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When a classical master equation (CME) is used to describe the nonadiabatic dynamics of a molecule at metal surfaces, we show that in the regime of reasonably strong molecule-metal couplings, the CME can be reduced to a Fokker-Planck equation with an explicit form of electronic friction. For a single metal substrate at thermal equilibrium, the electronic friction and random force satisfy the fluctuation-dissipation theorem. When we investigate the time scale for an electron transfer (ET) event between the molecule and metal surface, we find that the ET rates show a turnover effect (just as in Kramer's theory) as a function of frictional damping. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4927237]

I. INTRODUCTION

When nuclei interact nonadiabatically with a manifold of electronic states, e.g., an adsorbate at a metal surface, there is a drastic breakdown of the Born-Oppenheimer approximation. For a closed system, with only a few degrees of freedom (DoFs), there exist some exact methodologies for studying this breakdown, including numerical exact approaches, such as Numerical Renormalization Group (NRG),[1–3] Multi-Configuration Time-Dependent Hartree (MCTDH),[4] and Path Integral Monte Carlo (PIMC).[5] These methods are very powerful tools for solving model problems, but are difficult to apply to large, realistic (atomistic) systems.

A much simpler (but more approximate) approach for treating large-scale (atomistic) nonadiabatic dynamics near a metal surface is via a generalized Langevin dynamics (LD), whereby one runs effectively adiabatic molecular dynamics by including friction and a random force from the bath.[6,7] One such stochastic model of friction has been given by Head-Gordon and Tully (HGT), based on a smeared view of nonadiabatic couplings.[8] This model of electronic friction was derived for small electron-phonon (el-ph) couplings and zero temperature and can be extended to the finite temperature case somewhat naturally.[9] Another stochastic model of Langevin dynamics was derived by von Oppen and coworkers based on a nonequilibrium Green function formalism and scattering matrix approaches that are applicable in and out of equilibrium.[10,11] Similar results were achieved using influence functionals.[12,13]

For large systems, surface hopping (SH) is yet another appealing approach for modeling (approximately) dynamics with el-ph couplings.[14,15] Now, traditionally, SH has been restricted to the case that molecules interact with a limited (i.e., a handful) of electronic states. To go beyond this limited case and treat a (infinite) manifold of electronic states, e.g., the case of a molecule near a metal surface, Shenvi *et al.* have proposed an independent electron surface hopping (IESH).[16] According to the IESH scheme, one discretizes the continuum

and, by assuming independent one electron states, one can run reasonably large simulations that can capture vibrational relaxation.[17]

In a series of recent papers,[18,19] we have explored still another SH methodology—based on a classical master equation (CME)—to describe the dynamics of a molecule near a metallic system. According to this CME approach, the influence of the metal surface enters as hopping rates between two potential energy surfaces (PESs). Essentially, if the molecule is charged, the nuclei move on one potential surface, and if the molecule is uncharged, the nuclei move on another. This method is valid when two conditions are met. First, as usual for SH methods, classical mechanics must be a good approximation for the nuclear motion, that is, $\hbar\omega \ll kT$, where ω is a characteristic nuclear frequency and T is the temperature. Second, the CME should provide a good approximation for the kinetics of the electron transfer (ET) between molecule and metal. The CME is a perturbative expansion in metal-molecule coupling and will be accurate when the effect of molecular level broadening associated with the metal-molecule charge-transfer interaction can be disregarded, i.e., $kT \gg \Gamma$, where Γ is the corresponding width. (However, see Ref. 19 for an approximate workaround to incorporate broadening approximately.)

By using such a SH approach to construct and solve the CME, we have shown that an ensemble of SH trajectories admits a unique steady state solution no matter how we prepare the initial states. This solution is a manifestation of relaxation associated with the repeated electron exchange with a thermal electronic bath, similar in nature to the frictional effects described in Refs. 10–13. Now, the latter works consider the case of strong molecule-metal couplings ($\hbar\omega \ll \Gamma$), where the nuclear motion loses its surface hopping character and can be described as motion on a single potential of mean force accompanied by electronic thermal noise and friction. By contrast, the CME is valid (see above) both in the limit of strong metal-molecule coupling ($\Gamma \gg \hbar\omega$) and weak metal-molecule coupling ($\Gamma \ll \hbar\omega$). It is, therefore, of interest to compare

SH dynamics versus mean field LD both in the weak and the strong metal-molecule coupling regimes, both numerically and analytically.

In this paper, we show that in the strong molecule-metal coupling limit, the CME can indeed be mapped onto a Fokker-Planck (FP) equation with (electronic) frictional damping and a random force. This FP equation can be formulated easily as an equivalent Langevin equation. Furthermore, the fluctuation-dissipation theorem is satisfied automatically for the case of a molecule near one equilibrium metallic bath. Our results are identical to those obtained in Ref. 10 in the limit $kT \gg \Gamma$.

The final objective of this paper is to study the effect of friction on the ET rate. This can be done in two ways: either (i) changing the metal-molecule coupling or (ii) adding a nuclear phonon bath. In either case, we find a Kramer turnover effect.

The structure of this paper is as follows. In Sec. II, we derive a FP equation from the CME. In Sec. III A, we compare dynamical observables from a FP equation versus those from a CME. In Sec. III B, we analyze the effect of friction on ET. We conclude in Sec. IV.

A word about notation is in order. Below, we use dimensionless position x ($X = x\sqrt{\frac{\hbar}{m\omega}}$) and momentum p ($P = p\sqrt{m\omega\hbar}$). Here, X and P are the usual position and momentum operators. m and ω are the mass and frequency of an oscillator, respectively.

II. ELECTRONIC FRICTION

A. Classical master equation

For this paper, we will restrict ourselves to a generalized version of the Anderson-Holstein (AH) model. Our model Hamiltonian describes an impurity energy level (molecule) coupled both to a vibrational DoF and a continuum of electronic states,

$$H = H_s + H_b + H_c, \tag{1}$$

$$H_s = E(x)d^+d + \frac{1}{2}\hbar\omega(x^2 + p^2), \tag{2}$$

$$H_b = \sum_k (\epsilon_k - \mu)c_k^+ c_k, \tag{3}$$

$$H_c = \sum_k V_k(c_k^+ d + d^+ c_k), \tag{4}$$

where d (d^+) and c_k (c_k^+) are the annihilation (creation) operators for an electron in the impurity (subsystem) and in the continuum (bath), and x and p are (dimensionless) position and momentum operators for the nuclei. For now, $E(x)$ can be an arbitrary function of nuclear position. For the original AH model, $E(x) = \sqrt{2}gx + E_d$.

