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Temperature-driven irreversible generalized Langevin equation can capture the nonequilibrium dynamics of two dissipated coupled oscillators

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Kawai and Komatsuzaki [J. Chem. Phys. **134**, 114523 (2011)] recently derived the nonequilibrium generalized Langevin equation (GLE) for a nonstationary system using the projection operator technique. In the limit when the environment is slowly changing (that is, a quasi-equilibrium bath), it should reduce to the irreversible GLE approach (iGLE) [J. Chem. Phys. **111**, 7701 (1999)]. Kawai and Komatsuzaki, however, found that the driven harmonic oscillator, an example of a nonequilibrium system does not obey the iGLE presumably because it did not quite satisfy the limiting conditions of the latter. Notwithstanding the lack of a massive quasi-equilibrium bath (one of the conditions under which the iGLE had been derived earlier), we found that the temperature-driven iGLE (T-iGLE) [J. Chem. Phys. **126**, 244506 (2007)] can reproduce the nonequilibrium dynamics of a driven dissipated pair of harmonic oscillators. It requires a choice of the function representing the coupling between the oscillator coordinate and the bath and shows that the T-iGLE representation is consistent with the projection operator formalism if only dominant bath modes are taken into account. Moreover, we also show that the more readily applicable phenomenological iGLE model is recoverable from the Kawai and Komatsuzaki model beyond the adiabatic limit used in the original T-iGLE theory.

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I. INTRODUCTION

To investigate the behavior of a system within a complex environment, such as a bimolecular reaction within a solution or molecular rearrangement in liquid crystals, the dynamics of the system are often simplified by identifying a specific coordinate (reaction path, configuration parameter, etc.) characterizing the process. If the thermal equilibrium between the system and environment (bath) is established, then well-developed methods can be applied to describe this process. Such methods include diffusion models for investigating spatial and/or reactional fluxes [1–4], approaches based on the Langevin equation (LE) for calculating molecular flows and relaxation mechanisms [5–7], and transition state theory and its consequent improvements for obtaining rate constants and reactive trajectories [8–14].

In nonequilibrium cases, the interrelations between the system and bath coordinates do not obey the fluctuation-dissipation theorems critical to the balance of forces expressed in the LE. Moreover, nonvanishing heat flows between the system and the bath do not allow a strict definition of the temperature [15]. Consequently, to our knowledge, the contraction of a nonequilibrium bath so as to describe the system dynamics within a small reduced coordinate space has not yet been specified generally. The current work further develops and clarifies the applicability of the nonequilibrium LE-based theory.

When the bath can be represented as a set of harmonic oscillators (often referred to as Zwanzig's approach) [16–18], then in many cases the analytical solution to the problem can be obtained. The effective substitution of the bath variables by harmonic modes has recently been used to build an LE-based approach for deriving the reduced equations of motion (EoMs) in the nonequilibrium regime [15,19–21]. In this algorithm, the nonstationarity of the environment has been modeled by introducing a temporal dependence in the parameters of the bath modes. The resulting EoM describes the dissipative dynamics of the nonequilibrium subsystem with the help of a limited set of functions defining the system-bath interaction. In many practical applications these functions can be obtained either experimentally or numerically and are no more abstract than the friction coefficient in the LE. Presumably, the phenomenological character of this EoM allows one to use it in a wide range of practical applications.

In the equilibrium regime, the motion of a chosen particle in a dense medium at a constant temperature, T, can be described by use of the generalized Langevin equation (GLE),

$$m\dot{v}(t) = F[x(t)] - \int_0^t \gamma(t,t')v(t')\,dt' + \xi(t), \qquad (1)$$

where $\gamma(t,t') = \gamma_{\text{th}}(t-t')$ is the stationary and nonlocal friction kernel representing the delayed response of the solvent. The mean force, $F[x(t)]$, results from the averaging over all the solvent degrees of freedom and will be ignored in the remainder of this work for simplicity without loss of generality. The stationarity reveals itself as a dependence on the time difference, that is, a one-time argument rather than two. The fluctuation-dissipation relation (FDR) for the random stationary force $\xi(t) = \xi_{\text{th}}(t)$ reads

$$\langle \xi_{\text{th}}(t)\xi_{\text{th}}(t')\rangle = k_{\text{B}}T\gamma_{\text{th}}(t-t'). \qquad (2)$$

This equation naturally appears when the particles coordinates are bilinearly coupled to the bath modes [22,23]. Even when they are not rigorously bilinear, the GLE approximately captures much of the dynamics of the chosen particle because the nonlinear terms typically correspond to small contributions at higher order. Interestingly, such nonlinearities have been addressed recently, though challenges remain [24]. Meanwhile,

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the nonlocal or colored friction is represented through the fact that the friction kernel $\gamma_{\rm th}(\cdot)$ is not a Dirac δ function. This nonlocality establishes the time scale of the relaxation of the solvent in response to the motion of the chosen particle. It cannot be ignored if the time scales of interest with respect to the chosen particle are on the order of those of the solvent dynamics. This limit can be approached when the solvent is effectively representable through only a few collective coordinate modes such as has been seen in limiting cases of dense media [25,26].

Although no longer a surprise to the chemistry community, it is remarkable that the GLE is also applicable to the treatment of chemical reactions in liquids. Indeed, the local limit, that is, the Langevin equation, has given rise to the much celebrated treatment of one-dimensional chemical reactions that gave rise to the Grote-Hynes rate formula [27,28]. It forms the basis for the description of a large number of chemical reactions using a chosen reaction coordinate coupled to a statistical bath [29–37]. Moreover, the bath can be colored [38–41], space-dependent [42], or even nonstationary [19,43,44]. This begs the question as to whether this framework could also be of use in describing the dynamics of chemical reactions (and more general systems) when the environments are far from equilibrium.

