

Stochastic dynamics with a mesoscopic bath

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We consider the effects of bath size on the nature of the dynamics and transport properties for two simple models in which the bath is composed of a collinear chain of harmonic oscillators. The first model consists of an untwisted rotating chain (elastic rotor) for which we obtain a non-Markovian equation analogous to the generalized Langevin equation for the rotational degrees of freedom. We demonstrate that the corresponding memory function oscillates with a frequency close to that of the lowest mode of the chain. The second model considered consists of a tagged oscillator in a finite harmonic chain. For this model, we find an additional harmonic force in the generalized Langevin equation for the terminal atom that does not appear in the equation of motion for the semi-infinite chain. It is demonstrated that the force constant for the additional harmonic force scales as $1/N$, where N is the number of oscillators in the chain. Using an exact representation for the velocity correlation function, the transport properties of the model are discussed.

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I. INTRODUCTION

The dynamics of a system interacting with a bath has been the subject of sustained study for decades. While the equilibrium properties of the system are essentially insensitive to bath properties, the character of the relaxation processes usually depends crucially on the temporal and spatial scales of the dynamics of the bath [1]. One systematic approach for examining how the physical characteristics of the bath influence the dynamics of the system is based on the Zwanzig-Mori projection operator formalism which provides an exact but formal procedure for the elimination of irrelevant bath variables. The elimination procedure leads to the generalized Langevin equation (GLE) in which the total force acting on the variable of interest is represented as a sum of a colored noise term $F(t)$ and a non-Markovian dissipative term containing a memory function satisfying the fluctuation-dissipation relation. A particular decomposition of the total force into fluctuating and regular parts in the GLE is not unique, and corresponds to a specific choice of the projection operator. Some forms of the projection operator lead to equations for the relevant variables that differ from the GLE but conserve the non-Markovian character of the dissipation (see, for example, [2]).

If the bath variables evolve much faster than the variable of interest, one can expect that the dissipative memory function decays rapidly to zero and can be approximated by a δ function on time scales relevant to the dynamics of the system. This assumption is of vital importance in many applications, including the Brownian dynamic simulation method and its numerous variations. For a large system in which a full molecular dynamics simulation becomes very expensive, it is desirable to consider explicitly only the dynamics of relevant variables while fast variables (referred to as bath variables) are treated phenomenologically through a model incorporating fluctuating and dissipative forces acting on the relevant variables. For a few model systems, such as a heavy isotope in a chain of linear oscillators, the validity of the stochastic equation of motion has been demonstrated analytically in the thermodynamic limit [3] and numerically for a

finite bath [4]. The aim of this paper is to consider two elementary situations when the fact that the bath is finite cannot be neglected and may lead to effects surviving in the thermodynamic limit.

The coupling of a system to a sufficiently large bath often causes the dynamics of the system to appear to be stochastic and irreversible. While this situation is quite common, there are situations in which the bath produces an almost regular, rather than stochastic, force acting on the system. In fact, one can anticipate that, if only a small number of bath modes couple effectively with a system, the dynamics of the system appears more deterministic than stochastic in spite of the fact that the number of bath degrees of freedom may be very large. A simple model that exhibits behavior of this kind is an elastic untwisted rotor, which we consider in Sec. II. The elastic rotor system is modeled as a finite collinear chain of harmonic oscillators rotating as a whole around one of its ends. For this system, we focus on the dynamics of the angular velocity of the chain, while intrinsic vibrational degrees of freedom are treated as irrelevant bath variables. Vibrations of the bath lead to fluctuations of the moment of inertia of the rotor and therefore to fluctuations of the angular velocity of the chain. It will be shown that, even in the case in which a wide separation of time scales exists between the rotational and bath motions, their coupling does not lead to Brownian rotational motion, but rather gives a regular contribution which oscillates with a frequency close to that of the lowest vibrational mode of the bath. Although effects of quasimonochromatic external noise have been investigated recently [5], microscopic models leading to the intrinsic harmonic noise have not been considered.

While obviously oversimplified, the elastic rotor model captures the main physical features of rotation-translational coupling, and is relevant to the dynamics of long, linear molecules, stiff fragments of branched polymer systems, and many other molecular systems. Although rotation-vibrational coupling is usually relatively small, it may be an important factor in the dynamics of orientational ordering of linear molecules anchored to a surface and other processes of molecular nanotechnology. Moreover, the model can provide

valuable insight into the intrinsic rotational dynamics of macromolecules with complex three-dimensional structures such as DNA, since in many cases only fixed-conformation dynamics of polymer fragments is important [10].

In Sec. III, the dynamics of a tagged particle in a finite harmonic oscillator assembly is considered. The motion of a tagged particle in harmonic systems has been the subject of intensive study over many years and still continues to attract attention in the context of investigating the spatiotemporal evolution of the initial energy pulse [6]. In this article, we focus on the dynamics of a terminal atom of an anchored and finite chain. This model has been considered by many authors in the semi-infinite chain limit, mainly in the context of studies of gas/surface interactions and condensed-phase reaction dynamics [7,8] where the GLE can be derived by explicitly integrating the equations of motion for the bath variables [7]. We shall show that for the case of a finite chain an additional harmonic force appears in the GLE. In Sec. IV, we discuss transport properties of the finite chain system using the exact representation for the velocity autocorrelation function.

II. ELASTIC ROTOR

Consider an elastic rotor system governed by the Hamiltonian

$$H = \frac{P_\phi^2}{2I} + H_b + U(\phi), \quad (1)$$

where the Hamiltonian of the nonrotating chain (referred to as the “bath”) is

$$H_b = \frac{1}{2m} \sum_{i=1}^N p_i^2 + \frac{m\omega^2}{2} \sum_{i=1}^N (q_i - q_{i-1})^2, \quad (2)$$

and q_i and p_i are the displacements and momenta of the $N+1$ atoms of the chain, respectively. The chain rotates as a whole in an external potential $U(\phi)$ around an axis perpendicular to the chain and passing through the terminal atom anchoring the end of the chain. The anchoring atom is assumed to be fixed at the origin, $q_0=0$. In Eq. (1) the conjugate momentum P_ϕ of the rotation angle ϕ is the angular momentum of the chain, $P_\phi = I\dot{\phi}$, while the moment of inertia is $I = \sum_{i=1}^N m(x_i^0 + q_i)^2$, where $x_i^0 = ia$ is the position of atom i in equilibrium. We write the moment of inertia in the form $I(t) = I_r + \delta I(t)$, where