In the diabatic picture, there are two classes of PESs—those with the impurity occupied (denoted as 1) and those with the impurity unoccupied (denoted as 0),

$$H_\alpha = V_\alpha + \frac{1}{2}\hbar\omega p^2, \alpha = 0, 1 \tag{5}$$

$$V_0 = \frac{1}{2}\hbar\omega x^2, \tag{6}$$

$$V_1 = \frac{1}{2}\hbar\omega x^2 + E(x). \tag{7}$$

In a CME, we define the classical phase space probability densities $P_0(x,p,t)$ ($P_1(x,p,t)$) for the nuclear DoFs at time t, assuming that the impurity is unoccupied (occupied) and the nuclei is at position x with momentum p. The time evolution of phase space probability densities is governed by[19,20]

$$\frac{\partial P_0(x,p,t)}{\partial t} = \{H_0(x,p), P_0(x,p,t)\} - \gamma_{0\to1}P_0(x,p,t)$$
$$+ \gamma_{1\to0}P_1(x,p,t), \tag{8}$$

$$\frac{\partial P_1(x,p,t)}{\partial t} = \{H_1(x,p), P_1(x,p,t)\} + \gamma_{0\to1}P_0(x,p,t)$$
$$- \gamma_{1\to0}P_1(x,p,t), \tag{9}$$

where {} is the Poisson bracket,

$$\{A, B\} = \frac{1}{\hbar}\left(\frac{\partial A}{\partial x}\frac{\partial B}{\partial p} - \frac{\partial B}{\partial x}\frac{\partial A}{\partial p}\right). \tag{10}$$

$\gamma_{0\to1}$ and $\gamma_{1\to0}$ are the hopping rates. In the case of a one electronic bath,

$$\gamma_{0\to1} = \frac{\Gamma}{\hbar}f(E), \tag{11}$$

$$\gamma_{1\to0} = \frac{\Gamma}{\hbar}(1 - f(E)). \tag{12}$$

Here, f is the Fermi function, and Γ is the hybridization function,

$$\Gamma(\epsilon) = 2\pi \sum_k |V_k|^2 \delta(\epsilon_k - \epsilon), \tag{13}$$

which is assumed to be a constant (i.e., the wide band approximation).

B. Fokker-Planck equation

Let us now write down the CME explicitly for the case of one bath,

$$\hbar\frac{\partial P_0(x,p,t)}{\partial t} = -\hbar\omega p\frac{\partial P_0(x,p,t)}{\partial x} + \hbar\omega x\frac{\partial P_0(x,p,t)}{\partial p}$$
$$- \Gamma f(E)P_0(x,p,t)$$
$$+ \Gamma(1 - f(E))P_1(x,p,t), \tag{14}$$

$$\hbar\frac{\partial P_1(x,p,t)}{\partial t} = -\hbar\omega p\frac{\partial P_1(x,p,t)}{\partial x} + (\hbar\omega x + \frac{dE}{dx})$$
$$\times \frac{\partial P_1(x,p,t)}{\partial p} + \Gamma f(E)P_0(x,p,t)$$
$$- \Gamma(1 - f(E))P_1(x,p,t). \tag{15}$$

We define new densities $A(x,p,t)$ and $B(x,p,t)$ as follows:

$$P_0(x,p,t) = (1 - f(E))A(x,p,t) + B(x,p,t), \tag{16}$$
$$P_1(x,p,t) = f(E)A(x,p,t) - B(x,p,t). \tag{17}$$

Note that $A(x,p,t) = P_0(x,p,t) + P_1(x,p,t)$, which is the total probability density. We would like to find a FP equation describing the time evolution of $A(x,p,t)$.

To that end, if we plug Eqs. (16) and (17) into Eqs. (14) and (15) and add them up, we find

$$\hbar\frac{\partial A(x,p,t)}{\partial t} = -\hbar\omega p\frac{\partial A(x,p,t)}{\partial x}$$
$$+(\hbar\omega x + \frac{dE}{dx}f(E))\frac{\partial A(x,p,t)}{\partial p}$$
$$- \frac{dE}{dx}\frac{\partial B(x,p,t)}{\partial p}. \tag{18}$$

Next, using $B(x,p,t) = f(E)P_0(x,p,t) - (1 - f(E))P_1(x,p,t)$, together with Eqs. (14) and (15), we find

$$\hbar \frac{\partial B(x,p,t)}{\partial t} = -\hbar \omega p \frac{\partial B(x,p,t)}{\partial x} + \hbar \omega p A \frac{\partial f(E)}{\partial x}$$
$$+ \hbar \omega x \frac{\partial B(x,p,t)}{\partial p}$$
$$- \frac{dE}{dx} f(E)(1 - f(E)) \frac{\partial A(x,p,t)}{\partial p}$$
$$+ \frac{dE}{dx}(1 - f(E)) \frac{\partial B(x,p,t)}{\partial p} - \Gamma B(x,p,t).$$

$$(19)$$

Eqs. (18) and (19) are valid under the CME assumptions $kT \gg \hbar \omega$, Γ. We now further make the strong coupling assumption that the inverse lifetime of the impurity is much larger than the oscillator frequency, $\Gamma \gg \hbar \omega$, which implies that the oscillator reaches local equilibrium quickly. Thus, $B(x,p,t)$ should be small relative to $A(x,p,t)$, and one might hope that $B(x,p,t)$ should change slowly with respect to x, p, t. (The validity of these assumptions can be inferred from the data below.) These assumptions allow us to ignore several terms in Eq. (19), and we find

$$B(x,p,t) \approx -\frac{dE}{dx} \frac{1}{\Gamma}(1 - f(E))f(E) \frac{\partial A(x,p,t)}{\partial p}$$
$$+ \frac{\hbar \omega}{\Gamma} pA \frac{\partial f(E)}{\partial x}.$$

$$(20)$$

If we substitute Eq. (20) back into Eq. (18), we arrive at a FP equation (using the fact that $\frac{\partial f(E)}{\partial x} = -\frac{dE}{dx} f(E)(1 - f(E)) \frac{1}{kT}$),

