Study of a Microscopic Model for Two-Level System Dynamics in Glasses

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We propose a model for the low-temperature excitations in glasses, which have been the object of recent investigations by means of nonlinear optical techniques. The experimental evidence strongly suggests the presence in these amorphous materials of configurational two-level systems, which are coupled via the phonon field to the chromophore whose optical response is being probed. A microscopic description for the relevant interactions is developed and the connections between the exact dynamics within this description and the stochastic sudden-jump model are drawn by means of a path integral method.

1. Introduction

The low-temperature acoustic and thermal properties of crystals and glasses are very different. In glasses, acoustic experiments in which saturation is measured, and the anomalous temperature dependence of quantities like the heat capacity (quasilinear at low T) and thermal conductivity (roughly quadratic), suggest the presence of localized two-level systemlike excitations in these disordered materials¹⁻³ that are not present in ordered solids. This model of a glass consisting of a random array of two-level systems (TLS's) is now well supported by both experiments (such as single particle optical measurements4-6, the presence of spectral diffusion as detected by nonlinear optical techniques,⁷ etc.), and by numerical simulations.^{8,9} In general, it is believed that these two-level systems are configurational in nature: a particle or, more likely, a group of particles can tunnel between two local minima of the multidimensional potential energy surface. These two minima are separated by a potential barrier, which is typically much higher than the temperatures at which the experiments are conducted (usually around 1 K). The two-level systems are characterized by two parameters: E, the energy difference between the two configurations, assuming that they are separated by an infinite barrier, and Δ , the tunneling amplitude, which is proportional in the WKB approximation to $e^{-\lambda}$, where λ is the overlap of the two wavefunctions, each localized in one of the wells (see Figure 1).

The study of the spectrum¹⁰ of optical probes placed in these sorts of materials has revealed the presence of spectral diffusion.¹¹⁻¹³ This phenomenon permits the experimental study of the relaxation and dynamics of the TLS's mentioned above. In the particular case of an optical impurity surrounded by a glassy medium, the spectral diffusion is related to fluctuations of the absorption frequency due to rearrangements in the environment. At low temperatures, these rearrangements seem to correspond to the relaxation of the glass TLS's.^{7,14,15}

The quantity of interest in the interpretation of these nonlinear optical experiments is

$$A[s(\tau)] = \langle \langle \exp\{i \int_0^i d\tau \, s(\tau) \sum_{j=1}^N \Delta \omega_j(\tau) \} \rangle \rangle$$

in photon echo experiments^{16–18} or its Fourier transform in holeburning.¹¹ The term $\sum_{j=1}^{N} \Delta \omega_j(\tau)$ is the fluctuating part of the chromophore's frequency due to the interactions with the perturbers in the glass. $s(\tau)$ is a piecewise constant function taking the values $0, \pm 1$. Its particular form is determined by the type of experiment we are performing.¹⁶



Figure 1. Double-well potential given by the section of the multidimensional potential energy surface of the glass along the collective coordination $Q.^3$ At low temperature it is only necessary to take into account the lower two states, characterized by wavefunctions localized in each of the wells. This two-level system is characterized by two parameters: the energy splitting (E) and the tunneling matrix element (Δ) .

The angular brackets $(\langle \langle ... \rangle \rangle)$ in the expression for $A[s(\tau)]$ stand for the averages that have to be performed in order to make a direct connection to the experimental measurements: First, we have to carry out an average over the ensemble of perturbers. By the ergodic hypothesis, we can evaluate it by performing instead an average over the dynamics taking place in the chromophore's environment (in this case, the time evolution of the two-level systems). Second, we must carry out a configurational average over the positions of the TLS's. Finally, we have to evaluate the average over the parameters characterizing the perturbers, in this case, over the energy splitting (E), and the tunneling amplitude (Δ) of the TLS's.