In regimes where the temperature of the environment is time-dependent [15,45], $T = T(t)$, the amplitude of the stochastic force changes in accordance with the transformation

$$\xi(t) = \sqrt{\frac{T(t)}{T(0)}}\,\xi_{\rm th}(t). \tag{3}$$

This modification of the stochastic force amplitude has been verified in the bilinear coupling model by direct consideration of the influence of the harmonic bath modes with changing energy on the projected coordinate of motion [45].

In nonequilibrium systems, the friction kernel can also be influenced by irreversible internal processes that may be or may not be connected to the temperature change. Its effect can be taken into account by a corresponding modification of the GLE. In the case of a nonstationary environment at *constant* temperature, for the irreversible version of GLE (iGLE), as proposed in Refs. [19] and [20], the friction kernel and stochastic force read, respectively,

$$\gamma_{\rm iGLE}(t,t') = g(t)g(t')\gamma_{\rm th}(t-t') \quad \text{and} \tag{4}$$

$$\xi_{\rm iGLE}(t) = g(t)\xi_{\rm th}(t), \tag{5}$$

where the function $g(t)$ defines the coupling strength between the particle and the bath. The coupling function $g(t)$ is sensitive to changes in the interactions between the system and the bath as well as the bath itself. It is a dimensionless function with the condition $g(t_0) = 1$ chosen so that the friction is captured by $\gamma_{\rm th}(t_0)$ for some arbitrary t_0. In preceding work [15,19–21], this time was chosen to be $t_0 = 0$, although it may acquire any value, including the infinite past or future, at which a thermodynamic equilibrium is established. Equation (1) with $\gamma(t,t')$ and $\xi(t)$ from Eqs. (4) and (5) was called the irreversible GLE (iGLE) [21] so as to emphasize the fact that the system undergoes a nonequilibrium irreversible process.

Though more general than the GLE, the iGLE does not capture all possible forms of nonstationarity in the solvent response. This had led to further generalizations that are capable of correctly surmising more general nonstationary responses [15,46–52]. Nevertheless, the iGLE retained the advantage that it could be recovered [20] through the use of a projection operator technique ignoring small higher-order corrections in the force expansion akin to how the GLE is recovered from the Zwanzig Hamiltonian with the only cost being that the system be initiated at thermal equilibrium at time 0. Recently Kawai and Komatsuzaki [51] showed that the projection operator technique can give rise to a nonmultiplicative nonstationary kernel at the expense of allowing the potential of mean force to be time-dependent. This introduces additional complexity in both the construction of the equations of motion, which may be difficult to do in arbitrary systems, and in their propagation. As such, it is important to understand the degree to which their theory actually extends the iGLE in theory and in practice. In this article we recapitulate the derivation of the nonstationary GLEs, both the iGLE and the Kawai and Komatsuzaki GLE, so as to clarify these theoretical differences. In order to explore the practical differences of the two approaches, we revisit the model system, that is, a driven harmonic oscillator, that Kawai and Komatsuzaki [51] recently reported as demonstrating the insufficiency of the iGLE. We find that most of the reduced dynamics of this system can nevertheless be captured by the simple framework of the temperature-dependent iGLE (T-iGLE), thereby revealing the practical advantages of the original iGLE framework.

II. THEORY: GENERALIZED IGLE VERSUS T-IGLE

In Ref. [15], a new Zwanzig-type Hamiltonian has been proposed to allow for an arbitrary (although moderately slow) change of the environmental temperature. In this Hamiltonian, the oscillatory bath modes are subject to a parametric variation ("squeezing" oscillators): The effective masses and frequencies of the bath modes are prescribed to vary with time through a specified protocol. It results in the change of the energy (and temperature) of the bath and the corresponding corrections to the GLE, leading to the temperature-driven iGLE, T-iGLE, with the friction and random force equal to

$$\gamma_{\rm TiGLE}(t,t') = \frac{T(t)}{T(t_0)}\,g(t)g(t')\gamma_{\rm th}[\tau(t)-\tau(t')], \tag{6}$$

$$\xi_{\rm TiGLE}(t) = \frac{T(t)}{T(t_0)}\,g(t)\xi_{\rm th}[\tau(t)]. \tag{7}$$

The effective time in the T-iGLE,

$$\tau(t) = \int_{t_0}^{t} \frac{T(s)}{T(t_0)}\,ds, \tag{8}$$

is a functional of the temperature and goes "faster" when the temperature increases. Such a correction in the time dependence alters the intensity of the stochastic force. In so doing, it introduces a nonlinear correlation in the stochastic force not apparent in the multiplicative form of the iGLE.

The iGLE and T-iGLE formalisms have the advantage that they can be readily used to model large systems interacting with complex environments. For example, if the environment can be distinctly subdivided into several uncorrelated parts (baths with different properties such as temperature, response time, etc.), then the friction and the random force are expressed as sums over bath reservoirs,

$$\gamma_{\text{TiGLE}}(t,t') = \sum_k \frac{T_k(t)}{T_k(t_0)} g_k(t) g_k(t') \gamma_{(\text{th})k}[\tau_k(t) - \tau_k(t')], \tag{9}$$

$$\xi_{\text{TiGLE}}(t) = \sum_k \frac{T_k(t)}{T_k(t_0)}\, g_k(t) \xi_{(\text{th})k}[\tau_k(t)]. \tag{10}$$

Note that Eqs. (4), (6), and (9) imply the nonequilibrium kernels can be simply retrieved from equilibrium ones. This property is directly connected to the adiabaticity of the nonequilibrium process and a sufficient separation between the particle motion and any possible resonances to and between the bath reservoirs. Therefore, the applicability of the (T-)iGLE theory implies the existence of a hierarchy of characteristic times bracketing that of the motion of the tagged particle, τ_{part},

$$\tau_{\text{bath}} < \tau_{\text{part}} < \tau_{\text{noneq}}. \tag{11}$$

The fastest time scale, τ_{bath}, corresponds to the fluctuations of the bath modes. The slowest processes are quantified through τ_{noneq} and are characteristic of the nonequilibrium changes in the collective bath (that is, the environment). These slow time scales can therefore be seen in the nonequilibrium relaxation of macroscopic parameters such as temperature, density, etc.

