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Nonlinear Momentum Relaxation of an Impurity in a Harmonic Chain

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A microscopic derivation of the generalized Langevin equation for arbitrary powers of the momentum of an impurity in a harmonic chain is presented. As a direct consequence of the Gaussian character of the conditional momentum distribution function, nonlinear momentum coupling effects are absent for this system and the Langevin equation takes on a particularly simple form. The kernels which characterize the decay of higher powers of the impurity momentum depend on the ratio of the masses of the impurity and bath particles, in contrast to the situation for the momentum Langevin equation for this system. The simplicity of the harmonic chain dynamics is exploited in order to investigate several features of the relaxation, such as the factorization approximation for time-dependent correlation functions and the decay of the kinetic energy autocorrelation function.

KEY WORDS: Brownian motion; linear harmonic chain; Langevin equation; energy relaxation; Gaussian non-Markovian process.

1. INTRODUCTION

In the past the study of the Brownian motion of an impurity particle suspended in a fluid has relied heavily upon a phenomenological approach.[1]

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More recently, however, attempts have been made to derive and understand the limitations of the phenomenological equations by adopting a molecular viewpoint.[2-4] Unfortunately, due to the complex nature of the motion of the bath in which the impurity (B) particle is suspended, microscopic derivations cannot proceed very far without making some important assumptions concerning the dynamics of the B-particle motion relative to that of the bath. Typically, one assumes that the friction kernel, which characterizes the decay of the B-particle momentum, decays on a time scale which is short compared to that of the B-particle motion. The disparity between these time scales is gauged by the mass ratio, $\lambda^2 = m/M$, where m is the mass of a bath particle and M is the mass of the B particle. In general, for fluid systems, such an assumption is not justified and the reduction of the microscopic equations to the phenomenological form must be made with caution.[5]

In this article we consider several aspects of the microscopic approach to the treatment of Brownian motion for an impurity in a harmonic chain. The relative simplicity of the bath dynamics permits an explicit test of many assumptions which are made in the treatment of this problem for fluids. From previous work on this problem[6] it might appear that the harmonic chain will not exhibit many of the features which are of central importance in the study of this problem for fluids. For example, it is known that for the harmonic chain the generalized Langevin equation for the B-particle momentum takes the form

$$\frac{dP(t)}{dt} = -\frac{1}{M}\int_0^t dt_1\, K_0(t_1)P(t - t_1) + \left(\frac{\beta}{M}\right)^{1/2} F_0(t) \tag{1}$$

where $K_0(t)$ is a correlation function of the random force $F_0(t)$ for the B particle fixed in the fluid. Hence, $K_0(t)$ is independent of the mass ratio, in contrast to the general case.

However, as we will show in Section 3, the analog of Eq. (1) for higher powers of the B-particle momentum does not assume such a simple form; instead we find

$$\frac{dH_j(P,t)}{dt} = -\frac{1}{M}\int_0^t dt_1\, i\Omega_{jj}(t_1)H_j(P, t - t_1) + \left(\frac{\beta}{M}\right)^{1/2} F_j^{+}(t) \tag{2}$$

In Eq. (2), $H_j(P)$ is a member of an orthogonal set of polynomials of the B-particle momentum, $F_j^+(t)$ is the corresponding random force, and $i\Omega_{jj}(t)$ is a friction kernel. For the harmonic chain the friction kernels are just the mode coupling terms introduced in our earlier studies of Brownian motion, and since no off-diagonal terms appear in Eq. (2), the friction coefficients do not contain any long-lived components due to nonlinear B-particle momentum coupling.[7] However, $F_j^+(t)$ does not reduce to $F_0(t)$ and as a consequence $i\Omega_{jj}(t)$ is λ dependent and has many features in common with the friction coefficients for fluids. Although many-particle collective properties for the harmonic chain are quite different from those of fluids, single-particle properties do exhibit similar qualitative features.[8] A study of the Langevin equations which govern the relaxation of higher powers of the B-particle momentum is also of interest for this system since simple extensions of usual approaches may not yield correct results. For example, the use of a retarded Fokker–Planck equation correctly yields the momentum correlation function but not the kinetic energy correlation function.[9]

Frequently, the mass ratio λ^2 is used as an expansion parameter for various dynamical quantities. However, the only proof[3] of the existence of such an expansion rests upon the assumed validity of factorization properties of time-dependent correlation functions. Since exact results are obtainable for even somewhat complex correlation functions for the harmonic chain, it is possible to test such approximations against exact calculations. These calculations are carried out in Section 4. Although in the present work the discussion of factorization will be couched within the framework of the Brownian motion problem, the question of the validity of the factorization of time-dependent correlation functions is of general interest in many relaxation problems, for example, in recent studies of nonlinear mode coupling effects (e.g., Ref. 10).

The particularly simple form of Eq. (2) for the harmonic chain permits a direct calculation of the damping kernel $i\Omega_{jj}$ from the known forms for the momentum correlation functions of this system. In Section 5 we exploit this connection to investigate the properties of $i\Omega_{22}$, which characterizes the decay of the kinetic energy autocorrelation function. This kernel has a rich structure as a function of frequency and mass ratio, in contrast to the force correlation function which governs the decay of the B-particle momentum.

2. HARMONIC LATTICE MODEL

This section is devoted to a review of some of the pertinent information, previously obtained, concerning the one-dimensional harmonic lattice model. The model system consists of an impurity particle of mass M embedded in a one-dimensional chain of identical particles of mass m. Furthermore, it is assumed that all of the particles interact merely by nearest-neighbor harmonic forces. In the present work the restriction $M \geqslant m$ will also be imposed. The Hamiltonian for the total system is given by

$$H = \frac{p_0^2}{2M} + \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{\alpha}{2} \sum_{j=1}^{N} (x_j - x_{j+1})^2 + \frac{\alpha}{2} [(x_0 - x_1)^2 + (x_0 - x_N)^2]$$

$$\equiv \frac{p_0^2}{2M} + H_0 \tag{3}$$

where x_j is the displacement of the jth particle from its equilibrium position, p_j is its momentum, and $\alpha = m\omega_0^2/4$, with ω_0 the fundamental lattice frequency. It will be convenient for our subsequent discussions to introduce a scaled dimensionless momentum variable,

$$P = \lambda(\beta/m)^{1/2}p_0, \qquad \text{where} \quad \beta = (k_{\mathrm{B}}T)^{-1}$$

The Liouville operator for this system may be written as

$$iL = iL_0 + \lambda iL_{\mathrm{B}} = iL_0 + \lambda\left(\frac{\beta}{m}\right)^{1/2}\left(P\frac{\partial}{\partial\beta x_0} + F\frac{\partial}{\partial P}\right) \tag{4}$$

where F is the force on the impurity (B) particle and L_0 is the Liouville operator for the bath in the field of the fixed B particle.

Two quantities of interest for this system, the time-dependent conditional momentum distribution function and momentum autocorrelation function (acf) of the B particle, have been obtained by Rubin.[11] He found that the B-particle conditional momentum distribution is Gaussian and may be expressed in terms of the normalized momentum acf $\pi(t) = \langle P(t)P\rangle$ (the angle brackets denote a full system equilibrium average) as

$$f(P', P, t) = \{2\pi[1 - \pi(t)^2]\}^{-1/2} \exp - \frac{[P' - P\pi(t)]^2}{2[1 - \pi(t)^2]} \tag{5}$$

Rubin also obtained an expression for $\pi(t)$ in terms of a contour integral. A somewhat more tractable form for the B-particle momentum acf was found by Kashiwamura and several other investigators,[12]

$$\pi(t) = J_0(\omega_0 t) - 2(\mu - 1)\sum_{n\geq 1}^{\infty}(1 - 2\mu)^{n-1}J_{2n}(\omega_0 t) \tag{6}$$

In Eq. (6), J_n is an nth-order Bessel function and $\mu = \lambda^2$.