Assuming that these averages are independent of each other, that that perturbers are distributed at random and uniformly throughout the glass, and that the dynamics of different two-level systems are uncorrelated, $\mathcal{A}[s(\tau)]$ is given by

$$A[s(\tau)] = \exp\{-\rho \int_{V} d\vec{r} \left[1 - \langle \exp(i \int_{0}^{t} s(\tau) \Delta \omega_{r}(\tau) d\tau) \rangle \right]\}$$

where $\Delta \omega_{\bar{r}}(\tau)$ now stands for the fluctuation of the chromophore's frequency due to a perturber located at position \bar{r} . The remaining averages (denoted by $\langle \rangle$) are the history average and the average over the TLS parameters (Δ and E).

The objective of this paper is to show how the history average can be performed by assuming a realistic microscopic model for the low-temperature excitations in the glass where the chromophore is embedded. Previous attempts to model the environ-

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ment dynamics assume simply that the chromophore absorption frequency is shifted in a stochastic fashion. In particular, the sudden-jump model is presumed to be the proper description for this case: The actual dynamics of the two-level system are replaced by a two-state stochastic process, where $\Delta \omega_{\vec{r}}(\tau) = a(\vec{r}) h(\tau)$, where $a(\vec{r})$ gives the strength of the TLS-chromophore interaction and $h(\tau)$ is a random-telegraph variable taking the values ± 1 . The physical picture is that the TLS is jumping between its two configurations (in a semiclassical sense; the transitions actually occur through tunneling, but the description can be made in terms of classical jump rates). In one of the configurations of the TLS the chromophore's frequency takes the value $\omega_0 + a(\vec{r})$, and in the other one, $\omega_0 - a(\vec{r})$.

We shall show that, provided that the dynamics of the perturbers are uncorrelated, a stochastic sudden-jump model of the sort described above can be derived rigorously from a microscopic Hamiltonian, which includes the chromophore, the acoustic phonons, and the configurational two-level systems.

The paper is organized as follows: In section 2, we review some results obtained by means of the sudden-jump model. We shall recast the history average in terms of a summation over paths, each of which is a given a different weight according to the properties of the stochastic process. This approach will prove useful for the comparison with the microscopic model. In section 3, we propose a microscopic Hamiltonian, a generalization of the spin-boson model, in which two spins are coupled to the boson field. Our objective is to describe the dynamics of the lowtemperature excitations of glasses (acoustic phonons and twolevel systems) and how they affect the chromophore's absorption. The physical picture is the following: The chromophore (one of the pseudospins) and the TLS (the other pseudospin) are both coupled to the same set of phonons, which act as a boson field. This field mediates an elastic dipole-dipole interaction between the chromophore and the two-level system, which is responsible for the fluctuations of the chromophore's frequency that are the origin of the spectral diffusion observed in the optical experiments mentioned above. Section 4 contains a summary of the results obtained in this investigation.

2. Stochastic Sudden-Jump Model

In this section, we calculate the stochastic history average of quantities like

$$\langle \exp(-i \int_{0}^{t} \mathrm{d}\tau \ \Delta \omega_{\bar{r}}(\tau)) \rangle$$
 (1)

assuming that $\Delta \omega_{\bar{r}}(t) = a(\bar{r}) h(t)$ is the fluctuating part of the chromophore's frequency due to a perturber located at position \bar{r} (with the chromophore at the origin). The angular brackets $(\langle ... \rangle)$ denote the stochastic average. In the sudden-jump model $h(\tau)$ behaves like a random telegraph signal, taking over a discrete set of values (in this case ± 1 , since only TLS's are thought to be relevant). The upward and downward rates (W_2 and W_1 , respectively) are unequal, and they satisfy a detailed balance relation: $W_2/W_1 = e^{-\beta E}$ at a temperature $T = 1/(K_B\beta)$ (see Figure 2).

