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Initial Condition Effects for a Brownian Particle in a Harmonic Chain

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The influence of initial deviations from bath equilibrium on the motion of a Brownian particle in a harmonic chain is investigated by exact calculation. These initial condition effects, which are excluded by convention in standard projection operator treatments of relaxation processes, are found to be relatively long-lived, contrary to usual assumption. For weak, localized initial deviations from bath equilibrium these effects on the motion are small in magnitude and may be accounted for by a modified initial condition on the particle velocity. For initial deviations involving many bath particles these effects are more substantial and retention of their time dependence in the particle equation of motion is generally required.

KEY WORDS: Brownian motion; linear harmonic chain; Langevin equation; velocity correlation functions.

1. INTRODUCTION

The mechanical system of a heavy particle in a harmonic chain has been the object of extensive study, initiated by Hemmer[(1)] and Rubin,[(2),2] as a dynamical model for Brownian (B) motion. The microscopic derivation of the stochastic Langevin and Fokker–Planck equation descriptions of the particle

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[2] For a correction to Ref. 2a see Ref. 3.

motion and the behavior of the velocity correlation function have been topics of particular study.[3]

A dynamical aspect of B particle motion in a harmonic lattice which has received essentially no attention is the question of the nature of initial condition effects on the particle motion. Thus, if only the B particle velocity initially deviates from equilibrium, the average equation of motion for the B particle velocity can be found by projection operation methods[(5)] as

$$M(d\bar{V}/dt)(t) = -\int_0^t ds\, K(t-s)\bar{V}(s) \tag{1}$$

where M is the B particle mass and $K(t)$ is a friction kernel. [Under suitable limiting conditions of large mass and long times, Eq. (1) can be approximated by the damping law

$$M(d\bar{V}/dt)(t) = -\zeta\bar{V}(t); \qquad \zeta \equiv \int_0^\infty dt\, K(t) \tag{2}$$

which is the prediction of the stochastic B motion equations.] If, however, the bath particles are *not* initially in equilibrium, Eq. (1) will be amended to read

$$M(d\bar{V}/dt)(t) = I(t) - \int_0^t ds\, K(t-s)\bar{V}(s) \tag{3}$$

where the initial condition term $I(t)$ contains the explicit effects of the initial bath nonequilibrium state.

In standard projection operator approaches to the B motion problem the bath is conventionally chosen to be in equilibrium initially and $I(t)$ vanishes identically. Related assumptions are also made in a variety of relaxation problems[4] so that initial condition effects similarly vanish by construction. The effects of finite $I(t)$ have often been intuitively (and tacitly) assumed to be short-lived and thus unimportant, so that after some supposed short transient time Eq. (1) or its Markovian modification Eq. (2) would be suitable descriptions. We have recently shown,[(8)] however, that for a large B particle in a fluid, initial condition effects are rather long-lived, in contradiction with this assumption. This study was not strictly dynamical, however, since the predictions of macroscopic hydrodynamics were invoked in the analysis. In the present paper we investigate the lifetimes and effects on the particle motion of the initial condition term $I(t)$ by exact dynamical calculations for a B particle in a linear oscillator chain when there are initial deviations from equilibrium in the B particle neighborhood. We again find that initial

[3] For examples of the extensive literature see, in addition to the references cited in this paper, the references cited by Refs. 4, 10 and 12.

[4] See, e.g., Refs. 6. For additional information on initial condition effects for the Boltzmann equation regime see Refs. 7.

condition effects are relatively long-lived, although their numerical importance is small for a sufficiently heavy B particle and weak disturbances.

In Section 2 we present the formal description of the model and initial condition effects on the B particle motion. Explicit results and numerical computations are presented for single-bath-particle and collective-bath-particle initial condition effects in Sections 3 and 4, respectively. Some mathematical details are relegated to the appendices.

2. GENERAL FORMULATION

2.1. B Particle Equations of Motion

The Hamiltonian for a Brownian particle of mass M linearly coupled to a linear harmonic oscillator chain with periodic boundary conditions and nearest-neighbor interactions is given by

$$H = \frac{P^2}{2M} + \sum_{|j|=1}^{N} \frac{p_j^2}{2m} + \frac{\alpha}{2} \sum_{\substack{j=-N \\ (\neq 0,1)}}^{N} (q_j - q_{j-1})^2 + \frac{\alpha}{2} [(Q - q_1)^2 + (Q - q_{-1})^2] \tag{4}$$

where $(p_j = mv_j, q_j)$ are the momenta and positions (relative to equilibrium positions) of the $2N$ bath particles of mass m, while $P = MV$ and Q denote the momentum and (relative) position of the B particle. Here $\alpha = m\omega_0{}^2/4$, where ω_0 is the fundamental frequency of the lattice. In the following we will only consider results for this model in the infinite lattice limit $N \to \infty$.

The linear equations of motion for the B particle associated with Eq. (4) have been previously solved[9] as an initial value problem with the result expressed in terms of the natural time scale for the system $\tau = \omega_0 t$ as

$$V(\tau) = \sum_j \{G_j(\tau)v_j(0) + \omega_0 \dot{G}_j(\tau) q_j(0)\} \tag{5}$$

with $v_0(\tau) \equiv V(\tau)$ and $q_0(\tau) \equiv Q(\tau)$. The coefficients $G_j(\tau)$ and $\dot{G}_j(\tau)$ are related to the velocity correlation functions ($\beta^{-1} = kT$)

$$G_j(\tau) = \beta m_j \langle v_j V(\tau) \rangle, \tag{6}$$

and

$$\omega_0 \dot{G}_j(\tau) = \omega_0\, dG_j(\tau)/d\tau = -\beta \langle F_j V(\tau) \rangle \tag{7}$$

where F_j is the force on particle j, as can be seen by multiplying Eq. (5) by v_j and forming the canonical ensemble equilibrium average, here denoted by angular brackets. An explicit form for $G_j(\tau)$ has been derived by Kashiwamura,[9] Fujiwara *et al.*,[10] and Cukier.[11] For values of the mass ratio $\mu = m/M \leqslant 1$ one has

$$G_j(\tau) = [1 + (\mu - 1)^{(1-\delta_{j0})}] \times [J_{2|j|}(\tau) - 2(\mu - 1) \sum_{p \geq 1}^{\infty} (1 - 2\mu)^{p-1} J_{2|j|+2p}(\tau)] \quad (8)$$

where δ_{j0} is the Kronecker delta and J denotes a Bessel function of integer order:

$$J_{2j}(\tau) = (2/\pi) \int_0^{\pi/2} d\theta \cos(\tau \sin\theta) \cos(2j\theta) \quad (9)$$