The extended form of the FDR now reads

$$\langle \xi_{\text{TiGLE}}(t) \xi_{\text{TiGLE}}(t') \rangle = k_{\text{B}} T_{\text{eff}}(t,t') \gamma_{\text{TiGLE}}(t,t'), \tag{12}$$

where

$$T_{\text{eff}}(t,t') = \frac{\sum_k \frac{T_k(t)T_k(t')}{T_k(t_0)} g_k(t) g_k(t') \gamma_{(\text{th})k}[\tau_k(t) - \tau_k(t')]}{\gamma_{\text{TiGLE}}(t,t')} \tag{13}$$

is the "effective temperature," a parameter responsible for the relation between the friction kernel and the random force correlation function. Within the framework of the T-iGLE approach, this parameter depends on both initial and final times. The form of these equations becomes compatible with that of Komatsuzaki-Kawai if $T_{\text{eff}}(t,t') = T(t')$ [15]. This latter condition can arise if any of the following conditions are met: the temperature changes uniformly for all the bath modes [i.e., $T_k(t) = T(t)$], there is effectively only one bath mode, or the system is in the near-equilibrium limit.

III. A MODEL SYSTEM

Although the T-iGLE approach has been derived in those cases in which the system and bath time scales are nonresonant, we show here that it is also applicable to the special case of the driven harmonic oscillator investigated in Ref. [51]. Therein, a chosen harmonic oscillator, described by the coordinate q_1, is bilinearly coupled to a special-bath oscillator, q_2. In turn, the latter is influenced by a Langevin bath directly. This system can be viewed as a simplified version of the model analyzed in Ref. [53]. In the latter, a four-atom chain, rather than a single atom, is dissipated at both ends. In the larger system, the temperature associated with the vibrational mode of the central dimer was found not to be uniquely defined. As derived from the correlations of the bond momentum, it is somewhat larger than if it is calculated via the relative velocity of the central dimer. This nontrivial situation results from nonzero interactions of the dimer with the end atoms; such interactions lead to the coupling of the bond momenta of the neighbors. While this issue is absent in the smaller system, it does indicate that these types of simple models can give rise to unusual dynamics capable of testing the nonequilibrium theories we are developing.

The EoMs of the dissipated two-dimensional model system are

$$\begin{aligned} \frac{dq_1}{dt} &= p_1, \\ \frac{dp_1}{dt} &= -\omega_1^2 q_1 + a\omega_2^2 (q_2 - a q_1), \\ \frac{dq_2}{dt} &= p_2, \\ \frac{dp_2}{dt} &= -\zeta p_2 - \omega_2^2 (q_2 - a q_1) + \eta(t), \\ \langle \eta(t)\eta(t') \rangle &= 2 k_{\text{B}} T_0 \zeta \delta(t - t'). \end{aligned} \tag{14}$$

The Langevin bath for the special-bath oscillator is represented by the friction constant ζ and the random force $\eta(t)$. The special-bath oscillator q_2 acts as the conduit of interaction between the chosen oscillator q_1 and the local bath $\eta(t)$. The projection of q_2 results in a driven one-dimensional GLE describing the motion of q_1. As in Ref. [51], the system is prepared in a highly nonequilibrium state: the initial temperatures of the first (chosen) particle and the Langevin bath are $k_{\text{B}} T_0 = k_{\text{B}} T_1^{\text{initial}} = 1/2$, whereas the initial temperature of the special-bath particle is three times larger: $k_{\text{B}} T_2^{\text{initial}} = 3/2$. The values of other parameters are $a = 0.5$, $\omega_1 = 1$, $\omega_2 = 2$, and $\zeta = 0.2$.

The limitations of the iGLE for the first particle as emphasized in Ref. [51] are based on the fact that it does not adequately describe the dynamical behavior of the two-oscillator system: (1) The friction kernel of this system does not fall into the form encoded in Eqs. (4) and (5), because the factors $g(t)$ and $g(t')$ cannot shift the locations of the zeros of the equilibrium friction kernel. (2) The iGLE neglects the nonequilibrium nature of the free energy of the first oscillator. Their conclusions stem from observation of the correlation functions obtained through numerical simulations of the system specified by Eq. (14). The difficulties in applying the iGLE to the current problem are directly connected to the violation of the time scales used in deriving the (T-)iGLE. Indeed, in Ref. [51], there is no pronounced time separation: the vibration frequency of the special-bath oscillator is only two times larger than that of the chosen particle. Moreover, τ_{noneq} is about a period of the bath oscillator q_2, so that inequality (11) is not fulfilled. The lack of a large time-scale separation between the chosen oscillator mode and the special-bath mode therefore creates a challenge to any reduced dimensional description aimed at contracting the special-bath mode.

Within the framework of the (T-)iGLE approach, the free energy (and the mean forces associated with it) adiabatically changes together with the bath properties, so that at any moment of time the free energy depends on the tagged particle coordinates only. On the contrary, in Ref. [51] the mean force has evident dependence on the velocity of the first particle,

$\dot{q}_1$. It is caused by a strong correlation between the first and second particles and resembles the "momentum coupling" in the molecular chain investigated in Ref. [53]. Note that the contribution of the velocity-dependent part quickly disappears (at $t \sim 15$ of the time scale seen in Fig. 2 of Ref. [51]). Since the nonequilibrium effects on the friction properties last longer, up to $t + t' \sim (30 + 40) = 70$, the rest of this article is devoted to the analysis of the friction kernel and its connection to the T-iGLE. (Note that we found that the scale of t' should be 100 times less than that reported in Kawai and Komatsuzaki [51] in order to reproduce the results shown in their Fig. 3. Our analysis below therefore reports time in our present units and ignores differences related to this factor.)