$$I_r = ma^2 \sum_{i=1}^N i^2 = \frac{1}{6} ma^2 N(N-1)(2N-1) \quad (3)$$

is the moment of inertia of the rigid chain in which the atoms are frozen in their equilibrium positions, and

$$\delta I(t) = 2ma \sum q_i(t) + m \sum q_i^2(t) \quad (4)$$

is the fluctuating part of I . We focus on the angular velocity of the chain $\dot{\phi} = P_\phi/I$, which, in general, is nonlinearly

coupled to the bath variables $\{q_i, p_i\}$. We restrict ourselves to the regime when $\dot{\phi}(t)$ is small compared with the lowest mode ω_0 of the unperturbed chain, namely, $\dot{\phi} \ll \omega_0$. This condition of a wide separation of time scales for rotational and vibrational motion is simultaneously the condition of weak rotation-vibration coupling and guarantees that the displacements of atoms are close to those in a nonrotating chain provided the kinetic energy of the harmonic atoms is not too high. When this condition holds, the fluctuating part of the moment of inertia is small,

$$|\delta I(t)| \ll I_r, \quad (5)$$

and the angular velocity can be approximated as a linear function of δI ,

$$\dot{\phi} \approx \frac{P_\phi}{I_r} \left(1 - \frac{\delta I}{I_r} \right). \quad (6)$$

It should be stressed that inequality (5) does not imply that the displacements of all atoms are small. In fact, the fluctuations in the unperturbed system are $\langle q_i^2 \rangle = i/(\beta m \omega^2)$, where β is the inverse temperature, which increases with i and may be comparable to or even larger than a for a long enough chain. However, since $\delta I \sim \sum i q_i \sim \sum i^{3/2}$ scales as $N^{5/2}$, the ratio $\delta I/I_r \sim 1/\sqrt{N} \ll 1$.

In the weak coupling approximation, the Hamiltonian for the system can be decomposed as

$$H = H_r + H_b + H_c, \quad (7)$$

where H_r is the Hamiltonian of the rigid chain,

$$H_r = \frac{P_\phi^2}{2I_r} + U(\phi), \quad (8)$$

H_b is the bath Hamiltonian defined in Eq. (2) above, and H_c is the coupling term,

$$H_c = -\frac{1}{2} \left(\frac{P_\phi}{I_r} \right)^2 \delta I. \quad (9)$$

It is interesting to note that the coupling of the system to the bath occurs through the kinetic energy term of the system due to the form of the Hamiltonian in generalized coordinates. This is quite different from the more common form of the coupling through an interaction potential for the system and bath [9].

It is useful to describe the dynamics of the bath in terms of the normal coordinates $\{Q_j, P_j\}$ for unperturbed bath motion corresponding to a nonrotating chain with one fixed end. The normal mode transformation is of the form

$$q_i = \frac{1}{\sqrt{m}} \sum_{j=0}^{N-1} A_{ij} Q_j, \quad p_i = \sqrt{m} \sum_{j=0}^{N-1} A_{ij} P_j, \quad (10)$$

where the eigenvectors have the components

$$A_{ij} = \frac{2}{\sqrt{2N+1}} \sin\left(\pi i \frac{2j+1}{2N+1}\right), \quad (11)$$

and satisfy orthogonality conditions with respect to both indices,

$$\sum_{i=1}^N A_{ij} A_{ik} = \delta_{jk}, \quad \sum_{j=0}^{N-1} A_{ij} A_{kj} = \delta_{ik}. \quad (12)$$

The transformed bath Hamiltonian in the normal coordinate representation is

$$H_b = \frac{1}{2} \sum_{j=0}^{N-1} \{P_j^2 + \omega_j^2 Q_j^2\}, \quad (13)$$

where

$$\omega_j = 2\omega \sin\left(\frac{\pi}{2} \frac{2j+1}{2N+1}\right) \quad (14)$$

are the normal mode frequencies of the bath. In terms of normal coordinates, the variation of the moment of inertia in Eq. (9) for the coupling Hamiltonian H_c takes the form

$$\delta I = \sum_{j=0}^{N-1} \{Q_j^2 + 2B_j Q_j\}, \quad (15)$$

where the constant vector B_j is defined as

$$B_j = \sqrt{m} \sum_{i=1}^N x_i^0 A_{ij} = \sqrt{ma} \sum_{i=1}^N i A_{ij}. \quad (16)$$

Explicitly calculating the sum, one obtains

$$B_j = 2a \left(\frac{m}{2N+1} \right)^{1/2} \left(\frac{\omega}{\omega_j} \right)^2 \sin\left(\pi N \frac{2j+1}{2N+1}\right), \quad (17)$$

where the sine can be approximated by $(-1)^j$ if $N \gg 1$.

The Liouville operator corresponding to the Hamiltonian (7) can be written as

$$\mathcal{L} = \mathcal{L}_r + \mathcal{L}_b + \mathcal{L}_c, \quad (18)$$

where the Liouville operators for the rigid chains and for the isolated bath are

$$\mathcal{L}_r = \frac{P_\phi}{I_r} \frac{\partial}{\partial \phi} - \frac{\partial U}{\partial \phi} \frac{\partial}{\partial P_\phi}, \quad (19)$$

$$\mathcal{L}_b = \sum_{j=0}^{N-1} \left\{ P_j \frac{\partial}{\partial Q_j} - \omega_j^2 Q_j \frac{\partial}{\partial P_j} \right\}, \quad (20)$$

respectively. The coupling term gives rise to the Liouvillian $\mathcal{L}_c$ which can be conveniently decomposed into two parts, $\mathcal{L}_c = \mathcal{L}_c^{(1)} + \mathcal{L}_c^{(2)}$, where

$$\mathcal{L}_c^{(1)} = \left(\frac{P_\phi}{I_r} \right) \sum_{j=0}^{N-1} (Q_j + B_j) \frac{\partial}{\partial P_j}, \quad (21)$$

$$\mathcal{L}_c^{(2)} = -\frac{P_\phi}{I_r} \frac{\delta I}{I_r} \frac{\partial}{\partial \phi}. \quad (22)$$

Using the Liouville operators, one obtains an evolution equation for the rotation angle $\phi(t)$,

$$I_r \ddot{\phi}(t) = -\frac{dU(\phi)}{d\phi} - \dot{\phi}(t) \dot{I}(t), \quad (23)$$

to leading order in the small parameter $\delta I/I_r$. The term $-\dot{\phi} \dot{I}$, where

$$\dot{I} = \mathcal{L} \delta I = 2 \sum_{j=0}^{N-1} (Q_j + B_j) P_j, \quad (24)$$

can be interpreted as a fluctuating torque due to intrinsic noise. Our aim is to derive an equation of motion for rotational motion that does not explicitly include bath variables. In what follows, we shall express the function $\dot{I}(t)$ through $\dot{\phi}(t)$, eliminating vibrational degrees of freedom using the projection operator technique.

