


## Open quantum systems in thermal nonergodic environments

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We analyze the dynamics of an open system coupled to a nonergodic environment for which the correlation function does not decay, leading to a failure of the weak coupling and Markov approximations standard in open systems. We show that nonergodicity appears for environments at finite temperatures that have non-Gaussian statistics and do not fulfill the eigenstate thermalization hypothesis. We illustrate our statements by considering a thermal spin-boson environment that models a gas of dye molecules, and show that nondecaying correlations are connected to a  $1/f$  noise that extends to zero frequencies. This suggests the idea that nonergodic environments may be at the origin of the  $1/f$  behavior observed in other hybrid environments such as the ones encountered in superconducting qubits.

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### I. INTRODUCTION

Quantum mechanical systems coupled to an environment, i.e., open quantum systems, appear in a wide range of fields such as soft and condensed matter physics, quantum chemistry, quantum optics, or biology [1,2]. They are also relevant in quantum technological devices where quantum mechanical properties, crucial to their performance, are affected by the environmental noise. In all these contexts, a system of interest ( $H_S$ ) is considered to be coupled to the environment ( $H_E$ ) through an interaction of the form  $H_I = BS$ , where  $B$  and  $S$  are the environment and system coupling operators, respectively [1–6], such that the total Hamiltonian reads

$$H = H_E + H_S + BS. \quad (1)$$

The dynamics of the system mean values, described with its reduced density operator  $\rho_S(t) = \text{tr}_E\{\rho(t)\}$  [with  $\rho(t)$  being the total state at the time  $t$ ], is strongly conditioned by the different moments of the noise operator  $B$  with respect to the environment initial state  $\rho_E$ . When the environment is a set of harmonic oscillators in a Gaussian state and linearly coupled to the system, its statistics is Gaussian and all higher-order moments are either zero or can be written in terms of the second-order one, the correlation function

$$C_{\tilde{B}}(t) = \text{tr}_E\{\tilde{B}(t)\tilde{B}(0)\rho_E\}, \quad (2)$$

via the Wick's theorem. Here we have defined a renormalized operator,

$$\tilde{B} = B(t) - \text{tr}\{B(0)\rho_E\}, \quad (3)$$

accordingly redefining the system Hamiltonian as

$$\tilde{H}_S = H_S + \text{Str}\{B(0)\rho_E\}. \quad (4)$$

We assume, in addition, that the environment is initially in a thermal state,  $\rho_E = \rho_E^{\text{th}} = e^{-\beta H_E}/Z_E$ , with  $Z_E$  the partition function and  $\beta$  the inverse temperature. Thus,  $[\rho_E, H_E] = 0$

and, therefore,  $C_{\tilde{B}}(t_1, t_2) = \text{tr}_E\{\tilde{B}(t_1)\tilde{B}(t_2)\rho_E(0)\}$  depends only on the time difference,  $t = t_1 - t_2$ , i.e.,  $C_{\tilde{B}}(t_1, t_2) \equiv C_{\tilde{B}}(t)$ . Recent progress in noise spectroscopy in superconducting qubits [7,8] has revealed the non-Gaussian nature of their environment, in particular the  $1/f$  noise produced by surface impurities [9,10]. The non-Gaussianity affects the reduced dynamics of the system in the strong-coupling regime, when higher-order moments are relevant. Yet, in the weak coupling (when  $g \approx \|H_I\|$  is small compared to all other energy scales),  $\rho_S(t)$  is dominated by the correlation function (2), which suggests that Gaussian and non-Gaussian statistics may be hard to distinguish.

Here, we argue that this might not be the case. The details are as follows:

(i) We present a class of environments with non-Gaussian statistical properties that already manifest in the weak-coupling limit, as they display a nondecaying correlation,  $\lim_{t \rightarrow \infty} C_{\tilde{B}}(t) = C_0$ .

(ii) We argue that a finite  $C_0$  is linked to the statistical properties of the  $H_E$  eigenstates, and that it dramatically affects the accuracy of the weak-coupling approximation and the related Lindblad equation.

Indeed, in classical statistical physics, it is known that for a system of noninteracting or weakly interacting particles, the long-time decay of the correlation is linked to ergodicity as defined by the Khinchin theorem [11–13]. Thus, for a system in equilibrium, the ergodic property ( $\lim_{T \rightarrow \infty} \int_0^T B(t) dt = \text{av}[B]$ ) is fulfilled iff  $\lim_{t \rightarrow \infty} C_{\tilde{B}}(t) = 0$ , where  $C_{\tilde{B}}(t) = \text{av}\{\tilde{B}(t)\tilde{B}\}$  and  $\text{av}[\cdot]$  denotes an ensemble average. Hence, nonergodic environments do not fulfill the *sufficient condition* derived by Davies [14,15] for a well-defined weak-coupling limit,

$$\int_0^\infty dt |C_{\tilde{B}}(t)| (1 + |t|)^\epsilon < \infty, \quad (5)$$

with  $\epsilon > 0$ , and, in accordance, they have been shown to produce a failure in the standard weak-coupling approximation [16]. This paper analyzes under which conditions such nonergodic environments appear, and explains how they lead to a highly system-environment correlated state that invalidates the Born approximation, and therefore the closely linked weak-coupling approximation. Moreover, we show that besides the trivial Gaussian case, the decay to zero of  $C_{\tilde{B}}(t)$  may be linked to the eigenstate thermalization hypothesis (ETH), which states that the properties of a quantum system, in our case the environment, evolve at long times towards those in a thermal state [17–20]. We analyze an environment of dye molecules described with a spin-boson model [21–23] and show how nonergodicity can emerge in such realistic and nonexotic scenarios. Finally, we relate the nonergodicity to the appearance of a  $1/f$  noise spectrum that extends to zero frequencies.

This paper is organized as follows: In Sec. II, we present general statements on the correlation function of the environment based on its spectral decomposition in terms of environment eigenstates. We analyze the decay of such function and connect it to the statistical properties of the coupling operator, the notion of typicality, and the ETH ansatz. In Sec. III, we study the consequences of having a correlation function that decays to a finite offset value and how it leads to a failure of the weak-coupling approach and the Lindblad description of an open quantum system. In Sec. IV, we show how a hybrid environment described by a spin-boson model can induce a nondecaying correlation function. To this aim, we present matrix product state (MPS) simulations of such a function for an increasing number of bosons in the environment and different values of the environment parameters. As it is shown, the correlation function presents an offset for certain environment parameters. However, although we have performed the MPS simulations for an increasing number of environment oscillators and the offset appears to remain stable, our numerical solution does not allow us to give any prediction of the survival of the offset for a bosonic continuum. In addition, we show the connection between the emergence of an offset and the  $1/f$ -noise phenomena. Finally, in Sec. V, we present the conclusions and outlook of our investigation.

## II. ENVIRONMENT CORRELATION FUNCTION

### A. General form and the onset of an offset

General statements on  $C_{\tilde{B}}(t)$  can be made when representing it in its eigenbasis. Let  $\rho_E = \sum_k \eta_k |\epsilon_k\rangle\langle\epsilon_k|$  be an equilibrium state of the environment, with  $|\epsilon_k\rangle$  its eigenstates. Thus, Eq. (2) can be written as

$$C_{\tilde{B}}(t) = \sum_{l,k,\omega_{kl} \neq 0} \eta_k |B^{kl}|^2 e^{i\omega_{kl}t} + C_0, \quad (6)$$

where  $\omega_{kl} = \epsilon_k - \epsilon_l$ ,  $B^{kl} = \langle\epsilon_l|B|\epsilon_k\rangle$ , and

$$C_0 = \sum_k \eta_k (B^{kk})^2 - \left( \sum_k \eta_k B^{kk} \right)^2 + d_0. \quad (7)$$

It is expected that for a sufficiently large environment, the time-dependent term in Eq. (6) decays for  $t \gg 1/\min\{|\omega_{kl}|\}$ .

The correlation function, however, may contain a finite offset  $C_0 > 0$  if

(a) at least two (or more) eigenstates of  $H_E$  are degenerated (a contribution cast in the term  $d_0$ ). Unless the system exhibits accidental degeneracy [24,25], degeneracies are rare as they are easily removed by the presence of a very small perturbation.

(b) Alternatively, we require that  $\sum_k \eta_k (B^{kk})^2 > \langle B \rangle^2$  (assuming  $d_0 = 0$ ), for which a necessary condition is that the sum in  $k$  includes at least two eigenstates for which  $\eta_k (B^{kk})^2 \neq 0$  is fulfilled.

When we have a dense environment spectrum, as is often the case, more aspects come into play to determine the decay or nondecay of the correlation. To show this, let us first rewrite Eq. (6) in terms of  $\omega_{kl}$  and  $E_{kl} = \epsilon_k + \epsilon_l$  as  $C_{\tilde{B}}(t) = \sum_{E_{kl}} \eta(E_{kl}) C_{E_{kl}}(t)$ , with

$$C_{E_{kl}}(t) = \sum_{\omega_{kl}} \eta(\omega_{kl}) |\tilde{B}(\omega_{kl}, E_{kl})|^2 e^{i\omega_{kl}t}. \quad (8)$$

Note that here we have considered the renormalized operator  $\tilde{B}$  given by Eq. (3) and assumed no degeneracies, so that  $B^{kl}$  is fully determined by the eigenenergies  $\epsilon_k$  and  $\epsilon_l$ . Moreover, the coefficients of the thermal state have been rewritten as  $\eta_k = \eta(E_{kl})\eta(\omega_{kl})/Z_E$ , with  $\eta(E_{kl}) = e^{-\beta E_{kl}/2}$  and  $\eta(\omega_{kl}) = e^{-\beta\omega_{kl}/2}$ . In the continuum limit of Eq. (8),  $C_E(t)$  can be considered as the Fourier transform of  $F_E(\omega) = \eta(\omega) |\tilde{B}(\omega, E)|^2$ . Thus, following the Paley-Wiener theorem, it is possible to state that if  $F_E(\omega)$  is smooth and  $N$  times differentiable in a finite support  $\omega \in [-\omega_m, \omega_m]$ , with  $2\omega_m$  a finite bandwidth, then there is always a coefficient  $C_N$  for which

$$C_E(t) \leq C_N (1 + |t|)^{-N}, \quad (9)$$

i.e., the correlation function decays to zero. We note that since  $\eta(\omega)$  is a smooth function, the smoothness condition for  $F_E(\omega)$  is determined by  $|\tilde{B}(\omega, E)|^2$ . Clearly, the appearance of an offset is strongly related to the statistics of matrix elements  $B^{kl}$ , specifically to the diagonal ones. Moreover, for dense spectra, it also depends on the smoothness of the function  $F_E(\omega)$  defined above. Thus, setting more precise analytical conditions for the emergence of an offset is a nontrivial task as it requires one to access the analytical form of the environment eigenstates or a closed form of the coupling operator  $B$  in that basis. However, it is possible to set the conditions for a zero offset, that is, an always decaying correlation function, as we shown in the next section.