In the general case of a Brownian motion problem (e.g., a B particle suspended in a fluid) exact expressions for the momentum distribution function and momentum acf of the B particle have not been obtained. The usual procedure employed extensively in the past has consisted in utilizing projection operator techniques to obtain an exact relationship between the B-particle momentum acf and the random force acf. In the following section we consider the generalized Langevin equation for an arbitrary power of the B-particle momentum. In the course of the calculation we will discuss the relation of our results to previous investigations of Brownian motion in fluids and the harmonic chain.

3. GENERALIZED LANGEVIN EQUATION FOR POWERS OF THE B-PARTICLE MOMENTUM

In this section we derive generalized Langevin equations for a set of orthogonal polynomials constructed from powers of the B-particle momentum. The discussion is closely related to our earlier study[5,7] of nonlinear momentum coupling effects on B-particle motion in fluids. For fluids such nonlinear coupling effects are responsible for the slow decay of the kernel which characterizes the decay of the B-particle momentum in Mori's formulation[4] of this problem. However, by making use of the Gaussian property of the harmonic chain, it is easy to demonstrate that such nonlinear momentum coupling effects are absent. The absence of these nonlinear coupling terms leads to an especially simple form for the generalized Langevin equation. In the latter part of this section we will study several general features of the kernels which enter in the Langevin equations.

We begin by deriving a generalized Langevin equation for an arbitrary power of the B-particle momentum. It is convenient to work with an orthogonal set of momentum functions $H_j(P)$,

$$H_j(P) = [\exp(+P^2/2)](-\partial/\partial P)^j \exp(-P^2/2); \; H_1 = P, \; H_2 = P^2 - 1 \quad (7)$$

As in earlier investigations of Brownian motion, we can derive a generalized Langevin equation by applying the operator identity

$$\exp[(A + B)t] = \exp(At) + \int_0^t dt_1 \{\exp[A(t - t_1)]\} B \exp(A + B)t_1 \quad (8)$$

with $A = iL$, $B = -\mathscr{P}iL$, and $\mathscr{P}$ *a* projection operator which averages over an equilibrium bath distribution,

$$\rho_b = [\exp(-\beta H_0)] \Big/ \int dx^N \, dp^N \exp(-\beta H_0)$$

$$\mathscr{P}\mathscr{O} = \int dx^N \, dp^N \, \rho_b \mathscr{O} \equiv \langle \mathscr{O} \rangle_b \quad (9)$$

to

$$\frac{dH_j(P)}{dt} = \lambda \left(\frac{\beta}{m}\right)^{1/2} F \frac{\partial H_j(P)}{\partial P} = j\lambda \left(\frac{\beta}{m}\right)^{1/2} F H_{j-1}(P) \quad (10)$$

in order to obtain

$$\frac{dH_j(P, t)}{dt} = \frac{\lambda^2}{m} \int_0^t dt_1 \{\exp[iL(t - t_1)]\} \left(\frac{\partial}{\partial P} - P\right) K^+(t_1) \frac{\partial H_j(P)}{\partial P} + \lambda \left(\frac{\beta}{m}\right)^{1/2} F_j^+(t) \quad (11)$$

The random force $F_j^+(t)$ is defined by

$$F_j^+(t) = e^{i(1-\mathscr{P})Lt} F \, \partial H_j(P)/\partial P \quad (12)$$

and $K^+(t)$ is the force correlation function introduced by Mazur and Oppenheim,

$$K^+(t) = \beta\langle FF^+(t)\rangle_b = \beta\langle Fe^{i(1-\mathscr{P})Lt}F\rangle_b \tag{13}$$

We note that this correlation "function" is an operator in momentum space.

Equation (11) can be used to derive an equation of motion for the correlation function of powers of the B-particle momentum. As in our earlier studies of nonlinear momentum coupling effects, we carry out the calculation in two steps; first we average Eq. (11) over an equilibrium bath distribution to obtain

$$\frac{d\mathscr{P}H_j(P,t)}{dt} = \frac{\lambda^2}{m}\int_0^t dt_1\, \mathscr{G}(t-t_1)\left(\frac{\partial}{\partial P} - P\right)K^+(t_1)\frac{\partial}{\partial P}H_j(P) \tag{14}$$

where we have used the fact that $\mathscr{P}F_j^+(t) = 0$. The propagator $\mathscr{G}(t) = \langle e^{iLt}\rangle_b$ is related to the conditional momentum distribution in Eq. (6) by

$$\begin{aligned}\mathscr{P}H_j(P,t) &= \langle H_j(P,t)\rangle_b = \int dP'\, H_j(P')f(P',P,t)\\ &= \int dP'\, H_j(P')\mathscr{G}(t)\,\delta(P-P') = \mathscr{G}(t)H_j(P)\end{aligned} \tag{15}$$

In many of the subsequent calculations it will prove convenient to introduce a field theory notation frequently used in quantum mechanics. To this end we define a set of basis vectors

$$u_j(P) = \phi(P)^{1/2}H_j(P) \equiv |j\rangle \tag{16}$$

$$\langle j|k\rangle = j!\,\delta_{jk} \tag{17}$$

and introduce creation C and destruction D operators on these vectors[7,13]

$$C = \frac{P}{2} - \frac{\partial}{\partial P}, \qquad D = \frac{P}{2} + \frac{\partial}{\partial P} \tag{18}$$

with properties

$$C|j\rangle = |j+1\rangle, \qquad D|j\rangle = j|j-1\rangle \tag{19}$$

Transformed operators will be denoted by a tilde,

$$\tilde{\sigma}(P) = \phi(P)^{1/2}\sigma(P)\phi(P)^{-1/2} \tag{20}$$

In Eqs. (16) and (20), $\phi(P) = (2\pi)^{-1/2}\exp(-P^2/2)$ is a normalized Maxwellian distribution function. In this notation Eq. (14) takes the form

$$d|j,t\rangle/dt = -(\lambda^2/m)\int_0^t dt_1\, \tilde{\mathscr{G}}(t-t_1)C\tilde{K}^+(t_1)D|j\rangle \tag{21}$$

where

$$|j, t\rangle = \tilde{\mathscr{G}}(t)|j\rangle \tag{22}$$

If we make use of the fact that the $|j\rangle$ form a complete set

$$\sum_{l=0}^{\infty} |l\rangle(l!)^{-1}\langle l| = 1 \tag{23}$$

and Eq. (19), we can write Eq. (21) as

$$d|j, t\rangle/dt = -\sum_{l=1}^{\infty} \int_0^t dt_1\, |l; t - t_1\rangle i\Omega_{lj}(t_1) \tag{24}$$

where we have defined the coupling factors

$$i\Omega_{lj}(t_1) = (\lambda^2/m)\langle l|C\tilde{K}^+(t_1)D|j\rangle/l! \tag{25}$$

The coupled equations for the momentum correlation functions are easily obtained by taking the scalar product with $|k\rangle$,

$$d\pi_{kj}(t)/dt = -\sum_{l=1}^{\infty} \int_0^t dt_1\, \pi_{kl}(t - t_1)i\Omega_{lj}(t_1) \tag{26}$$

where

$$\pi_{kj}(t) = \langle k|j; t\rangle/k! \tag{27}$$

and is related to the conditional probability by

$$\begin{aligned}\pi_{kj}(t) &= \int dP\, \phi(P)H_k(P)\mathscr{G}(t)H_j(P) \\ &= \int dP\, \phi(P)H_k(P) \int dP'\, H_j(P')f(P', P, t)\end{aligned} \tag{28}$$

Making use of the expression for $f(P', P, t)$ given in Section 2 and performing the integrals, one obtains the familiar consequence of a Gaussian conditional distribution,

$$\pi_{kj}(t) = \pi_{jj}(t)\, \delta_{kj} = \pi(t)^j\, \delta_{kj} \tag{29}$$

and hence

$$d\pi_{jj}(t)/dt = -\int_0^t dt_1\, \pi_{jj}(t - t_1)i\Omega_{jj}(t_1) \tag{30}$$

As a direct consequence of the Gaussian character of the conditional distribution, the equations of motion for the various correlation functions decouple, but are non-Markovian.