The starting point is the operator identity

$$e^{(B+C)t} = e^{Bt} + \int_0^t d\tau e^{B(t-\tau)} C e^{(B+C)\tau}. \quad (25)$$

Differentiating Eq. (25) and defining $B = \mathcal{L}$ and $C = \mathcal{P}\mathcal{L}$, where $\mathcal{P}$ is an arbitrary operator, one obtains

$$e^{\mathcal{L}t} \mathcal{L} = e^{\mathcal{L}t} \mathcal{P}\mathcal{L} + \mathcal{F}(t) + \int_0^t d\tau e^{\mathcal{L}(t-\tau)} \mathcal{P}\mathcal{L} \mathcal{F}(\tau), \quad (26)$$

where $\mathcal{F}(t) = e^{\mathcal{Q}\mathcal{L}t} \mathcal{Q}\mathcal{L}$, and $\mathcal{Q} = 1 - \mathcal{P}$. Then for any dynamical variable $A(t) = e^{\mathcal{L}t} A$ one can write the evolution equation for $A(t)$ as

$$\dot{A}(t) = e^{\mathcal{L}t} \mathcal{P} \dot{A} + F(t) + \int_0^t d\tau e^{\mathcal{L}(t-\tau)} \mathcal{P} \mathcal{L} F(\tau), \quad (27)$$

$$F(t) = e^{\mathcal{Q}\mathcal{L}t} \mathcal{Q}\mathcal{L}A. \quad (28)$$

Here and below a dynamical function A with its time argument omitted denotes an initial value, namely, $A \equiv A(0)$. Let us define the operator $\mathcal{P}$ by the equation

$$\mathcal{P}B = \langle B \rangle \equiv \int \rho_b B d\Gamma_b, \quad (29)$$

where B is an arbitrary dynamical variable, $\rho_b = Z_b^{-1} e^{-\beta H_b}$ is the equilibrium distribution function for the isolated bath, and $d\Gamma_b = \prod_{j=0}^{N-1} dQ_j dP_j$ is the bath phase space element. With this definition, the operator $\mathcal{P}$ satisfies the properties of a projection operator since $\mathcal{P}^2 = \mathcal{P}$. Other important properties of the operator include $\mathcal{P}\mathcal{L}_b = 0$ and $\mathcal{P}F(t) = 0$, the first of which can be proved by integration by parts and noting that $\mathcal{L}_b \rho_b = 0$, while the second property follows from the fact that $\mathcal{P}F(t) \sim \mathcal{P}\mathcal{Q} = 0$.

Since $\mathcal{P}$ commutes with $\mathcal{L}_r$, the term $\mathcal{P}\mathcal{L}F(t)$ appearing in the integral in Eq. (27) is reduced to $\mathcal{P}\mathcal{L}_c F(t) = \mathcal{P}(\mathcal{L}_c^{(1)} + \mathcal{L}_c^{(2)})F(t)$. The contribution from $\mathcal{L}_c^{(1)}$ can be calculated by integrating by parts,

$$\mathcal{P}\mathcal{L}_c^{(1)}F(t) = - \int (\mathcal{L}_c^{(1)}\rho_b)F(t) d\Gamma_b. \quad (30)$$

Noting that

$$\mathcal{L}_c^{(1)}\rho_b = -\frac{\beta}{2}\left(\frac{P_\phi}{I_r}\right)^2 \dot{I}\rho_b, \quad (31)$$

we obtain

$$\mathcal{P}\mathcal{L}_c^{(1)}F(t) = \frac{\beta}{2}\left(\frac{P_\phi}{I_r}\right)^2 \langle \dot{I}F(t) \rangle. \quad (32)$$

The contribution from $\mathcal{L}_c^{(2)}$, given by

$$\mathcal{P}\mathcal{L}_c^{(2)}F(t) = -\frac{P_\phi}{I_r^2} \frac{d}{d\phi} \langle \delta I F(t) \rangle, \quad (33)$$

is proportional to the small parameter $\delta I/I_r$ and will be neglected. Under these circumstances, Eq. (27) takes the form

$$\dot{A}(t) = e^{\mathcal{L}t} \langle \dot{A} \rangle + F(t) + \frac{\beta}{2} \int_0^t d\tau e^{\mathcal{L}(t-\tau)} \left(\frac{P_\phi}{I_r}\right)^2 \langle \dot{I}F(\tau) \rangle. \quad (34)$$

If the dynamical variable of interest A is taken to be the moment of inertia I , the first term on the right hand side of Eq. (34) vanishes since $\langle \dot{I} \rangle = 0$, and the force is of the form

$$F(t) = e^{(\mathcal{L}_b + \mathcal{L}_0)t} \dot{I}, \quad (35)$$

where $\mathcal{L}_0 = \mathcal{Q}(\mathcal{L}_r + \mathcal{L}_c)$. The force $F(t)$ can be calculated exactly if one neglects the quadratic term in Eqs. (4) and (15) for δI . This corresponds to the approximation where the centrifugal force $f_c(x_i)$ acting on a particular i th atom does not depend on its displacement but is determined by the equilibrium position of the atom in the chain, $f_c(x_i) \approx m\dot{\phi}^2 x_i^0$. It then follows that

$$\delta I = 2 \sum_{j=0}^{N-1} B_j Q_j, \quad \dot{I} = 2 \sum_{j=0}^{N-1} B_j P_j, \quad (36)$$

and the operator $\mathcal{L}_c^{(1)}$ is reduced to

$$\mathcal{L}_c^{(1)} = \left(\frac{P_\phi}{I_r}\right)^2 \sum_{j=0}^{N-1} B_j \frac{\partial}{\partial P_j}. \quad (37)$$