$$\hbar \frac{\partial A(x,p,t)}{\partial t} = -\hbar \omega p \frac{\partial A(x,p,t)}{\partial x} + \frac{\partial U(x)}{\partial x} \frac{\partial A(x,p,t)}{\partial p}$$
$$+ \hbar \gamma_e \frac{\partial}{\partial p}(pA(x,p,t)) + \hbar \gamma_e \frac{kT}{\hbar \omega} \frac{\partial^2 A(x,p,t)}{\partial p^2}.$$

$$(21)$$

Here, γ_e is the electronic friction

$$\gamma_e = \frac{1}{\Gamma} \frac{\omega}{kT} f(E)(1 - f(E)) \left(\frac{dE}{dx} \right)^2,$$

$$(22)$$

and $\frac{\partial U(x)}{\partial x}$ is the mean force

$$\frac{\partial U(x)}{\partial x} = \hbar \omega x + \frac{dE}{dx} f(E).$$

$$(23)$$

We can write the potential of mean force explicitly (up to a constant),

$$U(x) = \frac{1}{2} \hbar \omega x^2 - \frac{1}{\beta} \log(1 + \exp(-\beta E(x))).$$

$$(24)$$

Eqs. (21)-(23) are the main results of this paper. In Appendix A 1, we show that these equations are consistent with those of Ref. 10 in the limit $kT \gg \Gamma$. Also in Appendix A 1, we give a very rough sketch about how our model might connect with the Head-Gordon/Tully electronic friction model. Note that our results are not restricted to a harmonic approximation for the nuclear motion (see Appendix A 2 for the general form of the FP equation in standard units).
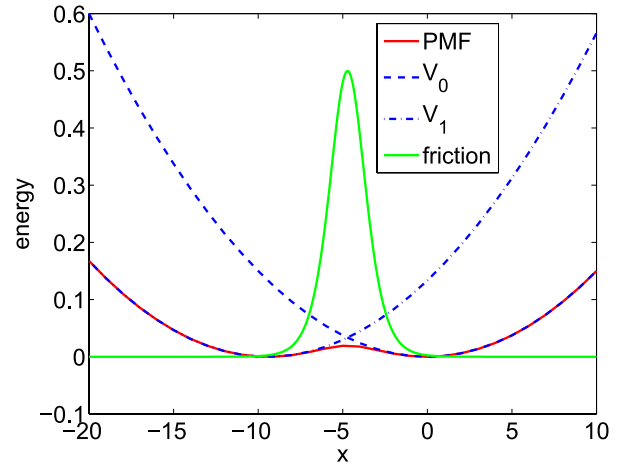

FIG. 1. Potential of mean force (PMF, Eq. (24)) and electronic friction (Eq. (22)) as a function of position for the AH model; V_0 (Eq. (6)) and V_1 (Eqs. (7) and (25)) are the two diabatic PESs. $g = 0.02$, $\hbar \omega = 0.003$, $\Gamma = 0.01$, $\bar{E}_d = 0$, and $kT = 0.01$. Here, the electronic friction is plotted in units of $\frac{g^2 \omega}{\Gamma kT}$.

To better understand Eqs. (21)-(23), we will consider here and below the original AH model, where $E(x)$ is chosen to linearly depend on x,

$$E(x) = \sqrt{2}gx + E_d.$$

$$(25)$$

We define the renormalized energy as $\bar{E}_d \equiv E_d - E_r$, where $E_r = g^2/\hbar \omega$ is the reorganization energy. In Fig. 1, we plot the potential of mean force and electronic friction as a function of x for the AH model. Note that the friction shows a peak where the two PESs cross and multiple surface effects are important. At this point, electrons are exchanged near the metal Fermi energy, where the partial occupation of the metal single-electron levels facilitates this exchange.

C. Equilibrium solution

Before we analyze numerically the behavior of the electronic friction model in Eqs. (21)-(23), a few analytical results about the equilibrium are appropriate.

The electronic friction in the FP equation (Eq. (21)) guarantees that the total system density $A(x,p,t)$ reaches thermal equilibrium. Let us show that this equilibrium (with Eqs. (20) and (21)) will be identical to the equilibrium distribution from the CME.

As shown previously, the simple equilibrium solution for the CME is (for the case of one bath)

$$P_0^{CME}(x,p) = C \exp \left(-\frac{1}{2} \beta \hbar \omega (x^2 + p^2) \right),$$

$$(26)$$

$$P_1^{CME}(x,p) = C \exp \left(-\frac{1}{2} \beta \hbar \omega (x^2 + p^2) - \beta E(x) \right).$$

$$(27)$$

C is a normalization factor, determined by $\int \int dx dp \left(P_0^{CME}(x,p) + P_1^{CME}(x,p) \right) = 1$.

Now, from Eq. (21), one can show easily that the equilibrium solution for the FP equation is

$$A(x,p) = C \exp \left(-\frac{1}{2} \beta \hbar \omega p^2 - \beta U(x) \right).$$

$$(28)$$

From Eq. (20), moreover, we find that B(x,p) vanishes at equilibrium. Thus, Eqs. (16) and (17) are reduced to

$$P_0(x,p) = (1 - f(E))A(x,p), \tag{29}$$

$$P_1(x,p) = f(E)A(x,p). \tag{30}$$

With the explicit form for the potential of mean force in Eq. (24), it is straightforward to show that Eqs. (29) and (30) give the same results as Eqs. (26) and (27).

III. RESULTS

A. Electronic friction-Langevin dynamics (EF-LD)

Finally, we will now study the dynamics of the electronic friction/FP model and compare these dynamics with dynamics from the CME.

For the CME, phase space densities can be propagated using a SH algorithm in real time.[18] In short, we use a swarm of trajectories to sample phase space densities. For each trajectory, we assume the oscillator moves on one potential surface 1 (or 0). At each time step, we generate a random number $\zeta \in [0,1]$. If $\zeta > \gamma_{1 \to 0} dt$ (or $\zeta > \gamma_{0 \to 1} dt$), the oscillator will continue moving on potential surface 1 (or 0) for a single time step of length dt. Otherwise, the oscillator will hop to potential surface 0 (or 1) and move a single time step on potential surface 0 (or 1). If the oscillator hops, the position and momentum are **not** adjusted.