IV. NONEQUILIBRIUM FRICTION KERNEL IN A MODEL SYSTEM

Investigating the expression for the nonequilibrium friction kernel in the iGLE model, Eq. (4), Kawai and Komatsuzaki [51] reasonably claim that the zeros of this kernel must coincide with zeros of the equilibrium friction kernel. However, the time squeezing effect (8), being the origin of the shift in the zeros, as implemented in the temperature-driven approach, Eqs. (6)–(10), was not considered.

We analyze the structure of the friction kernel as it is given in the supplementary material of Ref. [51]. We recapitulate this result noting that it is based on the accurate solution for the pair correlation functions of the dynamic variables. If the latter are united in a vector

$$\Gamma = (q_1 \quad p_1 \quad q_2 \quad p_2), \tag{15}$$

then the 4×4 correlation matrix is

$$\mathbf{G} = \langle \Gamma^{\mathrm{T}} \Gamma \rangle \equiv \begin{pmatrix} \mathbf{G}_{11} & \mathbf{G}_{12} \\ \mathbf{G}_{21} & \mathbf{G}_{22} \end{pmatrix}, \tag{16}$$

where $\mathbf{G}_{ij}$ are 2×2 matrices and $\langle \cdot \rangle$ denotes the averaging over the distribution. The matrix $\mathbf{G}$ represents the full solution for the problem (14) and obeys the differential equation [Eq. (S6) in the supplementary material of Ref. [51]]

$$\frac{d}{dt}\mathbf{G}(t) = \mathbf{L}^{\mathrm{T}}\mathbf{G} + \mathbf{G}\mathbf{L} + 2k_{\mathrm{B}}T_0\zeta\mathbf{E} \tag{17}$$

with

$$\mathbf{L} = \begin{pmatrix} 0 & -\omega_1^2 - a^2\omega_2^2 & 0 & a\omega_2^2 \\ 1 & 0 & 0 & 0 \\ 0 & a\omega_2^2 & 0 & -\omega_2^2 \\ 0 & 0 & 1 & -\zeta \end{pmatrix} \tag{18}$$

incorporating the coefficients from system (14) and $\mathbf{E}$ being the matrix with only one nonzero element, $E_{44} = 1$.

The projection operator [Eq. (S10) in Ref. [51]] is defined by

$$\mathbf{P} = \begin{pmatrix} \hat{\mathbf{1}} & \mathbf{G}_{11}^{-1}\mathbf{G}_{12} \\ \hat{\mathbf{0}} & \hat{\mathbf{0}} \end{pmatrix}, \tag{19}$$

where $\hat{\mathbf{0}}$ and $\hat{\mathbf{1}}$ are 2×2 zero and identity matrices, correspondingly, and $\mathbf{G}_{ij}$ are taken from Eq. (16).

In the most general case, the friction kernel found by Kawaii and Komatsuzaki [51] reads as follows:

$$\gamma(t,t') = \frac{a^2\omega_2^4}{\langle p_1^2(t')\rangle}[(1 - \mathbf{P}^{\mathrm{T}}(t))\mathbf{W}(t,t')(1 - \mathbf{P}(t'))]_{33}, \tag{20}$$

which recasts Eq. (S35) found in the supplementary material of Ref. [51] slightly within our notation. The matrix $\mathbf{W}$ is found by integrating two equations [Eqs. (S34) and (S33) in Ref. [51]]:

$$\frac{d}{dt'}\mathbf{W}(t',t') = \mathbf{Y}^{\mathrm{T}}(t')\mathbf{W}(t',t') + \mathbf{W}(t',t')\mathbf{Y}(t') + 2k_{\mathrm{B}}T_0\zeta\mathbf{E}, \tag{21}$$

when $t = t'$ and

$$\frac{d}{dt}\mathbf{W}(t,t') = \mathbf{Y}^{\mathrm{T}}(t)\mathbf{W}(t,t') \tag{22}$$

for $t > t'$ with the initial condition $\mathbf{W}(0,0) = \mathbf{G}(0)$ and

$$\mathbf{Y}(t) = [1 - \mathbf{P}(t)]\,\mathbf{L} + \frac{d\mathbf{P}}{dt} \tag{23}$$

as also seen in Eq. (S21) in Ref. [51].

With these preliminaries, we can now obtain a formal expression for the friction kernel (which is the only new result in this section),

$$\begin{aligned}\gamma(t,t') = \frac{a^2\omega_2^4}{\langle p_1^2(t')\rangle}[&P_{13}(t)P_{13}(t')W_{11}(t,t') - P_{13}(t)W_{13}(t,t') - P_{13}(t')W_{31}(t,t') + W_{33}(t,t') + P_{13}(t)P_{23}(t')W_{12}(t,t') \\ &+ P_{23}(t)P_{13}(t')W_{21}(t,t') + P_{23}(t)P_{23}(t')W_{22}(t,t') - P_{23}(t)W_{23}(t,t') - P_{23}(t')W_{32}(t,t')],\end{aligned} \tag{24}$$

which allows us to make comparisons between the T-iGLE and the Komatsuzaki-Kawai theory below. The elements, P_{ij} and W_{ij}, of the projection operator $\mathbf{P}$ and matrix $\mathbf{W}$ included in this equation can be found numerically according to the scheme described in Ref. [51].

The form of Eq. (24) resembles that of Eq. (9), in which the cross-correlated bath terms are also included. While the functions $W_{ij}(t,t')$ originate from the correlation functions of the form $\langle \xi_i(t)\xi_j(t')\rangle$, [51] the factors P_{ij} can be associated with the coupling functions, $g_k(t)$.

