, equal-mass particles, one obtains

$$\rho(\tau) = J_0(\tau) \tag{25}$$

and for $\mu = \frac{1}{2}$,

$$\rho(\tau) = J_0(\tau) + J_2(\tau) \tag{26}$$

In the combined weak-coupling limit, $\mu \to 0$, $\tau \to \infty$, $\mu\tau = \text{const}$, and thermodynamic limit, $N \to \infty$, one obtains from the spectral representation, Eq. (21), the well-known result[2]

$$\lim_{\substack{\tau\to\infty\\ \mu\to 0\\ \mu\tau=c}} \rho(\tau) = e^{-\mu\tau} \tag{27}$$

The physical basis of the weak-coupling limit is the existence of processes occurring on different time scales. Processes which occur slowly relax to equilibrium in the "mean field" of the fast processes. In the present example, the equal-mass particles relax on a time scale of $1/\omega_0$, while the momentum of the heavy particle ($M \gg m$) relaxes on a time scale measured by the mass ratio $\mu = m/M$. This latter time scale is slow compared to the $1/\omega_0$ time scale of the mass-m particles. In the limit when $\mu = 0$, the momentum of the heavy particle is a constant of the motion.

To obtain information about the form of the momentum autocorrelation function for nonzero $\mu \leqslant 1$, we have numerically integrated Eq. (22). In Fig. 1, we plot $\rho(\tau)$ versus τ for various values of μ. The time is measured in units of the maximum frequency ω_0 of the lattice, which is typically of order 10^{-13} sec. The damped oscillatory behavior is clearly evident from this figure, but for $\mu = 0.1$, one already has behavior suggesting exponential decay. A log plot of these data in Fig. 2 shows that, for all intents and purposes, one has reached the weak-coupling limit when $\mu = 0.1$. A comparison of the values of $\exp(-\mu\tau)$ and $\rho(\tau)$ of Eq. (22) for $\mu = 0.1$ in Table I shows that they differ by only 1% for $\tau \geqslant 6$, i.e., for times longer than about 6×10^{-13} sec.

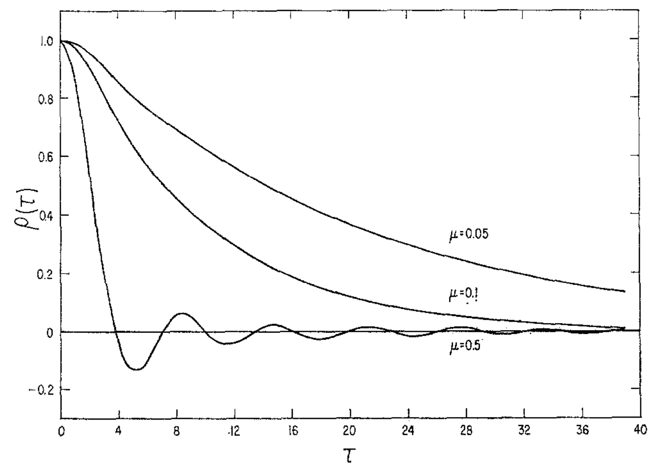

Fig. 1. Normalized momentum autocorrelation function $\rho(\tau, \mu)$ for $\mu = 0.05$, 0.1, and 0.5. The scaled time τ is measured in units of the maximum frequency ω_0 of the lattice.

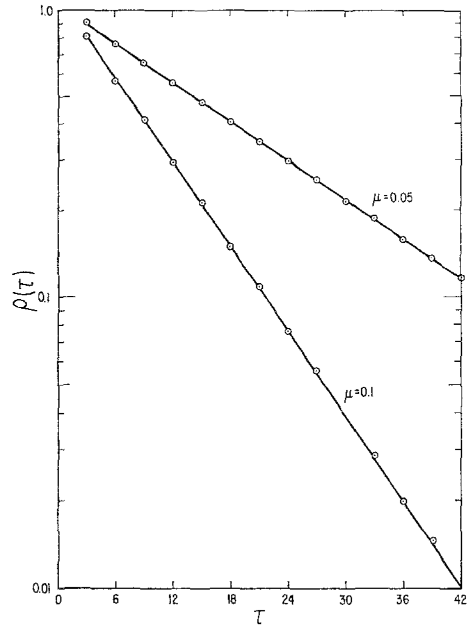

Fig. 2. A logarithmic plot of $\rho(\tau, \mu)$ versus τ for $\mu = 0.5$ and $\mu = 0.1$. The circles are data points; the data are closely approximated by a straight line.