The probability weight for a path such as the one indicated in Figure 2 is¹⁹

$$P(t_1, t_2, ..., t_{2n}, t) = W_1^n W_2^n e^{-W_2 t_1} e^{-W_1 (t_2 - t_1)} e^{-W_2 (t_3 - t_2)} ... e^{-W_1 (t_{2n} - t_{2n-1})} e^{-W_2 (t - t_{2n})}$$

For the sake of concreteness, we shall calculate the average in eq 1 for a free-induction decay (FID) experiment $(s(\tau) = 1$ for all τ). There are four possible different types of paths that contribute to the free-induction decay signal (see Figure 3). We



Figure 2. Sudden-jump model: The stochastic variable $h(\tau)$ can take the values ± 1 . The process is characterized by upward (W_2) and downward (W_1) jump rates that satisfy a detailed balance relation $W_2/W_1 = e^{-\beta E}$ at a temperature $T = 1/(K_B\beta)$. In the stochastic model, E is simply an arbitrary parameter defining the temperature scale. The microscopic model proposed identifies it with the energy splitting of the perturbing TLS.

shall assume that the probability of starting at the state +1 (-1) is proportional to $W_2(W_1)$; i.e. the initial state is an equilibrium one. The average is then given by

$$\langle \exp(ia\int_{0}^{t} d\tau h(\tau)) \rangle = \frac{1}{2R} [W_{2} \{e^{-W_{1}t}e^{iat} + \sum_{n=1}^{\infty} W_{1}^{n} W_{2}^{n} \int_{0}^{t} dt_{2n} \int_{0}^{t_{2n}} dt_{2n-1} \dots \int_{0}^{t_{2}} dt_{1} \times e^{iat}e^{2iat_{1}} \dots e^{-2iat_{2n}}e^{-W_{1}t_{1}}e^{-W_{2}(t_{2}-t_{1})} \dots e^{-W_{1}(t-t_{2n})} + \sum_{n=0}^{\infty} W_{1}^{n+1} W_{2}^{n} \int_{0}^{t} dt_{2n+1} \int_{0}^{t_{2n+1}} dt_{2n} \dots \int_{0}^{t} dt_{1} e^{-iat} \times e^{2iat_{1}} \dots e^{-2iat_{2n}}e^{2iat_{2n+1}}e^{-W_{1}t_{1}}e^{-W_{2}(t_{2}-t_{1})} \dots e^{-W_{1}(t_{2n+1}-t_{2n})}e^{-W_{2}(t-t_{2n+1})} \} +$$

 W_1 {complex conjugate + interchange 1 \leftrightarrow 2}]

The following definitions shall be useful:

$$R = \frac{W_1 + W_2}{2}$$
$$W_- = \frac{W_1 - W_2}{2}$$
$$(Y^{\pm})^2 = a^2 - R^2 \pm 2iaW_-$$
$$\theta = a + iW_-$$

Consider the first term, corresponding to path 1 in Figure 3:

$$\begin{aligned} (\mathbf{I}) &= e^{-W_{1}t} e^{iat} \sum_{n=1}^{\infty} W_{1}^{n} W_{2}^{n} \int_{0}^{t} dt_{2n} \dots \int_{0}^{t_{2}} dt_{1} e^{2i\theta t_{1}} \dots e^{-2i\theta t_{2n}} \\ &= e^{-W_{1}t} e^{iat} \sum_{n=1}^{\infty} W_{1}^{n} W_{2}^{n} \int_{0}^{t} dt_{1} e^{-2i\theta t_{1}} \frac{t_{1}^{n-1}}{(n-1)!} \frac{(t-t_{1})^{n}}{n!} \\ &= e^{-W_{1}t} e^{i(a-\theta)t} t\theta \sum_{n=1}^{\infty} \frac{W_{1}^{n} W_{2}^{n}}{n!} [j_{n-1}(\theta t) + ij_{n}(\theta t)] \left(\frac{t}{2\theta}\right)^{n} \\ &= e^{-Rt} \Big[\cos(Y^{+}t) - \cos(\theta t) + i\frac{\theta}{Y^{+}} \sin(Y^{+}t) - i\sin(\theta t) \Big] \end{aligned}$$

The function $j_n(x)$ is a spherical Bessel function of *n*th order.²⁰ For the second type of path

(II) =

$$e^{-W_{2}t}e^{-iat}\sum_{n=0}^{\infty}W_{1}^{n+1}W_{2}^{n}\int_{0}^{t}dt_{2n+1}\dots\int_{0}^{t_{2}}dt_{1}e^{2i\theta t_{1}}\dots e^{-2i\theta t_{2n}}e^{2i\theta t_{2n+1}}$$

$$=W_{1}e^{-Rt}\frac{\sin(Y^{+}t)}{V^{+}}$$



Figure 3. Paths contributing to the average required for the free-induction decay experiments in the stochastic sudden-jump model.