V. FRICTION KERNEL AT LARGE TIMES

One can solve Eq. (17) at $t \to \infty$ to obtain

$$\mathbf{G}(t \to \infty) = \begin{pmatrix} k_{\mathrm{B}}T_0/\omega_1^2 & 0 & ak_{\mathrm{B}}T_0/\omega_1^2 & 0 \\ 0 & k_{\mathrm{B}}T_0 & 0 & 0 \\ ak_{\mathrm{B}}T_0/\omega_1^2 & 0 & \left(a^2\omega_1^{-2} + \omega_2^{-2}\right)k_{\mathrm{B}}T_0 & 0 \\ 0 & 0 & 0 & k_{\mathrm{B}}T_0 \end{pmatrix}. \tag{25}$$

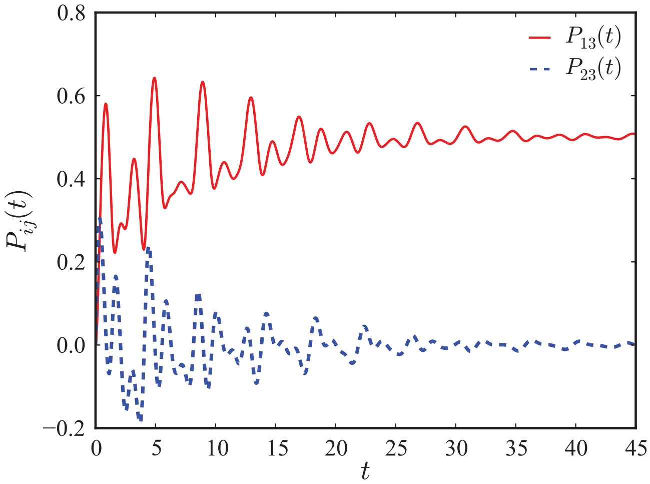

FIG. 1. (Color online) The coefficients P_{13} and P_{23} as functions of time.

Note that not all off-diagonal elements are zero because the interaction between the oscillator and the bath in Eq. (14) stems from the Hamiltonian contribution

$$\omega_2^2(q_2 - aq_1)^2/2 = \omega_2^2\big(a^2q_1^2 - 2aq_1q_2 + q_2^2\big)\big/2, \tag{26}$$

which necessarily includes a nontrivial cross-correlation term. Consequently, the correlation between the bath mode q_2 and the tagged coordinate q_1 never disappears completely.

At large times, Eqs. (19) and (25) reduce to $P_{13}(t \to \infty) = a$ and $P_{23}(t \to \infty) = 0$ (see Fig. 1). Thus, only four terms in Eq. (24) survive at large times, resulting in

$$\gamma(t,t') \to \frac{a^2\omega_2^4}{k_{\rm B}T_0}[a^2W_{11}(t,t') - aW_{13}(t,t') - aW_{31}(t,t') + W_{33}(t,t')]. \tag{27}$$

The formal structure of this equation is the same as that of the interaction potential (26) (indexes 1 and 3 correspond to the phase space variables q_1 and q_2, accordingly). Moreover, all four elements of the matrix $\mathbf{W}$ in the above equation do not vanish at $t,t' \to \infty$, giving

$$W_{11} = k_{\rm B}T_1/\omega_1^2 \quad (\forall\, t \text{ and } t'), \tag{28}$$

$$W_{13} = W_{31} \to ak_{\rm B}T_1/\omega_1^2, \tag{29}$$

$$W_{33} \to a^2k_{\rm B}T_1/\omega_1^2 + k_{\rm B}T_0\big/\big(a^2\omega_2^4\big)\cdot\gamma_{\rm th}(t-t') \tag{30}$$

in accordance with the fact that the correlations between coordinates q_1 and q_2 in the matrix $\mathbf{G}$ do not completely fade away. Note that $\gamma_{\rm th}$ in Eq. (30) is the equilibrium (thermal) friction kernel,

$$\gamma_{\rm th}(t) = a^2\omega_2^2\exp(-\zeta t/2)\left[\cos(\nu t) + \frac{\zeta}{2\nu}\sin(\nu t)\right], \tag{31}$$

where $\nu \equiv \sqrt{\omega_2^2 - \zeta^2/4}$. This equation differs slightly from that of Eq. (88) in Ref. [51] by a sign change in the second term in brackets.

In the next section we demonstrate that the T-iGLE theory gives satisfactory results upon suitable choice of the independent bath modes and corresponding coupling functions, $g_k(t)$.

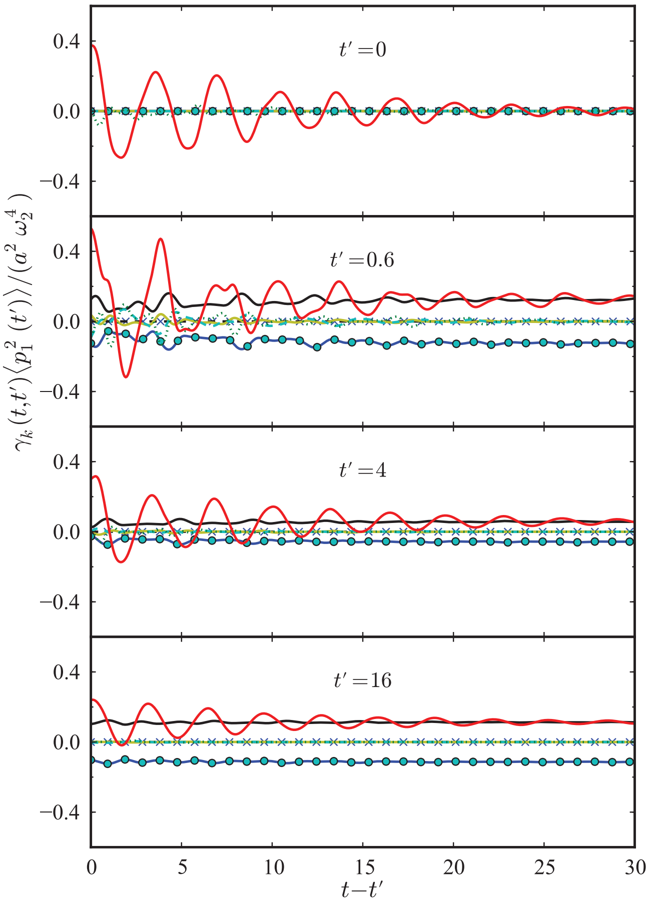

FIG. 2. (Color online) The behavior of each of the nine terms inside of the brackets of Eq. (24) shown as a function of time difference $(t-t')$ for different t', as indicated. The terms are shown according to the following order: (1) $P_{13}(t)P_{13}(t')W_{11}(t,t')$ as black solid curve, (2) $-P_{13}(t)W_{13}(t,t')$ as cyan circles, (3) $-P_{13}(t')W_{31}(t,t')$ as blue solid curve, (4) $W_{33}(t,t')$ as red solid curve, (5) $P_{13}(t)P_{23}(t')W_{12}(t,t')$ as black dashed curve, (6) $P_{23}(t)P_{13}(t')W_{21}(t,t')$ as blue crosses, (7) $P_{23}(t)P_{23}(t')W_{22}(t,t')$ as yellow solid curve, (8) $-P_{23}(t)W_{23}(t,t')$ as green dotted curve, and (9) $-P_{23}(t')W_{32}(t,t')$ as cyan dashed curve.