Table I. Comparison of $\exp(-\mu\tau)$ and $\rho(\mu, \tau)$ of Eq. (22) for $\mu = 0.1$

τ	$\exp(-\mu\tau)$	$\rho(\mu, \tau)$
0	1.000	1.000
3	0.741	0.819
6	0.549	0.570
9	0.407	0.415
12	0.301	0.292
15	0.223	0.212
18	0.165	0.159
21	0.122	0.108
24	0.090	0.076
27	0.067	0.056
30	0.050	0.039
33	0.037	0.028
36	0.027	0.020

Note that there is an initial transient period where the autocorrelation function must be Gaussian for any μ.[8] On the other hand, for long times, i.e., times τ greater than the exponential decay time $1/\mu$, one has a correction of damped oscillatory form to the weak-coupling limit. These contributions to $\rho(\tau)$ are, however, less than 0.1 % of the initial value $\rho(0)$.

It should be noted that the mass ratio appears as the square root in the Hamiltonian, Eq. (5), so that one has exponential relaxation of the autocorrelation function for a value of 0.3 of the "small" parameter in the Hamiltonian.

For the case of finite N, we must find the eigenfrequencies of the secular equation (10) which are the solutions of the transcendental equation (17). There are only $N + 1$ modes which are pertinent to this problem: the zero-frequency mode due to the translational invariance of the lattice and N modes arising from the symmetric modes of the unperturbed lattice. The antisymmetric modes have a node at the position of the heavy-mass particle and thus do not influence its dynamical behavior. These N frequencies $\{s_k\}$ for $k = 1, 2, ..., 2N - 1$ are easily found numerically from Eqs. (17) and (19) and are used to obtain the X_{0k}^2 with the help of Eqs. (12) and (13). The momentum autocorrelation function was then calculated by carrying out the summation in Eq. (16). In Fig. 3, we plot the calculated values of $\rho_N(\mu, \tau)$ versus τ for various small values of N.

As has been pointed out by Rubin[3] and others, one expects that for times less than those required for a signal to propagate around the lattice, the autocorrelation function should closely approximate the $N \to \infty$ result.

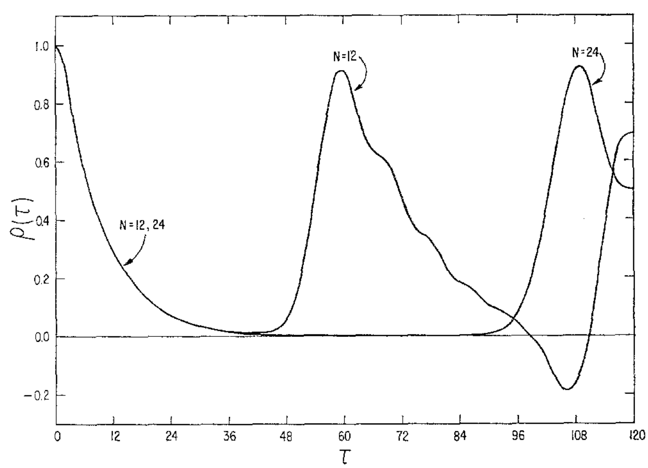

Fig. 3. Normalized momentum autocorrelation function $\rho_N(\tau, \mu)$ for $2N + 1$ particles with $N = 12$ and $N = 24$ and $\mu = 0.1$.

This is due to the fact that there is, to a good approximation, no way for the signal to know that it is traveling in a finite lattice until it reaches the boundaries. For a signal traveling in the lattice with the speed of sound, the time τ ($=\omega_0 t$) required to propagate around a lattice of $2N$ mass points is $\tau \sim 2N$. For times $\tau < 2N$, the results for the finite lattice should thus be numerically indistinguishable from those of the infinite lattice. This is borne out by the calculations presented here. Furthermore, for relatively small values of μ, for which $\rho(\tau)$ decays fairly rapidly, the finite-N results are in excellent agreement with the thermodynamic limit results even when N is only of the order of 50. Thus even in a harmonic system where one has coherent signal propagation, small-N results are quite accurate in describing the dynamics of local perturbations. One must, of course, restrict such statements to systems with potentials whose range is small compared to the size of the system, as otherwise the boundaries would be "felt" by the signal at all times.