For the FP equation, we use EF-LD,

$$\hbar \dot{p} = -\frac{\partial U}{\partial x} - \hbar \gamma_e p + \xi, \tag{31}$$

$$\hbar \dot{x} = \hbar \omega p, \tag{32}$$

where ξ is the random force that is assumed to be a Gaussian variable with a norm $\sigma = \sqrt{2\hbar\gamma_e kT/(\omega dt)}$ (which satisfies the fluctuation-dissipation theorem[21,22]). Again, dt is the time step interval. We use 4th order Runge-Kutta to integrate Eqs. (31) and (32). Below, unless stated otherwise, we use 10 000 trajectories for SH and EF-LD simulations.

1. Electronic population

First, we look at the electronic population in the impurity as a function of time. For EF-LD, to calculate the electronic population, we make the following approximation:

$$N(t) = \int dx\,dp\,P_1(x,p,t) \approx \int dx\,dp\,f(E)A(x,p,t)$$
$$\equiv \langle f(E) \rangle. \tag{33}$$

At long times, when $B(x,p,t)$ vanishes, Eq. (33) gives the same population as the CME, as shown in Sec. II C. That being said, for short times, SH dynamics and FP dynamics can be extremely different.

In Fig. 2, we simulate electronic population in the impurity for both SH and EF-LD, where we prepare the initial states of the oscillators in one well with a Boltzmann distribution at temperature kT. Note that, because the potential of mean force is a mixture of two diabatic PESs, the initial ($t = 0$) electronic populations from EF-LD are not equal to 1. Furthermore, observe that SH and EF-LD dynamics disagree strongly at short times; agreement occurs only at long times. Clearly, EF-LD is not reliable for calculating electronic population in general. In fact, EF-LD would be useless for simulating the early time dynamics of a photoexcited system where the nuclear distribution was completely uncorrelated with electronic population.

2. Kinetic energies and momentum-momentum correlation functions

Whereas EF-LD does not yield a robust treatment of impurity population, the model is much more reliable for measuring nuclear observables.

In Fig. 3, we look at the average kinetic energy as the oscillator relaxes after being prepared initially with an inflated temperature of $5kT$ (in a Boltzmann distribution). Fig. 4 plots the momentum-momentum correlation. Both plots show that, with increased Γ, EF-LD agrees with SH. Finally, Fig. 5 shows that, for the AH model, EF-LD works best when g (the el-ph coupling) is not too large.

(a)   (b)
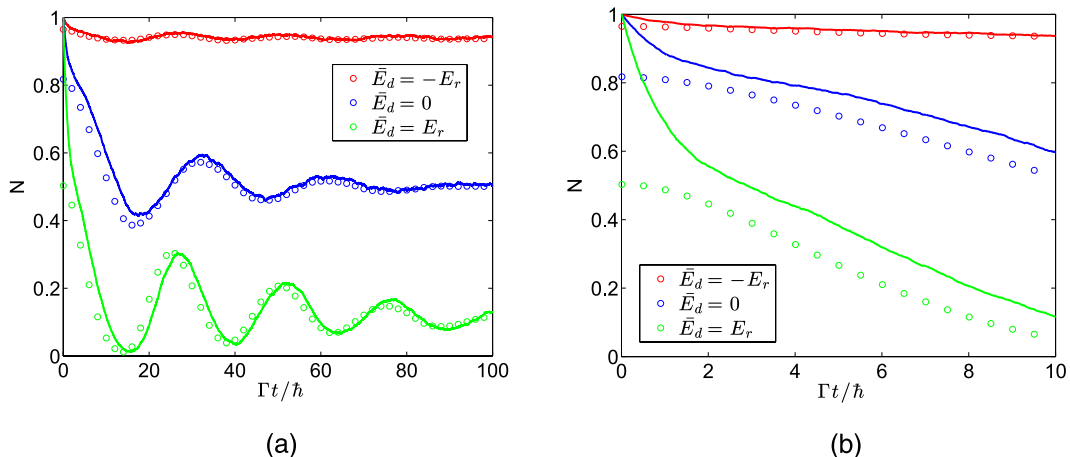
FIG. 2. Electronic population in the impurity from EF-LD (circles) and SH (lines): (a) long time dynamics, (b) short time dynamics. $g = 0.02$, $\hbar\omega = 0.003$, $\Gamma = 0.01$, and $kT = 0.05$. Note that EF-LD and SH agree only at long times; at short times, EF-LD is unreliable.
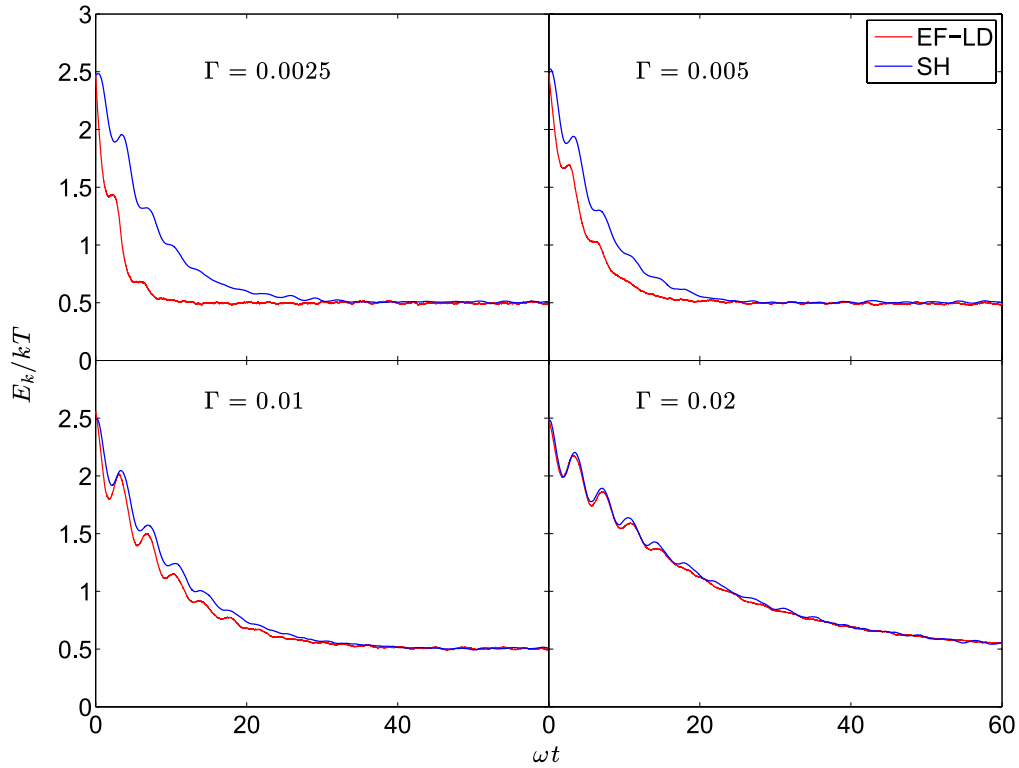
FIG. 3. The effect of electronic friction on phonon relaxation. Here, we plot the average kinetic energy as a function of time. $kT = 0.05$, $\hbar\omega = 0.003$, $g = 0.02$, and $\bar{E}_d = 0$. We prepare the initial states satisfying a Boltzmann distribution with a temperature $5kT$. Note that EF-LD agrees with SH increasingly well as Γ increases.