An important consequence of the decoupling of the set of relaxation equations is the elimination of slowly decaying components from the jth-order kernel. For example, if we consider the case where $j = 1$ (decay of the momentum autocorrelation function), we have demonstrated previously[5,7] that in the general case the Mori kernel [see Eq. (A.2)] has a slowly decaying component stemming from the coupling of the B-particle momentum to higher powers of the B-particle momentum. However, since such coupling is absent in the harmonic chain, any residual, slowly decaying terms which may appear in the force kernels must be attributed to bath effects.

Equation (30) also implies the diagonal property

$$i\Omega_{kj}(t) = i\Omega_{jj}(t)\,\delta_{kj} \tag{31}$$

and it follows that Eq. (11) can be written in the generalized Langevin form[4]

$$dH_j(P,t)/dt = -\int_0^t dt_1\, i\Omega_{jj}(t_1)H_j(P, t-t_1) + \lambda(\beta/m)^{1/2}F_j^{+}(t) \tag{32}$$

Equation (31) also leads to the conclusion that the Mori and Mazur–Oppenheim treatments of the harmonic chain are equivalent (see Appendix A).

We also note that although for several exactly soluble master equation models (e.g., see Ref. 14) one can show that the analog of $i\Omega_{kj}(t_1)$ [for these models $i\Omega_{kj}(t_1) \propto \delta(t_1)$] is diagonal, the harmonic chain provides the only example where such decoupling occurs for $i\Omega_{kj}(t_1)$ with the time dependence explicitly determined from the microscopic equations of motion of the system.

We can utilize the explicit specification of time dependence of the $i\Omega_{kj}(t_1)$ to deduce some general properties of $\langle j|\tilde{K}^{+}(t)|j\rangle$. Repeated use of Eq. (8) with $A = iL_0$ and $B = \lambda(1-\mathscr{P})i\tilde{L}_{\mathrm{B}}$ leads to

$$\begin{aligned}\langle j|\tilde{K}^{+}(t)|j\rangle = j!\,K_0(t) + \sum_{n=1}^{\infty}\int_0^{t_1} dt_1 \int_0^{t_1} dt_{2\ldots}\int_0^{t_{2n-1}} dt_{2n} \\ \times (\lambda^2\beta/m)^n\beta\langle j|\langle F\{\exp[iL_0(t-t_1)]\}(1-\mathscr{P}) \\ \times (aC+bD)\cdots(1-\mathscr{P})(aC+bD)[\exp(iL_0t_{2n})]F\rangle_b|j\rangle\end{aligned} \tag{33}$$

where we have written $i\tilde{L}_{\mathrm{B}}$ in the form

$$i\tilde{L}_{\mathrm{B}} = (\beta/m)^{1/2}(aC+bD) \tag{34}$$

with

$$a = \partial/\partial\beta x_0, \qquad b = F + (\partial/\partial\beta x_0) \tag{35}$$

In Eq. (33), $K_0(t)$ is the fixed particle force correlation function,

$$K_0(t) = \beta\langle j|\langle F[\exp(iL_0t)]F\rangle_b|j\rangle/j! = \beta\langle F[\exp(iL_0t)]F\rangle_b \tag{36}$$

The correlation function in Eq. (33) may be decomposed into a sum of terms containing products of C and D operators. First one may observe that all correlation functions in this sum that do not contain an equal number of C and D operators vanish. This may be readily demonstrated by making use of Eqs. (19) and (17). By making use of the properties of the harmonic chain, one can show that

$$\beta(1-\mathscr{P})a[\exp(iL_0t)]F = -(1-\mathscr{P})K_0(t) = 0 \tag{37}$$

[4] See Refs. 18–20 for the alternative Gaussian non-Markovian Fokker-Planck approach.

and as a result each term in the expansion in Eq. (33) must begin with a D operator on the extreme right. As an immediate consequence,

$$(m/\lambda^2)i\Omega_{11}(t) = \langle 0|\tilde{K}^+(t)|0\rangle = K_0(t) \tag{38}$$

since $D|0\rangle = 0$. This matrix element characterizes the decay of the momentum correlation function and Eq. (38) is just the result obtained earlier by Deutch and Silbey.[6] No such simple form results for the matrix elements that characterize the decay of the higher powers of the B-particle momentum.[5] We illustrate this by considering $\langle 1|K^+(t)|1\rangle$.

It is easy to show that terms to *all* orders in λ contribute but that each term contains only contributions that come from a strict alternation of C and D operators, $CDCD\ldots CD$. It is clear that, starting from the right in a typical term, we must begin with D because of Eq. (37) and follow this with C since $D^2|1\rangle = 0$. If we assume that the next contribution comes from a C operator, direct calculation using Eq. (37) leads to

$$\begin{aligned}(1 - \mathscr{P})a(-[iL_0(t_{2n-2} - t_{2n})]\}F\langle F[\exp(iL_0t_{2n-1})]F\rangle_b \\ - [\exp(iL_0t_{2n-2})]F\langle F\{\exp[iL_0(t_{2n-1} - t_{2n})]\}F\rangle_b) = 0\end{aligned} \tag{39}$$

Hence two consecutive C operators produce a zero contribution and C must be followed by D. By the repetitive use of such arguments one may easily show that any term must assume the alternating CD form or else its matrix element will vanish, and thus for $(m/2\lambda^2)i\Omega_{22}(t) = \langle 1|\tilde{K}^+(t)|1\rangle$

$$\begin{aligned}\langle 1|\tilde{K}^+(t)|1\rangle = K_0(t) + \sum_{n=1}^{\infty}\int_0^t dt_1\int_0^{t_1} dt_2\ldots\int_0^{t_{2n-1}} dt_{2n}(\lambda^2\beta/m)^n \\ \times \beta\langle F\{\exp[iL_0(t - t_1)]\}(1 - \mathscr{P}) \\ \times a\{\exp[iL_0(t_1 - t_2)]\}(1 - \mathscr{P})b\ldots(1 - \mathscr{P})b[\exp(iL_0t_{2n})F\rangle_b\end{aligned} \tag{40}$$

where we have used the fact that $CD\ldots CD|1\rangle = |1\rangle$. For the higher order matrix elements no simple pattern for the C and D operators results. Hence we see that even for the harmonic lattice the higher order matrix elements have a much richer structure than $\langle 0|\tilde{K}^+(t)|0\rangle$, and therefore we can investigate many properties of such matrix elements which are important in the study of Brownian motion in fluids. In the following sections we will study the validity for this system of the factorization approximation for time-dependent correlation functions as well as several other aspects of the λ expansions of $\tilde{K}^+(t)$.

[5] It is for this reason that Deutch and Silbey were unable to find a corresponding simple form for the Fokker–Planck equation.

4. FACTORIZATION APPROXIMATION FOR TIME-DEPENDENT CORRELATION FUNCTIONS

As mentioned previously, a knowledge of the properties of the kernel $K^+(t)$ is essential in any study of Brownian motion. Typically, the existence of a λ expansion of $K^+(t)$ or its matrix elements is assumed, but in one case Mazur and Oppenheim[3] were able to prove the validity of such an expansion. This proof, however, was based on an assumption concerning the long-time behavior of certain correlation functions appearing in the λ expansion of $K^+(t)$. More explicitly, for correlation functions which are governed by fixed particle dynamics the factorization approximation states

$$\langle A(t_1)[\exp(iL_0 t)]B(t_2)\rangle_b = \langle A(t_1)\rangle_b \langle B(t_2)\rangle_b \tag{41}$$

for $t > t_b$, where t_b is some characteristic bath relaxation time and t_1 and t_2 refer to a collection of positive times. If one is interested in the Langevin equation for the B-particle momentum, only $\langle 0|K^+(t)|0\rangle$ appears and from Eq. (38) the factorization approximation need not be considered. However, for the Langevin equation for higher powers of the B-particle momentum one is faced with the full complexity of the λ expansion and the problem is very similar to the fluid case. In this section we utilize the simplicity of the harmonic chain dynamics to investigate in more detail the validity of such an approximation.