Expressions for $G_j(\tau)$ are also available[9,11] for $\mu > 1$ and exhibit undamped oscillations due to a light impurity localized mode.[12]

The basic starting point for our subsequent analysis of initial condition effects will be the *exact* "generalized Langevin equation" for the B particle in a harmonic lattice derived by Deutch and Silbey[5] by projection operator methods as

$$F(t) = M(d/dt)V(t) = F^{\dagger}(t) - \int_0^t ds\, K(t - s)V(s) \quad (10)$$

or

$$F(\tau) = m(\omega_0/\mu)(d/d\tau)V(\tau) = F^{\dagger}(\tau) - \omega_0^{-1} \int_0^{\tau} ds\, K(\tau - s)V(s) \quad (11)$$

in terms of the reduced time $\tau = \omega_0 t$ which we henceforth employ. In Eq. (11), $F^{\dagger}(\tau)$ is the M-independent force exerted by the bath oscillators at time τ on the *fixed* B particle and the M-independent friction kernel

$$K(\tau) = \beta\langle FF^{\dagger}(\tau)\rangle \quad (12)$$

with $\beta = (kT)^{-1}$, is the equilibrium time correlation of this force. The kernel $K(\tau)$ also governs the time development of the normalized B particle velocity correlation function $G_0(\tau) = (M\beta)\langle VV(\tau)\rangle$ according to

$$dG_0(\tau)/d\tau = -(\mu/m\omega_0^2) \int_0^{\tau} ds\, K(\tau - s)G_0(s) \quad (13)$$

For nonquadratic interaction potentials, the time development of the "random" force $F^{\dagger}(\tau)$ and $K(\tau)$ is governed by M-dependent Mori-projection operator dynamics. In this more general case the reduction to fixed particle quantities is only approximate.[8]

For the present model $K(\tau)$ has been evaluated by several authors[13] as

$$K(\tau) = (\zeta\omega_0/2)[J_0(\tau) + J_2(\tau)] = \zeta\omega_0 J_1(\tau)/\tau \tag{14}$$

with the friction constant given by

$$\zeta = \omega_0^{-1}\int_0^\infty d\tau\, K(\tau) = m\omega_0 \tag{15}$$

For asymptotically long times one finds the slow decay[14] $K(\tau) \sim \tau^{-3/2}\cos(\tau - 3\pi/4)$. It is important to note for our further considerations that the strict validity of the Markovian result Eq. (2) requires a complete separation of time scales for correlations associated with a slowly moving B particle and the bath in the presence of the *fixed* particle, e.g., $G_0(\tau)$ and $K(\tau)$, respectively. In units reduced by ω_0, the characteristic time of the former is $O(\mu^{-1})$ for small μ (cf. Section 3). The long lifetime of $K(\tau)$ will generally preclude this complete time-scale separation and results in deviations from the exponential decay in Eq. (2).

2.2. Initial Condition Effects

With an average over the initial distribution of the entire system denoted by a superior bar, the average equation of motion for the B particle is obtained from Eq. (11) as

$$\begin{aligned}\bar{F}(\tau) = \frac{\zeta}{\mu}\frac{d}{d\tau}\bar{V}(\tau) &= \overline{F^\dagger(\tau)} - \omega_0^{-1}\int_0^\tau ds\, K(\tau - s)\bar{V}(s) \\ &\equiv I(\tau) + \bar{F}_{\mathrm{fr}}(\tau)\end{aligned} \tag{16}$$

where the initial condition term $I(\tau) \equiv \overline{F^\dagger(\tau)}$ and we have defined the average frictional force $\bar{F}_{\mathrm{fr}}(\tau)$ due to the *motion* of the B particle by the second line. The explicit dependence of the average velocity $\bar{V}(\tau)$ on the initial velocity $\bar{V}(0) \equiv V_0$ and $I(\tau)$ is given by

$$\bar{V}(\tau) = V_0 G_0(\tau) + (\mu/\zeta)\int_0^\tau ds\, G_0(\tau - s)I(s) \tag{17}$$

as is easily verified from Eqs. (16) and (13).[5] Equations (16) and (17) thus describe the B particle motion in terms of $I(\tau)$.

We can now express $I(\tau)$ in terms of the initial deviations $\bar{v}_j(0)$ and $\bar{q}_j(0)$ from bath equilibrium as follows. First the general solution Eq. (5) for $V(\tau)$ is differentiated with respect to τ. Then the generalized Langevin equation (11) is introduced for the resulting time derivatives of $V(\tau)$ in the correlation

[5] The exact generalized Fokker–Planck equation for the present model[15] also yields Eqs. (16) and (17).

functions $G_j(\tau)$ and $\dot{G}_j(\tau)$, Eqs. (6) and (7). For example, $G_j(\tau)$ satisfies

$$(\zeta/\mu)\dot{G}_j(\tau) = \beta\langle p_j F^\dagger(\tau)\rangle - \omega_0^{-1}\int_0^\tau ds\, K(\tau - s)G_j(s) \tag{18}$$

with a similar result for $\ddot{G}_j(\tau)$. Finally, an average over an initial system distribution yields the equation of motion (16) with $I(\tau)$ given as the sum of individual particle contributions:

$$\begin{aligned} I(\tau) = \overline{F^\dagger(\tau)} &= \beta \sum_j [\langle p_j F^\dagger(\tau)\rangle \bar{v}_j(0) - \langle F_j F^\dagger(\tau)\rangle \bar{q}_j(0)] \\ &\equiv \sum_j [\alpha_j(\tau)\bar{v}_j(0) + \beta_j(\tau)\bar{q}_j(0)], \qquad \alpha_0 = 0 \end{aligned} \tag{19}$$

For $j \neq 0$, $\beta_j = \omega_0\dot{\alpha}_j$; for $j = 0$, $\beta_j = -K(\tau)$, Eq. (14). Thus the dynamics of initial condition effects are determined by the correlation functions of the *fixed* particle force $F^\dagger(\tau)$ and the momentum of, or force on, bath particle j. We also note that, since $I(\tau)$ is thus *independent* of μ, the previously mentioned persistent oscillatory behavior for $\mu > 1$ which precludes an approach to equilibrium is due only to the frictional term in Eq. (16), i.e., only $\bar{F}_{\text{fr}}(\tau)$ is undamped oscillatory.