Overall, our conclusions are as follows. On the one hand, Ref. 19 shows our SH approach agrees well with the quantum master equation (QME), both when $\Gamma \ll \hbar\omega$ or $\Gamma \gg \hbar\omega$. On the other hand, here we have shown the EF-LD agrees well with SH only in the limit that $\Gamma \gg \hbar\omega$ and when the initial conditions are quasi-equilibrium. Because both SH and EF-LD are computationally inexpensive with roughly the same cost, for now we presume SH approach will be more useful than
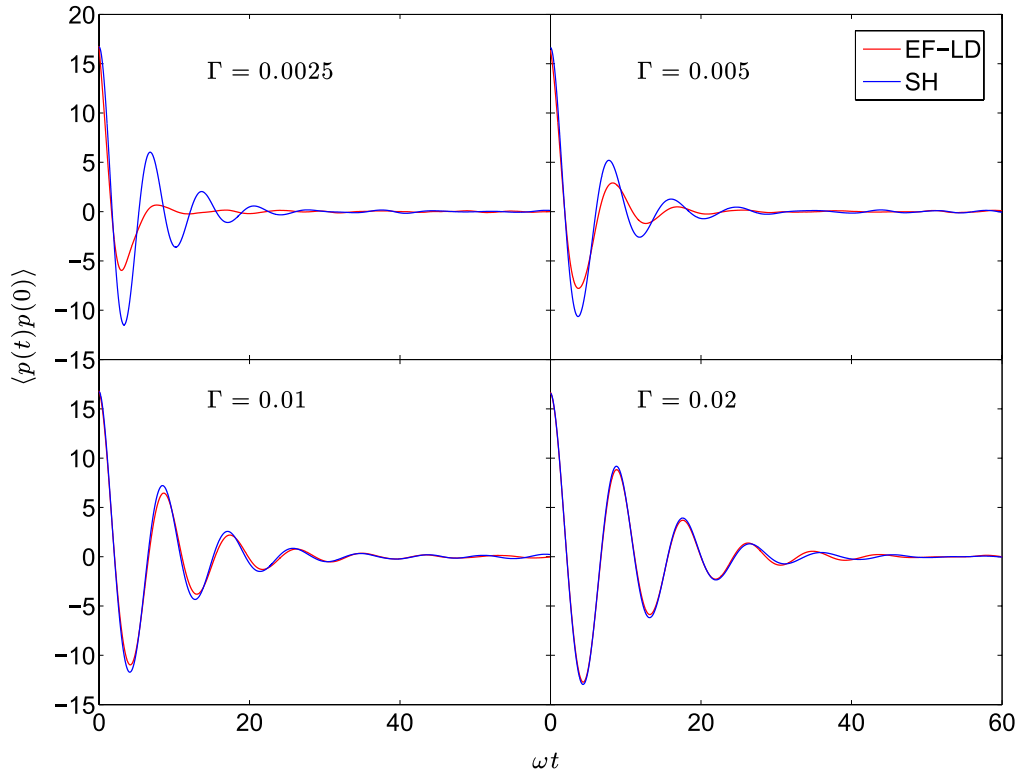

FIG. 4. The effect of electronic friction on the momentum-momentum correlation function. $kT = 0.05$, $\hbar\omega = 0.003$, $g = 0.02$, and $\bar{E}_d = 0$. 100 trajectories have been used to calculate the momentum-momentum correlation function. Note that EF-LD agrees better with SH for large Γ.
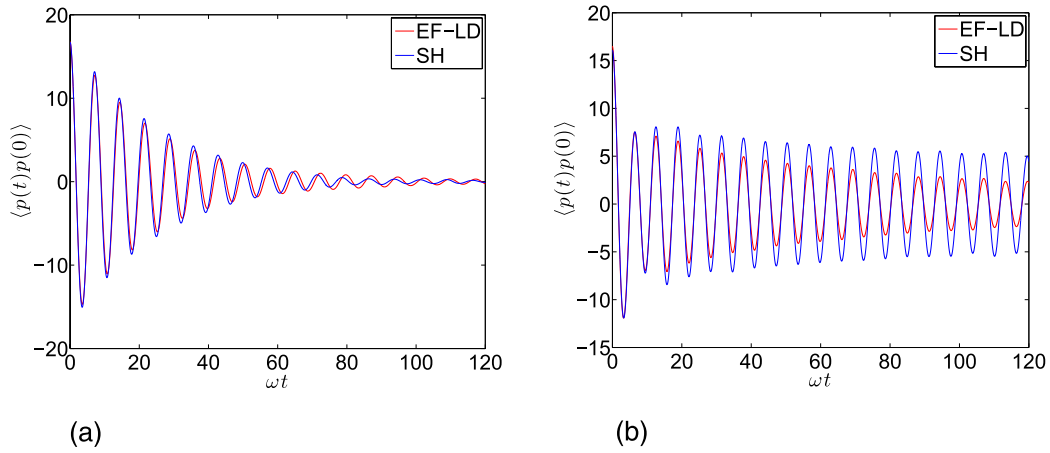
FIG. 5. The effect of electronic friction on the momentum-momentum correlation function. $kT = 0.05$, $\Gamma = 0.01$, $\hbar\omega = 0.003$, and $\bar{E}_d = 0$. 100 trajectories have been used to calculate the momentum-momentum correlation function. Note that EF-LD agrees better with SH when g is smaller. (a) $g = 0.01$. (b) $g = 0.04$.
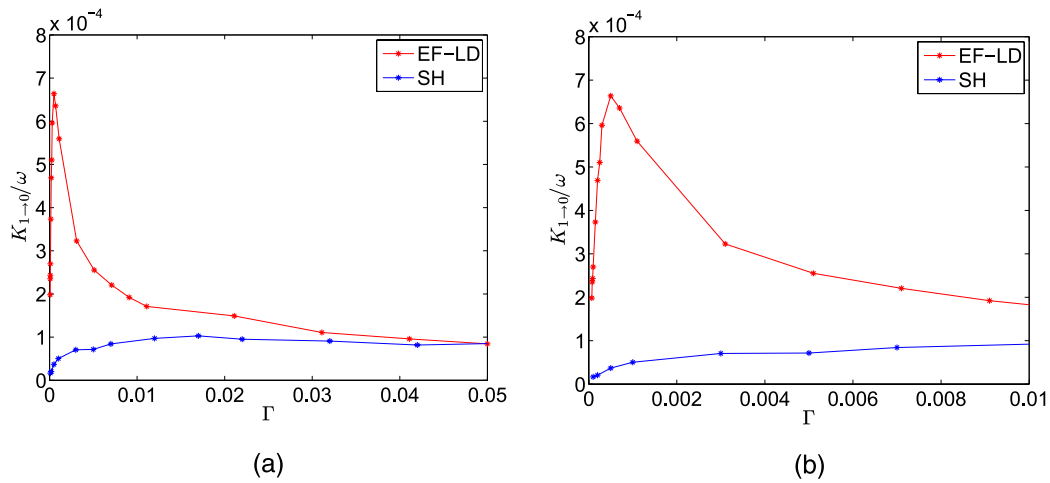