From Eq. (33) we can write the operator expansion

$$\begin{aligned}\tilde{K}^+(t) &= K_0(t) + \sum_{n=1}^{\infty} (\lambda^2\beta/m)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{2n-1} dt_{2n} \\ &\quad \times \beta\langle F\{\exp[iL_0(t-t_1)]\}(1-\mathscr{P})(aC+bD) \\ &\quad \times \cdots (1-\mathscr{P})(aC+bD)[\exp(iL_0 t_{2n})]F\rangle_b \\ &\equiv K_0(t) + \sum_{n=1}^{\infty} \lambda^{2n} K_n(t)\end{aligned} \tag{42}$$

For the harmonic chain the expressions for $K_n(t)$ simplify considerably by making repeated use of Eq. (37) in the form

$$(\partial/\partial\beta x_0)\{\exp[iL_0(t_i - t_j)]\}F = -\langle F_i F_j\rangle_b \tag{43}$$

where we have introduced the fixed particle force notation

$$F_i = [\exp(iL_0 t_i)]F \tag{44}$$

We also note that as a consequence of Eq. (43) [since $P(t)$ is Gaussian, its corresponding random force $F_0(t)$—Eq. (1)—is also Gaussian],

$$\langle F_1 F_2 \ldots F_{2n}\rangle_b = \sum_{\substack{\text{all} \\ \text{pairs}}} \langle F_i F_j\rangle_b \langle F_k F_l\rangle_b \ldots \tag{45}$$

Using Eqs. (43) and (45), it is straightforward to write expressions for the $K_n(t)$ in terms of products of fixed particle force autocorrelation functions. Explicit expressions for $K_1(t)$ and $K_2(t)$ are

$$K_1(t) = m^{-1} \int_0^t dt_1 \int_0^{t_1} dt_2 \, L(t, t_1, t_2) CD$$
$$\equiv K^{(1)}(t) CD \tag{46}$$

with

$$L(t, t_1, t_2) = -K_0(t_1) K_0(t - t_2) - K_0(t) K_0(t_1 - t_2) \tag{47}$$

and

$$K_2(t) = m^{-2} \int_0^t dt_1 \dots \int_0^{t_3} dt_4 \{ M_1(t, t_1, \dots, t_4) CCDD$$
$$+ M_2(t, t_1, \dots, t_4) CDCD \} \tag{48}$$

with

$$\begin{aligned} M_1(t, t_1, \dots, t_4) &= K_0(t - t_3) K_0(t_1 - t_4) K_0(t_2) + K_0(t - t_4) K_0(t_1 - t_3) K_0(t_2) \\ &\quad + K_0(t - t_2) K_0(t_1) K_0(t_2 - t_4) + K_0(t) K_0(t_1 - t_3) K_0(t_2 - t_4) \\ &\quad + K_0(t) K_0(t_1 - t_4) K_0(t_2 - t_3) + K_0(t) K_0(t_1 - t_4) K_0(t_2 - t_3) \end{aligned} \tag{49}$$

$$\begin{aligned} M_2(t, t_1, \dots, t_4) &= K_0(t - t_2) K_0(t_1 - t_4) K_0(t_3) + K_0(t - t_4) K_0(t_1 - t_2) K_0(t_3) \\ &\quad + K_0(t - t_2) K_0(t_1) K_0(t_3 - t_4) + K_0(t) K_0(t_1 - t_2) K_0(t_3 - t_4) \end{aligned} \tag{50}$$

Since the fixed particle force correlation function is known for the harmonic chain,[12]

$$K_0(t) = m\omega_0 J_1(\omega_0 t)/t \tag{51}$$

the properties of the integrands of the $K_n(t)$ operators are therefore completely specified. We can now use these results to test the validity of the factorization approximation. We will consider $K^{(1)}(t)$ in some detail. From Eq. (42) the term proportional to CD in the expansion of $\tilde{K}^+(t)$ is

$$\langle F\{\exp[iL_0(t - t_1)]\}(1 - \mathscr{P}) a \{\exp[iL_0(t_1 - t_2)]\}(1 - \mathscr{P}) b \exp(iL_0 t_2) F \rangle_b \tag{52}$$

which by direct calculation is given in Eq. (47) for the harmonic chain (the other terms, i.e., the coefficients of CC, DC, and DD, vanish for this system). The factorization approximation states that this correlation function is zero for $t - t_1 > t_b$, $t_1 - t_2 > t_b$, or $t_2 > t_b$ corresponding to the three possible breaking points. The restriction of the breaking approximation to positive times also requires that $t \geqslant t_1 \geqslant t_2$. This inequality is also implied by the time integral in Eq. (46). If we assume that the fixed particle force correlation function in Eq. (51) decays to zero in a time t_b

$$K_0(t) \simeq 0, \qquad t > t_b \tag{53}$$

then it is easy to verify that Eq. (47) exactly satisfies the factorization approximation. Similar considerations apply to Eqs. (49) and (50). Thus we see that for the harmonic chain the *mechanics* of the factorization approximation are exactly satisfied.

Although the mechanics of the factorization approximation is exactly satisfied for this model, the oscillatory character of the fixed particle force correlation function [Eq. (51)] precludes the definition of a well-defined relaxation time t_b. (We note that a bath relaxation time is also not well defined for the fluid case.) Hence, it is useful to examine some of the consequences of the factorization in more detail. Mazur and Oppenheim have demonstrated that as a direct consequence of the factorization approximation, $K^{(1)}(t)$ [Eq. (46)] is zero for $t > 3t_b$. For the harmonic chain it is possible to compute $K^{(1)}(t)$ explicitly and test this conclusion in more detail. Using Eqs. (46), (47), and (51), we can write

$$K^{(1)}(\tau) = -m\omega_0^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \left\{ \frac{J_1(\tau_1)J_1(\tau - \tau_2)}{\tau_1(\tau - \tau_2)} + \frac{J_1(\tau)J_1(\tau_1 - \tau_2)}{\tau(\tau_1 - \tau_2)} \right\} \tag{54}$$

where $\tau_i = \omega_0 t_i$. Performing the double time integral (see Appendix B), we find

$$\begin{aligned} K^{(1)}(\tau) = -m\omega_0^2 [&\{J_1(\tau)/\tau\}\{J_0(\tau) + 1\} - 1 \\ &+ \{\tau J_0(\tau) + \tfrac{1}{2}\pi\tau[H_0(\tau)J_1(\tau) - H_1(\tau)J_0(\tau)]\} \\ &\times\{\tau J_0(\tau) + \tfrac{1}{2}\pi\tau[H_0(\tau)J_1(\tau) - H_1(\tau)J_0(\tau)] - J_1(\tau)\}] \end{aligned} \tag{55}$$

where $H_0(\tau)$ and $H_1(\tau)$ are Struve functions.[17] In Fig. 1 we plot and compare the time behavior of $K_0(\tau)$ and $K^{(1)}(\tau)$. The oscillations in $K^{(1)}(\tau)$ are much more pronounced and decay much more slowly than those of $K_0(\tau)$. Such long-time behavior is expected from an examination of the asymptotic forms of these functions,

$$K_0(\tau) \sim m\omega_0^2 \left(\frac{2}{\pi}\right)^{1/2} \frac{\cos(\tau - 3\pi/4)}{\tau^{3/2}} \tag{56}$$

and

$$K^{(1)}(\tau) \sim -m\omega_0^2 \left(\frac{2}{\pi}\right)^{1/2} \frac{\cos(\tau - 3\pi/4)}{\tau^{1/2}} \tag{57}$$

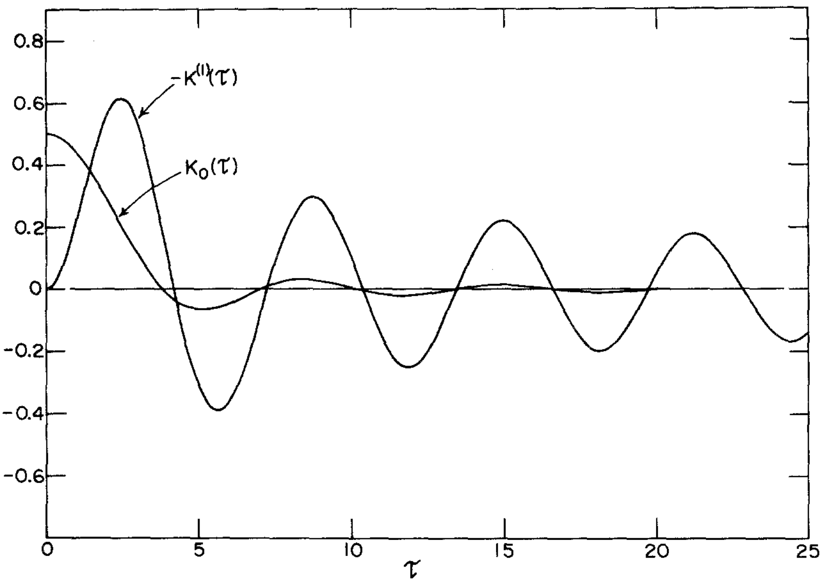

Fig. 1. Comparison of $K_0(\tau)$ [Eq. (51)] and $-K^{(1)}(\tau)$ [Eq. (55)]. Results are plotted in units of $m\omega_0^2$.