Adding up the contributions from all four paths, we obtain

$$\langle \exp(ia \int_0^t d\tau \ h(\tau)) \rangle = \frac{e^{-Rt}}{R} \left[R \cos(Y^+ t) + (R^2 - iaW_-) \frac{\sin(Y^+ t)}{Y^+} \right]$$
(2)

which is the final expression for the FID experiment.

In order to facilitate the comparison with the microscopic model, we shall calculate a simpler average in which the $h(\tau)$ is restricted to have the value +1 at the beginning of the interval in question: h(0) = +1. This corresponds to computing only the contributions from the first and second paths of Figure 3:

$$\Theta(t) \equiv \langle \exp(ia \int_0^t \mathrm{d}\tau \ h(\tau)) \rangle_{h(0)=+1}$$

The Laplace transform of this quantity is given by

$$\tilde{\Theta}(s) = \frac{s + ia + W_1 + W_2}{s^2 + a^2 + W_2(s - ia) + W_1(s + ia)}$$
(3)

3. Microscopic Model for TLS Dynamics

In this section, we shall provide for the theoretical description that justifies the use of the stochastic sudden-jump model to model the dynamics of TLS's in glasses. Our starting point is a microscopic Hamiltonian in terms of the degrees of freedom of the chromophore, one TLS and a bath of harmonic oscillators, which represent the phonons. This Hamiltonian contains linear coupling of the glass TLS's with the phonons and between the chromophore and the phonons. The TLS-chromophore direct coupling is obtained by elimination of the chromophore-phonon interaction by means of a polaron transformation. In this fashion, the effective elastic dipole interaction between the chromophore and each of the TLS's is derived from a microscopic model in such a way that its physical origin is explicitly displayed: The phonon (deformation) field is the mediator of the interaction.^{7,21,22} Assuming that the dynamics of the TLS's are not correlated, it shall be sufficient to deal with pairwise interactions one at a time. The Hamiltonian for one two-level system interacting with the chromophore is

$$H = -\frac{\omega_0}{2}\sigma_{z0} + \frac{E}{2}\sigma_{z1} - \frac{\Delta}{2}\sigma_{z1} + H_b + \sum_q c_q^0(b_q + b_{-q}^+)\sigma_{z0} + \sum_q c_q^1(b_q + b_{-q}^+)\sigma_{z1}$$
(4)

where it has been assumed that the tunneling matrix element is not modulated by the phonon coordinate. The chromophore Hamiltonian has been truncated to that of a pseudospin with S = 1/2, assuming that the experiments are carried near resonance with the optical transition of frequency ω_0 . The 0 subindex refers to the chromophore, and the 1 subindex to the TLS with asymmetry E and tunneling splitting Δ (in a localized basis; see Figure 1). $H_b = \sum_q \omega_q b_q^+ b_q$ represents the Hamiltonian for the harmonic lattice, with q being a set of quantum numbers (analogous to those for polarization and wave vector in crystals) characterizing the normal modes. The following definitions should be useful for clarifying the notation:

$$\sigma_{z0} = |g\rangle\langle g| - |e\rangle\langle e|; \quad \sigma_{x0} = |g\rangle\langle e| + |e\rangle\langle g| \qquad (5a)$$

where g(e) is the ground (excited) state of the chromophore, and

$$\sigma_{z1} = |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|; \quad \sigma_{x1} = |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow| \tag{5b}$$

where $\uparrow(\downarrow)$ is the upper (lower) state of the TLS. The polaron transformation mentioned above is given by

$$U = \exp\left\{-\sum_{q} \frac{c_q^0}{\omega_q} (b_q^+ - b_{-q})\sigma_{z0}\right\}$$