VI. RESULTS AND DISCUSSION

All nine terms in the square brackets of Eq. (24) denoted as $\gamma_k(t,t')\langle p_1^2(t')\rangle/(a^2\omega_2^4)$ are depicted in Fig. 2. Four dominant terms, $P_{13}(t)P_{13}(t')W_{11}(t,t')$, $-P_{13}(t)W_{13}(t,t')$, $-P_{13}(t')W_{31}(t,t')$, and $W_{33}(t,t')$, corresponding to those in Eq. (27), are shown as a black solid curve, cyan circles, blue and red solid lines, accordingly. Retaining only these nontrivial terms in Eq. (24) results in the approximate fiction kernel,

$$\gamma_{\rm appr}(t,t') = \frac{a^2\omega_2^4}{\langle p_1^2(t')\rangle}[P_{13}(t)P_{13}(t')W_{11}(t,t') - P_{13}(t)W_{13}(t,t') - P_{13}(t')W_{31}(t,t') + W_{33}(t,t')], \tag{32}$$

which deviates only slightly from the true one (see Fig. 3). Other terms in Eq. (24) represent the bath modes, which do not contribute significantly to the dynamics. Below we show that the terms in the above equation originate from the single bath reservoir associated with the coupling coordinate, $q_2 - aq_1$.

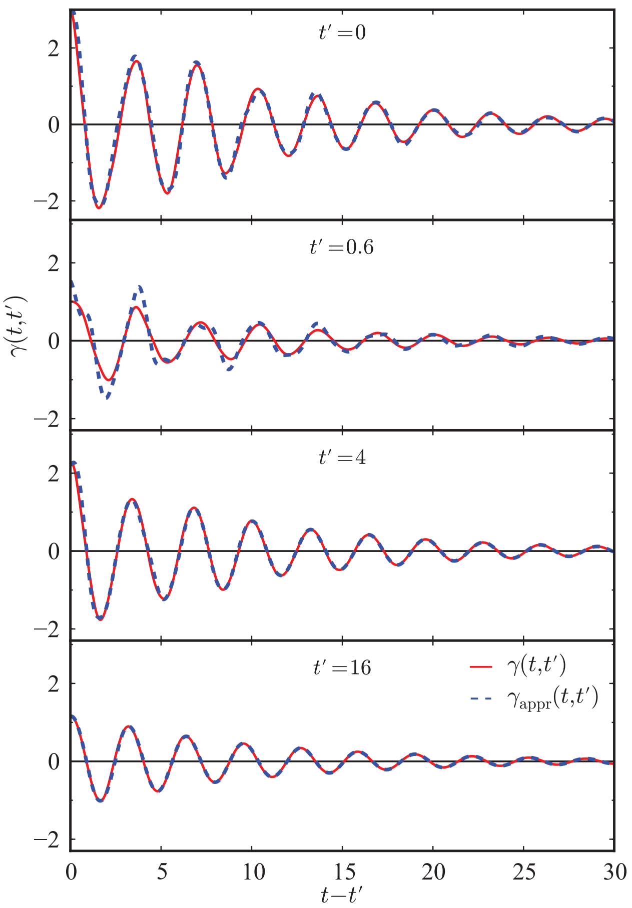

FIG. 3. (Color online) The friction kernel $\gamma(t,t')$ in Eq. (24) (solid red curves), and its approximation $\gamma_{\rm appr}(t,t')$ in Eq. (32) (dashed blue curves) as a function of the time difference at various initial times t'.

The starting point in the multibath T-iGLE approach, Eqs. (9) and (10), is the assumption that different bath reservoirs do not correlate with each other when acting on the tagged particle [15]. It presumes the random force correlation functions between different reservoirs are negligibly small, reflecting the independence (orthogonality) of the random forces. Evidently, this is not the case for the system under investigation [see Eqs. (28)–(30)]. However, the nonvanishing terms appear to cancel each other at large times, allowing the resulting function to approach zero. Since at large times this resulting friction kernel corresponds to the only thermodynamically equilibrated bath mode, it is reasonable to assume that the combination of the four dominant terms in Eq. (32) represents a single independent set of environmental coordinates. That is the environment can be represented by a single-bath reservoir.

By combining the terms in Eq. (32), we regroup the system coordinates in a way that leads to an effective separation of the bath modes to prevent their dependencies on each other. [An analogous procedure was performed in Ref. [47] to restore the coupling function $g(t)$ for a particle diffusing in a two-reservoir bath: a binary mixture of hard spheres.] On the one hand, this procedure implies some arbitrariness in the choice as allowed by the phenomenological character of the iGLE approach. On the other hand, there is no more arbitrariness than in the intuitive notion that the sole connection between the bath and the tagged particle is realized via the combined coordinate $q_2 - aq_1$. Evidence for the fact that the T-iGLE includes only one bath can be found in the one-parameter dependence of the temperature $\langle p_1^2(t')\rangle$ in Eq. (32). Such one-parameter dependence is found also in the effective temperature in Eq. (13) in the case when the temperature is the same for the whole bath reservoir.