Since $\mathcal{L}_0 \mathcal{L}_b^n \dot{I} = 0$ for $n=0,1,2,\dots$, Eq. (35) implies that

$$F(t) = e^{\mathcal{L}_b t} \dot{I} \equiv \dot{I}_b(t). \quad (38)$$

Substituting this result into Eq. (34) leads finally to the equation

$$\dot{I}(t) = \dot{I}_b(t) + \frac{\beta}{2} \int_0^t d\tau \dot{\phi}^2(\tau) \langle \dot{I}_b(t-\tau) \rangle, \quad (39)$$

where we have used the fact that $P_\phi(t)/I_r = \dot{\phi}(t)$ to leading order in the small parameter $\delta I/I_r$. Equation (23) for the angle can therefore be written in the form

$$I_r \ddot{\phi}(t) = -U'(\phi) + \gamma(t), \quad (40)$$

where $\gamma(t)$ is the torque describing the influence of the intrinsic noise; its ‘‘stochastic’’ and regular non-Markovian constituents are, respectively,

$$\gamma_s(t) = -\dot{\phi}(t)\dot{I}_b(t), \quad (41)$$

$$\gamma_r(t) = -4ma^2 \dot{\phi}(t) \int_0^t d\tau \dot{\phi}^2(\tau) K(t-\tau), \quad (42)$$

where the dimensionless memory function satisfies the fluctuation-dissipation relation

$$K(t) = \frac{\beta}{8ma^2} \langle \dot{I}_b \dot{I}_b(t) \rangle. \quad (43)$$

Under the dynamics of the unperturbed bath described by the Liouville operator $\mathcal{L}_b$, the normal modes evolve as

$$Q_j^0(t) = Q_j \cos(\omega_j t) + \omega_j^{-1} P_j \sin(\omega_j t), \quad (44)$$

$$P_j^0(t) = P_j \cos(\omega_j t) - \omega_j Q_j \sin(\omega_j t), \quad (45)$$

and the corresponding correlation functions are

$$\langle Q_j^0(t) Q_{j'}^0 \rangle = \delta_{jj'} \beta^{-1} \omega_j^{-2} \cos(\omega_j t), \quad (46)$$

$$\langle P_j^0(t) P_{j'}^0 \rangle = \delta_{jj'} \beta^{-1} \cos(\omega_j t). \quad (47)$$

Consequently, the memory function $K(t)$ can be expressed as

$$\begin{aligned} K(t) &= \frac{\beta}{2ma^2} \sum_{j,j'=0}^{N-1} B_j B_{j'} \langle P_j^0(t) P_{j'}^0 \rangle \\ &= \frac{1}{2ma^2} \sum_{j=0}^{N-1} B_j^2 \cos(\omega_j t). \end{aligned} \quad (48)$$

Using the expression in Eq. (17) for B_j , the memory function for large N is

$$K(t) = \frac{1}{N} \sum_{j=0}^{N-1} \left(\frac{\omega}{\omega_j}\right)^4 \cos(\omega_j t). \quad (49)$$

Examination of Eq. (49) reveals that the first term in the sum ($j=0$) exceeds the others by a factor of at least 3^4 , and gives the main contribution to $K(t)$. As a result, the memory function is a nearly harmonic function oscillating with the frequency of the lowest mode $\omega_0 \sim \omega/N$. The implications of this result are quite transparent, since the lowest mode cor-

responds to the displacements of all atoms in the chain in the same direction. Collective motion of this kind gives the dominant contribution to the variation of the moment of inertia and therefore is coupled more strongly to the rotational variables than modes of higher frequencies. In the continuum limit, interpreted as the simultaneous limits $N \rightarrow \infty$ and $a, m \rightarrow 0$ with fixed $aN = L$, $mN = M$, and $ka = g$, the frequency ω_0 takes the finite value $\sqrt{g/(ML)} = (L/c)^{-1}$, where $c = \sqrt{gL/M}$ is the velocity of sound in the continuum.

Equation (40) is nonlinear and difficult to solve analytically except in the case of free rotation in which $U'(\phi) = 0$ and P_ϕ is an integral of the motion. In this case $\delta I(t) = \delta I_1(t) + \delta I_2(t)$, where

$$\delta I_1(t) = 2 \sum_{j=0}^{N-1} B_j Q_j^0(t) \quad (50)$$

is the approximate variation of the moment of inertia for the nonrotating chain, and

$$\delta I_2(t) = 2 \dot{\phi}_0^2 \sum_{j=0}^{N-1} \left(\frac{B_j}{\omega_j} \right)^2 \cos(\omega_j t) \quad (51)$$

is the variation due to rotation. In Eq. (51) $\dot{\phi}_0 = P_\phi / I_r$ is the angular velocity of the rigid chain. Noting that in both sums the main contribution comes from the element with $j=0$, one can check that

$$\delta I_1 / I_r \sim (\beta m \omega^2 a^2 N)^{-1/2} \ll 1, \quad (52)$$

$$\delta I_2 / I_r \sim (\dot{\phi}_0 / \omega_0)^2. \quad (53)$$

It is clear from these considerations that the condition $\delta I / I_r \ll 1$ indeed implies that a wide time scale separation for rotary and vibrational motions exists, $\dot{\phi} / \omega_j \ll 1$. Since $\dot{\phi} \sim P_\phi / I_r \sim 1/N^3$ and $\omega_0 \sim 1/N$, this condition imposes a lower bound for N for a given value of P_ϕ , namely, $N \gg (P_\phi / m a^2 \omega)^{1/2}$.

Note also that for the case of free rotation the dynamics can be solved without dropping the quadratic term in the expression for δI . In fact, using the additional coordinate transformation $\tilde{Q}_j = Q_j - \lambda_j^2 B_j$ with

$$\lambda_j^2(P_\phi) = \left(\frac{\dot{\phi}_0}{\omega_j} \right)^2, \quad \tilde{\omega}_j^2(P_\phi) = \omega_j^2 - \dot{\phi}_0^2, \quad (54)$$

and leaving momenta unchanged, the Hamiltonian (7) assumes the form

$$H = \frac{1}{2} \sum_{j=0}^{N-1} (P_j^2 + \tilde{\omega}_j^2 \tilde{Q}_j^2) + H_0(P_\phi), \quad (55)$$

where $H_0(P_\phi)$ does not depend on the bath variables. Since the above transformation is canonical, the new coordinates $\{\tilde{Q}_j, P_j\}$ evolve as normal modes of the unperturbed bath according to Eqs. (44) and (45). Then, expressing δI in terms

of $\tilde{Q}_j$, one can get the results obtained above but with shifted frequencies $\tilde{\omega}_j \approx \omega_j - \dot{\phi}_0^2 / 2\omega_j$.