It remains to evaluate the correlation functions $\alpha_j(\tau)$ and $\beta_j(\tau)$ in $I(\tau)$. This can be most readily accomplished by solving Eq. (18) for $\alpha_j(\tau) = \beta\langle p_j F^\dagger(\tau)\rangle$ in terms of $G_j(\tau)$ and $K(\tau)$, which are known by Eqs. (8) and (14), and then finding $\beta_j(\tau)$ as $\beta_j(\tau) = \omega_0\dot{\alpha}_j(\tau)$. Since $\alpha_j(\tau)$ is independent of μ, we may set $\mu = 1$ in Eq. (8) for convenience and find, using standard Bessel function identities,[14] the explicit results

$$\begin{aligned} \alpha_j(\tau) &= 2\zeta|j|J_{2|j|}(\tau)/\tau, \qquad && j \neq 0 \\ &= 0, && j = 0 \end{aligned} \tag{20}$$

and

$$\begin{aligned} \beta_j(\tau) &= \tfrac{1}{4}\zeta\omega_0[J_{2|j|-2}(\tau) - J_{2|j|+2}(\tau)], \qquad && j \neq 0 \\ &= -\zeta\omega_0 J_1(\tau)/\tau, && j = 0 \end{aligned} \tag{21}$$

Both $\alpha_j(\tau)$ and $\beta_j(\tau)$ for small j are displayed in Fig. 1 and show damped oscillations as the effect of the equilibrium fluctuation in the velocity of or force on bath particle j is experienced by the fixed B particle. As both functions decay asymptotically[14] for long times as $\sim$(trigonometric function) $\times\ \tau^{-3/2}$, the initial condition term $I(\tau)$ will generally be *long-lived* on the τ time scale and, if only small j contribute, will be of essentially the *same* lifetime as the friction kernel $K(\tau)$, Eq. (14). This is the same general phenomenon we have previously found[8] for the case of an immersed B particle in a fluid.

In the following sections we investigate the explicit effects of initial conditions on the average B particle motion. For brevity, we limit our further

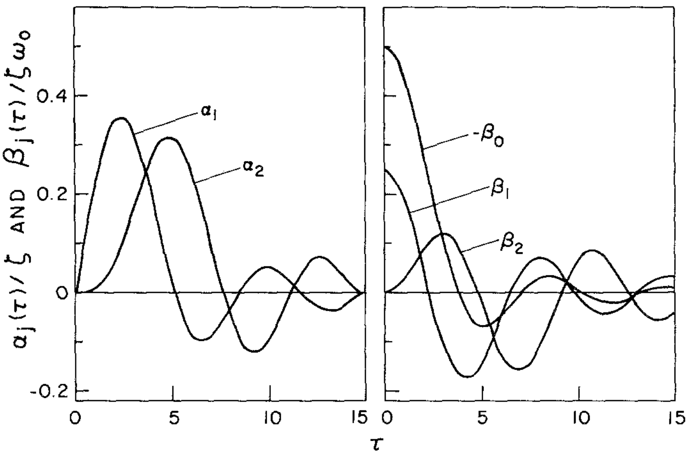

Fig. 1. $\alpha_j(\tau)/\zeta$ and $\beta_j(\tau)/\zeta\omega_0$ versus τ for small j values.

considerations to initial deviations from equilibrium in momentum but not position, i.e., we henceforth assume that $\bar{q}_j(0) = 0$ for all j.

We note here that initial condition effects also occur as corrections to the standard Fokker–Planck equation and are discussed elsewhere.[15]

3. SINGLE-PARTICLE INITIAL CONDITION EFFECTS

In this section we explicitly examine initial condition effects on the B particle motion for the case where, in addition to the B particle velocity, only the average velocity of a *single* bath particle j deviates initially from equilibrium. We focus attention on the calculation of the average quantities $\bar{V}^{(j)}(\tau)$, $I^{(j)}(\tau)$, and $\bar{F}_{fr}{}^{(j)}(\tau)$ for this case. Although we will present numerical calculations for only the case $j = 1$, we obtain here results for general j which we will employ in Section 4.

The average B particle velocity $\bar{V}^{(j)}(\tau)$ is most easily computed by averaging Eq. (5) over the initial system distribution to find

$$\bar{V}^{(j)}(\tau) = V_0[G_0(\tau) + a_j G_j(\tau)] \tag{22}$$

where we have defined $a_j \equiv \bar{v}_j(0)/\bar{V}(0) = \bar{v}_j(0)/V_0$ to gauge the magnitude of the initial deviation of bath particle j. Except for the special values $\mu = 1$ or $1/2$, the Bessel function series (8) for the correlation functions $G_j(\tau)$ is inconvenient for calculation. A more useful integral representation when

$\mu \leqslant 1$ is available, however, as[11]

$$G_j(\tau) = (2/\pi)\mu^{(1-\delta_{j0})} \int_0^{\pi/2} d\theta \cos(\tau \sin \theta) A(\mu, \theta) \times [\mu \cos^2 \theta \cos(2|j|\theta) - (1 - \mu) \sin \theta \cos \theta \sin(2|j|\theta)] \tag{23}$$

where we have defined

$$A(\mu, \theta) = [\mu^2 + (1 - 2\mu) \sin^2 \theta]^{-1} \tag{24}$$

so that Eq. (22) can be written as

$$\bar{V}^{(j)}(\tau) = \left(\frac{2\mu V_0}{\pi}\right) \int_0^{\pi/2} d\theta \cos(\tau \sin \theta) A(\mu, \theta) C_j(\mu, \theta) \tag{25}$$

where

$$C_j(\mu, \theta) = [1 + a_j \mu \cos(2|j|\theta)] \cos^2 \theta - a_j(1 - \mu) \sin \theta \cos \theta \sin(2|j|\theta) \tag{26}$$

For the initial condition term it follows from Eqs. (19) and (20) that $I^{(j)}(\tau)$ is given by

$$\begin{aligned} I^{(j)}(\tau) &= 2\zeta V_0 a_j |j| J_{2|j|}(\tau)/\tau \\ &= (4\zeta V_0 a_j |j|/\pi\tau) \int_0^{\pi/2} d\theta \cos(\tau \sin \theta) \cos(2|j|\theta) \end{aligned} \tag{27}$$

where we have used Eq. (9) for $J_{2|j|}(\tau)$. With the aid of the relation $b \cos(bx) = d \sin(bx)/dx$ and an integration by parts, Eq. (27) can be expressed as

$$I^{(j)}(\tau) = (\zeta V_0)(2a_j/\pi) \int_0^{\pi/2} d\theta \sin(\tau \sin \theta) \cos \theta \sin(2|j|\theta) \tag{28}$$