The system approaches thermodynamic equilibrium at infinitely large times, hence, the reference time must be chosen equal to $t_0 = \infty$. As mentioned above, the form of Eq. (24) suggests that $g_k(t)$ can be associated with $P_{ij}(t)$. In the nominal one-reservoir case, it is reasonable to set

$$g(t) = P_{13}(t)/P_{13}(\infty) = P_{13}(t)/a. \tag{33}$$

Comparing Eq. (6) with Eq. (32), one should expect that

$$\begin{aligned}\gamma_{\rm th}&[\tau(t)-\tau(t')]\\ &\approx \gamma_{\rm th}^{\rm appr}[\tau(t)-\tau(t')]\\ &= \frac{T(t_0)}{T(t)}\frac{a^4\omega_2^4}{\langle p_1^2(t')\rangle}\big[W_{11}(t,t') - P_{13}^{-1}(t')W_{13}(t,t')\\ &\quad -P_{13}^{-1}(t)W_{31}(t,t') + P_{13}^{-1}(t)P_{13}^{-1}(t')W_{33}(t,t')\big],\end{aligned} \tag{34}$$

where the equality (33) is used and $T(t)$ is the temperature of the bath mode. According to the T-iGLE theory, this temperature is defined through the total energy of the bath oscillators, $\sum \frac{1}{2}(\omega_k^2 q_k^2 + p_k^2)$ under the condition of weak coupling between the tagged and bath coordinates. Since in the present case, the coupling constant a is not small and does not allow a full separation of the bath mode, the contributions from the combined coordinate $q_2 - aq_1$ is included in the definition

$$T(t) = \tfrac{1}{2}\big(\omega_2^2\langle q_2 - aq_1\rangle^2 + \langle p_2^2\rangle\big) \tag{35}$$

of the bath temperature instead.

The bath temperature is also included into the effective time τ from Eq. (8). It results in a shift of the zeros of the friction

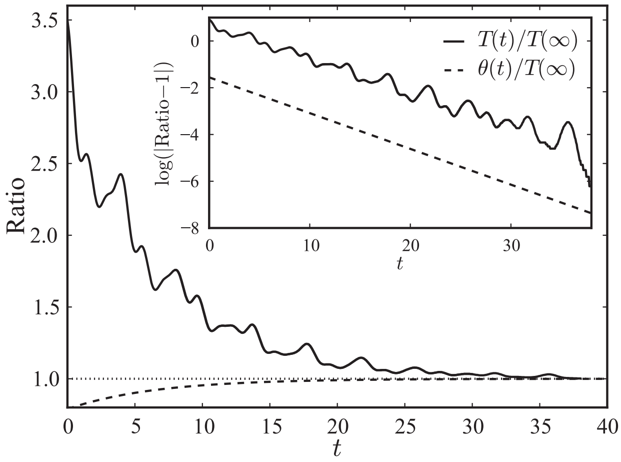

FIG. 4. The ratio $T(t)/T(\infty)$ of the bath mode temperature at time t to that at $t = \infty$ is shown as a function of time (solid curve). The ratio $\theta(t)/T(\infty)$ of the auxiliary factor $\theta(t)$ to $T(\infty)$, is also shown as a function of time (dashed curve). The logarithms of the corresponding relaxation functions $|\text{Ratio} - 1|$ are shown in the insert.

kernel. However, using a modified $T(t)$ from Eq. (8) does not lead to the desired result: the ratio $T(t)/T(\infty)$ (Fig. 4, solid curve) is much higher than the actual shift of zeros. To overcome this problem, the auxiliary parameter $\theta(t)$ was introduced in Eq. (8) with the help of a simple fit

$$\frac{\theta(t)}{T(\infty)} = 1 - 0.211\exp(-0.153\,t) \tag{36}$$

(Fig. 4, dashed curve). Although it has the same dimension as temperature [which is required by the formal use of Eq. (8)], its role is to redefine the time scale for the bath mode. Interestingly, the fitted relaxation rate in the exponent of Eq. (36) is close to the relaxation rate of $T(t)$ (that is, both curves in the inset in Fig. 4 have the same slope up to a sign).

To better understand why the factor $\theta(t)$ does not coincide with the bath temperature, one need only refer to the fundamental construction of the T-iGLE theory. According to Ref. [15], the temperature of an oscillating bath mode is associated with its energy. The latter is expressed via the angle-action variables as

$$T_i(t) \sim E_i(t) = \omega_i(t) I_i. \tag{37}$$

Here I_i is the action which remains nearly constant in the adiabatic T-iGLE theory. The time scale of the relaxing environment is thereby dictated by a slowly changing bath frequency, which is directly connected to the bath temperature. However, in the present case, in which the bath is represented by a single bath mode q_2 and the frequency ω_2 is constant, the nonstationarity of the bath manifests itself through a change in the action variable I_2. As a consequence, the system temperature takes the special case of Eq. (37), $T(t) \sim \omega_2 I_2(t)$, and is evidently not equal, or proportional, to the auxiliary parameter $\theta(t)$ associated with the bath response. The necessity for the correction embodied through $\theta(t)$ is thus a manifestation of the fact that this model includes a single dominant bath mode, whose dynamics is far away from the assumed adiabaticity conditions. Specifically, the recurrences in the dynamics of this bath mode are not available within the assumed structure of the T-iGLE wherein the bath is nonresonant, adiabatic, and massive. [Note that including nonadiabatic effects in the T-iGLE requires the inclusion of higher order terms in the near-adiabatic expansion of the bath mode response to the perturbation (see Ref. [15]). Such an expansion can be performed readily and will be published elsewhere.]