To conclude this section, we consider the dynamics of rotational motion beyond the rigid-rod approximation by taking into account the coupling between vibrational and rotational motions. We have derived a stochastic equation for the angular velocity which has essentially non-Markovian character. Because of the dominant role of the lowest vibrational modes, it may be more convenient in practice to consider the dynamics of the slowest vibrational modes explicitly and neglect altogether the coupling of the system to the faster modes. As a compromise to integrating the equations of motion of all degrees of freedom, one can consider the Newtonian dynamics of the lowest modes and treat the remaining degrees of freedom stochastically. In this case the system of equations to solve includes equations of motion for the modes with $j=0, 1, \dots, N_0-1$, and the stochastic equation for rotary motion

$$I_r \ddot{\phi}(t) = -U'(\phi) + 2 \sum_{j=0}^{N_0-1} B_j P_j(t) + \gamma(t). \quad (56)$$

In this equation the random torque $\gamma(t)$ has the same form as before except that it no longer includes contributions from the first N_0-1 modes. The corresponding memory function appearing in $\gamma(t)$,

$$K(t) = \frac{1}{N} \sum_{j=N_0}^{N-1} \left(\frac{\omega}{\omega_j} \right)^4 \cos(\omega_j t), \quad (57)$$

is an oscillating and decaying function of time for $t \sim 1/\omega_0$, while on longer time scales it exhibits more complex behavior (Fig. 1).

III. TAGGED OSCILLATOR DYNAMICS

In light of the important finite length effects observed in the elastic rotor system, it is worthwhile to explore the effects of a finite bath of mesoscopic scale on the dynamics of the terminal atom in a collinear harmonic chain. The issue of finite bath effects should be particularly relevant to the study of transport properties of tagged particles in finite assemblies, such as atomic clusters of mesoscopic size.

Consider a chain consisting of $N+2$ harmonically coupled atoms labeled as $i=0, 1, \dots, N, N+1$ in which the position of the first atom is fixed, $q_0=0$. The Hamiltonian for the system is

$$H = \frac{1}{2m} \sum_{i=1}^{N+1} p_i^2 + \frac{m\omega^2}{2} \sum_{i=1}^{N+1} (q_i - q_{i-1})^2. \quad (58)$$

In the limit $N \rightarrow \infty$, it has been shown that the coordinate of the terminal atom $q_{N+1}(t) \equiv q(t)$ satisfies the generalized Langevin equation [7]

$$\ddot{q}(t) = -\omega^2 \int_0^t d\tau \Lambda(t-\tau) \dot{q}(\tau) + F(t), \quad (59)$$

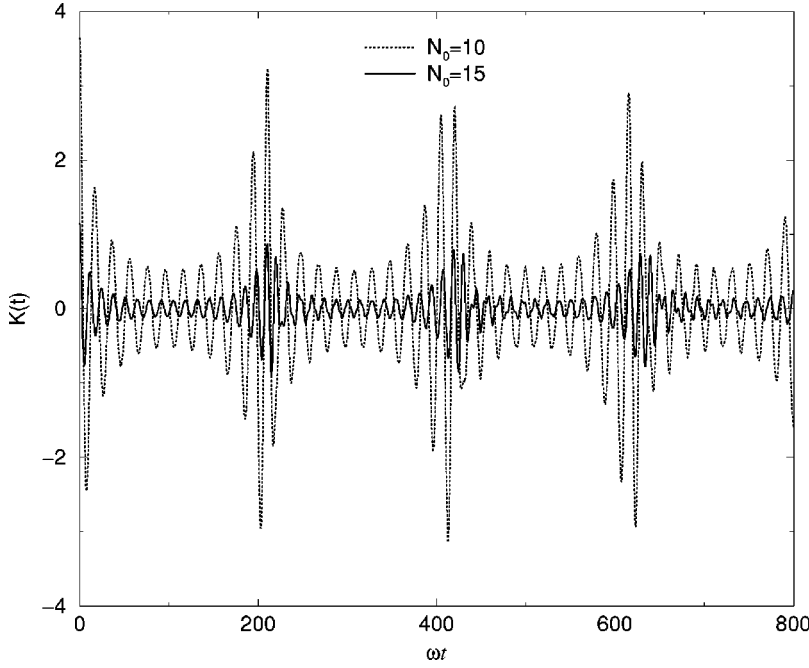


FIG. 1. The memory function given by Eq. (57) for the chain with $N=100$.

where the force $F(t)$ is a function of all initial displacements and velocities except $\dot{q}$, and the memory function is expressed in terms of Bessel functions

$$\Lambda(t) = J_0(2\omega t) + J_2(2\omega t) = J_1(2\omega t)/\omega t. \quad (60)$$

To examine the effects of finite chain lengths, let us decompose the Hamiltonian as $H = H_s + H_c + H_b$, where

$$H_s = \frac{p^2}{2m} + \frac{kq^2}{2}, \quad H_c = -\frac{1}{2}kqq_N, \quad (61)$$

$k = m\omega^2$ is the spring constant, and the bath Hamiltonian is

$$H_b = \frac{1}{2m} \sum_{i=1}^N p_i^2 + \frac{m\omega^2}{2} \sum_{i=1}^N (q_i - q_{i-1})^2 + \frac{kq_N^2}{2}. \quad (62)$$

One can recognize H_b as the Hamiltonian of a chain consisting of $N+2$ atoms with fixed positions for the first ($i=0$) and last ($i=N+1$) atoms. This Hamiltonian can be diagonalized,

$$H_b = \frac{1}{2} \sum_{j=1}^N (P_j^2 + \omega_j^2 Q_j^2), \quad (63)$$

$$\omega_j = 2\omega \sin\left(\frac{\pi j}{2(N+1)}\right), \quad (64)$$

by means of the transformations

$$q_i = \frac{1}{\sqrt{m}} \sum_{j=1}^N A_{ij} Q_j, \quad p_i = \sqrt{m} \sum_{j=1}^N A_{ij} P_j, \quad (65)$$

with normalized eigenvectors

$$A_{ij} = \left(\frac{2}{N+1}\right)^{1/2} \sin\left(\frac{\pi i j}{N+1}\right). \quad (66)$$

The Hamiltonian H_c in normal coordinates reads

$$H_c = -\sum_{j=1}^N \Gamma_j Q_j q, \quad (67)$$

where the coupling coefficient $\Gamma_j = kA_{Nj}/\sqrt{m}$ can be written as

$$\Gamma_j = -\frac{k}{\sqrt{m}} \left(\frac{2}{N+1}\right)^{1/2} (-1)^j \sin\left(\frac{\pi j}{N+1}\right). \quad (68)$$