### B. The role of the statistical typicality and ETH

An environment obeying statistical typicality [26–28] violates condition (b). Indeed, statistical typicality means that for all  $k$ ,  $B^{kk} \approx \text{tr}_E\{\rho_E^{\text{th}} B\}$ , which leads to a zero offset due to the normalization condition  $\sum_k \eta_k = 1$ . This conjecture can be justified if the bath is classically chaotic, and therefore is linked to the ergodic condition described in Sec. I [26].

On the other side, the correlation function will also decay to zero under ETH conditions. Indeed, following the ETH ansatz, the matrix element of the observable  $\tilde{B}$  between two

eigenstates can be written as [29]

$$\tilde{B}^{kl} = \mathcal{B}\left(\frac{1}{2}E_{kl}\right)\delta_{kl} + e^{-S(\frac{1}{2}E_{kl})/2}f_0(E_{kl}, \omega_{kl})R_{kl}, \quad (10)$$

where  $S(E)$  is the thermodynamic entropy at energy  $E$ , and  $R_{kl}$  is a random real or complex variable with zero mean and unit variance ( $\overline{R_{kl}^2} = 1$  or  $\overline{|R_{kl}|^2} = 1$ , with  $\overline{\dots}$  representing the noise average). The function  $\mathcal{B}(E)$  is the expectation value of the observable in the microcanonical ensemble at energy  $E$ , which in the thermodynamic limit corresponds to its canonical average and therefore is a constant. Considering  $C_{\tilde{B}}(t) = \sum_{l,k} \eta_k |\tilde{B}^{kl}|^2 e^{i\omega_{kl}t}$  and performing the noise average, we find that it can be written as a function of Eq. (8), but now with

$$|\tilde{B}(\omega_{kl}, E_{kl})|^2 = f_0^2(\omega_{kl}, E_{kl})e^{-S(\frac{1}{2}E_{kl})}. \quad (11)$$

According to the ETH ansatz,  $f_0$  is a smooth function, and therefore  $C_{\tilde{B}}(t)$  will decay to zero according to Eq. (9).

Hence, systems whose classical analog is chaotic or, more generally, for which ETH is suitable will present no offset. However, the opposite is not necessarily true: the fact that a system is integrable does not mean that the autocorrelation function of some of its observables may have an offset. An example of this is an environment of harmonic oscillators, where  $B = \sum_{\lambda} g_{\lambda}(b_{\lambda} + b_{\lambda}^{\dagger})$ , with  $b_{\lambda}(b_{\lambda}^{\dagger})$  annihilation (creation) operators [30]. If  $\rho_E$  is in equilibrium, it is fulfilled that  $B^{kk} = 0$  and therefore there is no offset (see Appendix C).

### III. WEAK-COUPLING MASTER EQUATION FOR A SYSTEM COUPLED WITH A NONERGODIC ENVIRONMENT

The ETH ansatz leads to a correlation given by Eq. (9) that fulfills the convergence criteria (5), with an  $\epsilon$  such that  $N > \epsilon + 1$  [notice that  $C_{\tilde{B}}(t)$  is just a linear combination of  $C_E(t)$ ]. A correlation function with an offset will not only dissatisfy Eq. (5), but it will also lead to an ill-defined weak-coupling master equation and to the absence of a Lindblad limit. To see this, we analyze the weak-coupling master equation up to second order in the coupling parameter,

$$\frac{d\rho_S(t)}{dt} = \int_0^t d\tau C_{\tilde{B}}(\tau)[S(t-\tau)\rho_S(t-\tau), S(t)] + \text{H.c.}, \quad (12)$$

where  $C_{\tilde{B}}(t)$  is given by Eq. (6). We now consider the spectral decomposition  $S(t) = \sum_{ab} L_{ab} e^{iE_{ab}t} \langle a|S|b\rangle$ , with  $L_{ab} = \langle a|b\rangle$  and  $E_{ab} = E_a - E_b$ , in terms of the eigenbasis of  $\tilde{H}_S = \sum_a E_a |a\rangle\langle a|$ , and split the terms into those depending on the decaying part of the correlation,  $\alpha_B(t)$ , and those depending on  $C_0$ , with  $C_{\tilde{B}}(t) = \alpha_B(t) + C_0$ . Then, by assuming a fast decay of  $\alpha_B$ , such that  $\gamma_i(\omega) = \int_0^t d\tau \alpha_B(\tau) e^{i\omega\tau} \approx \int_0^{\infty} d\tau \alpha_B(\tau) e^{i\omega\tau}$ , and also considering the secular approxima-

tion, we find ( see the appendices)

$$\begin{aligned} \frac{d\rho_S(t)}{dt} = & -i \sum_{ab} \Delta_{ab} [L_{ab} L_{ab}^{\dagger}, \rho_S(t)] \\ & + \sum_{ab} \gamma_{ab} \left[ L_{ab} \rho_S(t) L_{ab}^{\dagger} - \frac{1}{2} \left\{ L_{ab}^{\dagger} L_{ab}, \rho_S(t) \right\} \right] \\ & + C_0 \int_0^t d\tau e^{iE_{ab}\tau} [L_{ab} \rho_S(\tau), L_{ab}^{\dagger}] + \text{H.c.} \end{aligned} \quad (13)$$

The terms proportional to the offset do not allow the equation to be in a Lindblad form. Thus, as discussed in the appendices, the thermal state  $\rho_S^{\text{th}} = \exp(-\beta H_S)/Z_S$  is no longer a steady state of such equation. Moreover, Eq. (13) is no longer consistent with its second-order time-local counterpart (see Appendix A), reflecting a failure of the standard weak coupling and thus the related Born approximation that assumes  $\rho(t) = \rho_S(t) \otimes \rho_E$ . A way to see this is to express

$$\rho_S = \sum_k \eta_k \rho_S^k(t), \quad (14)$$

where we define  $\rho_S^k = \text{tr}_E \{U(t)(\rho_S(0) \otimes \rho_E^k)U^{-1}(t)\}$ , with  $U(t) = \exp(-iHt)$  and  $\rho_E^k = |\epsilon_k\rangle\langle\epsilon_k|$ . The interesting aspect of this decomposition is that for each term  $\rho_S^k$ , we consider a master equation by rewriting the total Hamiltonian as follows:

$$H = H_S^k + H_E + S\tilde{B}^k, \quad (15)$$

where we have defined  $H_S^k = H_S + S B^{kk}$  and  $\tilde{B}^k = B - B^{kk}$ , and  $B^{kk} = \langle\epsilon_k|B|\epsilon_k\rangle$ . Note we do this for every case  $k$ , but the result is always the same Hamiltonian because we always subtract and sum the term  $S B^{kk}$ . Having done that, we find that the resulting correlation function,

$$C_{\tilde{B}^k}(t) = \text{tr}_E \{ \rho_E^k \tilde{B}^k(t) \tilde{B}^k(0) \} = \sum_{k \neq l} |B^{kl}|^2 e^{i\omega_{kl}t}, \quad (16)$$

will, in principle, decay in time. Thus, the dynamics of each  $\rho_S^k(t)$  depending on such well-behaved correlation function will be compatible with the perturbative and Markov approximations in the weak-coupling limit. The important point is that the resulting master equation will be different for each  $k$  mostly because it will depend on a different  $H_S^k$ . This formal derivation shows that contrary to what is assumed in the Born approximation, the total system-environment state is correlated,  $\rho(t) = \sum_k \eta_k \rho_S^k \otimes \rho_E^k$  [31].

### IV. THE SPIN-BOSON MODEL AS HYBRID ENVIRONMENT

To illustrate the emergence of an offset in the environment correlation function, we consider a realistic model consisting of  $M$  independent organic dye molecules. Each molecule have a complex structure consisting of two electronic internal states strongly affected by a discrete set of rovibronic modes [32]; thus, it can be treated as a two-party, i.e., hybrid, system that can be well described by means of a variant of the well-known spin-boson model, referred to as the Dicke-Holstein model [33],

$$H_E = \sum_j \left\{ H_{\sigma_j} + \sum_{\lambda} (\omega_{j\lambda} b_{j\lambda}^{\dagger} b_{j\lambda} + \sigma_j^z x_{j\lambda}) \right\}, \quad (17)$$

where the index  $j$  runs over all molecules. Here the electronic part is written as  $H_{\sigma_j} = \frac{1}{2}\Omega_j\hat{n}_j \cdot \vec{\sigma}_j$ , where  $\hat{n}_j = \Omega_j^{-1}(-\Delta_j, 0, \varepsilon_j)$  is a unitary vector, and  $\vec{\sigma}_j = (\sigma_j^x, \sigma_j^y, \sigma_j^z)$  is the vector of Pauli matrices. We have defined the Rabi-like frequency  $\Omega_j = \sqrt{\Delta_j^2 + \varepsilon_j^2}$ , with  $\Delta_j$  and  $\varepsilon_j$  being the spin-tunneling strength and flip-flop energy, respectively. We have set  $\hbar = 1$ .