FIG. 6. (a) Electron transfer rate as a function of Γ; (b) a zoomed in picture of (a) in the range $\Gamma \in [0, 0.01]$. $g = 0.02$, $\hbar\omega = 0.003$, $\bar{E}_d = 0$, and $kT = 0.01$. The electronic friction varies as $1/\Gamma$, so that over damped dynamics occur as $\Gamma \to 0$.

EF-LD in the limit $kT \gg \Gamma$. In other words, EF-LD would appear useful only for physical intuition.

B. The effect of friction on barrier crossings

1. Electronic friction

The potential of mean force for the AH model is a double well with a barrier (Fig. 1), and the friction increases as Γ decreases (see Eq. (22)). Thus, in the context of EF-LD, the electron transfer rate as a function of friction (or Γ) should give a turnover effect just as in standard transition state theory.

In Fig. 6, we plot ET rates as a function of Γ for both EF-LD and SH. When calculating ET rates from SH dynamics, we fit the long time electronic population to an exponential function, which should yield total ET rates,

$$K_T = K_{1\to0} + K_{0\to1}. \tag{34}$$

To determine the forward rates ($K_{1\to0}$), we invoke detailed balance,[23] so that

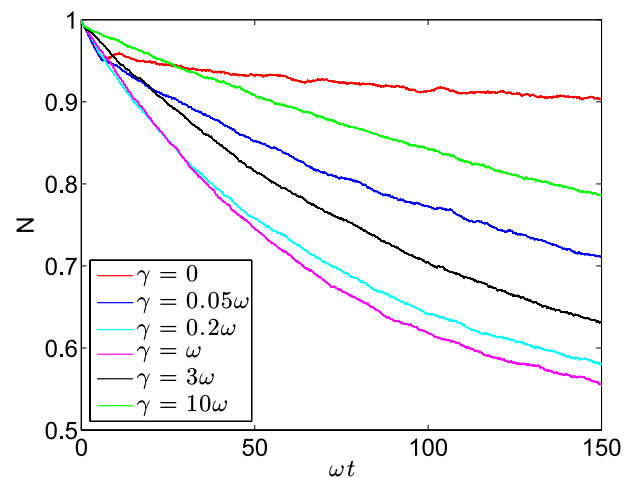$$K_{1\to0} = K_{0\to1}\exp(\beta\bar{E}_d). \tag{35}$$

FIG. 7. Electronic population in the impurity as a function of time with different phonon frictions. $g = 0.02$, $\hbar\omega = 0.003$, $\Gamma = 0.01$, $\bar{E}_d = 0$, and $kT = 0.01$.

To determine the ET rates from EF-LD, we fit the average position $\langle x \rangle$ as a function of time with an exponential. Again, by using the detailed balance in Eq. (35), we can determine the forward ET rates. This prescription allows us to extract
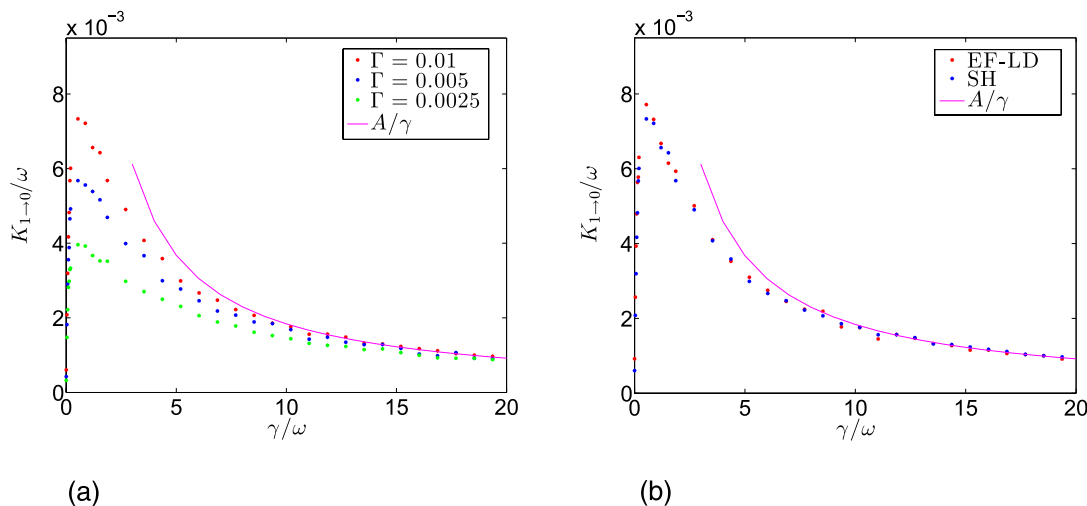
FIG. 8. ET forward rates as function of phonon friction γ from SH and EF-LD. $g = 0.02$, $\hbar\omega = 0.003$, $\bar{E}_d = 0$, and $kT = 0.01$. Note the agreement between EF-LD and SH. For large γ, we fit the ET rates as A/γ (where A is a fitting parameter), which indicates that ET decays as $1/\gamma$ for large friction. (a) ET forward rates from SH. (b) $\Gamma = 0.01$ for SH and EF-LD.