The equations of motion for the normal modes are

$$\ddot{Q}_j(t) = -\omega_j^2 Q_j(t) + \Gamma_j q(t), \quad (69)$$

for $j=1, \dots, N$, which have the solution

$$Q_j(t) = Q_j^0(t) + \frac{\Gamma_j}{\omega_j} \int_0^t d\tau q(\tau) \sin \omega_j(t - \tau), \quad (70)$$

where $Q_j^0(t)$ is the normal coordinate for the unperturbed bath given by Eq. (44). Using integration by parts, this can be written as

$$Q_j(t) = Q_j^0(t) + \frac{\Gamma_j}{\omega_j^2} \left\{ q(t) - q \cos \omega_j t - \int_0^t d\tau \dot{q}(\tau) \cos \omega_j(t - \tau) \right\}. \quad (71)$$

Substitution of this expression into the equation of motion for the terminal atom

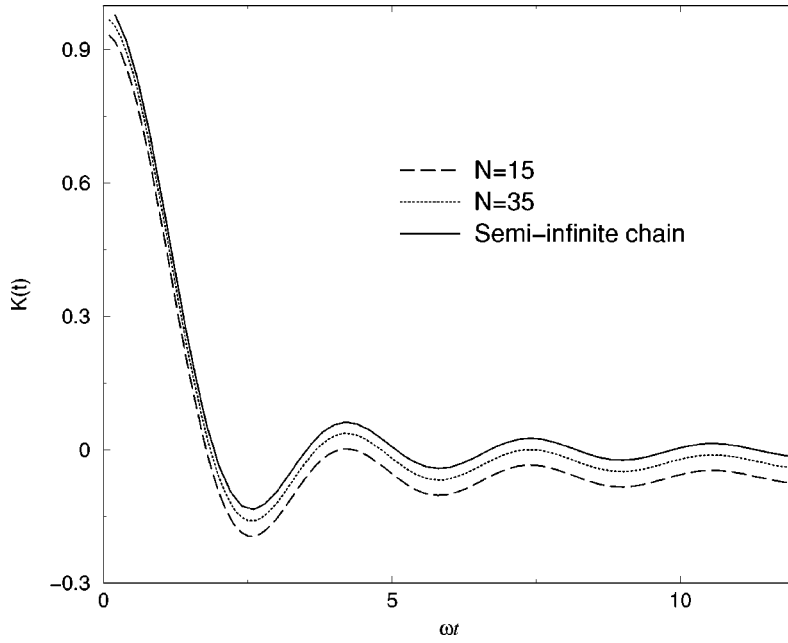


FIG. 2. The memory function $K(t)$ in Eq. (73) for different numbers of atoms N in the chain.

$$\ddot{q}(t) = -\omega^2 q(t) + \frac{1}{m} \sum_{j=1}^N \Gamma_j Q_j(t) \quad (72)$$

finally yields an equation in the form of a generalized Langevin equation:

$$\ddot{q}(t) = -\Omega^2 q(t) + F(t) - \omega^2 \int_0^t d\tau K(t-\tau) \dot{q}(\tau). \quad (73)$$

Here the “random” force $F(t) = F_s(t) + F_b(t)$ has a part $F_s(t)$ depending on the initial displacement of the terminal atom q ,

$$F_s(t) = -\frac{q}{m} \sum_{j=1}^N \left(\frac{\Gamma_j}{\omega_j} \right)^2 \cos(\omega_j t), \quad (74)$$

and a part $F_b(t)$ that is a function of the displacements and momenta of the remaining atoms of the chain (bath),

$$F_b(t) = \frac{1}{m} \sum_{j=0}^N \Gamma_j Q_j^0(t). \quad (75)$$

Comparing Eq. (73) with Eq. (59), we note the existence of an additional harmonic force with associated frequency

$$\Omega^2 = \omega^2 - \frac{1}{m} \sum_{j=0}^N \left(\frac{\Gamma_j}{\omega_j} \right)^2 = \frac{\omega^2}{N+1}. \quad (76)$$

The dimensionless memory function $K(t)$ in Eq. (73) has the form

$$K(t) = \frac{1}{m\omega^2} \sum_{j=1}^N \left(\frac{\Gamma_j}{\omega_j} \right)^2 \cos(\omega_j t). \quad (77)$$

Using Eqs. (46) and (47), $K(t)$ can be written in the form of the fluctuation-dissipation relation

$$K(t) = \frac{\beta m}{\omega^2} \langle F_b F_b(t) \rangle, \quad (78)$$

where the average is taken over the bath variables $\{Q_j, P_j\}$. Using expression (68) for the coupling coefficients Γ_j , one can write the memory function as

$$K(t) = \frac{2}{N+1} \sum_{j=1}^N \cos^2\left(\frac{\pi}{2} \frac{j}{N+1}\right) \cos(\omega_j t). \quad (79)$$

In the limit $N \rightarrow \infty$, the sum in the above expression can be converted into the integral

$$K(t) = \frac{4}{\pi} \int_0^{\pi/2} d\theta \cos^2 \theta \cos(2\omega t \sin \theta). \quad (80)$$

Keeping in mind the integral representation for Bessel functions

$$J_{2i}(z) = \frac{2}{\pi} \int_0^{\pi/2} d\theta \cos(2i\theta) \cos(z \sin \theta), \quad (81)$$

one can see that Eq. (80) gives the memory function $\Lambda(t)$ for the semi-infinite chain, Eq. (60). However, for finite chains of moderate length, the memory function $K(t)$ differs significantly from $\Lambda(t)$ (see Fig. 2). For times shorter than $T_r = N/\omega$, the time scale of the reflection of sound waves from the anchored part of the chain, $K(t)$ oscillates around a negative value that approaches zero as N increases. Note that the existence of a region of time for which the memory function is negative is not uncommon and has been discussed recently in Ref. [11].

The exact expression (79) for the memory function is not very convenient to use when the number of atoms is large but finite. Since the commonly used procedure of converting a sum to an integral quite often gives unsatisfactory results,

one may wish to have an alternative representation for series like (79). We address this problem in the next section.