The rovibronic part is represented by the bosonic creation (annihilation) operators  $b_{j\lambda}^\dagger$  ( $b_{j\lambda}$ ), with energies  $\omega_{j\lambda}$ , and reaction coordinate,

$$x_{j\lambda} = g_{j\lambda}(b_{j\lambda} + b_{j\lambda}^\dagger), \quad (18)$$

where  $g_{j\lambda}$  represents the coupling strength between the electronic and vibrational modes. Considering a linear dispersion, this quantity is determined by the spectral function  $J(\omega) = \sum_\lambda g_\lambda^2 \delta(\omega - \omega_\lambda)$ , which we consider Ohmic [34],

$$J(\omega) = r \frac{\omega}{\omega_c} \exp(-\omega/\omega_c) \theta(5\omega_c - \omega), \quad (19)$$

where  $r$  is a parameter that modules the spin-boson interaction strength,  $\theta(x)$  is the Heaviside function, and  $5\omega_c$  is the cutoff frequency. Here we set  $\omega_c = 1$  without loss of generality. The molecular environment is in a thermal state with inverse temperature  $\beta$ .

We consider an open system coupled to such hybrid environment through the standard interaction Hamiltonian  $H_I = BS$ , where  $S$  is an arbitrary system operator and  $B = \sum_j \sigma_j^x$ , such that  $C_{\bar{B}}(t)$  is a sum of single-molecule correlation functions (SMCFs), i.e.,  $C_{\bar{B}}(t) = \sum_j C_{\bar{B}}^{(j)}(t)$ , with  $C_{\bar{B}}^{(j)}(t) = \text{tr}\{\bar{\sigma}_j^x(t)\bar{\sigma}_j^x(0)\rho_E^{\text{th}}\}$ . Thus, since the molecules are not interacting, we only need to study the properties of the  $j$ th SMCF,  $C_{\bar{B}}^{(j)}(t)$ , which we tackle with exact diagonalization for up to three vibrational modes (see Appendix D) and MPS for more. In the following, we drop the index  $j$  for simplicity.

### A. Single-molecule environment

For certain parameter regimes, the analysis of the SMCF is quite simple. To show this, we apply the polaron transformation to the single-molecule environment Hamiltonian, resulting in

$$H_{\text{SM}} = E_0 + \frac{1}{2}\varepsilon\sigma^z + \sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda - \frac{1}{2}\Delta(\sigma^+ e^K + \sigma^- e^{-K}),$$

with  $E_0 = \sum_\lambda g_\lambda^2/\omega_\lambda$ ,  $\sigma^+$  ( $\sigma^-$ ) being the raising (lowering) spin-1/2 operator, and  $K = 2\sum_k \frac{g_k}{\omega_k}(b_k^\dagger - b_k)$  (see Appendix B). Thereby, there exists two trivial cases for which the SMCF is analytically accessible:

(i) First, if the spin-tunneling strength  $\Delta = 0$ , the environment Hamiltonian becomes separable, rendering the well-known pure-dephasing limit. The eigenstates are separable spin-boson bare states:  $|\epsilon_k\rangle = |s, \mathbf{n}\rangle$ , with  $s = 0, 1$  labeling the electronic state of the molecule, and  $|\mathbf{n}\rangle \equiv |n_1 \cdots n_L\rangle$  its respective multimode Fock state. Accordingly, the offset  $C_0 = 0$ , since  $B^{kk} = \langle \epsilon_k | \sigma^x | \epsilon_k \rangle = 0$ , for all  $k$ . Furthermore, after some analytics, it is possible to prove that  $C_{\bar{B}}(t) \propto e^{-\Gamma_\beta(t)}$ , where  $\Gamma_\beta(t) = 8\sum_\lambda (g_\lambda/\omega_\lambda)^2 \sin^2(\omega_\lambda t/2) \coth(\beta\omega_\lambda/2)$  (see Appendix B).

(ii) The second case is when  $r = 0$ , which corresponds to a spin-boson environment with no interaction between the electronic and vibrational parts.  $H_{\text{SM}}$  is again separable and, as shown in the appendices, the SMCF reduces to  $\text{Re}\{C_{\bar{B}}(t)\} = (\varepsilon/\Omega)^2 \cos(\Omega t) + C_0$ , with the offset given by  $C_0 = (\Delta/\Omega)^2 \text{sech}^2(\beta\Omega/2)$ . Thus, a nonzero offset requires that  $\Delta \neq 0$  and a finite temperature  $\beta^{-1} > 0$ . Nonetheless, the offset disappears at zero temperatures, even when  $r \neq 0$ . This is shown by rewriting the thermal weights of  $\rho_E^{\text{th}}$  as

$$\eta_k = \frac{e^{-\beta\epsilon_k}}{\sum_k e^{-\beta\epsilon_k}} = \frac{e^{-\beta(\epsilon_k - \epsilon_0)}}{1 + \sum_{k \neq 0} e^{-\beta(\epsilon_k - \epsilon_0)}}, \quad (20)$$

where  $\epsilon_0 < \epsilon_k$  is the ground state. By setting  $\beta \rightarrow \infty$ , we find that  $\eta_k \rightarrow 1$ , iff  $\epsilon_k = \epsilon_0$ , and zero otherwise. Thus, in the zero-temperature limit, the only eigenstate involved in Eq. (7) is the ground state, such that the condition (b) is no longer fulfilled, and therefore  $C_0 = 0$ .

Away from the above cases, the dynamics of the environment displays a competition between the dephasing and the spin coherence. While the offset appears when  $\Delta \neq 0$ , resulting in an oscillatory behavior of the SMCF, the role of  $r$  is to induce a damping. In this scenario, the eigenstate structure of the Hamiltonian is analytically and numerically hard to access, particularly when dealing with many vibrational modes. However, since any eigenstate can be written as a linear combination of the spin-boson bare states, i.e.,  $|\epsilon_k\rangle = \sum_{\mathbf{sn}} c_{\mathbf{sn}}^{(k)} |s, \mathbf{n}\rangle$ , we can infer that a minimal requirement for the offset is that the eigenstates display a mixing of at least two spin states, that is,  $B^{kk} = \langle \epsilon_k | \sigma^x | \epsilon_k \rangle = \sum_{\mathbf{n}} (c_{1\mathbf{n}}^{(k)} c_{0\mathbf{n}}^{(k)*} \langle 0 | \sigma^x | 1 \rangle + c_{0\mathbf{n}}^{(k)} (c_{1\mathbf{n}}^{(k)})^* \langle 1 | \sigma^x | 0 \rangle) \neq 0$ . While spin coherences are required for a finite offset, certain entangled eigenstates may have zero contribution. For instance, an entangled eigenstate of the form  $|\epsilon_k\rangle = c_{0,\mathbf{n}}^{(k)} |0, \mathbf{n}\rangle + c_{1,\mathbf{m}}^{(k)} |1, \mathbf{m}\rangle$ , with  $|\mathbf{n}\rangle \neq |\mathbf{m}\rangle$ , leads to  $\langle \epsilon_k | \sigma^x | \epsilon_k \rangle = 0$ .

In general, the coherence-dephasing competition can be qualitatively characterized in terms of the ratio  $r/\Delta$ . For intermediate values of  $r/\Delta$ , we consider the matrix product state (MPS) formalism [35,36], implemented in the MPS library [37,38], to compute the SMCF. This is shown in Fig. 1 for different values of  $\Delta$  [Fig. 1(a)] and different numbers  $L$  of bosonic modes [Fig. 1(b)], which shows that the offset does not appear to depend significantly on the environment size, at least for the number of modes and the timescale that we are able to consider here.

Our analysis (see details in Appendix B 3) suggests that the best fitting function for the real part of the non-normalized SMCF,  $C_{\bar{B}}(t) = \text{tr}_E\{\sigma^x(t)\sigma^x(0)\rho_E^{\text{th}}\}$ , in Fig. 1 is

$$f(t) = A_0 \cos(\omega_0 t) e^{-B_0 t^a} + \tilde{C}_0 e^{-t/T_0}. \quad (21)$$

Thus, the short-time non-Markovian decay is dominated by the first factor, which represents a nonexponential decay since  $a \approx \sqrt{2} > 1$ , while the long-time limit dynamics is dominated by an exponential decay with a characteristic correlation time  $T_0$  that takes different values. Indeed, towards the limit  $r/\Delta \rightarrow 0$ , the correlation time  $T_0$  tends to grow larger and the corresponding term tends to a constant value  $\tilde{C}_0$ , at least at the timescales here considered. Once the norm  $(\text{tr}_E\{\sigma^x \rho_E\})^2$  is subtracted, this value appears to provide a finite offset. However, we shall stress here that our numerical method

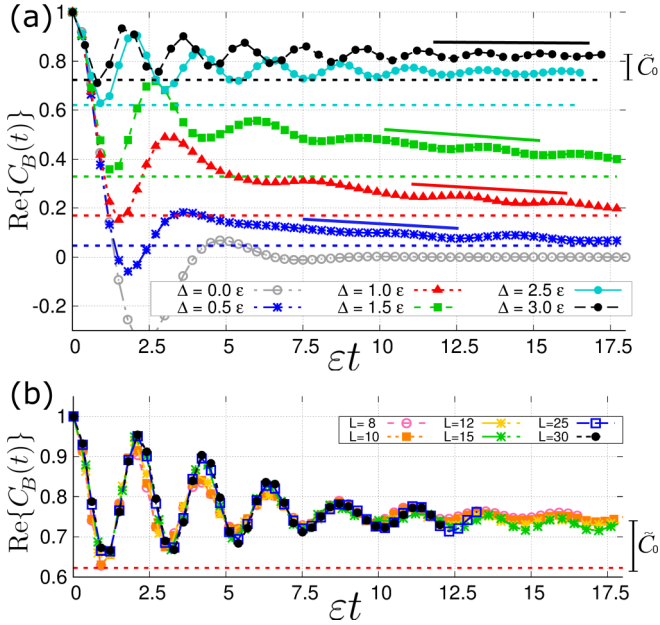


FIG. 1. SMCF: (a) Real part of the nonrenormalized SMCF computed using the MPS library [37], for different values of  $\Delta$  with  $r = 0.25$  for an eight-mode ( $L = 8$ ) dye molecule. (b) Scaling of the nonrenormalized SMCF with the number of bosonic modes  $L$  for  $r = 0.25\epsilon$  and  $\Delta = 2.5\epsilon$ . These calculation was done for  $\beta = 1$  and local MPS dimension  $d_{\text{MPS}} = 10 \dots 15$ , which showed to be sufficient for good convergence of our results. In both plots, the horizontal dashed lines are the corresponding renormalization terms  $(\text{tr}_E\{\sigma^x \rho_E\})^2$ .

only allows us to consider a limited number of oscillators [see Fig. 1(b)] and to reach a finite time in our simulations. Thus, we cannot predict with certainty what may happen at longer times and when adding more environment oscillators. The transition into a continuum of modes may be a crucial aspect to consider, as the property of returning to equilibrium strongly relies on the system composed of a continuum part [39]. A molecular environment with a finite number of modes such as the one described here is nonetheless a physically realistic and relevant scenario, where it is reasonable to expect an offset and thus information about the initial state being preserved.