ET rates without ever calculating the electronic population explicitly.

In Fig. 6, we see that, according to EF-LD, there is a large turnover effect in the ET rate as a function of Γ. This Kramer turnover is a well-known function of overdamping. For SH dynamics, we do not see such a large effect, but there is an optimal range of Γ that maximizes the ET rate (around $\Gamma = 0.015$). Note that EF-LD should not (and does not) agree with SH dynamics for small Γ ($\Gamma \leq \hbar\omega$). The rates in Fig. 6 are quite slow and SH and EF-LD are in near agreement for $\Gamma \geq 0.01$.

2. Imposition of external (phonon) frictional bath

As seen in Fig. 6, we obtain a pronounced turnover in the rate as a function of Γ from the EF-LD dynamics when this dynamics fails to correctly describe system behavior ($\Gamma \ll \hbar\omega$). For comparison with standard descriptions of environmental (phonon) effects on reaction rates, we next simulate the effect of a thermal environment (solvent motions) by adding standard (Markovian and position independent) frictional damping γ and the associated random force that together satisfy the fluctuation-dissipation theorem with the same temperature as the electronic bath.

Fig. 7 shows electronic population in the impurity as a function of time with different phonon frictions from SH. Here, we are operating in the limit $E_r \gg kT$. If we compare Fig. 2 against Fig. 7, we find that, except for an early time transient, Fig. 7 has no oscillations in the electronic population. When we increase the phonon friction from 0 to ω, the ET rates increase. Thereafter, increasing the phonon friction reduces the ET rates. Thus, again, we find a Kramer's turnover effect.[22,23]

In Fig. 8(a), we plot the forward ET rates ($K_{1 \to 0}$) as a function of phonon frictions from SH, which shows the turnover phenomenon clearly. Moreover, the ET rates tend to agree for large phonon friction regardless of Γ. Note the relative scale of ET rates between Figs. 6 and 8. A simple fit shows that the ET rate scales as $1/\gamma$, as would be expected from Kramer's

theory. As Fig. 8(b) shows, ET rates from EF-LD agree well with results from SH.

IV. CONCLUSION

In this paper, we have found a FP equation to characterize a CME for an impurity subsystem coupled to an electronic continuum and a nuclear DoF. (If the nuclear DoF is harmonic, we assume that we are in the limit of $\Gamma \gg \hbar\omega$.) We have found an explicit form for the electronic friction and random force. For the case of one bath, the FP equation satisfies the fluctuation-dissipation theorem automatically. In equilibrium, we have shown that the FP equation gives the same solution as the CME. For the transient dynamics, EF-LD agrees well with SH for large Γ if we focus on nuclear properties and we assume that the system begins close enough to equilibrium (i.e., not photoexcitation). Finally, we also have investigated the effect of friction on ET rates, where we have found an analog to the Kramer's turnover effect.

Looking forward, several questions arise. First, recent experiments[24,25] have suggested that electronic friction cannot treat electron-molecule scattering at a metal surface. However, Wodtke *et al.* have used the Head-Gordon/Tully prescription for frictional dynamics (which we cannot fully recover in our theory). It will be interesting to see how the electronic frictional model described here in Eq. (22) performs (compared to both the more robust SH calculation and to experiments).

Second, there are many other exciting questions to address in the regime of nonequilibrium dynamics, including the instability as induced by current.[26,27] This work is ongoing.

APPENDIX: THE HEAD-GORDON/TULLY FRICTION MODEL AND BEYOND THE HARMONIC APPROXIMATION

In contrast with the body of this paper, we now work in standard units, where X and P have units of position and momentum.

1. A rough sketch relating our model of electronic friction to the Head-Gordon/Tully (HGT) model

In this paper, we have derived the von Oppen model of electronic friction (Eq. (22)) starting from a SH picture of nuclear-electronic dynamics (i.e., the classical master equation). Now in the literature, there is a different model of electronic friction, due to HGT. As presented in Ref. 8, in practice, the HGT model has been used for *ab initio* calculations of clusters where there is at least a small band gap. In such a case, the HGT frictional damping parameter can be written down as[16]

$$\gamma = \pi \hbar d_{j,j+1}^2, \tag{A1}$$

where j is the highest occupied adiabatic orbital and $j+1$ is the lowest unoccupied adiabatic orbital. $d_{j,j+1}$ is the derivative

coupling between orbital j and $j+1$. In this appendix, we would like to make a heuristic sketch for how one might try to reconcile Eq. (22) (which was derived at large temperature) and Eq. (A1) (which was derived at zero temperatures). The argument goes as follows.

In the context of a true many-body calculation, with an infinite number of electronic DoFs, a natural extension of Eq. (A1) would be to assume that the damping term varies as

$$\gamma = \pi \hbar \sum_{\alpha,\alpha'} d_{\alpha,\alpha'}^2, \tag{A2}$$

where α and α' index the adiabatic orbitals below and above the Fermi level. For a Hamiltonian of the form in Eqs. (1)-(4), we can then rewrite the electronic friction as

$$\gamma = \pi \hbar \sum_{\alpha,\alpha'} d_{\alpha,\alpha'}^2 = \pi \hbar \sum_{\alpha,\alpha'} \frac{|\langle \alpha| \frac{\partial H}{\partial X} |\alpha'\rangle|^2}{(\epsilon_\alpha - \epsilon_{\alpha'})^2}$$

$$= \pi \hbar \left(\frac{dE}{dX}\right)^2 \sum_{\alpha,\alpha'} \frac{|\langle \alpha|d^+d|\alpha'\rangle|^2}{(\epsilon_\alpha - \epsilon_{\alpha'})^2}, \tag{A3}$$

where we have used Hellmann-Feynman theorem. Converting the sum to an integral in energy domain, and using a Green function formalism, we can represent d^+d explicitly in the adiabatic basis,[28]

$$\sum_{\alpha,\alpha'} \frac{|\langle \alpha|d^+d|\alpha'\rangle|^2}{(\epsilon_\alpha - \epsilon_{\alpha'})^2} = \int_{-\infty}^{\epsilon_F} d\epsilon_1 \rho(\epsilon_1) \int_{\epsilon_F}^{\infty} d\epsilon_2 \rho(\epsilon_2) \frac{1}{2\pi\rho(\epsilon_1)} \frac{\Gamma}{(\epsilon_1 - E(X))^2 + (\Gamma/2)^2}$$

$$\times \frac{1}{2\pi\rho(\epsilon_2)} \frac{\Gamma}{(\epsilon_2 - E(X))^2 + (\Gamma/2)^2} \frac{1}{(\epsilon_1 - \epsilon_2)^2}. \tag{A4}$$

$\rho(\epsilon_1)$ ($\rho(\epsilon_2)$) is the density of states at ϵ_1 (ϵ_2).