The frictional force

$$\bar{F}_{\mathrm{fr}}^{(j)}(\tau) = (\zeta/\mu)\, d\bar{V}^{(j)}(\tau)/d\tau - I^{(j)}(\tau)$$

can now be found from Eqs. (16), (25), and (28) as

$$\bar{F}_{\mathrm{fr}}^{(j)}(\tau) = -(\zeta V_0)(2/\pi) \times \int_0^{\pi/2} d\theta\, [\sin(\tau \sin \theta)] A(\mu, \theta)(\cos \theta) D_j(\mu, \theta) \tag{29}$$

where

$$D_j(\mu, \theta) = (\sin \theta \cos \theta)[1 + a_j \mu \cos(2|j|\theta)] + \mu a_j(\mu - \sin^2 \theta) \sin(2|j|\theta) \tag{30}$$

If we specialize now to the nearest-neighbor case $j = 1$, define $a_1 \equiv a$, and include the a dependence in the notation, we find that $I^{(1)}(\tau; a)$ is self-evident from Eq. (28), while $\bar{V}^{(1)}(\tau; a)$ and $\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a)$ are given by Eqs. (25) and (29), with the expressions for $C_1(\mu, \theta)$ and $D_1(\mu, \theta)$ given, respectively, by

$$C_1(\mu, \theta) = (\cos^2 \theta)(1 + a\mu - 2a \sin^2 \theta) \tag{31}$$

and

$$D_1(\mu, \theta) = (\sin \theta \cos \theta)(1 + a\mu + 2a\mu^2 - 4a\mu \sin^2 \theta) \tag{31a}$$

where standard trigonometric identities have been employed.

Unless μ is small, there is essentially no time scale separation; the initial condition term is as long-lived as the frictional force, and both, as well as the velocity, show damped oscillatory behavior. For example, for $\mu = 1/2$, it follows from Eqs. (27)–(31a) that

$$\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a) = -[1 + a + 2a(d^2/d\tau^2)][2I^{(1)}(\tau; a)/a]$$

and from Eqs. (25), (27), (9), and (14) that

$$\bar{V}^{(1)}(\tau; a) = (V_0/\tau)[2J_1(\tau) + 3aJ_3(\tau)]$$

Here we focus on the small-μ regime, where the velocity and force (after an initial transient period) are slowly decaying in approximately exponential fashion,[16] as in stochastic theory. Initial condition effects on the velocity are displayed in Fig. 2, where the added force on the B particle due to $I^{(1)}(\tau; a)$ (a "pull" due to the bath particle initial velocity on the right) leads to a small increased (over $a = 0$) velocity of the particle. The effect is long-lived, but is small in magnitude for a massive B particle if a is small. This magnitude is of order μa [cf. Eq. (36)], so if $\mu a \sim 1$, the initial condition effect will be appreciable even for small μ.

In Fig. 3 we compare the initial condition term $I^{(1)}(\tau; a)$ with the deviation

$$D^{(1)}(\tau; a) = -[\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a) + \zeta \bar{V}^{(1)}(\tau; a)] \tag{32}$$

of the frictional force from time local friction due to the finite lifetime of $K(\tau)$. These are comparable in the initial time regime, but $D^{(1)}(\tau; a)$ persists well past the lifetime of $I^{(1)}(\tau; a)$, since the former is associated with a moving B particle and the latter with a fixed particle. Past an initial period $\tau \leqslant 5$, both terms are roughly 1–10% of the actual frictional force $\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a)$ for small a and μ. Our results conform with those of Cukier *et al.*[16] and indicate that finite lifetime effects are typically numerically small even when more stringent formal conditions for their neglect are not strictly satisfied.

It is instructive to consider alternate expressions for the average velocity and frictional force for finite a in terms of the corresponding quantities when

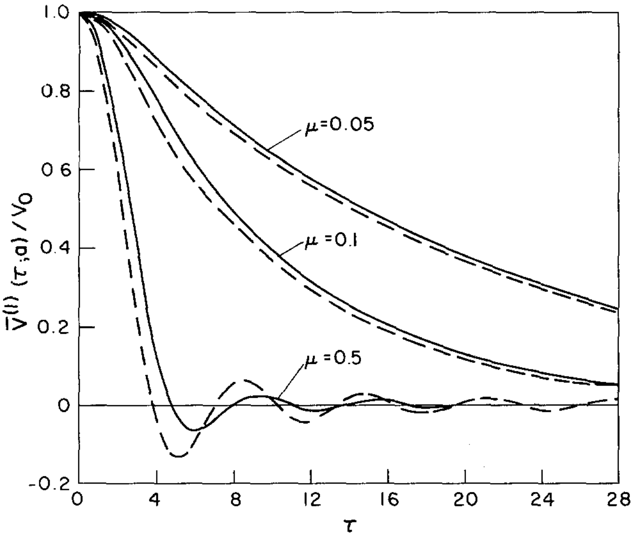

Fig. 2. Particle velocity $\bar{V}^{(1)}(\tau; a)/V_0$ (——) versus τ for $a = 0.5$ and several μ values. (– – –) The velocity with no initial condition effects, $\bar{V}(\tau; 0)/V_0$, Eq. (35).