Thus, with all the assumptions made above, the functions $g(t)$ and $T(t)$ can be optimized to reproduce the equilibrium friction kernel of the two-oscillator model as shown in Fig. 5. The T-iGLE theory fails only at small times, $t' < 0.6$, when the system is very far from equilibrium (the case with $t' = 0$

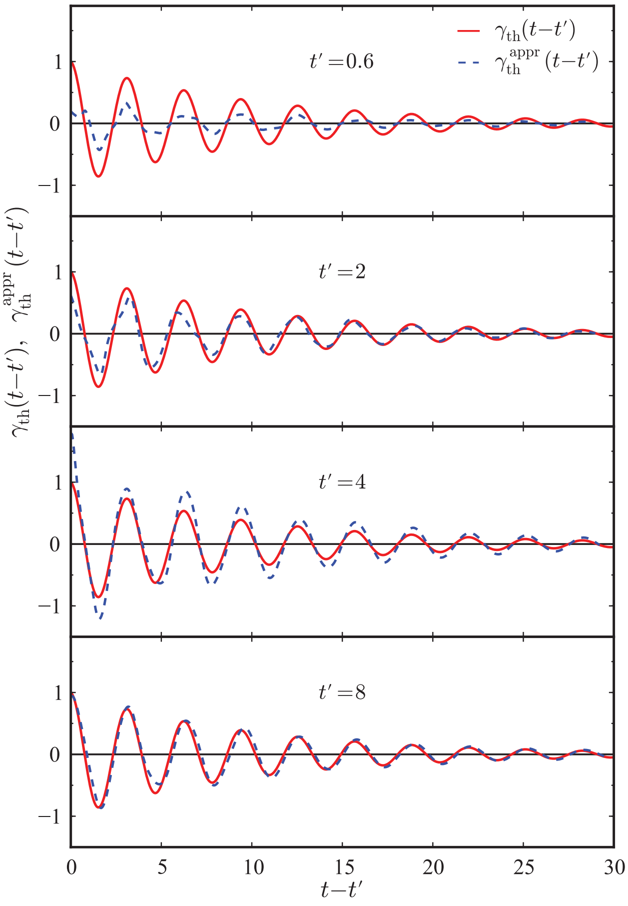

FIG. 5. (Color online) The equilibrium friction kernel $\gamma_{\rm th}(t-t')$, Eq. (31) (solid red curves), and its approximation, Eq. (34) (dashed blue curves), as functions of time difference at various initial times, t'.

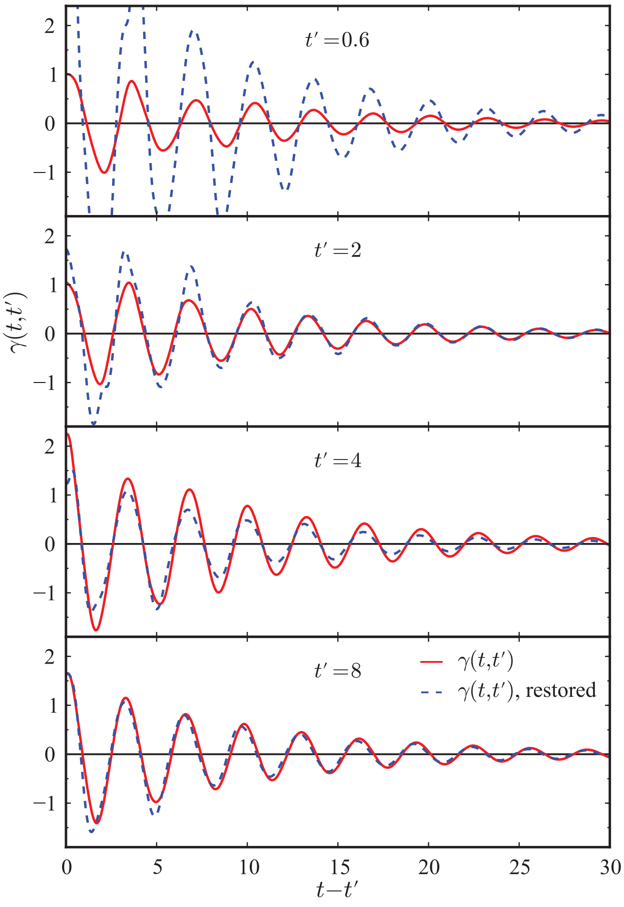

FIG. 6. (Color online) The original friction kernel $\gamma(t,t')$, Eq. (24) (solid curves), and its approximation (dashed curves) as functions of time difference at various initial times, t'.

is not presented). At intermediate times ($t' = 2,4$) the results become satisfactory. At larger times (only $t' = 8$ is shown) the approximate friction kernels are practically identical to the equilibrium one.

To restore the original friction kernel from the equilibrium one, expression (6) is used with the equilibrium friction kernel (31), bath temperature (35), coupling function (33), and the effective time (8) with $\theta(t)$ instead of the actual temperature $T(t)$. The results are illustrated in Fig. 6. As observed in the previous figure, the larger the time, the better the agreement between the Komatsuzaki-Kawai and T-iGLE approximations. Note that the nonequilibrium behavior lasts up to $t = 70$, as observed in the simulations. Thus, the T-iGLE approach, initially prepared for large-dimensional systems, is able to reproduce the major part of the dynamics of the low-dimensional model.

VII. CONCLUSIONS

The present article adds to our increasing understanding of nonequilibrium responses. The recent work of Kawai and Komatsuzaki [51] extended the framework for reduced dimensional models to describe nonequilibrium response. The model they used to illustrate this extension, however, can be captured as shown in this work within the less-general T-iGLE formalism. The fact that the nonequilibrium nature of these systems can be encoded in larger-dimensional projected models does not diminish the need for nontrivial memory in the most reduced dimensional systems. However, it does illustrate the fact that the complexity of these systems can be captured with an appropriate mixture of treatments. It is thus notable that the T-iGLE, as well as iGLE and GLE, can under some assumptions be reproduced within the framework of Kawai and Komatsuzaki's [52] projection operator formulation in those cases when the nonequilibrium behavior arises from external time-dependent perturbations to the system. However, the T-iGLE and iGLE approaches accommodate a wider class of baths and the self-consistent coupling between a given subsystem and the collective dynamics of an ensemble of such systems [46]. It remains a challenge to construct a rigorous representation of such multiscale dynamics.

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