### B. Many-molecule environment

Finally, when considering the case of  $M$  molecules, the total offset is enhanced since  $C_0 = \sum_j C_0^{(j)}$ . Moreover, the ensemble of molecules behaves at long times as a collection of exponentially decaying two-level systems, each having different internal parameters and thus different decay rates  $1/T_0$ . As it is well known, this type of system leads to a  $1/f$  spectrum between the frequency ranges of  $[1/T_{\text{max}}, 1/T_{\text{min}}]$ , where  $T_{\text{max}}(T_{\text{min}})$  are the maximum (minimum) correlation times [10,40,41]. Interestingly, contrary to the standard case where no offset is considered, here we find that some molecules have extremely long and even infinite decay times  $T_0 = T_{\text{max}} \sim \infty$ , which implies that the  $1/f$  extends towards the zero-frequency limit. Interestingly,  $1/f$  behavior has been experimentally observed to extend to low frequencies (at least up

to the lowest frequency that can be measured) in the context of superconducting qubits, which are coupled to similar hybrid environments [41–43].

## V. CONCLUSIONS AND OUTLOOK

We argue that a necessary condition for the existence of a well-defined weak-coupling approximation and valid Born approximation is to have a correlation function that decays to zero in time, a feature that is fulfilled for Gaussian and ETH environments but not in general. To illustrate this, we show that a spin-boson environment in a thermal state has a nondecaying correlation function, and show how this connects with the presence of a  $1/f$  spectrum that in contrast to previous analysis, extends to zero frequencies. This work opens several interesting research avenues. First, quantum devices such as superconducting qubits are affected by similar hybrid environments [7,8] and  $1/f$  noise [10,40,41], and thus a rigorous analysis of the convergence of a weak-coupling expansion and the related Lindblad equation may be relevant. Second, this work may be helpful to understand the dynamics of impurities coupled to materials that do not fulfill ETH, for instance, those presenting dynamical localization or Hilbert space fragmentation, where the emergence of an offset has also been described [44–46]. Other environments where an offset is present can also be found in the context of quantum chemistry [47]. Further, the offset is linked to strong memory effects and to the inability of the environment to bounce back to its equilibrium state after interacting with the system, which renders interesting to characterize the non-Markovianity [48–50]. Finally, the nonergodicity of the environment may be harnessed to recover the open system information by developing appropriate correction protocols.

## ACKNOWLEDGMENTS

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## APPENDIX A: MASTER EQUATION FOR CORRELATION FUNCTIONS WITH AN OFFSET

Up to second order in the weak-coupling parameter, and in the interaction picture with respect to  $\tilde{H}_S$ , the master equation reads [1]

$$\frac{d\rho_s(t)}{dt} = \int_0^t d\tau C_{\tilde{B}}(t, t - \tau)[S(t - \tau)\rho_s(t - \tau), S(t)] + \text{H.c.},$$

where we have crucially considered the Born approximation, by which, within the right-hand side term, one can reply the total density operator as  $\rho(t - \tau) \approx \rho_s(t - \tau) \otimes \rho_E$ . In addition, we have already taken into account that the environment is in equilibrium, so that the environment correlation function satisfies the condition  $C_{\tilde{B}}(t, t - \tau) = C_{\tilde{B}}(\tau)$ . The above

equation can now be separated into two terms,

$$\begin{aligned} \frac{d\rho_s(t)}{dt} &= \int_0^t d\tau \sum_{lj} \alpha_B(\tau) [S(t-\tau)\rho_s(t-\tau), S(t)] + \text{H.c.} \\ &+ C_0 \int_0^t d\tau \sum_{lj} [S(t-\tau)\rho_s(t-\tau), S(t)] + \text{H.c.}, \end{aligned} \quad (\text{A1})$$

where we have separated  $C_{\bar{B}}(t) = \alpha_B(t) + C_0$  in terms of the time-dependent part and the offset. Moreover, we assume that  $\alpha_B(t)$  decays very fast, so that it is a good approximation to consider  $\rho_s(t-\tau) \approx \rho_s(t)$ . Nevertheless, such replacement cannot be made in the term that depends on the offset, where the integrand is not ensured to have a fast decay. We now assume that

$$S(t) = \sum_{ab} L_{ab} e^{iE_{ab}t} \langle a|S|b \rangle, \quad (\text{A2})$$

where  $L_{ab} = |a\rangle\langle b|$ , in terms of the eigenstates and eigenvalues of  $\tilde{H}_S$ . Therefore, we find that

$$\begin{aligned} \frac{d\rho_s(t)}{dt} &= -i \sum_{ab,cd} \Delta_{ab,cd}^t [L_{ab} L_{cd}^\dagger, \rho_s(t)] \\ &+ \sum_{ab,cd} \gamma_{ab,cd}^t \left[ L_{ab} \rho_s(t) L_{cd}^\dagger - \frac{1}{2} \{ L_{cd}^\dagger L_{ab}, \rho_s(t) \} \right] \\ &+ C_0 e^{i(E_{ba}-E_{dc})t} \int_0^t d\tau e^{iE_{ab}\tau} [L_{ab} \rho_s(\tau), L_{cd}^\dagger] + \text{H.c.}, \end{aligned} \quad (\text{A3})$$

with  $E_{ba} = E_b - E_a$ , and the coefficients defined as

$$\begin{aligned} \gamma_{ab,cd}^t &= e^{i(E_{ba}-E_{dc})t} \gamma(E_{ba}) \langle a|S|b \rangle \langle d|S|c \rangle, \\ \Delta_{ab,cd}^t &= e^{i(E_{ba}-E_{dc})t} \Sigma(E_{ba}) \langle a|S|b \rangle \langle d|S|c \rangle, \end{aligned} \quad (\text{A5})$$

where we have defined

$$\begin{aligned} \gamma(\omega) &= \text{Re} \left\{ \int_0^\infty \alpha_B(\tau) e^{i\omega\tau} d\tau \right\}, \\ \Sigma(\omega) &= \text{Im} \left\{ \int_0^\infty \alpha_B(\tau) e^{i\omega\tau} d\tau \right\}. \end{aligned} \quad (\text{A6})$$

At this point, we realize that up to the second order that is considered, the convoluted Eq. (A3) should be equivalent to its time-local counterpart. This is because the terms on its right-hand side are already of second order, and therefore we can make the replacement  $\rho_s(\tau) = \rho_s(t) + \mathcal{O}(g^2)$  to find

$$\begin{aligned} \frac{d\rho_s(t)}{dt} &= -i \sum_{ab,cd} \Delta_{ab,cd}^t [L_{ab} L_{cd}^\dagger, \rho_s(t)] \\ &+ \sum_{ab,cd} \gamma_{ab,cd}^t [L_{ab} \rho_s(t) L_{cd}^\dagger - \frac{1}{2} \{ L_{cd}^\dagger L_{ab}, \rho_s(t) \}] \\ &+ C_0 e^{i(E_{ba}-E_{dc})t} \int_0^t d\tau e^{iE_{ab}\tau} [L_{ab} \rho_s(t), L_{cd}^\dagger] + \text{H.c.} \end{aligned} \quad (\text{A7})$$

Nonetheless, if the offset is large, the two equations will differ significantly, signaling the failure of the weak coupling.

Indeed, when the offset is large, the time-local master equation (A8) becomes increasingly unstable, as the coefficients related to  $C_0$  grow unbounded. In contrast, the convoluted equation appears to be more stable, but reflects a dependency or memory over the whole trajectory of  $\rho_s(\tau)$  that suggests a strong non-Markovian character and thus compromises the weak-coupling assumption. To see this, we proceed further, and consider the standard secular approximation in Eq. (A3), to find

$$\begin{aligned} \frac{d\rho_s(t)}{dt} &= -i[H_{\text{eff}}, \rho_s(t)] \\ &+ \sum_{ab} \gamma_{ab} \left[ L_{ab} \rho_s(t) L_{ab}^\dagger - \frac{1}{2} \{ L_{ab}^\dagger L_{ab}, \rho_s(t) \} \right] \\ &+ C_0 \int_0^t d\tau e^{iE_{ab}\tau} [L_{ab} \rho_s(\tau), L_{ab}^\dagger] + \text{H.c.}, \end{aligned} \quad (\text{A8})$$

where we have defined  $H_{\text{eff}} = \sum_{ab} \Delta_{ab} L_{ab} L_{ab}^\dagger$ ,  $\gamma_{ab} = \gamma(E_{ba}) \langle a|S|b \rangle \langle b|S|a \rangle$ , and  $\Delta_{ab} = \Sigma(E_{ba}) \langle a|S|b \rangle \langle b|S|a \rangle$ . In the long-time limit, we formally have

$$\begin{aligned} \frac{d\rho_s(t)}{dt} &= -i[H_{\text{eff}}, \rho_s(t)] + \sum_{ab} \gamma_{ab} [L_{ab} \rho_s(t) L_{ab}^\dagger \\ &- \frac{1}{2} \{ L_{ab}^\dagger L_{ab}, \rho_s(t) \}] \\ &+ C_0 \sum_{ab} [L_{ab} \rho_s(t, E_a - E_b) L_{ab}^\dagger \\ &- \frac{1}{2} \{ L_{ab}^\dagger L_{ab}, \rho_s(t, E_a - E_b) \}], \end{aligned} \quad (\text{A9})$$

which depends on the quantity

$$\rho_s(t, \omega) = \int_0^t d\tau e^{i\omega\tau} \rho_s(\tau). \quad (\text{A10})$$