In order to test the conclusion that $K^{(1)}(\tau) \sim 0$ for $\tau > 3\tau_b$, we estimate τ_b by the third zero in $K_0(\tau)$. As can be seen from Fig. 1, the amplitudes of the oscillations are small and the infinite-time integral is well approximated by $\int_0^{\tau_b} K_0(\tau)\,d\tau$ (about 2.4% error). If we let τ^* be the ninth zero of $K^{(1)}(\tau)$ ($\tau^* > 3\tau_b$), then we can compute $\int_{\tau^*}^{\infty} d\tau\, K^{(1)}(\tau)$ in order to determine how well the conclusions of the breaking approximation are satisfied. Direct calculation indicates that this contribution is about 15% of the value of the infinite-time integral.

Hence, in summary, one can conclude that although the mechanics of the factorization approximation are exactly satisfied for the harmonic chain, because of the oscillatory nature of the solutions and the lack of a well-defined relaxation time, the factorization approximation may yield poor estimates of the higher correlation functions. [We should also point out that if we examine the force correlation function $\langle Fe^{iLt}F\rangle_b$ rather than $K^+(t)$, the infinite-time integral of the analog of $K^{(1)}(t)$ does not exist. This points out the difference between these correlation functions and shows that the full force correlation function does not possess a λ expansion.[3]] In the following section we examine some properties of the λ expansion of a particular matrix element of $\tilde{K}^+(t)$,

$$i\Omega_{22}(t) = (\lambda^2/m)2\langle 1|\tilde{K}^+(t)|1\rangle$$

which characterizes the decay of the square of the B-particle momentum.

5. ENERGY RELAXATION IN THE HARMONIC CHAIN

The results of the previous sections provide an especially convenient route to obtain more information about the structure of the kernels $i\Omega_{jj}$, which characterize the decay of the higher powers of the B-particle momentum. As we mentioned earlier, these higher matrix elements are not equal to the fixed particle force correlation function and display a more complex behavior as a function of λ and t or ϵ (frequency).

The principal feature of our earlier results that permits such a detailed study of these higher matrix elements is the fact that the equations of motion decouple. As a result we can simply relate the Laplace transform of $i\Omega_{jj}(t)$,

$$i\Omega_{jj}(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t} i\Omega_{jj}(t)$$

to the momentum correlation functions, which are known for the harmonic lattice. This relationship follows directly from the Laplace transform of Eq. (30),

$$i\Omega_{jj}(\epsilon) = [\pi_{jj}(\epsilon)]^{-1} - \epsilon = [\pi^j(\epsilon)]^{-1} - \epsilon \tag{58}$$

where

$$\pi^j(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t} \pi(t)^j \tag{59}$$

Although $\pi(t)$ is known explicitly for the harmonic chain [Eq. (6)], the Laplace transforms of arbitrary powers of $\pi(t)$ are difficult to compute. However, a fairly detailed study of $i\Omega_{22}(\epsilon)$ is possible. This matrix element is of considerable interest since it characterizes the decay of the kinetic energy of the B particle.[6] Also, as noted in Section 3, terms to all orders in λ contribute and it is in this sense similar to the kernels that appear in the study of B-particle motion in fluids.

It is well known that under certain conditions it is justifiable to replace a frequency-dependent kernel by its zero-frequency limit (Markov approximation). Below we examine $i\Omega_{22}(\epsilon = 0)$ and test the appropriateness of the Markov approximation for $\pi_{22}(t)$ by comparison with the exact results. The kernel $i\Omega_{22}(\epsilon = 0)$ may be calculated with the aid of Eqs. (6), (58), and (C.1). Some details on the evaluation of the pertinent integrals are given in Appendix C; we simply quote the result:

$$\begin{aligned} &\mu^{-1} i\Omega_{22}(\lambda, \epsilon = 0) \\ &= \frac{\pi\omega_0(1 - 2\lambda^2)}{\lambda^2 - (\lambda^4 + 2\lambda^2 - 1)(1 - 2\lambda^2)^{-1/2}\tan^{-1}[(1 - 2\lambda^2)^{1/2}/\lambda^2]}, \quad \mu \le \tfrac{1}{2} \\ &= \frac{\pi\omega_0(1 - 2\lambda^2)}{\lambda^2 - (\lambda^4 + 2\lambda^2 - 1)(2\lambda^2 - 1)^{-1/2}\tan^{-1}[(2\lambda^2 - 1)^{1/2}/\lambda^2]}, \quad \mu \ge \tfrac{1}{2} \end{aligned} \tag{60}$$

[6] Specifically, Eq. (30) with $j = 2$ governs the acf π_{22} of the kinetic energy fluctuation $P^2 - \langle P^2 \rangle = H_2(P)$.

We have explicitly indicated the λ dependence of $i\Omega_{22}$ on the left-hand side of Eq. (60). Figure 2 is a plot of the results in Eq. (60). Perhaps the most striking feature is the fact that for $\mu = 1$, $i\Omega_{22}(1, 0) = 0$ and as a result the Markov approximation to the kinetic energy correlation function,

$$\pi_{22}(t) \simeq \exp[-i\Omega_{22}(\lambda, 0)t] \tag{61}$$

does not lead to decay. For this special value of λ, Eq. (6) reduces to the exact result

$$\pi(t) = J_0(\omega_0 t) \tag{62}$$

and the result $i\Omega_{22}(1, 0) = 0$ follows directly from the fact that $\int_0^\infty dt\, [J_0(\omega_0 t)]^2$ diverges. We note that the B-particle kinetic energy is ergodic for this value of μ.[16]

Figures 3 and 4 compare the Markov approximation to the decay of $\pi_{22}(t) = \pi(t)^2$ for various values of λ. The Markov approximation provides a fair approximation to the exact correlation function except for values of λ near $\lambda = 1$, where it must necessarily fail. The Markov approximation of course predicts exponential decay, while the exact result is a damped oscillatory function. However, since $\pi_{22}(t)$ is highly damped so that the magnitude of the oscillations is small beyond the first zero, the overall decay is fairly well predicted.

For fluids where very little is known about the structure of the kernels that characterize the decay of the B-particle momentum and its powers, frequently, as mentioned earlier, the validity of a λ expansion is assumed.

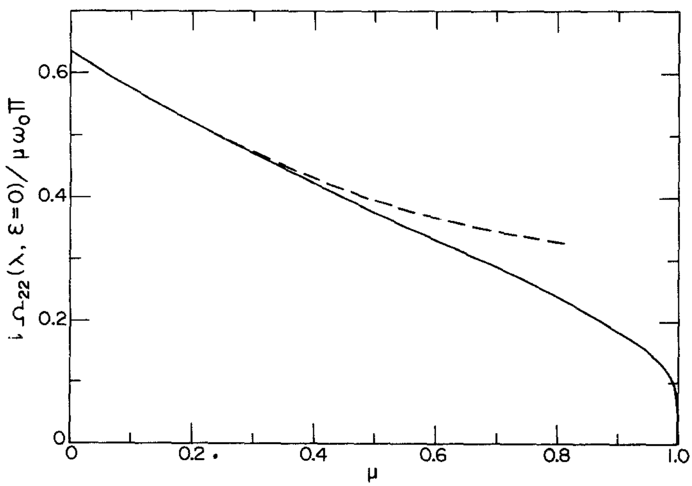

Fig. 2. $i\Omega_{22}(\lambda, \epsilon = 0)/\mu\omega_0\pi$ as a function of $\mu = \lambda^2$. The dashed line is a plot of the approximation in Eq. (63).