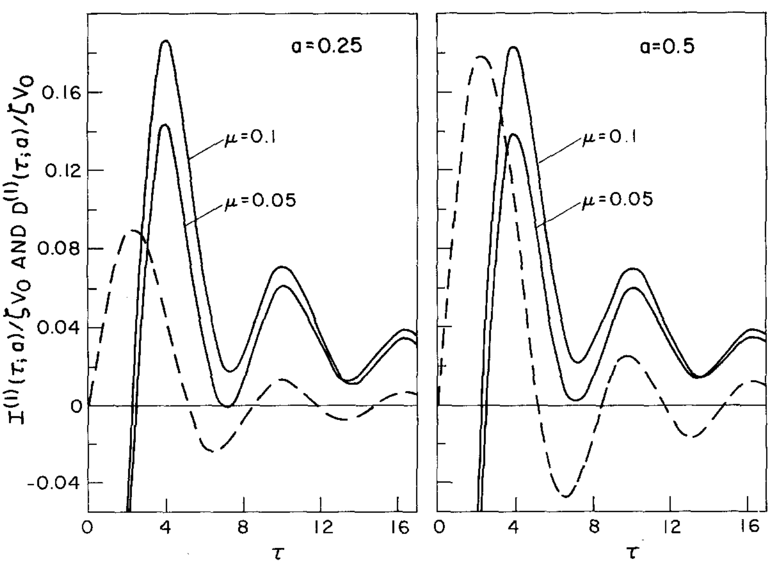

Fig. 3. Initial condition term $I^{(1)}(\tau; a)/\zeta V_0$ (– – –) and deviation from time local friction $D^{(1)}(\tau; a)/\zeta V_0$ (——) versus τ for several a and μ values. $D^{(1)}(\tau = 0; a) = -\zeta V_0$.

$a = 0$ (no initial condition effects). It is shown in Appendix A that Eqs. (25) and (29) for $j = 1$ can be written as

$$\bar{V}^{(1)}(\tau; a) = \bar{V}(\tau; 0) + \frac{\mu a}{1 - 2\mu}[\bar{V}(\tau; 0) - 2V_0\tau^{-1}J_1(\tau)] \tag{33}$$

and

$$\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a) = \bar{F}_{\mathrm{fr}}(\tau; 0) + \frac{\mu a}{1 - 2\mu}[\bar{F}_{\mathrm{fr}}(\tau; 0) + 4\zeta V_0\tau^{-1}J_2(\tau)] \tag{34}$$

with the unperturbed average particle velocity and frictional force given by

$$\bar{V}(\tau; 0) \equiv G_0(\tau)V_0 \tag{35}$$

and $\bar{F}_{\mathrm{fr}}(\tau; 0) = (\zeta/\mu)(d/d\tau)\bar{V}(\tau; 0)$ from Eqs. (16) and (17). For small μ, $\bar{V}(\tau; 0)$ $[\propto G_0(\tau)]$ will be slowly decaying on the τ time scale, and for times long compared to the lifetime of $J_1(\tau)/\tau$ $[\propto K(\tau)]$ one has the approximation

$$\bar{V}^{(1)}(\tau; a) \simeq [1 + \mu a]\bar{V}(\tau; 0) \tag{36}$$

and similarly,

$$\bar{F}_{\mathrm{fr}}^{(1)}(\tau; a) \simeq (1 + \mu a)\bar{F}_{\mathrm{fr}}(\tau; 0) \tag{37}$$

Equations (36) and (37) are equivalent to a *modified* initial condition on the B particle velocity $\bar{V}(0) = V_0 \to (1 + \mu a)V_0$, due to the added velocity arising from the initial condition effect and applicable after an initial transient period. The origin of this effect is most clearly seen from the general result (17). For small μ the separation of time scales for a fixed and a moving B particle yields the approximate result

$$\bar{V}(\tau; a) \simeq \bar{V}(\tau; 0) + (\mu/\zeta V_0)\bar{V}(\tau; 0)\int_0^\infty ds\, I(s; a) \tag{38}$$

which for the present case with Eq. (27) yields again Eq. (36),

$$\bar{V}^{(1)}(\tau; a) \simeq (1 + \mu a)\bar{V}(\tau; 0) \tag{39}$$

for times long compared to the lifetime of $I^{(1)}(\tau; a)$. The exact velocity and the approximate velocity with modified initial condition are compared favorably in Table I.

In the formal weak coupling limit ($\equiv$Lim)

$$\mu \to 0, \quad \tau \to \infty, \qquad \mu\tau = \text{fixed and } O(1) \tag{40}$$

which enforces *strict* time scale separation, it is well known that $\bar{V}(\tau; 0)$ is exponential,[2,11] as in the stochastic theory:

$$\mathrm{Lim}\ \bar{V}(\tau; 0) = V_0 \exp(-\mu\tau) \tag{41}$$

Table I. Comparison of Exact B Particle Velocity $\bar{V}^{(1)}(\tau;a)/V_0$ and Approximate Velocity with Modified Initial Condition, Eq. (36), for the Single-Particle Case

	$a = 0.25, \mu = 0.1$		$a = 0.5, \mu = 0.05$		$a = 0.5, \mu = 0.1$	
τ	Exact	Approx.	Exact	Approx.	Exact	Approx.
0	1.000	1.025	1.000	1.025	1.000	1.050
4	0.747	0.742	0.882	0.878	0.771	0.762
8	0.475	0.474	0.711	0.711	0.488	0.485
12	0.302	0.299	0.576	0.574	0.312	0.307
16	0.195	0.194	0.467	0.466	0.200	0.198
20	0.124	0.124	0.378	0.377	0.128	0.126
24	0.079	0.078	0.306	0.305	0.082	0.080
28	0.051	0.051	0.248	0.248	0.052	0.052

In the same limit we find from Eq. (33) that

$$\operatorname{Lim} \bar{V}^{(1)}(\tau; a) = V_0 \exp(-\mu\tau) \tag{42}$$

unless a is very large $[=O(\mu^{-1})]$. Thus transient initial condition effects are completely suppressed since, although their lifetime is long on the fixed-particle time scale τ, they are both short-lived on the moving-particle time scale $(\sim\mu^{-1})$ [as is the friction kernel $K(\tau)$] and negligible in magnitude when μ is made arbitrarily small [cf. Eq. (17)].

On the other hand, Rubin[2a,3] has shown that for finite μ [lifetime of $K(\tau)$ nonnegligible]

$$G_0(\tau) = \bar{V}(\tau; 0)/V_0 = e^{-\tau/Q} + Q^{-1}[\Delta(\tau) + e^{-\tau/Q}] \tag{43}$$

is correct to first order in $Q^{-1} = \mu/(1 - \mu)$, where $\Delta(\tau)$ is a certain combination of Bessel functions. It then follows from Eq. (33) that when $a > Q^{-1}$,

$$\bar{V}^{(1)}(\tau; a)/V_0 = e^{-\tau/Q} + Q^{-1}[\Delta(\tau) + (1 + a)e^{-\tau/Q} - a\tau^{-1}J_1(\tau)] \tag{44}$$

is correct to order Q^{-1}. For nonnegligible a the initial condition correction can be comparable to the contribution of the finite lifetime of $K(\tau)$ to the deviation of $\bar{V}^{(1)}(\tau; a)$ from the decay $\exp(-\tau/Q)$.