IV. CORRELATION FUNCTIONS

In this section we discuss properties of the normalized velocity autocorrelation function (VAF) of atom i , defined by $C_i(t) = \langle \dot{q}_i(t) \dot{q}_i \rangle / \langle \dot{q}_i^2 \rangle$, where the average is taken over coordinates and momenta of the whole system. The VAF determines the transport properties of the chain through its connection with the diffusion constant of the i th atom, $D_i = \langle \dot{q}_i^2 \rangle \int_0^\infty dt C_i(t)$. For a harmonic chain with periodic boundary conditions, $C_i(t) = J_0(2\omega t)$ in the limit of large N , and the diffusion constant takes on the nonzero value $D = (2m\omega\beta)^{-1}$ [12]. Some authors [13,14] have interpreted the finite diffusion constant for a tagged oscillator as a consequence of the zero-frequency mode present in a system with periodic boundary conditions. To support this conclusion, Florencio and Lee [13] considered a harmonic chain with both ends fixed to remove the zero-frequency mode. The system, governed by the Hamiltonian in Eq. (62), has a VAF for atom i given by [15]

$$C_i(t) = J_0(2\omega t) - J_{4i}(2\omega t). \quad (82)$$

Since the integral $\int_0^\infty dt J_n(at) = 1/a$ does not depend of the Bessel function index n , this expression indeed leads to a vanishing diffusion coefficient. This result is correct, however, only for atoms near the fixed ends with finite indices i . For atoms in the bulk of the infinite chain, one has to take the limit $i \rightarrow \infty$ *before* calculation of the diffusion constant. Then $C_i(t) \rightarrow J_0(2\omega t)$, so the dynamics of atoms located in the bulk of the chain with fixed ends is the same as that in the periodic system in the limit $N \rightarrow \infty$. Actually, the nonzero diffusion constant for a bulk atom is a general property of infinite one-dimensional harmonic chains. It is a manifestation of the delocalization of atoms in the limit $N \rightarrow \infty$ and does not depend on the type of boundary condition. For example, for the chain with one fixed end considered in the previous section, one can see that the fluctuations $\langle q_i^2 \rangle = i/m\beta\omega^2$ diverge with increasing i while $\langle (q_i - q_{i-1})^2 \rangle = 1/m\beta\omega^2$ is finite for any i .

The velocity autocorrelation function for the terminal atom of the semi-infinite chain can be obtained from the generalized Langevin equation (59). In fact, since $\langle F(t) \dot{q} \rangle = 0$, the equation of motion for the VAF is

$$\dot{C}(t) = -\omega^2 \int_0^t d\tau \Lambda(t-\tau) C(\tau). \quad (83)$$

Using the Laplace transform, one can verify that $C(t)$ coincides with the memory function $\Lambda(t) = J_1(2\omega t)/\omega t$ and yields a nonzero diffusion constant.

The result in Eq. (82) can be derived by expressing the velocities in terms of normal modes, Eqs. (65), which gives

$$C_i(t) = \frac{2}{N+1} \sum_{j=1}^N \sin^2\left(\frac{\pi i j}{N+1}\right) \cos\left(2\omega t \sin \frac{\pi j}{2(N+1)}\right). \quad (84)$$

Converting this sum into an integral in the limit $N \rightarrow \infty$ yields

$$C_i(t) = \frac{4}{\pi} \int_0^{\pi/2} d\theta \sin^2(2i\theta) \cos(2\omega t \sin \theta) = J_0(2\omega t) - J_{4i}(2\omega t). \quad (85)$$

This expression has the evident drawback of not being invariant with respect to the transformation $i \rightarrow (N+1) - i$, that is, for instance, $C_1(t) \neq C_N(t)$. Note that the same shortcoming is also evident in Hamilton's result for displacements [16]

$$q_i(t) = \sum_{j=1}^{\infty} \left(q_j(0) + m^{-1} p_j(0) \int_0^t dt \right) [J_{2(i-j)}(2\omega t) - J_{2(i+j)}(2\omega t)], \quad (86)$$

while the exact formula

$$q_i(t) = \sum_{j=1}^N \left(q_j(0) + m^{-1} p_j(0) \int_0^t dt \right) \sum_{k=1}^N A_{jk} A_{ik} \cos(\omega_k t) \quad (87)$$

has the desirable symmetry. The trouble arises, of course, from the fact that the conversion from a sum to an integral in Eqs. (84) and (87) can be done only if the label i is finite. Below we shall obtain an exact representation for the VAF that is particularly convenient in the case of the large but finite N .

Using the generating function

$$\cos(z \sin \theta) = J_0(z) + 2 \sum_{i=1}^{\infty} J_{2i}(z) \cos(2i\theta) \quad (88)$$

for the Bessel functions, Eq. (84) can be written as

$$C_i(t) = R_i J_0(2\omega t) + \sum_{j=1}^{\infty} S_{ij} J_{2j}(2\omega t), \quad (89)$$

where

$$R_i = \frac{2}{N+1} \sum_{k=1}^N \sin^2\left(\frac{\pi k i}{N+1}\right) = \sum_{k=1}^N A_{ik}^2 = 1, \quad (90)$$

$$S_{ij} = \frac{4}{N+1} \sum_{k=1}^N \sin^2\left(\frac{\pi i k}{N+1}\right) \cos\left(\frac{\pi j k}{N+1}\right). \quad (91)$$

Using the formula

$$\sum_{k=1}^N \cos(kz) = -1 + \cos \frac{zN}{2} \sin \frac{z(N+1)}{2} \sin^{-1} \frac{z}{2}, \quad (92)$$

which holds if $\sin z/2 \neq 0$, one can show that S_{ij} is zero for every i and j except for three sets of j :

$$\{j_1\} = 2(N+1)s, \quad (93)$$

$$\{j_2\} = 2(N+1)s - 2i, \quad (94)$$

$$\{j_3\} = 2(N+1)(s-1) + 2i, \quad (95)$$

where $s=1,2,3,\dots$. Note that for all j from the set $\{j_1\}$, $S_{ij}=2$, while for all j in the sets $\{j_2\}$ and $\{j_3\}$, $S_{ij}=-1$. Using these results, we finally have

$$C_i(t) = J_0(2\omega t) + 2 \sum_{j \in \{j_1\}} J_{2j}(2\omega t) - \sum_{j \in \{j_2\}, \{j_3\}} J_{2j}(2\omega t). \quad (96)$$

It is easy to see that this expression is invariant under the transformation $i \rightarrow (N+1) - i$, as the sets $\{j_2\}$ and $\{j_3\}$ transform into each other while the set $\{j_1\}$ is invariant under the transformation. In the limit $N \rightarrow \infty$, the Bessel functions with indices proportional to N or higher vanish. Then, for atoms near the origin of the chain (finite i), we have Eq. (82), while the equation

$$C_i(t) = J_0(2\omega t) - J_{4(N+1-i)}(2\omega t) \quad (97)$$

holds for atoms near the other end of the chain at index $N+1-i$. Clearly Eq. (82) and Eq. (97) give the same expression for the symmetric atoms with labels i and $N+1-i$. For atoms in the bulk of the chain where both i and $|i-N|$ are of the order of N , we have $C_i(t) = J_0(2\omega t)$ in the limit $N \rightarrow \infty$, as in the case of periodic boundary conditions. For these atoms, we obtain a finite diffusion coefficient $D = 1/2\beta\omega m$.