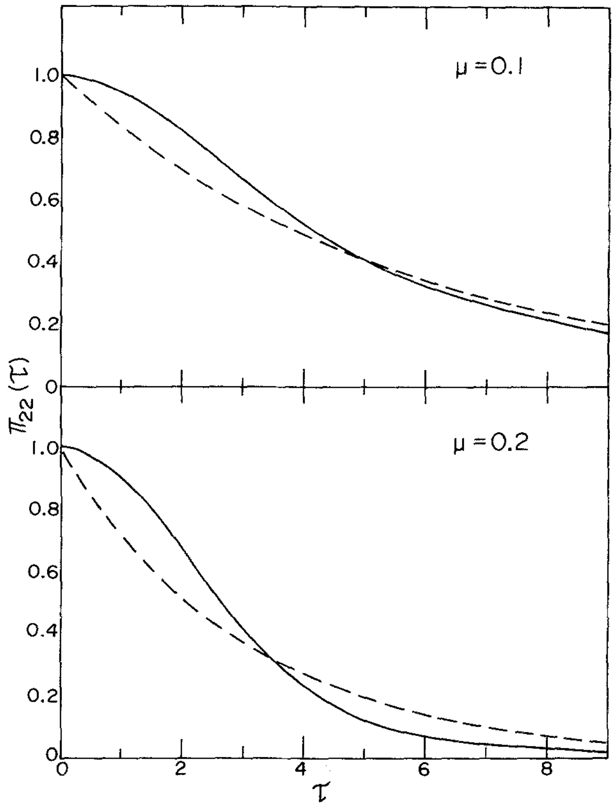

Fig. 3. Comparison of Markov approximation (— — —) with the exact result (———) for $\pi_{22}(\tau)$ for $\mu = 0.1$ and 0.2.

For the special case considered above, it is clear from Eq. (60) that $i\Omega_{22}(\lambda, 0)$ is an analytic function of λ. The first few terms in the λ expansion are

$$\mu^{-1} i\Omega_{22}(\lambda, 0) = 2\omega_0[1 - \lambda^2 + \lambda^4/2! \cdots] \tag{63}$$

and provide an excellent approximation for small λ (see Fig. 2).[7]

The general behavior of $i\Omega_{22}(\lambda, \epsilon)$ as a function of ϵ for various values of λ is given in Fig. 5. Although a closed expression for arbitrary λ and ϵ was not obtained, several special cases which span the range of interesting values can be explicitly given. For $\mu = 0$, $i\Omega_{22}(0, \epsilon)$ reduces to the fixed particle force correlation function and we can write

$$\mu^{-1} i\Omega_{22}(0, \epsilon) = 2\omega_0^2[(\epsilon^2 + \omega_0^2)^{1/2} + \epsilon]^{-1} \tag{64}$$

In addition, for both $\mu = \frac{1}{2}$ and $\mu = 1$, Eq. (6) reduces to simple forms and again $i\Omega_{22}$ can be explicitly computed. For $\mu = \frac{1}{2}$ we find

$$\mu^{-1} i\Omega_{22}(2^{-1/2}, \epsilon) = \pi\omega_0[2\mathscr{I}(x)]^{-1} - \epsilon \tag{65}$$

[7] The first term in Eq. (63) is the standard Fokker–Planck prediction.[9]

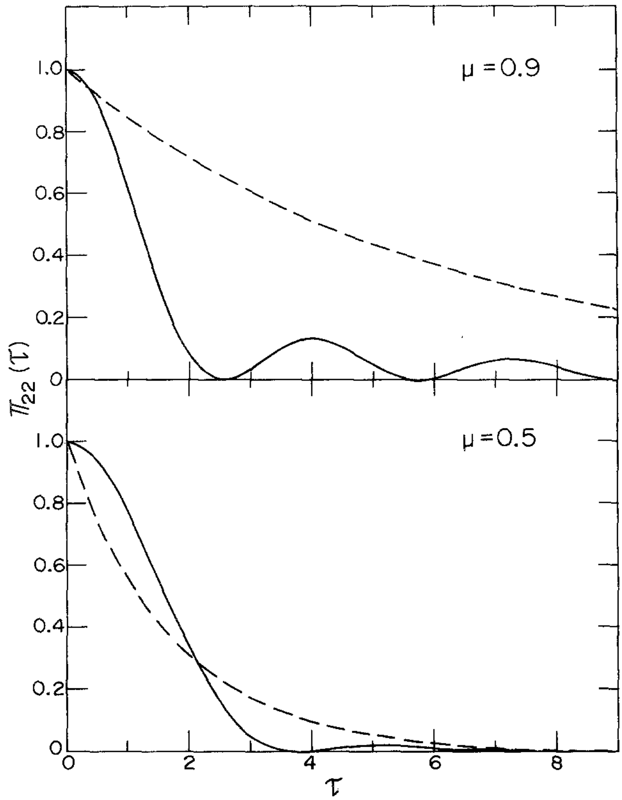

Fig. 4. Same as Fig. 3 for μ = 0.5 and 0.9.

where

$$\mathscr{I}(x) = \frac{4\pi}{3x}\left[\frac{1-x}{1-(1-2x)^2}\right]^{1/2}\{P_{-1/2}(1-2x) - (1-2x)P_{1/2}(1-2x)\} \tag{66}$$

with $x = 4\omega_0^2/(4\omega_0^2 + \epsilon^2)$, and $P_{1/2}$ and $P_{-1/2}$ are half-order Legendre functions.[15]. For $\mu = 1$ we find

$$\mu^{-1} i\Omega_{22}(1, \epsilon) = \frac{\pi(\epsilon^2 + 4\omega_0^2)^{1/2}}{2\mathbb{K}[2\omega_0/(\epsilon^2 + 4\omega_0^2)^{1/2}]} - \epsilon \tag{67}$$

where $\mathbb{K}$ is a complete elliptical integral of the first kind.[17] The results for other values of λ in Fig. 5 were computed numerically. The plots indicate that for small values of μ ($\mu \leq \frac{1}{2}$), $i\Omega_{22}(\lambda, \epsilon)$ is a monotonically decreasing function of ϵ, while for larger values of μ the function exhibits a maximum. A maximum for large values of μ is not unexpected since, as shown earlier, $i\Omega_{22}(1, 0)$ is

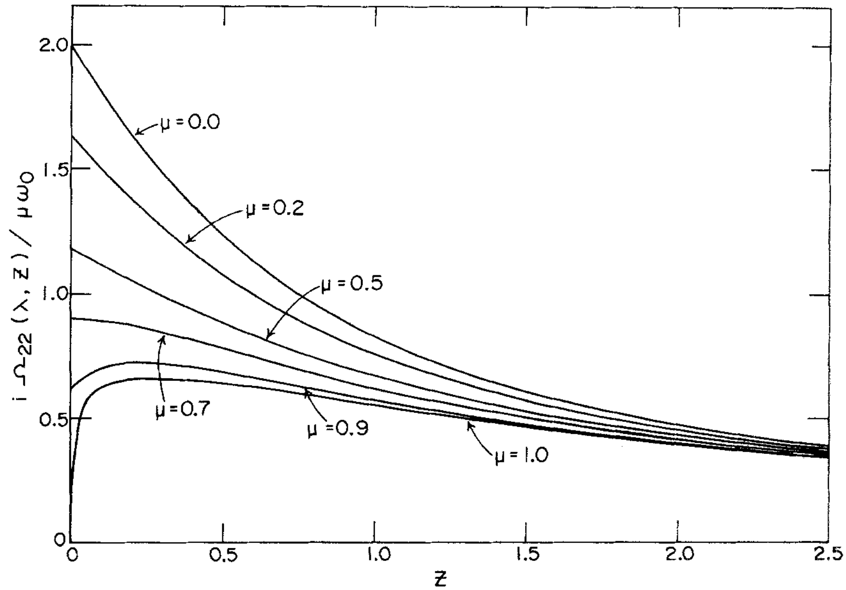

Fig. 5. $i\Omega_{22}(\lambda, z)/\mu\omega_0$ as a function of the reduced frequency $z = \epsilon/\omega_0$ for several values of μ.

zero. The kernel is well behaved for all values of λ and ϵ investigated but it is difficult to determine if the function is analytic in λ for finite frequency.[8]

All of the above results reflect only a portion of the full complexity of $\tilde{K}^+(t)$ since, as demonstrated in Section 3, the matrix elements of $\tilde{K}^+(t)$ depend only on selected terms in the λ expansion of this operator. The operator itself is much more difficult to examine than its matrix elements (see Section 4). However, the quantities of direct physical interest are the matrix elements of $\tilde{K}^+(t)$ since these characterize the decays of the various powers of the B-particle momentum.