4. MANY-PARTICLE INITIAL CONDITION EFFECTS

In this section we examine initial condition effects when the average velocities of the B particle and many bath particles initially deviate from their zero equilibrium values. Integral representations for the average velocity, frictional force, and initial condition terms are obtained for this case by summations over all j (noting that $a_0 = 1$) of the j-dependent integrals given in Eqs. (25), (28), and (29).

These sums can be evaluated for several choices of $a_j = \bar{v}_j(0)/V_0$. Here we focus on the special but interesting case where

$$a_j = a^{|j|}; \qquad |j| \geqslant 1 \tag{45}$$

with $|a| < 1$. If we take $a = \exp(-d/l)$, where d is the average interparticle spacing, then $a^{|j|} = \exp(-d|j|/l)$ corresponds to a *spatial* exponential decay in magnitude of initial deviations from velocity equilibrium centered at the B particle. The characteristic decay length in units of d is $L \equiv l/d$, so that $a = \exp(-1/L)$.

With the choice Eq. (45) one requires the sums[17]

$$\sum_{j=1}^{\infty} a^j \sin(2j\theta) = a \sin(2\theta)\, B(a, \theta) \tag{46}$$

and

$$\sum_{j=1}^{\infty} a^j \cos(2j\theta) = [a \cos(2\theta) - a^2] B(a, \theta) \tag{47}$$

where $B(a, \theta) = [(1 - a)^2 + 4a \sin^2 \theta]^{-1}$. With these summations in hand we obtain, after some algebra,

$$\begin{aligned} \bar{V}(\tau; a) = {} & V_0(2\mu/\pi)[(1 - a)^2 + (1 - a)2\mu a] \\ & \times \int_0^{\pi/2} d\theta \cos(\tau \sin\theta)(\cos^2\theta) A(\mu, \theta) B(a, \theta) \end{aligned} \tag{48}$$

for the velocity;

$$\begin{aligned} \bar{F}_{\mathrm{fr}}(\tau; a) = {} & -(\zeta V_0)(2/\pi) \int_0^{\pi/2} d\theta \sin(\tau \sin\theta)(\sin\theta \cos^2\theta) A(\mu, \theta) \\ & \times [(1 - 2\mu) + 2\mu(1 - a + 2\mu a) B(a, \theta)] \end{aligned} \tag{49}$$

for the frictional force; and

$$I(\tau; a) = \zeta V_0(8a/\pi) \int_0^{\pi/2} d\theta \sin(\tau \sin\theta)(\sin\theta \cos^2\theta) B(a, \theta) \tag{50}$$

for the initial condition term, which is plotted in Fig. 4 for several decay lengths L.

As in Section 3, unless μ is small, $\bar{F}_{\mathrm{fr}}(\tau; a)$ and $I(\tau; a)$ will decay on the same time scale. For example, for $\mu = 1/2$, it follows from Eqs. (49) and (50) that $I(\tau; a) = -a\bar{F}_{\mathrm{fr}}(\tau; a)$. For small μ, initial condition effects are now more substantial than in the single-particle case since $I(\tau; a)$ is larger in magnitude and longer lived. These are displayed in Figs. 5 and 6 for the velocity

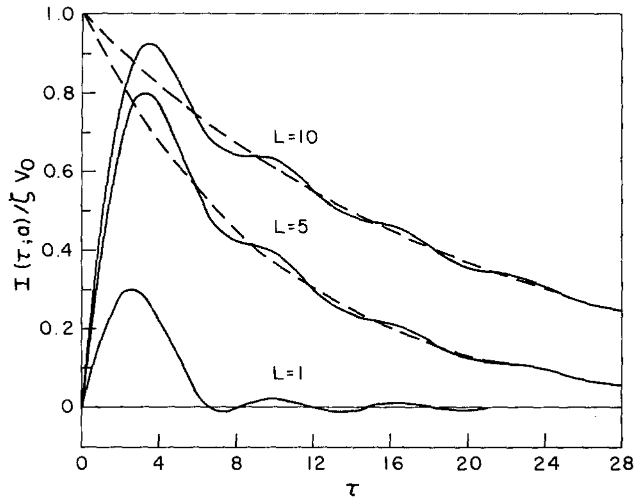

Fig. 4. Initial condition term $I(\tau; a)/\zeta V_0$ (——) versus τ for several values of the scaled decay length L. The corresponding a values are 0.368, 0.819, and 0.905. (– – –) $\exp(-\kappa\tau)$, Eq. (53).

$\bar{V}(\tau; a)$ and the deviation $D(\tau; a) = -[\bar{F}_{fr}(\tau; a) + \zeta\bar{V}(\tau; a)]$ from time local friction. When L is sufficiently large, $I(\tau; a)$ evidently dominates $D(\tau; a)$; this suggests that one may neglect the lifetime of $K(\tau)$ and approximate $G_0(\tau)$ by $\exp(-\mu\tau)$ [Eqs. (35) and (41)] in Eq. (17) to obtain in this

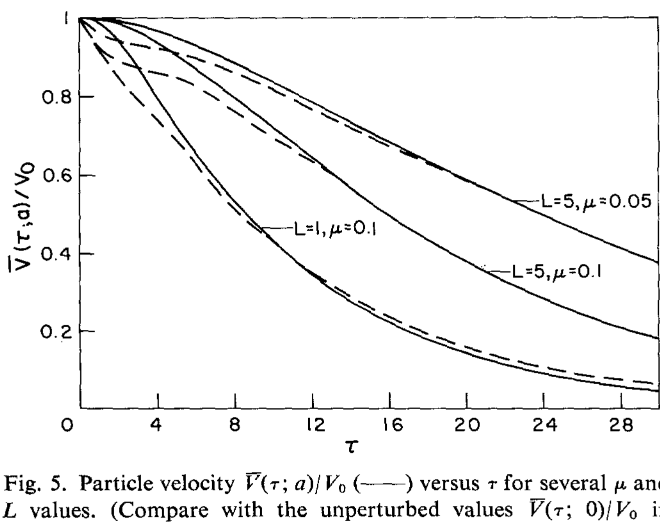

Fig. 5. Particle velocity $\bar{V}(\tau; a)/V_0$ (——) versus τ for several μ and L values. (Compare with the unperturbed values $\bar{V}(\tau; 0)/V_0$ in Fig. 2.) (– – –) The approximation (50a).