When projected into the system eigenbasis, one can calculate the rate equations as before,

$$\begin{aligned} \frac{d\langle m|\rho_s(t)|m \rangle}{dt} &= \sum_{b \neq m} (\gamma_{mb} \langle b|\rho_s(t)|b \rangle - \gamma_{bm} \langle m|\rho_s(t)|m \rangle) \\ &+ C_0 \left( \sum_{b \neq m} \langle b|\rho_s(t, E_m - E_b)|b \rangle \right. \\ &\left. - \langle m|\rho_s(t, E_m - E_b)|m \rangle \right). \end{aligned} \quad (\text{A11})$$

Thus, the steady-state condition is

$$\begin{aligned} &\sum_{b \neq m} (\gamma_{mb} P_{bb}^{\text{st}} - \gamma_{bm} P_{mm}^{\text{st}}) \\ &= -C_0 \sum_{b \neq m} [\langle b|\rho_s(t \rightarrow \infty, E_m - E_b)|b \rangle \\ &- \langle m|\rho_s(t \rightarrow \infty, E_m - E_b)|m \rangle]. \end{aligned} \quad (\text{A12})$$

In the standard case, we have that  $C_0 = 0$ , and thus one steady-state solution is the thermal one, i.e.,  $P_{bb}^{\text{st}} \sim \exp(-\beta E_b)$ , provided that the detailed balance is also fulfilled, i.e.,  $\gamma_{mb} = \exp(-\beta E_{mb})\gamma_{bm}$ . Nonetheless, when  $C_0 \neq 0$ , we find that  $P_{bb}^{\text{st}}$  is no longer a thermal state since it is given by

$$\begin{aligned} \gamma_{mb}P_{bb}^{\text{st}} - \gamma_{bm}P_{mm}^{\text{st}} &= -C_0[\langle b|\rho_s(t \rightarrow \infty, E_m - E_b)|b\rangle \\ &- \langle m|\rho_s(t \rightarrow \infty, E_m - E_b)|m\rangle], \end{aligned} \quad (\text{A13})$$

and thus it depends on the whole history of evolution, including the initial state.

## APPENDIX B: ENVIRONMENT IN EXTREME CASES

Here we briefly present the derivation of the formulas used in the main text for the following cases: (1) pure dephasing  $\Delta = 0$  and (2) spin coherence,  $r = 0$ . In addition, we also present a case (3) corresponding to weak-coupling derivation, which will allow us to justify in this limit the fitting functional used in the main text to characterize the single-molecule correlation function (SMCF). First, we stress that throughout the paper, we have only computed single-molecule correlation corresponding to the  $j$ th molecule due to the nondirect interaction between them. Hence the full environment Hamiltonian can be written as  $H_E = \sum_j H_E^{(j)}$  and the many-molecule polaron transformation gets defined then as  $U_{\text{full}} = U_{(1)} \otimes \cdots \otimes U_{(j)} \otimes \cdots \otimes U_{(N_{\text{mol}})}$ , where

$$U_{(j)} = \exp\left(\frac{1}{2}\sigma_j^z K_j\right), \quad (\text{B1})$$

with  $K_j = 2 \sum_{\lambda} \frac{g_{j\lambda}}{\omega_{j\lambda}} (b_{j\lambda}^\dagger - b_{j\lambda})$ . Henceforth, in the computation of the SMCF, we ignore the index  $j$ , and therefore we redefine  $H_E^{(j)} \equiv H_{\text{SM}}$ . Considering that the formula for the SMCF implies the computation of a trace, we can apply arbitrary unitary transformation  $U$  with which we can write

$$\begin{aligned} \langle \sigma^x(t)\sigma(0) \rangle_E &= \text{tr}_E \left\{ e^{-itH_{\text{SM}}} \sigma^x e^{itH_{\text{SM}}} \sigma^x \rho_E^{\text{th}}(0) \right\} \\ &= \text{tr}_E \left\{ e^{-it\bar{H}_{\text{SM}}} \bar{\sigma}^x e^{it\bar{H}_{\text{SM}}} \bar{\sigma}^x \bar{\rho}_E^{\text{th}}(0) \right\}, \end{aligned} \quad (\text{B2})$$

where

$$\begin{aligned} U e^{-itH_{\text{SM}}} U^{-1} &= \sum_p \frac{(-it)^p}{p!} U \underbrace{H_{\text{SM}} \cdots H_{\text{SM}}}_{p \text{ times}} U^{-1} \\ &= \sum_p \frac{(-it)^p}{p!} \underbrace{\bar{H}_{\text{SM}} \cdots \bar{H}_{\text{SM}}}_{p \text{ times}} \\ &= e^{-it\bar{H}_{\text{SM}}}, \end{aligned} \quad (\text{B3})$$

and where we have used the short notation  $\bar{H}_{\text{SM}} = UH_{\text{SM}}U^{-1}$ . It can also be shown that

$$\begin{aligned} \bar{\sigma}^x &= U\sigma^xU^{-1} = \sigma^+ e^K + \sigma^- e^{-K}, \\ \bar{\sigma}^z &= U\sigma^zU^{-1} = \sigma^z, \\ \bar{b}_\lambda &= Ub_\lambda U^{-1} = b_\lambda - \frac{g_\lambda}{\omega_\lambda} \sigma^z, \end{aligned}$$

with which  $H_{\text{SM}}$  gets transformed into

$$\begin{aligned} \bar{H}_{\text{SM}} &= \frac{\varepsilon}{2} \sigma^z + \sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda + \sum_\lambda \frac{g_\lambda^2}{\omega_\lambda} \\ &- \frac{\Delta}{2} (\sigma^+ e^K + \sigma^- e^{-K}). \end{aligned} \quad (\text{B4})$$

### 1. Pure-dephasing case

Let us first consider  $\Delta = 0$  and this Hamiltonian is separable, and thus  $e^{-it\bar{H}_{\text{SM}}} = e^{-\frac{1}{2}it\varepsilon\sigma^z} e^{-it\sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda}$ . Then, the SMCF can be expressed as

$$\begin{aligned} C_{\bar{B}}(t) &= \langle \bar{\sigma}^x(t)\bar{\sigma}^x(0) \rangle_E - \langle \bar{\sigma}^x \rangle_E^2 \\ &= e^{iet} \langle \sigma^+ \sigma^- \rangle_\sigma \langle e^{K(t)} e^{-K(0)} \rangle_R \\ &+ e^{-iet} \langle \sigma^- \sigma^+ \rangle_\sigma \langle e^{-K(t)} e^{K(0)} \rangle_R \\ &- \langle \sigma^+ \rangle_\sigma \langle e^{K(0)} \rangle_R - \langle \sigma^- \rangle_\sigma \langle e^{-K(0)} \rangle_R, \end{aligned} \quad (\text{B5})$$

where we have used the separability of  $\bar{H}_{\text{SM}}$  to write  $\rho_E^{\text{th}}(0) = \rho_\sigma \otimes \rho_R$ , with  $\rho_\sigma = e^{-\frac{1}{2}\beta\varepsilon\sigma^z}/Z_\sigma$  and  $\rho_R = e^{-\beta\sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda}/Z_R$ . Thus, the respective traces are denoted as  $\text{tr}_\sigma\{\cdots\rho_\sigma\} = \langle \cdots \rangle_\sigma$ , and  $\text{tr}_R\{\cdots\rho_R\} = \langle \cdots \rangle_R$ . Further, the operator  $K(x)$  is defined as

$$\begin{aligned} K(x) &= e^{ix\sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda} K e^{-ix\sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda} \\ &= 2 \sum_\lambda \frac{g_\lambda^2}{\omega_\lambda^2} (b_\lambda^\dagger e^{ix} - b_\lambda e^{-ix}), \end{aligned} \quad (\text{B6})$$

which satisfies

$$[K(x), [K(x), K(y)]] = [K(y), [K(x), K(y)]] = 0$$

and

$$[K(x), K(y)] = i8 \sum_\lambda \frac{g_\lambda^2}{\omega_\lambda^2} \sin[\omega_\lambda(x-y)]. \quad (\text{B7})$$

Therefore, we can use the Baker-Campbell-Hausdorff identity,

$$e^{K(x)} e^{-K(y)} = e^{K(x)-K(y) - \frac{1}{2}[K(x), K(y)]}, \quad (\text{B8})$$

and the thermal average,

$$\langle e^{\sum_\lambda (c_\lambda b_\lambda + d_\lambda b_\lambda^\dagger)} \rangle_R = e^{\sum_\lambda c_\lambda d_\lambda [2n(\omega_\lambda) + 1]}, \quad (\text{B9})$$

with the thermal distribution  $n(\omega_\lambda) = (e^{\beta\omega_\lambda} - 1)^{-1}$ , and the complex numbers  $c_\lambda$  and  $d_\lambda$ . With these formulas, we can compute the two-point thermal correlator of the type  $\langle e^{K(x)} e^{-K(y)} \rangle_R = \exp[\sum_\lambda \frac{g_\lambda^2}{\omega_\lambda^2} h_\lambda(\beta)]$  with

$$h_\lambda(\beta) = -2|\xi_\lambda(x, y)|^2 \coth(\beta\omega_\lambda/2) + i4\mu_\lambda(x, y), \quad (\text{B10})$$

and with

$$\begin{aligned} \xi_\lambda(x, y) &= i2e^{i\omega_\lambda(x+y)/2} \sin[\omega_\lambda(x-y)/2], \\ \mu_\lambda(x, y) &= \sin[\omega_\lambda(x-y)]. \end{aligned}$$

Considering this, together with the identity  $\langle e^{K(x)} e^{-K(y)} \rangle_R = \langle e^{K(y)} e^{-K(x)} \rangle_R^*$ , and that for a thermal initial state  $\langle \sigma^\pm \rangle_\sigma = 0$  and  $\langle \sigma^+ \sigma^- \rangle_\sigma = (1 + e^{-\beta\varepsilon})^{-1}$ , we obtain the final expression

for the SMCF,

$$C_{\bar{B}}(t) = \left( \frac{e^{i\epsilon t}}{1 + e^{-\beta\epsilon}} + \frac{e^{-i\epsilon t}}{1 + e^{\beta\epsilon}} \right) \times \exp \left[ -i4 \sum_{\lambda} \frac{g_{\lambda}^2}{\omega_{\lambda}^2} \sin(\omega_{\lambda} t) \right] \times \exp \left[ -8 \sum_{\lambda} \frac{g_{\lambda}^2}{\omega_{\lambda}^2} \sin^2(\omega_{\lambda} t/2) \coth(\beta\omega_{\lambda}/2) \right], \quad (\text{B11})$$

which implies no offset, as expected, for the pure-dephasing case.