APPENDIX A

In this appendix we show that the Mori generalized Langevin equation[(4)] for the B-particle momentum function, $H_j(P)$, reduces to Eq. (11) for the harmonic chain. Mori's generalized Langevin equation can be obtained by the procedure specified in Eqs. (8)–(11) if we select $A = iL$ and $B = \mathscr{P}_j^m iL$, where the projection operator $\mathscr{P}_j^m$ is defined by

$$\begin{aligned} \mathscr{P}_j^m &= H_j(P)(j!)^{-1}\langle H_j(P)\mathscr{O}\rangle \\ &= H_j(P)(j!)^{-1}\int dP\,\phi(P)H_j(P)\langle\mathscr{O}\rangle_b \end{aligned} \tag{A.1}$$

[8] For $\lambda^2 < 1$, analyticity has been proved by M. Kummer (Toledo Univ.).

The familiar result is

$$\frac{dH_j(P,t)}{dt} = -\frac{\lambda^2\beta}{m}\int_0^t dt_1\,\langle F_j F_j^m(t_1)\rangle (j!)^{-1} H_j(P, t - t_1) + \lambda\left(\frac{\beta}{m}\right)^{1/2} F_j^m(t) \tag{A.2}$$

where the Mori random force is defined by

$$F_j^m(t) = \{\exp[i(1 - \mathscr{P}_j^m)Lt]\}F_j \equiv \{\exp[i(1 - \mathscr{P}_j^m)Lt]\}F\frac{\partial H_j(P)}{\partial P} \tag{A.3}$$

To establish the equivalence, we first show that $F_j^+(t) = F_j^m(t)$ [$F_j^+(t)$ is defined in Eq. (12)] for the harmonic chain. First we note that the projection operator in Eq. (A.1) can be written as

$$\mathscr{P}_j^m = \mathscr{P}_j\mathscr{P} \tag{A.4}$$

where

$$\mathscr{P}_j = H_j(P)(j!)^{-1}\int dP\,\phi(P)H_j(P) \tag{A.5}$$

is a projection operator in momentum space. By making use of the identity

$$\exp[(A + B)t] = \exp(At) + \int_0^t dt_1\,\{\exp[(A + B)(t - t_1)]\}B\exp(At_1) \tag{A.6}$$

with $A = i(1 - \mathscr{P})L$ and $B = i(1 - \mathscr{P}_j^m)L - i(1 - \mathscr{P})L = \lambda(1 - \mathscr{P}_j)\mathscr{P}iL_B$, we obtain

$$F_j^m(t) = F_j^+(t) + \lambda\left(\frac{\beta}{m}\right)^{1/2}\int_0^t dt_1\,\{\exp[i(1 - \mathscr{P}_j^m)L(t - t_1)]\}$$
$$\times (1 - \mathscr{P}_j)\left(\frac{\partial}{\partial P} - P\right)K^+(t_1)\frac{\partial}{\partial P}H_j(P) \tag{A.7}$$

If we write $(1 - \mathscr{P}_j)$ as

$$(1 - \mathscr{P}_j) = \sum_{k\neq j} H_k(P)(k!)^{-1}\int dP\,\phi(P)H_k(P) \tag{A.8}$$

and insert in Eq. (A.7), we obtain

$$F_j^m(t) = F_j^+(t) + \lambda\left(\frac{\beta}{m}\right)^{1/2}\sum_{k\neq j}\int_0^t dt_1\,\{\exp[i(1 - \mathscr{P}_j^m)L(t - t_1)]\}H_k(P)$$
$$\times\frac{\langle k - 1|\tilde{K}^+(t_1)|j - 1\rangle}{(k - 1)!} \tag{A.9}$$

From Eq. (31) and the fact that the sum is restricted to $k \neq j$ it follows that

$$F_j^m(t) = F_j^+(t) \tag{A.10}$$

Hence as a direct consequence of the absence of nonlinear momentum mode coupling for this model, the Mori and Mazur–Oppenheim random forces are equal. It follows immediately that Eqs. (A.2) and (11) are identical. Equation (A.2) reduces to

$$\frac{dH_j(P,t)}{dt} = -j\frac{\lambda^2\beta}{m}\int_0^t dt_1\, H_j(P, t-t_1)\frac{\langle j-1|\tilde{K}^+(t_1)|j-1\rangle}{(j-1)!} + \lambda\left(\frac{\beta}{m}\right)^{1/2} F_j^+(t) \tag{A.11}$$

or using the definition of $i\Omega_{jj}$ in Eq. (25), we can write

$$\frac{dH_j(P,t)}{dt} = -\int_0^t dt_1\, i\Omega_{jj}(P, t_1)H_j(P, t-t_1) + \lambda\left(\frac{\beta}{m}\right)^{1/2} F_j^+(t) \tag{A.12}$$

which is identical to Eq. (32).

APPENDIX B

The purpose of this appendix is to derive an explicit expression for $K^{(1)}(t)$. We use Eq. (54) to define $A(\tau)$ and $B(\tau)$ as

$$K^{(1)}(\tau) = -m\omega_0^2[A(\tau) + B(\tau)] \tag{B.1}$$

with

$$A(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \frac{J_1(\tau_1)J_1(\tau-\tau_2)}{\tau_1(\tau-\tau_2)} \tag{B.2}$$

and

$$B(\tau) = \frac{J_1(\tau)}{\tau}\int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \frac{J_1(\tau_1-\tau_2)}{\tau_1-\tau_2} \tag{B.3}$$

We first consider $B(\tau)$. Equation (B.3) can be integrated by parts to yield

$$B(\tau) = J_1(\tau)\int_0^\tau dy\frac{J_1(y)}{y} - \frac{J_1(\tau)}{\tau}\int_0^\tau dy\, J_1(y) \tag{B.4}$$

where $y = \tau_1 - \tau_2$. The recursion relation

$$y\, dJ_n(y)/dy = yJ_{n-1}(y) - nJ_n(y) \tag{B.5}$$

may be used in the first integral in (B.4); thereafter both integrations can be performed. The final expression for $B(\tau)$ is

$$B(\tau) = J_1(\tau)\{\tau J_0(\tau) + \tfrac{1}{2}\pi\tau[J_1(\tau)H_0(\tau) - J_0(\tau)H_1(\tau)] - J_1(\tau)\} - [J_1(\tau)/\tau][1 - J_0(\tau)] \tag{B.6}$$

In Eq. (B.6), H_0 and H_1 are Struve functions. $A(\tau)$ may be readily evaluated by means of the following decomposition:

$$\begin{aligned} A(\tau) &= \int_0^\tau d\tau_1 \int_0^\tau d\tau_2 \frac{J_1(\tau)}{\tau_1} \frac{J_1(\tau - \tau_2)}{\tau - \tau_2} \\ &\quad + \int_0^\tau d\tau_1 \int_\tau^{\tau_1} d\tau_2 \frac{J_1(\tau - \tau_2)}{\tau - \tau_2} \frac{J_1(\tau_1)}{\tau_1} \\ &\equiv A_1(\tau) + A_2(\tau) \end{aligned} \tag{B.7}$$

After transforming variables it is easy to see that

$$\begin{aligned} A_1(\tau) &= \left[\int_0^\tau dy \frac{J_1(y)}{y} \right]^2 \\ &= \{\tau J_0(\tau) + \tfrac{1}{2}\pi\tau[J_1(\tau)H_0(\tau) - J_0(\tau)H_1(\tau)] - J_1(\tau)\}^2 \end{aligned} \tag{B.8}$$

Similarly, $A_2(\tau)$ may be expressed as

$$A_2(\tau) = -\int_0^\tau d\tau_1 \frac{J_1(\tau_1)}{\tau_1} \int_0^{\tau - \tau_1} dy \frac{J_1(y)}{y} \tag{B.9}$$

Once again employing Eq. (B.5), we find

$$A_2(\tau) = J_2(\tau) + J_0(\tau) - 1 \tag{B.10}$$

Combining Eqs. (B.6), (B.8), and (B.10) and using the recursion relation

$$yJ_{n-1}(y) + yJ_{n+1}(y) = 2nJ_n(y) \tag{B.11}$$

we obtain the result given in Eq. (55).