This "recurrence" time $\tau \sim 2N$ bears no relation to the Poincaré recurrence time, which refers to the recurrence of a particular phase point. These latter times are much longer than any time scale considered here.[9]

4. AUTOCORRELATION FUNCTION FOR LATTICE WITH LONG-RANGE INTERACTION

In this section, we turn our attention to the case of a harmonic lattice with long-range interactions. We consider here only the case of the infinite chain.

The Hamiltonian can be written as

$$H = (1/2M)\,P^2 + (1/2m)\sum_{k=1}^{2N} p_k^2 + \tfrac{1}{2}\sum_{k=0}^{2N}\sum_{j=0}^{2N} q_k A_{kj} q_j \tag{28}$$

where we take $q_0 = Q$. We impose periodic boundary conditions on the chain and assume that

$$A_{kj} = A_{|k-j|} \equiv A_l \tag{29}$$

This last condition expresses the physically realistic assumption that the interaction between two mass points depends only on their separation in the lattice. We take the interaction to be of the form

$$A_l = (\alpha/m)(1-\gamma)\,\gamma^{l-1}, \qquad 0 < \gamma < 1, \quad l = 1, 2, \ldots \tag{30}$$

Note that as $\gamma \to 0$, one recovers the nearest-neighbor interaction and as $\gamma \to 1$, one obtains an interaction of zero strength and infinite extent. The normalization factor $(1-\gamma)$ ensures that the total potential energy of the infinite system remains constant for all γ.

By procedures analogous to those used in obtaining Eq. (22), the spectral representation of the momentum autocorrelation function of the heavy particle is found to be

$$\rho(\mu, \gamma, \tau) = \mu \int_{-1}^{1} \frac{A(\omega, \gamma)}{\mu^2 + 2\mu(1 - \mu)\, \omega B(\omega, \gamma) + \omega^2(1 - \mu)^2 [A^2(\omega, \gamma) + B^2(\omega, \gamma)]} \times \cos \omega\tau \, d\omega \tag{31}$$

where

$$A(\omega, \gamma) = (1 - \gamma^2)/\{(1 - \omega^2)^{1/2}[(1 + \gamma)^2 - 4\gamma\omega^2]\} \tag{32}$$

$$B(\omega, \gamma) = 4\gamma\omega/[4\gamma\omega^2 - (1 + \gamma)^2] \tag{33}$$

$$\tau = [\omega_0/(1 + \gamma)^{1/2}]\, t \tag{34}$$

and where the frequency ω is now dimensionless, having been scaled by the maximum frequency ω_0. The autocorrelation function $\rho(\mu, \gamma, \tau)$ of Eq. (31) can easily be evaluated for different values of μ and γ by numerical integration and some representative results are displayed in Fig. 4. The same damped oscillatory behavior as shown in Fig. 1 for nearest-neighbor interactions is obtained in this case for intermediate values of μ and γ. For small enough μ and $\gamma < 1$, one again obtains an exponential decay of the autocorrelation function. As γ increases, i.e., as the range of interaction increases,

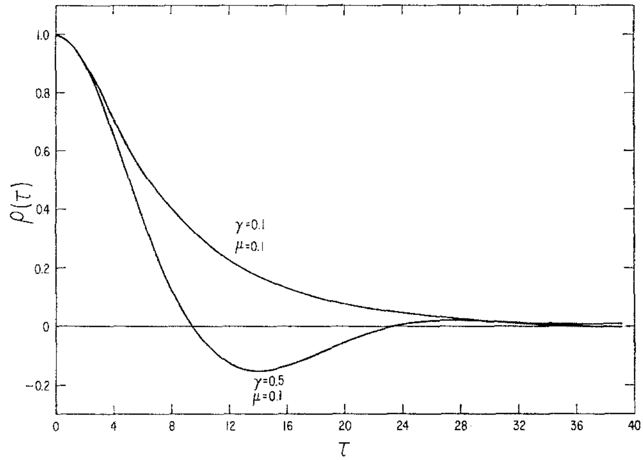

Fig. 4. Normalized momentum autocorrelation function $\rho(\tau, \mu, \gamma)$ for $\mu = 0.1$ and $\gamma = 0.1$ and $\gamma = 0.5$. For small values of γ, one still obtains exponential relaxation for small μ.