## 2. No dissipation

Let us now consider  $r \approx 0$ . The polaron-transformed Hamiltonian  $H_{\text{SM}}$  takes the the form

$$\bar{H}_{\text{SM}} = \frac{1}{2} \Omega \hat{n} \cdot \vec{\sigma} + \sum_{\lambda} \omega_{\lambda} b_{\lambda}^{\dagger} b_{\lambda}, \quad (\text{B12})$$

since  $g_{\lambda} \propto r \approx 0 \Rightarrow e^{\pm K} \approx 1$ . Here we have defined a Rabi-type frequency  $\Omega = \sqrt{\Delta^2 + \epsilon^2}$ , where  $\hat{n} = (n_x, n_y, n_z) = \Omega^{-1}(-\Delta, 0, \epsilon)$  is a unitary operator, and  $\vec{\sigma} = (\sigma^x, \sigma^y, \sigma^z)$ . To compute the SMCF, we directly use the identity

$$e^{i\alpha \hat{n} \cdot \vec{\sigma}} = \hat{1} \cos(\alpha) + i(\hat{n} \cdot \vec{\sigma}) \sin(\alpha), \quad (\text{B13})$$

with  $\alpha = \Omega_j t/2$ , and the separability of  $\bar{H}_{\text{SM}}$  to express

$$\begin{aligned} \sigma^x(t) \sigma^x(0) &= e^{i t \bar{H}_{\text{SM}}} \sigma^x e^{-i t \bar{H}_{\text{SM}}} \\ &= [\sigma^x \cos(\alpha) + i(n_x + n_z \sigma^z \sigma^x) \sin(\alpha)] \\ &\quad \times [\sigma^x \cos(\alpha) - i(n_x + n_z \sigma^z \sigma^x) \sin(\alpha)] \\ &= \cos^2(\alpha) + (n_x^2 - n_z^2) \sin^2(\alpha) \\ &\quad + 2n_x n_z \sigma^z \sigma^x \sin^2(\alpha) + i n_z \sigma^z \sin(2\alpha) \\ &= \cos^2(\Omega t/2) + \frac{\Delta^2 - \epsilon^2}{\Omega^2} \sin^2(\Omega t/2) \\ &\quad - 2 \frac{\epsilon \Delta}{\Omega^2} \sigma^z \sigma^x \sin^2(\Omega t/2) - i \frac{\epsilon}{\Omega} \sigma^z \sin(\Omega t), \end{aligned} \quad (\text{B14})$$

where we have used the identity  $\sin(2x) = 2 \cos(x) \sin(x)$ . After computing the thermal average,  $\langle \cdot \rangle_E|_{r=0}$  results in

$$\langle \sigma^x(t) \sigma^x(0) \rangle_E|_{r=0} = \frac{1}{\Omega^2} [\Delta^2 - \epsilon^2 + 2\epsilon^2 \cos^2(\Omega t/2)] - i \frac{\epsilon}{\Omega} \tanh(\beta\epsilon/2) \sin(\Omega t), \quad (\text{B15})$$

since  $\langle \sigma^z \sigma^x \rangle_E|_{r=0} = 0$  and  $\langle \sigma^z \rangle_E|_{r=0} = \tanh(\beta\epsilon/2)$ . For the renormalization term, we have

$$\begin{aligned} \langle \sigma^x \rangle_E|_{r=0} &= \text{tr}_{\sigma} \{ \sigma^x \rho_{\sigma} \} \text{tr}_R \{ \rho_R \} \\ &= \frac{1}{Z_E} \text{tr} \{ \sigma^x \exp(-\beta \hat{n} \cdot \vec{\sigma}) \} \\ &= -\frac{\Delta}{\Omega} \tanh(\beta\Omega/2), \end{aligned} \quad (\text{B16})$$

where we have again used the identity (B13), but this time considering  $i\alpha = -\beta\Omega/2$ . Furthermore, we have considered that the partition function can be written as

$Z_E = \cosh(\beta\Omega/2)$ . We finally arrive at the SMCF,

$$\begin{aligned} C_{\bar{B}}(t)|_{r=0} &= \langle \sigma^x(t) \sigma^x(0) \rangle_E - (\langle \sigma^x \rangle_E)^2 \\ &= \frac{\epsilon^2}{\Omega^2} \cos(\Omega t) + \frac{\Delta^2}{\Omega^2} \text{sech}^2(\beta\Omega/2) \\ &\quad - i \frac{\epsilon}{\Omega} \tanh(\beta\epsilon/2) \sin(\Omega t), \end{aligned} \quad (\text{B17})$$

where we have the trigonometrical identities  $\cos(2\theta) = 2 \cos^2(\theta) - 1$  and  $\text{sech}^2(x) = 1 - \tanh^2(x)$ . Clearly, the last term on the right side corresponds to the offset, that is,

$$C_0 = \frac{\Delta^2}{\Omega^2} \text{sech}^2(\beta\Omega/2) \in \mathbb{R}. \quad (\text{B18})$$

## 3. Weak coupling also for the initial state and the importance of having an environment in equilibrium

Another possibility to approach the SMCF is to consider the case in which the interaction between the electronic and vibrational parts of  $H_E$  is weak, such that the initial thermal state can be approximated as

$$\rho_E^{\text{th}} = \rho_{\sigma}^{\text{th}} \otimes \rho_R^{\text{th}} + \rho_{\text{corr}} \approx \rho_{\sigma}^{\text{th}} \otimes \rho_R^{\text{th}}, \quad (\text{B19})$$

where we consider that  $\rho_{\sigma}^{\text{th}} = \exp(-\beta H_{\sigma})/Z_{\sigma}$  and  $\rho_R^{\text{th}} = \exp(-\beta H_R)/Z_R$ , with  $Z_{\sigma,R}$  the partition functions, and  $H_R = \sum_{\lambda} \omega_{\lambda} b_{\lambda}^{\dagger} b_{\lambda}$ . Thus, we are neglecting the correlation term  $\rho_{\text{corr}}$ , which is of the order of  $r^2$ . Moreover, not only does this approximation restrict the results to a weak electron-boson coupling, but also it leads to an environment initial state that is no longer in equilibrium, which means that strictly speaking, the correlation function is no longer stationary, i.e.,  $C_{\bar{B}}(t_1, t_2) \neq C(t_1 - t_2)$ . We remind the reader that the stationary condition is crucial for a rigorous derivation of the weak coupling and Lindblad master equations. For simplicity, we concentrate in the case  $t_1 = t$  and  $t_2 = 0$ . Using the cyclic property of the trace, we write the correlation function as follows:

$$\langle \sigma^x(t) \sigma^x(0) \rangle_E = \text{tr}_{\sigma} \{ \sigma^x \tilde{\rho}_{\sigma}(t) \}, \quad (\text{B20})$$

where  $\tilde{\rho}_{\sigma}(t) = \text{tr}_R \{ e^{-it H_{\text{SM}}} \sigma^x \rho_{\sigma}^{\text{th}} \otimes \rho_R^{\text{th}} e^{it H_{\text{SM}}} \}$ . Therefore, we can use the eigenstates of the free spin part of the Hamiltonian  $H_{\sigma} = \frac{1}{2}(\epsilon \sigma^z - \Delta \sigma^x)$ , labeled by  $|\mu\rangle$  ( $\mu = \pm$ ), to express Eq. (B20) as

$$\langle \sigma^x(t) \sigma^x(0) \rangle_E = \sum_{\mu\nu} \langle \mu | \sigma^x | \nu \rangle \tilde{\rho}_{\nu\mu}(t), \quad (\text{B21})$$

with  $\tilde{\rho}_{\nu\mu}(t) = \langle \nu | \tilde{\rho}_{\sigma}(t) | \mu \rangle$ . Following [51], for instance, we can obtain the matrix element of  $\tilde{\rho}_{\sigma}$  by solving the following system of differential equations:

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_{++} &= -\gamma_{(+,+,+)} \tilde{\rho}_{++} + \gamma_{(-,+,+)} \tilde{\rho}_{--}, \\ \frac{\partial}{\partial t} \tilde{\rho}_{--} &= -\gamma_{(-,+,+)} \tilde{\rho}_{--} + \gamma_{(+,+,+)} \tilde{\rho}_{++}, \\ \frac{\partial}{\partial t} \tilde{\rho}_{-+} &= -i(\epsilon_- - \epsilon_+ + \sigma_{--} - \sigma_{++}) \tilde{\rho}_{-+} \\ &\quad + \left( \gamma_{(-,+,+)} - \frac{\gamma_{(+,+,+)} + \gamma_{(+,-,+)} }{2} \right) \tilde{\rho}_{-+}, \end{aligned} \quad (\text{B22})$$



where  $\gamma_{(\mu\nu,\mu'\nu')}$  are relevant damping coefficients and  $\sigma_{\pm,\pm}$  are the Lamb-shift terms. The initial conditions are set by  $\tilde{\rho}_\sigma(0) = \text{tr}_\sigma\{\sigma^x \rho_\sigma(0)\}$ . The solutions of the system of differential equation have the form

$$\begin{aligned}\tilde{\rho}_{++}(t) &= a_1 + b_1 e^{-\lambda t}, \\ \tilde{\rho}_{--}(t) &= a_2 + b_2 e^{-\lambda t}, \\ \tilde{\rho}_{+-}(t) &= b_3 e^{-\lambda_0 t},\end{aligned}\quad (\text{B23})$$

where  $\lambda = \gamma_{(-+,-+)} + \gamma_{(+,-,+)}$ . The  $a_j$  and  $b_j$  ( $j = 1, 2$ ) are real, while  $\lambda_0$  and  $b_3$  are complex, and all of them depend explicitly on the damping and the Lamb-shift coefficients, as well as on the initial state  $\tilde{\rho}_{\mu\nu}(0)$ . The nonrenormalized SMCF is then given by the function

$$\begin{aligned}\langle \sigma^x(t) \sigma_j^x(0) \rangle_E &= \langle -|\sigma^x|-\rangle a_1 + \langle +|\sigma^x|+\rangle a_2 \\ &+ e^{-\lambda t} (\langle -|\sigma^x|-\rangle b_1 + \langle +|\sigma^x|+\rangle b_2) \\ &+ \langle -|\sigma^x|+\rangle b_3 e^{-\lambda_0 t} + \langle +|\sigma^x|-\rangle b_3^* e^{-\lambda_0^* t}.\end{aligned}\quad (\text{B24})$$