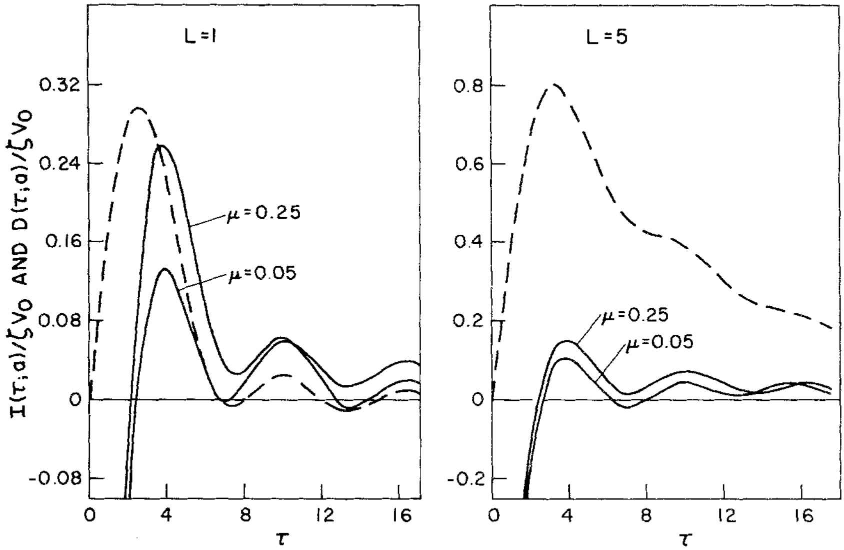

Fig. 6. Initial condition term $I(\tau; a)/\zeta V_0$ (– – –) and deviation from time local friction $D(\tau; a)/\zeta V_0$ (——) versus τ for several μ and L values. $D(\tau = 0; a) = -\zeta V_0$.

regime (large L, small μ)

$$\bar{V}(\tau; a) \simeq V_0 e^{-\mu\tau} + (\mu/\zeta)\int_0^\tau ds\, e^{-\mu(\tau-s)} I(s; a), \qquad \tau \gg 1 \tag{50a}$$

which retains the time dependence of $I(\tau; a)$. This is plotted in Fig. 5.

We can also discuss initial condition effects on the basis of alternate representations of Eqs. (48) and (50). In Appendix B we show that the initial condition term (50) can also be written as

$$I(\tau; a) = \zeta \frac{V_0}{2\kappa}\int_{-\infty}^{\infty} ds \frac{J_2(\tau - s)}{\tau - s} e^{-\kappa|s|} \tag{51}$$

where[6]

$$\kappa = (1 - a)(4a)^{-1/2} = \sinh(1/2L) > 0$$

If κ is very large (a, L small), corresponding to rapid spatial decay of initial nonequilibrium effects, the exponential in Eq. (51) is strongly peaked at $s = 0$ and one has, as $a, L \to 0$,

$$\begin{aligned} I(\tau; a) &\simeq \tau^{-1} J_2(\tau)(\zeta V_0/2\kappa)\int_{-\infty}^{\infty} ds\, e^{-\kappa|s|} \\ &\simeq (\zeta V_0) 4a J_2(\tau)/\tau \end{aligned} \tag{52}$$

[6] One can easily show using Bessel function bounds[14] that $|I(\tau; a)| \leqslant (\zeta V_0/\sqrt{8}\kappa^2)$.

which is simply the contribution from the next-nearest neighbors of the B particle, $|j| = 1$ [compare Eq. (27)]. If, however, κ is very small ($a \sim 1$, large L), a large portion of the chain initially departs from equilibrium. Naturally $I(\tau; a)$ is then very slowly decaying rather than a short-lived transient. In Appendix B we show that as $\kappa \to 0$ ($\kappa > 0$),

$$I(\tau; a) \simeq \zeta V_0 e^{-\kappa\tau} \simeq \zeta V_0 e^{-\tau/2L}, \qquad \tau \gg 1 \tag{53}$$

which is a decay on a *macroscopic* time scale (cf. Fig. 4).

It is also shown in Appendix B that the average particle velocity is related to $\bar{V}(\tau; 0)$, the unperturbed average velocity with $a = 0$, by

$$\bar{V}(\tau; a) = \tfrac{1}{2}(\kappa + \mu\sqrt{a}) \int_0^\infty ds\, \bar{V}(s; 0) e^{-\kappa|\tau - s|} + \tfrac{1}{2} V_0 e^{-\kappa\tau} \tag{54}$$

For small μ, unless κ is very small [$= O(\mu)$], the slow decay of $\bar{V}(s; 0)$ compared to that of the relatively strongly peaked factor $\exp(-\kappa|\tau - s|)$ yields the approximate result

$$\begin{aligned} \bar{V}(\tau; a) &\simeq \tfrac{1}{2}(\kappa + \mu\sqrt{a}) \bar{V}(\tau; 0) \kappa^{-1} (2 - e^{-\kappa\tau}) + \tfrac{1}{2} V_0 e^{-\kappa\tau} \\ &= [1 + (\mu/\kappa)\sqrt{a}] \bar{V}(\tau; 0), \qquad \kappa\tau \gg 1 \end{aligned} \tag{55}$$

which, as in Section 3, is equivalent to a modified initial condition for the velocity and is identical with the general approximate result Eq. (38) applied to the present case with $\int_0^\infty ds\, I(s; a) = V_0 \zeta \sqrt{a}/\kappa$ from Eq. (51). General adherence to Eq. (55) is displayed for small μ in Table II.