At this point, noting that Eq. (A2) (or Eq. (A4)) is a zero temperature result, one might propose incorporating finite temperature by including the Fermi-Dirac distribution and adding a small number ξ in the denominator. Eq. (A4) then becomes

$$\int d\epsilon_1 f(\epsilon_1) \int d\epsilon_2 (1 - f(\epsilon_2)) \left(\frac{1}{2\pi}\right)^2$$

$$\times \frac{\Gamma}{(\epsilon_1 - E(X))^2 + (\Gamma/2)^2}$$

$$\times \frac{\Gamma}{(\epsilon_2 - E(X))^2 + (\Gamma/2)^2} \frac{1}{(\epsilon_1 - \epsilon_2)^2 + \xi^2}. \tag{A5}$$

Assuming ξ is small, we can further approximate

$$\frac{1}{(\epsilon_1 - \epsilon_2)^2 + \xi^2} = \frac{\xi}{(\epsilon_1 - \epsilon_2)^2 + \xi^2} \frac{1}{\xi} \approx \pi \delta(\epsilon_1 - \epsilon_2) \frac{1}{\xi}. \tag{A6}$$

Then, the electronic friction becomes

$$\gamma \approx \pi \hbar \left(\frac{dE}{dX}\right)^2 \int \frac{d\epsilon_1}{\pi} f(\epsilon_1)(1 - f(\epsilon_1))$$

$$\times \left(\frac{\Gamma/2}{(\epsilon_1 - E(X))^2 + (\Gamma/2)^2}\right)^2 \frac{1}{\xi}. \tag{A7}$$

Finally, if we make the ansatz that temperature is the relevant broadening parameter and set ξ to be the order of temperature ($\xi \sim kT$), we get the same expression for the friction as in Ref. 10 (up to a constant factor). In the limit $\Gamma \ll kT$, we can ignore the level broadening and we recover

$$\gamma \sim \frac{\hbar}{\Gamma} \frac{1}{kT} f(E)(1 - f(E)) \left(\frac{dE}{dX}\right)^2, \tag{A8}$$

which is exactly the same as what we get from the CME (Eq. (22)) but now in standard units. See Eq. (A16).

We must emphasize that this "derivation" is highly *ad hoc*. On the one hand, given the leaps of faith in this derivation, the reader might well decide that the HGT model is a very different model of friction than the von Oppen model. One the other hand, this derivation does show some relevant features in common, for instance, both frictional models scale as g^2 and peak near the crossing region. Further research will be necessary to assess the connection derived here and the domain of validity of the HGT model.

2. Beyond the harmonic approximation for the motion of the nuclei

We will now show that the model of friction in Eq. (22) does not rely on a harmonic potential energy surface for the nuclei. Consider the general potential $U_0(X)$ for the nuclei,

$$H = H_s + H_b + H_c, \tag{A9}$$

$$H_s = E(X)d^+d + \frac{P^2}{2m} + U_0(X), \tag{A10}$$

$$H_b = \sum_k (\epsilon_k - \mu)c_k^+ c_k, \tag{A11}$$

$$H_c = \sum_k V_k(c_k^+ d + d^+ c_k). \tag{A12}$$

In such a case, the CME is[20]

$$\frac{\partial P_0(X,P,t)}{\partial t} = -\frac{P}{m}\frac{\partial P_0(X,P,t)}{\partial X} + \frac{dU_0}{dX}\frac{\partial P_0(X,P,t)}{\partial P}$$
$$- \frac{\Gamma}{\hbar}f(E)P_0(X,P,t)$$
$$+ \frac{\Gamma}{\hbar}(1-f(E))P_1(X,P,t), \tag{A13}$$

$$\frac{\partial P_1(X,P,t)}{\partial t} = -\frac{P}{m}\frac{\partial P_1(X,P,t)}{\partial X} + (\frac{dU_0}{dX}+\frac{dE}{dX})$$
$$\times \frac{\partial P_1(X,P,t)}{\partial P} + \frac{\Gamma}{\hbar}f(E)P_0(X,P,t)$$
$$- \frac{\Gamma}{\hbar}(1-f(E))P_1(X,P,t). \tag{A14}$$

Following the exact procedure as above in Eqs. (16)-(21), we can write the FP equation for the general case,

$$\frac{\partial A(X,P,t)}{\partial t} = -\frac{P}{m}\frac{\partial A(X,P,t)}{\partial X} + \frac{\partial U(X)}{\partial X}\frac{\partial A(X,P,t)}{\partial P}$$
$$+ \frac{\gamma_e}{m}\frac{\partial}{\partial P}(PA(X,P,t)) + \gamma_e kT\frac{\partial^2 A(X,P,t)}{\partial P^2}, \tag{A15}$$

where γ_e is the electronic friction

$$\gamma_e = \frac{\hbar}{\Gamma}\frac{1}{kT}f(E)(1-f(E))\left(\frac{dE}{dX}\right)^2, \tag{A16}$$

and $U(X)$ is the potential of mean force,

$$U(X) = U_0(X) - \frac{1}{\beta}\log(1+\exp(-\beta E(X))). \tag{A17}$$

The equivalent Langevin dynamics is

$$m\ddot{X} = -\frac{\partial U(X)}{\partial X} - \gamma_e\dot{X} + \xi(t), \tag{A18}$$

where $\xi(t)$ is the random force that satisfies

$$\langle \xi(t)\xi(t')\rangle = 2kT\gamma_e\delta(t-t'). \tag{A19}$$

Eq. (A16) is a general form of electronic friction that does not depend on any harmonic approximation.

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