one must go to smaller values of μ to obtain exponential relaxation. In the weak-coupling limit, which one can obtain from Eq. (31) by setting

$$\omega' = \omega/\mu, \qquad \tau' = \mu\tau$$

and holding τ' constant, one finds

$$\lim_{\substack{\mu\to 0\\ \tau\to\infty\\ \mu\tau=c, N\to\infty}} \rho_N(\mu, \gamma, \tau) = [(1+\gamma)/(1-\gamma)] \exp[-\mu\tau/(1-\gamma)^{1/2}] \tag{35}$$

The weak-coupling limit thus yields again an exponential relaxation for the momentum autocorrelation function. For $\gamma = 0$, Eq. (35) reduces to the nearest-neighbor interaction result (27).

It has been demonstrated[10] that for interactions which are of the form $A_{ij} = A_{|i-j|}$, exponential relaxation is obtained in the limit $\mu \to 0$ when the squared frequency distribution of the equal-mass system ($\mu = 1$) satisfies

$$G(\omega^2) \sim 1/\omega, \qquad \omega \to 0 \tag{36}$$

for small ω. Our interaction matrix satisfies this criterion since one finds from Eqs. (31)–(33) that for $\mu = 1$,

$$G(\omega^2) = [(1-\gamma^2)/\omega]\{[(1+\gamma)^2 - 4\gamma\omega^2](1-\omega^2)^{1/2}\}^{-1} \tag{37}$$

5. SUMMARY AND DISCUSSION

Starting with the Hamiltonian for a linear harmonic chain of $2N$ particles with one mass defect particle, we have calculated via analytical dynamics the momentum autocorrelation function of the mass defect particle for finite chains and for nonzero mass ratios μ. We have shown that one obtains, to a very good approximation, an exponential relaxation of the momentum autocorrelation function for mass ratios as high as $\mu = 0.1$ and for chains with only 50 particles. As is well known, passage to the thermodynamic and weak-coupling limits yields the result that the dynamics of the infinite-mass particle is rigorously described by a Fokker–Planck equation. This in turn yields the rigorous result that the momentum autocorrelation function of the infinite-mass particle has an exponential time decay. It is clear from the above results that, at least for the harmonic chain studied here, the Fokker–Planck equation (or, equivalently, the corresponding Langevin equation) can be used to describe, to a very good approximation, the dynamics of a heavy (but not necessarily infinitely heavy) particle in a finite chain. The thermodynamic limit and the weak-coupling limit, while necessary to obtain *rigorous analytic* results for the validity of stochastic equations of motions, are thus unnecessarily stringent conditions for the use of stochastic equations in describing the dynamics of the model considered here.

One important question which immediately arises is how applicable this conclusion is to other systems. Is this true in general or are these findings quite specific to the harmonic chain? We believe that our result on the validity (in an approximate rather than rigorous sense) of stochastic equations such as the master equation, the Fokker–Planck equation, or the Langevin equation far outside (whatever that may mean in any given case) the thermodynamic and weak-coupling limits is a very general one. Unfortunately, this must remain a conjecture for the time being, since we know of no general proof.

A somewhat related study has recently been carried out by Berne and Bishop[11] who investigated via computer calculations the onset of Brownian motion in a one-dimensional fluid. They found an exponential relaxation of the velocity autocorrelation function for clusters with mass $M \geqslant 25m$, where m is the mass single fluid particle. Their results thus point definitely in the same direction as ours.

The analytic treatments of this problem imply that the momentum autocorrelation function can be written as a series expansion in the coupling parameter μ where the leading term is given by the thermodynamic and weak-coupling limit result and where the correction terms, arising from finite-strength coupling and the finite size of the system, are proportional to powers of μ. As we have seen, these correction terms are very small in the example considered here. It should be pointed out that it is exceedingly difficult to demonstrate *analytically* that corrections to the "rigorous" stochastic equations are indeed proportional to powers of the coupling parameter. It is only very recently that it has been shown[12] that the Langevin equation and the Fokker–Planck equation for a heavy particle in a classical fluid do have correction terms proportional to the coupling parameter μ which are bounded for all times.

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