APPENDIX C

We outline here the evaluation of the integrals which are required to obtain Eq. (60). The expression for $\pi(t)$ [Eq. (6)] can also be written in integral form[12]

$$\pi(t) = \frac{2\mu}{\pi} \int_0^{\pi/2} d\theta \frac{\cos(\omega_0 t \sin\theta)\cos^2\theta}{\mu^2 + (1 - 2\mu)\sin^2\theta} \tag{C.1}$$

Making use of Eqs. (6), (58), and (C.1), we obtain

$$i\Omega_{22}(\lambda, 0) = [\pi^2(\epsilon = 0)]^{-1} \tag{C.2}$$

with

$$\begin{aligned} \pi^2(\epsilon = 0) = \frac{2\mu}{\pi} \Bigg[&\int_0^\infty dt\, J_0(\omega_0 t) \int_0^{\pi/2} d\theta \frac{\cos(\omega_0 t \sin\theta)\cos^2\theta}{\mu^2 + (1 - 2\mu)\sin^2\theta} \\ &- \int_0^\infty dt \int_0^{\pi/2} \frac{d\theta \cos(\omega_0 t)(\cos^2\theta)2(\mu - 1)}{\mu^2 + (1 - 2\mu)\sin^2\theta} \\ &\times \sum_{p \geq 1}^\infty (1 - 2\mu)^{p-1} J_{2p}(\omega_0 t) \Bigg] \end{aligned} \tag{C.3}$$

If the order of integrations is interchanged and the time integral is performed, we obtain

$$\pi^2(\epsilon = 0) = \frac{2\mu}{\pi\omega_0} \int_0^{\pi/2} \frac{d\theta \cos\theta}{\mu^2 + (1 - 2\mu)\sin^2\theta} - \frac{4\mu(\mu - 1)}{\pi\omega_0} \times \int_0^{\pi/2} \frac{d\theta \cos\theta}{\mu^2 + (1 - 2\mu)\sin^2\theta} \sum_{p\geq 1}^{\infty} [\cos(2p\theta)](1 - 2\mu)^{p-1} \quad \text{(C.4)}$$

With the aid of the identity

$$\sum_{p=0}^{\infty} \gamma^p \cos(\alpha p + \beta) = \frac{\cos\beta - \gamma\cos(\beta - \alpha)}{1 - 2\gamma\cos\alpha + \gamma^2} \quad \text{(C.5)}$$

Eq. (C.3) can be transformed to a tractable form

$$\pi^2(\epsilon = 0) = I_1 + I_2 + I_3 \quad \text{(C.6)}$$

with

$$I_1 = \frac{2\mu}{\pi\omega_0} \int_0^{\pi/2} \frac{d\theta \cos\theta}{\mu^2 + (1 - 2\mu)\sin^2\theta} \quad \text{(C.7)}$$

$$I_2 = -\frac{4\mu(\mu - 1)}{\pi\omega_0} \times \int_0^{\pi/2} \frac{d\theta \cos\theta \cos 2\theta}{[\mu^2 + (1 - 2\mu)\sin^2\theta][1 - 2(1 - 2\mu)\cos 2\theta + (1 - 2\mu)^2]} \quad \text{(C.8)}$$

and

$$I_3 = \frac{(1 - 2\mu)4\mu(\mu - 1)}{\pi\omega_0} \int_0^{\pi/2} \frac{d\theta \cos\theta}{[\mu^2 + (1 - 2\mu)\sin^2\theta][1 - 2(1 - 2\mu)\cos 2\theta + (1 - 2\mu)^2]} \quad \text{(C.9)}$$

The integrations in Eqs. (C.7)–(C.9) can readily be performed to obtain Eq. (60).

REFERENCES

1. N. Wax (ed.), *Noise and Stochastic Processes*, Dover, New York (1954).
2. J. L. Lebowitz and E. Rubin, *Phys. Rev.* **131**:2381 (1963); P. Résibois and H. T. Davis, *Physica (Utr.)* **30**:1077 (1964); J. L. Lebowitz and P. Résibois, *Phys. Rev.* **139**:1001 (1965); R. Kubo, *Rep. Progr. Phys.* **24**:255 (1966); R. I. Cukier and J. M. Deutch, *Phys. Rev.* **177**:240 (1969).

3. P. Mazur and I. Oppenheim, *Physica* (*Utr.*) **50**:241 (1970).
4. H. Mori, *Progr. Theor. Phys.* **33**:423 (1965).
5. J. T. Hynes, R. Kapral, and M. Weinberg, Microscopic theory of Brownian motion: Mori friction kernel and Langevin equation derivation, to be published.
6. J. M. Deutch and R. Silbey, *Phys. Rev. A* **3**:2049 (1971).
7. J. T. Hynes, Nonlinear fluctuations in master equation systems I. Velocity correlation function for the Rayleigh model, *J. Chem. Phys.* **62**:2972 (1975); J. T. Hynes, R. Kapral, and M. Weinberg, to be published.
8. M. Bishop and B. Berne, *J. Chem. Phys.* **59**:5337 (1973); J. T. Hynes, *J. Stat. Phys.* **11**:257 (1974).
9. E. L. Chang, R. M. Mazo, and J. T. Hynes, *Mol. Phys.* **28**:997 (1974).
10. J. A. McLennan, *Phys. Rev. A* **8**:1479 (1973). I. M. DeSchepper, H. Van Beyeren, and M. H. Ernst, *Physica* (*Utr.*) **75**:1 (1974); R. Kapral and M. Weinberg, *Phys. Rev. A* **8**:1008 (1973); T. Keyes and I. Oppenheim, *Phys. Rev. A* 8:937 (1973).
11. R. J. Rubin, *J. Math. Phys.* **1**:309 (1960).
12. S. Kashiwamura and E. Teramoto, *Progr. Theor. Phys. Suppl.* **23**:207 (1962); H. Nakazawa, *Progr. Theor. Phys. Suppl.* **36**:172 (1966); R. I. Cukier, *Physica* **61**:321 (1972); K. Wada, and J. Hori, *Prog. Theor. Phys.* **49**:129 (1973).
13. H. Akama and A. Siegel, *Physica* **31**:1493 (1965).
14. E. W. Montroll and K. E. Shuler, *J. Chem. Phys.* **45**:1110 (1957); B. Widom, *J. Chem. Phys.* **32**:913 (1960).
15. M. Abramowitz and I. Stegun (eds.), *Handbook of Mathematical Functions*, Dover, New York (1965).
16. R. I. Cukier and P. Mazur, *Physica* **53**:157 (1971).
17. I. Gradshteyn and I. Ryzhik, *Table of Products, Series and Integrals*, Academic Press, New York (1965).
18. R. I Cukier and K. E. Shuler, *J. Chem. Phys.* **57**:5612 (1972).
19. J. T. Hynes, R. Kapral, and M. Weinberg, Microscopic theory of Brownian motion: Non-linear Fokker-Planck equation, to be published.
20. S. A. Adelman, Fokker-Planck equations for simple non-Markovian systems, preprint.