For the case of a chain of $N+1$ atoms with one end fixed, the Hamiltonian takes the form (2) and the transformation to the normal modes is given by Eqs. (10) and (11). Then the VAF assumes the form

$$C_i(t) = \frac{4}{2N+1} \sum_{j=0}^{N-1} \sin^2\left(\pi i \frac{2j+1}{2N+1}\right) \cos(\omega_j t). \quad (98)$$

Following the same procedure used above, one again obtains Eq. (89) for the VAF with $R_i=1$. However, the summation over index j now runs from 0 to $N-1$, and the matrix S_{ij} has the form

$$S_{ij} = \frac{8}{2N+1} \sum_{k=0}^{N-1} \sin^2\left(\pi i \frac{2k+1}{2N+1}\right) \cos\left(\pi j \frac{2k+1}{2N+1}\right). \quad (99)$$

One can find again that $S_{ij}=0$ for any j except elements of the sets

$$\{j_1\} = (2N+1)s, \quad (100)$$

$$\{j_2\} = (2N+1)s - 2i, \quad (101)$$

$$\{j_3\} = 2(N+1)(s-1) + 2i, \quad (102)$$

where $s=1,2,3,\dots$. For the j from the first, second, and third sets we obtain $S_{ij}=2(-1)^s$, $(-1)^{s+1}$, and $(-1)^s$, respectively. These relations yield a correlation function $C_i(t)$ of the form

$$C_i(t) = J_0(2\omega t) + 2 \sum_{s=1}^{\infty} (-1)^s J_{s(4N+2)}(2\omega t) - \sum_{s=0}^{\infty} (-1)^s J_{s(4N+2)+4i}(2\omega t) - \sum_{s=1}^{\infty} (-1)^s J_{s(4N+2)-4i}(2\omega t). \quad (103)$$

In the limit of large N this expression leads to Eq. (82) for atoms near the fixed end (finite i), while for atoms near the free end we have

$$C_i(t) = J_0(2\omega t) + J_{4(N-i)+2}(2\omega t). \quad (104)$$

For the terminal atom ($i=N$), this equation gives $C(t) = J_1(2\omega t)/\omega t$, the result already obtained from the Langevin equation. The VAF (104) decays as $t^{-3/2}$, faster than the decay for the case of the periodic boundary condition, where the decay goes as $t^{-1/2}$, and the corresponding diffusion constant $D = 1/\beta\omega m$ is larger by a factor of 2. For the bulk atoms, only the function $J_0(2\omega t)$ survives in Eq. (103), just as in the case of periodic boundary conditions.

V. CONCLUDING COMMENTS

In this paper we have examined the influence of finite bath effects on the structure of non-Markovian stochastic equations. For a tagged oscillator in a finite collinear chain, the finite-size effects lead not only to strong modification of the memory function in the GLE, but also to an additional harmonic force whose spring constant scales as $1/N$. It should be noted, however, that if one rewrites the GLE so that the memory term involves oscillator positions rather than velocities, the corresponding equation has the same form for both the finite and (semi-)infinite chains. Moreover, in this case, for the time interval $t < N/\omega$, the corresponding memory function of the finite chain is very close to that of the infinite chain.

The elastic rotor system provides another model in which finite bath effects have important consequences. Although it is a simple matter to write down the GLE for the angular velocity in formal operator form using the Mori projection operator, the evaluation of the memory function is difficult using this approach. On the other hand, the projection operator defined in Eq. (29) can be used to obtain a stochastic equation for the variable of interest and an explicit expression for the memory function in a straightforward fashion. Although the same results can be obtained by the explicit integration of the equations of motion for the normal modes, the projection operator formalism allows one to analyze the stochastic nature of the system. The essentially non-Markovian character of the resulting equation for the angle in the elastic rotor system may be a serious obstacle for

numerical simulation of the thermal fluctuation effects with stochastic dynamics methods. The dominating role of the lowest bath modes suggests that explicit integration of the equations of motion for such modes may be a simple and effective generalization of the widely used rigid-rod approximation when intrinsic degrees of freedom are replaced by rigid constraints.

Among other phenomena for which the presented findings may be of potential importance, one can mention the dynamical properties of rodlike polymers and polymer fragments smaller than a persistence length. Dielectric relaxation and the Kerr effect in dilute solutions of rodlike polymers are usually interpreted in the context of a model of overdamped Brownian motion of a rigid rotor [17]. The only source of randomness in the model is assumed to arise from collisions with surrounding solvent molecules (external noise), while the coupling of rotation with fluctuating internal motions (internal noise) is completely ignored. Under these assumptions the frequency dependence of observables is characterized by a single relaxation time τ_r which is of the order of the inverse rotary diffusion coefficient $1/D_r$. This approach, originated by Debye, has been successfully applied for decades to many systems and phenomena [18]. It may not be adequate,

however, in the low damping regime when the viscosity of the solvent is small and the Brownian forces cause only a tiny perturbation during the period of the external ac field. In this case the fluctuation of the intramolecular degrees of freedom may be quite pronounced, and one may expect a cross-over from purely diffusive motion to more or less regular rotation modulated with the frequency of the predominating mode. This conclusion seems to be quite general and insensitive to the simplifying assumptions used in the present work. In particular, in the case of a semistiff chain, the dominating mode may be related to a bending motion of the chain rather than longitudinal vibrations. One may also speculate that for some combinations of parameters the collisions of the chain with solvent molecules could contribute significantly to the torque of the entire chain, while the effect of collisions on the longitudinal vibrations may be negligible on a characteristic time scale of the external field. Under these conditions, both intrinsic vibrations and solvent-chain collisions would act independently and contribute additively to the total torque. Further work is needed to elucidate the exact conditions under which the intrinsic vibrational motions dominate over solvent interactions and to describe their net effect on the dynamics of the system.

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