The behavior of the average B particle velocity can be examined in the weak coupling limit, Eq. (40), by inserting the velocity correlation function representation[10]

Table II. Comparison of Exact B Particle Velocity $\bar{V}(\tau; a)/V_0$ and Approximate Velocity with Modified Initial Condition, Eq. (55), for the Many-Particle Case

	$L = 1, \mu = 0.05$		$L = 2, \mu = 0.05$		$L = 3, \mu = 0.025$	
τ	Exact	Approx.	Exact	Approx.	Exact	Approx.
0	1.000	1.058	1.000	1.154	1.000	1.126
4	0.899	0.907	0.932	0.989	0.974	1.044
8	0.738	0.734	0.799	0.800	0.916	0.942
12	0.599	0.592	0.663	0.646	0.846	0.849
16	0.486	0.481	0.543	0.525	0.773	0.767
20	0.393	0.389	0.442	0.425	0.702	0.692
24	0.318	0.315	0.359	0.343	0.636	0.624
28	0.258	0.256	0.291	0.279	0.576	0.564

$$G_0(\tau) = \bar{V}(\tau; 0)/V_0$$
$$= (\gamma/2\mu) \int_{-\infty}^{\infty} ds\, [J_1(\tau - s)/(\tau - s)] e^{-\gamma|s|} \tag{56}$$

where $\gamma^2 = \mu^2/(1 - 2\mu)$, into Eq. (54). Under the weak coupling limit one again finds an exponential decay

$$\text{Lim}\ \bar{V}(\tau; a) = V_0 e^{-\mu|\tau|}, \qquad \kappa/\mu > 1 \tag{57}$$

so that initial condition effects are suppressed, as in the single-particle case, Eq. (42).

5. CONCLUDING REMARKS

In this paper we have considered the previously unexamined effects of local nonequilibrium bath initial states on the motion of a B particle in a linear chain by exact dynamical calculation. The resulting initial condition effects were found to be relatively long-lived, as is the friction kernel, but require a large initial deviation from equilibrium to exert a numerically pronounced influence on the motion. For a sufficiently massive B particle and weak initial deviations these effects can be approximately accounted for by a shift in the initial condition of the particle velocity. For extensive initial deviation from equilibrium the long-lived time dependence of the initial condition term must be retained in the particle equation of motion, while the finite lifetime of the friction kernel may be simultaneously neglected for a heavy particle.

APPENDIX A

Here we outline the derivation of Eqs. (33) and (34). It is easily seen from Eqs. (25) and (31) that $\bar{V}^{(1)}(\tau; a)$ satisfies

$$\bar{V}^{(1)}(\tau; a) = (1 + a\mu)\bar{V}(\tau; 0) + 2ad^2\bar{V}(\tau; 0)/d\tau^2 \tag{A.1}$$

where the unperturbed velocity $\bar{V}(\tau; 0)$, Eq. (35), is given by

$$\bar{V}(\tau; 0) = V_0(2\mu/\pi) \int_0^{\pi/2} d\theta \cos(\tau \sin\theta)(\cos^2\theta) A(\mu, \theta) \tag{A.2}$$

By differentiation of Eq. (A.2) and use of the identity[18]

$$J_1(\tau)/\tau = (2/\pi) \int_0^{\pi/2} d\theta \cos(\tau \sin\theta) \cos^2\theta \tag{A.3}$$

one finds that

$$(d^2/d\tau^2)\bar{V}(\tau; 0) = [\mu^2/(1 - 2\mu)][\bar{V}(\tau; 0) - V_0(\mu\tau)^{-1} J_1(\tau)] \tag{A.4}$$

which when inserted into Eq. (A.1) yields Eq. (33). The frictional force result, Eq. (34), follows by differentiation of Eq. (33) with respect to τ and use of Eqs. (16) and (27).

APPENDIX B

Here we outline the derivation of Eqs. (51) and (54) of the text. It is easily seen from Eqs. (50) and (9) that $I(\tau; a)$ satisfies

$$\ddot{I}(\tau; a) - \kappa^2 I(\tau; a) = -\zeta V_0 J_2(\tau)/\tau \equiv -E(\tau) \tag{B.1}$$

where $\kappa^2 = (1 - a)^2/4a$, with the boundary conditions that $I(\tau; a)$ vanishes for $\tau = 0$ and $\tau = \infty$. This equation can be solved by Fourier transformation; one finds that

$$\tilde{I}(\omega; a) \equiv \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} I(\tau; a) = (\omega^2 + \kappa^2)^{-1} \tilde{E}(\omega) \tag{B.2}$$

which can be inverted by the convolution theorem to find Eq. (51):

$$I(\tau; a) = (\zeta V_0/2\kappa) \int_{-\infty}^{\infty} ds\, [J_2(\tau - s)/(\tau - s)] e^{-\kappa|s|} \tag{B.3}$$

As $\kappa \to 0$ ($\kappa > 0$), this can be analyzed with the aid of the identity[14] $(d/d\tau) J_1(\tau)/\tau = -J_2(\tau)/\tau$ and the approximation that $J_1(\tau)/\tau$ acts like a delta function on the slow time scale of κ^{-1} to find

$$\begin{aligned} I(\tau; a) &= -\frac{\zeta V_0}{2\kappa} \frac{d}{d\tau} \int_{-\infty}^{\infty} ds \frac{J_1(\tau - s)}{\tau - s} e^{-\kappa|s|} \\ &\simeq \zeta V_0 e^{-\kappa\tau}, \qquad \tau \gg 1; \quad \kappa \to 0 \end{aligned} \tag{B.4}$$

The demonstration of Eq. (54) for $\bar{V}(\tau; a)$ proceeds along similar lines. It follows from Eqs. (48) and (23) that

$$(d^2/d\tau^2)\bar{V}(\tau; a) - \kappa^2 G_0(\tau) V_0 = -\tfrac{1}{2}\kappa[(1 - a) + 2\mu a] G_0(\tau) V_0 \tag{B.5}$$

whose solution by Fourier methods is

$$\begin{aligned} \bar{V}(\tau; a) &= \tfrac{1}{2}(\kappa + \mu\sqrt{a}) \int_{-\infty}^{\infty} ds\, G_0(s) V_0 e^{-\kappa|\tau - s|} \\ &= \tfrac{1}{2}(\kappa + \mu\sqrt{a}) \left[\int_0^{\infty} ds\, \bar{V}(s; 0) e^{-\kappa|\tau - s|} \right. \\ &\qquad \left. + V_0 e^{-\kappa\tau} \int_0^{\infty} ds\, G_0(s) e^{-\kappa s} \right] \end{aligned} \tag{B.6}$$

where we have used Eq. (35) and the time symmetry of $G_0(\tau)$. The last integral in Eq. (B.6) is the Laplace transform $\hat{G}_0(\kappa) = \int_0^\infty d\tau\, e^{-\kappa\tau} G_0(\tau)$ of $G_0(\tau)$ and can be evaluated via Eqs. (13) and (14) as[19]

$$\hat{G}_0(\kappa) = [\kappa + (\mu/\zeta\omega_0)\hat{K}(\kappa)]^{-1} = (\kappa + \mu\sqrt{a})^{-1} \tag{B.7}$$

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