Interestingly, the form of this solution is very similar to the one of the fitting functional [see Eq. (9) in the main text]. Indeed, once renormalized, i.e., after subtracting  $\langle \sigma^x \rangle^2$ , its real part takes the form

$$\begin{aligned}f^{r \ll 1}(t) &= \text{Re}\{\langle \sigma^x(t) \sigma^x(0) \rangle_E\} - \langle \sigma^x \rangle^2 \\ &= \tilde{A}_0 e^{-\text{Re}\{\lambda_0\}t} \cos(\text{Im}\{\lambda_0\}t) + C_0 e^{-\lambda t} \\ &+ b_0 - \langle \sigma^x \rangle^2.\end{aligned}\quad (\text{B25})$$

The first term on the right-hand side corresponds to an exponentially decaying damping,  $\sim e^{-\text{Re}\{\lambda_0\}t}$ . This is due to the fact that we are assuming the weak-coupling approximation between electrons and phonons, while the analogous term in the fitting function [see Eq. (9) in the main text] presents a non-Markovian structure,  $\sim e^{-B_0 t^a}$  with  $a \approx \sqrt{2} > 1$ . Notice that in the weak-coupling solution given by Eq. (B25), there is a constant term  $b_0$  that does not cancel with  $\langle \sigma^x \rangle^2$ . One may be tempted to say that this corresponds to an offset. However, we argue that such an offset is ill defined, as our initial nonequilibrium state (B19) produces a time-dependent renormalization factor,  $\langle \sigma^x \rangle_E \approx \text{tr}_E\{\rho_\sigma(t) \otimes \rho_R \sigma_x\}$ .

In contrast, we shall emphasize that the offset described in the main text corresponds to a correlation function of an environment in equilibrium. Indeed, in the main text, we take the full thermal initial state  $\rho_E^{\text{th}}$ , for which

$$\langle \sigma^x \rangle_E = \text{tr}_E\{e^{iH_E t} \sigma^x e^{-iH_E t} \rho_E^{\text{th}}\} = \text{tr}_E\{\sigma^x \rho_E^{\text{th}}\} \quad (\text{B26})$$

is time independent.

### APPENDIX C: CORRELATION FUNCTION IN THE HARMONIC LIMIT

Let us now consider the particular case of Gaussian environments. In this case, the environment should be formed by a set of independent harmonic oscillators, and thus we relabel the environment eigenstates and eigenenergies in terms of the standard indices: one referring to the oscillator  $\lambda$  and another one referring to its internal state  $n_\lambda$  that reflects the number of quanta in such oscillator (we consider a single molecule and

thus skip the index  $j$ ),

$$\begin{aligned}|\epsilon_k\rangle &\equiv |n_\lambda\rangle, \\ \epsilon_k &\equiv \epsilon_{n_\lambda} = \omega_\lambda(n_\lambda + 1/2).\end{aligned}\quad (\text{C1})$$

Thus, the correlation function can be written as

$$C_{\tilde{B}}(t) = \sum_{\lambda', n_{\lambda'}} \sum_{\lambda'', n_{\lambda''}} e^{-\beta \omega_{\lambda'}} |B^{n_{\lambda'}, n_{\lambda''}}|^2 e^{i(\epsilon_{n_{\lambda'}} - \epsilon_{n_{\lambda''}})t}.$$

To obtain Gaussian statistics, we furthermore need a linear coupling operator  $B = \sum_{\lambda} g_{\lambda} (a_{\lambda}^{\dagger} + a_{\lambda})$ , such that  $B^{n_{\lambda'}, n_{\lambda''}}$  is

$$\begin{aligned}\langle n_{\lambda'} | B | n_{\lambda''} \rangle &= \sum_{\lambda} \delta_{\lambda', \lambda} \delta_{\lambda'', \lambda} g_{\lambda} (\sqrt{n_{\lambda'} + 1} \delta_{n_{\lambda'}, n_{\lambda''} + 1} \\ &+ \sqrt{n_{\lambda''}} \delta_{n_{\lambda'}, n_{\lambda''} - 1}).\end{aligned}$$

Notice that here there is no need to renormalize since  $\langle n_{\lambda} | B | n_{\lambda} \rangle = 0$ , i.e., the coupling operator does not connect the same environment eigenstates, which means that  $\tilde{B} = B$ . In addition, we have

$$\begin{aligned}\delta_{n_{\lambda'}, n_{\lambda''} + 1} e^{i(\epsilon_{n_{\lambda'}} - \epsilon_{\lambda''})t} &= \delta_{n_{\lambda'}, n_{\lambda''} + 1} e^{i\omega_{\lambda} t}, \\ \delta_{n_{\lambda'}, n_{\lambda''} - 1} e^{i(\epsilon_{\lambda'} - \epsilon_{\lambda''})t} &= \delta_{n_{\lambda'}, n_{\lambda''} - 1} e^{-i\omega_{\lambda} t}.\end{aligned}\quad (\text{C2})$$

Considering, also, the Bose-Einstein statistics, i.e.,

$$N(\omega_{\lambda}) = \frac{\sum_{n_{\lambda}=0}^{\infty} n_{\lambda} e^{-\beta \omega_{\lambda}(n_{\lambda} + 1/2)}}{Z_{\lambda}} = \frac{1}{e^{\beta \omega_{\lambda}} - 1}, \quad (\text{C3})$$

and the detailed balance  $[N(\omega_{\lambda}) + 1]e^{-\beta \omega_{\lambda}} = N(\omega_{\lambda})$ , we find the standard correlation function for harmonic environments,

$$C_{\tilde{B}}(t) = \sum_{\lambda} g_{\lambda}^2 [(N(\omega_{\lambda}) + 1)e^{-i\omega_{\lambda} t} + N(\omega_{\lambda})e^{i\omega_{\lambda} t}]. \quad (\text{C4})$$

As it is well known, this function can be written in terms of the one-particle spectral density  $J(\omega) = g(\omega)^2 |\partial(\omega_{\lambda})/\partial \lambda|_{\lambda=\omega}^{-1}$  as

$$C_{\tilde{B}}(t) = \int_0^{\infty} d\omega J(\omega) \{ [N(\omega) + 1] e^{-i\omega t} + N(\omega) e^{i\omega t} \}. \quad (\text{C5})$$

As discussed in regard to Eq. (5) in the main text, as long as  $J(\omega)$  is a smooth function in frequencies [since  $N(\omega)$  is smooth],  $C_{\tilde{B}}(t)$  will decay to zero. This is the case in most physical models, where  $J(\omega)$  is a continuous differentiable function.

### APPENDIX D: ADDITIONAL NUMERICS ON THE OFFSET

We first compute the offset  $C_0$  using Eq. (4) in the main text by diagonalizing  $H_{\text{SM}}$  for a single-, two-, and three-mode molecule. As seen in the main text, the offset does not show any strong dependence on the number of modes  $L$ , and it is a smooth function of the parameters of interest. The results are shown in Fig. 2, where it can be noticed that the  $x$  and  $y$  axes are in a logarithmic scale. The figure also illustrates why the offset cancels towards the limit in which the environment Hamiltonian becomes separable, for instance, as the ratio  $r/\Delta \gg 1$ .

In addition, we compute the distribution of  $B^{kk} = \sigma_{kk}^x = \langle \epsilon_k | \sigma^x | \epsilon_k \rangle$ . The eigenenergies are rescaled as  $\epsilon'_k = (\epsilon_k - \epsilon_0)/\max\{(\epsilon_k) - \epsilon_0\}$ , such that  $0 \leq \epsilon'_k \leq 1$ . From this figure, it is easily noticed that whenever  $\Delta = 0$ , then  $B^{kk} = 0$  for all

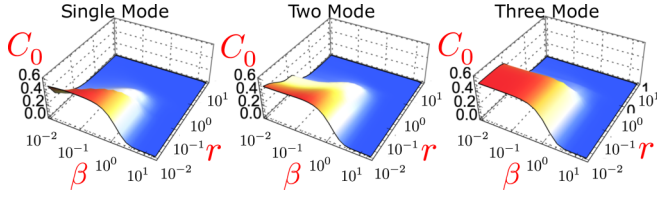


FIG. 2. Few-mode case: Offset. Offset as a function of the inverse of the temperature  $\beta$  and the environment interaction  $g_\lambda \propto r$  for a single-, two-, and three-mode molecule, with  $\Delta = \varepsilon = 1$ .

eigenstates, as expected, while for a very small value of  $\Delta$ , the distribution already gets spread around zero. The larger the value of  $\Delta$ , the broader the distribution, and, as seen in Fig. 3, when  $\Delta/r \gg 1$ , two peaks are getting formed around  $\pm 1$ , especially in the low-energy regime that is the relevant energy bandwidth for the computation of  $C_0$ . Such relevant bandwidth can be estimated by considering the thermal distribution  $\eta_k$  (black dashed lines).

Furthermore, to visualize the energy range in which the offset increases, we compute an effective participation-energy range  $\Delta E_\beta = \varepsilon_N - \varepsilon_0$  (light blue region), defined as the values in which the cumulative sum  $F_\beta(N) = \sum_{k=0}^N \eta_k (B^{kk})^2$  converges to their constant value  $F_\beta(N) \approx \lim_{N \rightarrow \infty} F_\beta(N)$ . This quantity might be helpful to evaluate the offset for thermal large systems, where only the first few eigenstates are accessible. Nonetheless, as concluded before, a nonzero offset implies the participation of at least two eigenstates.

To complete the analysis, in Fig. 4 we show the variation of the SMCF as the interaction strength  $r$  is increased. We can see that the larger the ratio  $r/\Delta$ , the more relevant the dephasing becomes and the faster the correlation function decays. To contrast these results, we additionally include the correlation function with parameters  $r = 0.25$  and  $\Delta = 2.5$  for which the appearance of a very large  $T_0$  is observed.

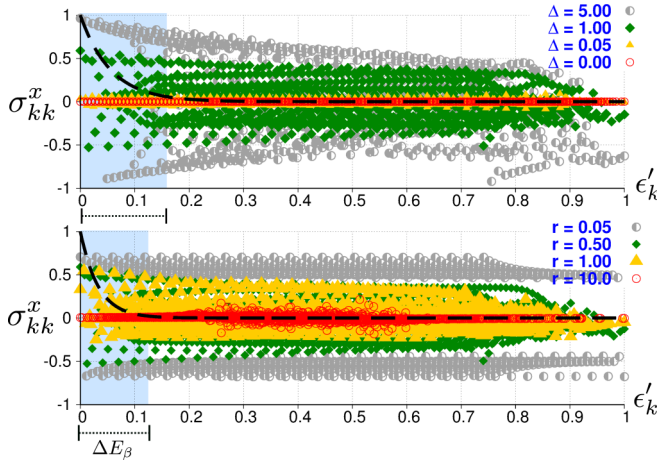


FIG. 3. Few-mode case: Statistics. Distribution of the single-eigenstate expectation of system-environment coupling operator  $B = \sigma^x$  as a function of (a) the tunneling strength  $\Delta$  with  $r = 0.25$ , and (b)  $r$  ( $\propto g_\lambda$ ) with  $\Delta = 1$ . The black dashed lines represent the thermal distribution for  $\beta = 0.5$ .

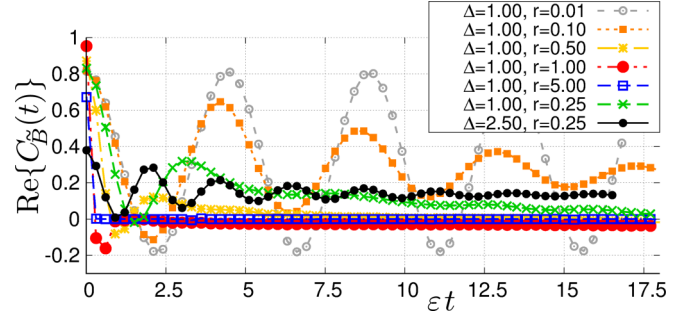


FIG. 4. Environment interaction. Single-molecule correlation function for different values of the environment interaction strength  $r$ , given  $\Delta = 1$  and  $\beta = 1$ .

### APPENDIX E: MANY-MOLECULE SCENARIO

A standard case is that in which the environment is composed of an ensemble of molecules. When they are independent, the total correlation function is given by  $C_{\bar{B}}(t) = \sum_{j=1}^M C_B^{(j)}(t)$ . In a realistic setup, the molecules in the ensemble are not identical, and the total correlation function shall depend on how the molecular parameters,  $\{\Delta_j, \varepsilon_j\}$ , are distributed. Let us assume that they follow a normalized distribution,  $\mathcal{P}(\{\Delta_j, \varepsilon_j\})$ . In the continuous limit, the correlation function can then be written as

$$\begin{aligned} C_{\bar{B}}(t) &= \frac{1}{M} \sum_j C_B(t, \{\Delta_j, \varepsilon_j\}) \\ &= \int_{\langle \Delta \rangle} \int_{\langle \varepsilon \rangle} \mathcal{P}(\Delta, \varepsilon) C_B(t, \Delta, \varepsilon) d\Delta d\varepsilon, \end{aligned} \quad (\text{E1})$$

with  $C_B^{(j)}(t) \equiv C_B(t, \{\Delta_j, \varepsilon_j\})$ , and  $\mathcal{P}(\Delta, \varepsilon)$  is the continuous distribution. A precise knowledge of this distribution may not be experimentally trivial to obtain.

Here, we consider a Gaussian probability distribution where  $\Delta$  and  $\varepsilon$  are treated as independent variables,

$$\begin{aligned} \mathcal{P}(\Delta, \varepsilon) &= \mathcal{P}(\Delta)\mathcal{P}(\varepsilon) \\ &= \left( \frac{1}{\sqrt{2\pi}\sigma^2} \right)^2 e^{-\frac{(\Delta-\bar{\Delta})^2}{2\sigma^2}} e^{-\frac{(\varepsilon-\bar{\varepsilon})^2}{2\sigma^2}}, \end{aligned} \quad (\text{E2})$$

where the distribution width  $\sigma$  is set as a tuning parameter. Considering such a Gaussian distribution (which leads to mean values  $\{\bar{\Delta}_j = 1, \bar{\varepsilon}_j = 1\}$ ), we randomly sample the parameter set  $\{\Delta_j, \varepsilon_j\}$  and compute the correlation function for each pair by solving the eigenspectrum of  $H_E^{(j)}$ .

In Fig. 5, we present the numerical results of the correlation function as a function of the total number of molecules  $M$ , each with a single active bosonic mode. Therein, it can be seen that the function exhibits a large offset in the presence of many molecules and, interestingly, the expected finite-size recurrence is washed out in the average. We shall emphasize that our results are valid for a finite number of modes for each molecule and limited to the timescale that is accessible to us. The fluctuations around the final offset value (light-yellow dashed line) are expected to disappear as the number of molecules involved is larger while  $\sigma$  also is increased. This calculation, for a higher number of modes, is not easily

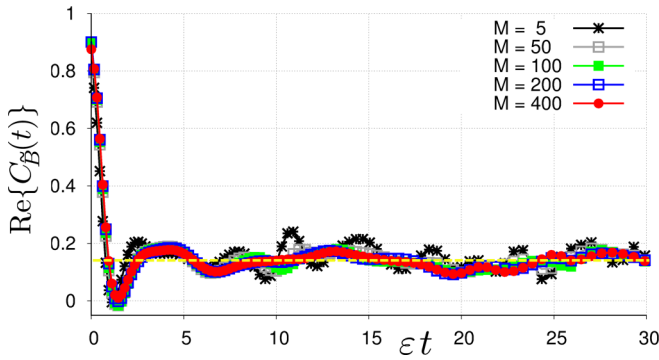


FIG. 5. Many-molecule offset. Many-molecule correlation function computed using the eigenstates and eigenvalues of  $H_E^{(j)}$ . The parameters are  $r = 0.25$ ,  $\beta = 1$ , and we randomly choose  $\{\Delta_j, \varepsilon_j\}$  around  $\overline{\Delta_j} = \overline{\varepsilon_j} = 1$ , and a distribution width  $\sigma = 0.3$ .

accessible due to the exponential growth of the Hilbert space of  $H_E^{(j)}$ .

#### APPENDIX F: THE $1/f$ NOISE

Another important aspect of the presence of an offset for some parameters is related to the bandwidth of the  $1/f$  noise. To show this, we compute the susceptibility function, which is the Fourier transform of  $C_B(t)$ . The  $1/f$  is observed at low frequencies, and therefore it will be dominated by the long-time or slowly decaying term of the fitting correlation function [see Eq. (9) in the main text], i.e.,

$$f^{\text{lt}}(t) = \tilde{C}_0 e^{-t/T_0}. \quad (\text{F1})$$

In order to compute the susceptibility, one should take into account a sum over an ensemble of molecules  $j$ , each with different parameters and therefore with different decay rates  $\nu_0^{(j)} = 1/T_0^{(j)}$ ,

$$F^{\text{lt}}(t) = \sum_j \tilde{C}_0^{(j)} e^{-\nu_0^{(j)} t}. \quad (\text{F2})$$

Thus, the susceptibility at low frequencies will be given by the Fourier transform of this function,

$$\begin{aligned} \chi_0(\omega) &= \sum_j \int_{-\infty}^{\infty} e^{-\nu_0^{(j)} |t|} e^{-i\omega t} \tilde{C}_0^{(j)} dt \\ &= \frac{c_1}{2\pi} \sum_j \tilde{C}_0^{(j)} \frac{\nu_0^{(j)}}{\omega^2 + \frac{(\nu_0^{(j)})^2}{4\pi^2}} \\ &\propto \frac{c_1}{2\pi} \int_{\nu_{\min}}^{\nu_{\max}} \mathcal{Q}(\nu_0) \tilde{C}_0(\nu_0) \frac{\nu_0}{\omega^2 + \frac{\nu_0^2}{4\pi^2}} d\nu_0, \quad (\text{F3}) \end{aligned}$$

with  $\nu_{\min} = 1/T_{\max}$  and  $\nu_{\max} = 1/T_{\min}$  very small. In the last equality, we have considered the limit of a very dense molecular ensemble and taken the sum as an integral with a certain probability distribution for decay rates, which we take as  $\mathcal{Q}(\nu_0) = 1/\nu_0$  [10,41]. Moreover, we assume a narrow bandwidth at low frequencies, such that  $\tilde{C}_0(\nu_0) \approx \tilde{C}_0$ , so that it can be taken out of the integral. The resulting integral is analytically accessible and allows one to obtain the  $1/f$  behavior since

$$\chi_0(\omega) \propto \frac{\tilde{C}_0}{\omega} \quad \text{if} \quad \frac{1}{T_{\max}} < \nu_0 < \frac{1}{T_{\min}}. \quad (\text{F4})$$

So far, we have carried the standard calculation of the  $1/f$  spectrum. The difference in our case is that due to the finite temperature, we find that  $\nu_{\min} = 1/T_{\max} = 0$  since there are some molecules with internal parameters that have an infinitely decaying correlation function. Previous models are often based on a weak-coupling approximation that leads to a correlation function (B25) that always decays with a finite rate  $\lambda$ . This leads to a  $1/f$  spectrum that is limited to the lower frequency,  $\frac{1}{T_{\max}} = \lambda_{\min}$ . In contrast, our model shows a  $1/f$  behavior that extends to zero frequency, and it is therefore in better agreement with experimental observations (see [41] and references therein).

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