Applying this unitary transformation, the Hamiltonian becomes

$$\tilde{H} = U^{\dagger} H U = -\frac{\omega_0}{2} \sigma_{z0} + \frac{E}{2} \sigma_{z1} - \frac{\Delta}{2} \sigma_{x1} + H_b + \sum_q c_q^1 (b_q + b_{-q}^+) \sigma_{z1} + \frac{a}{2} \sigma_{z0} \sigma_{z1}$$
(6)

where a has the radial and angular dependence of a dipole-dipole interaction.²² This is finally a good starting point for our applying approximate methods to calculate the pertinent time-correlation functions. Note that the last term has the basic ingredients of the system we want to study: the chromophore frequency fluctuates according to the dynamics of a perturber, which is relaxing to equilibrium.

Take, for instance, the free-induction decay experiment: in the absence of an external field, given the low temperatures at which these experiments are performed (0.1-10 K), the chromophore should be in its ground state $(\rho(0^-) = |g\rangle\langle g|)$. We can now apply an optical $\pi/2$ pulse at the right frequency in order to transfer population into coherence $(\rho(0^+) = |e\rangle\langle g| + |g\rangle\langle e| = \sigma_{x0}$, after the pulse). Obviously, if the chromophore were isolated (e.g., in the gas phase), the coherence would oscillate at a frequency ω_0 (neglecting collisions and electronic dephasing). In the glass matrix, the fluctuations due to the coupled perturbers lead to a signal which is decaying in time. The formal solution to the time evolution in terms of the global density matrix is

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt}; \quad \rho(0) = \rho_{b,\text{TLS}}^{\text{eq}}\sigma_{x0}$$

.

where initially both the bath and the TLS are in their equilibrium states.

The amplitude of the free-induction decay signal is proportional to

$$\langle M_x \rangle = Tr_{b,\text{TLS}} \{ \langle g | e^{-i\tilde{H}t} \rho(0) e^{i\tilde{H}t} | e \rangle + \langle e | e^{-i\tilde{H}t} \rho(0) e^{i\tilde{H}t} | g \rangle \}$$

$$= e^{-i\omega_0 t} \langle e^{iH_r t} e^{-iH_r t} \rangle + e^{i\omega_0 t} \langle e^{iH_r t} e^{-iH_r t} \rangle$$

where the angular brackets stand for a thermal average over both the bath and the TLS (i.e. $\langle ... \rangle \equiv Tr_{b,TLS} \{... \rho_{b,TLS}^{eq} \}$),

$$H_{g,e} = \frac{E_{g,e}}{2}\sigma_{z1} - \frac{\Delta}{2}\sigma_{x1} + H_b + V\sigma_{z1}$$
$$V = \sum_q c_q^1 (b_q + b_{-q}^+); \quad E_{g,e} = E \pm a$$

Let us examine the second term in $\langle M_x \rangle$ in detail:

$$\begin{aligned} \langle \mathbf{e}^{iH_{\mathbf{f}}}\mathbf{e}^{-iH_{\mathbf{f}}} \rangle &= Tr_{b,\text{TLS}} \{ \mathbf{e}^{iH_{\mathbf{f}}}\mathbf{e}^{-iH_{\mathbf{f}}}\rho_{b,\text{TLS}}^{\text{eq}} \} \\ &= \langle \langle \uparrow | \mathbf{e}^{iH_{\mathbf{f}}}\mathbf{e}^{-iH_{\mathbf{f}}} | \uparrow \rangle \rangle \frac{\mathbf{e}^{-(\beta E/2)}}{2\cosh(\beta E/2)} + \\ & \langle \langle \downarrow | \mathbf{e}^{iH_{\mathbf{f}}}\mathbf{e}^{-iH_{\mathbf{f}}} | \downarrow \rangle \rangle \frac{\mathbf{e}^{(\beta E/2)}}{2\cosh(\beta E/2)} \end{aligned}$$

Here, the outer angular brackets denote a thermal average over the bath only. Furthermore, for simplicity, we have assumed that $E \gg a$ and $E \gg \Delta$ so that the equilibrium density matrix for the TLS is given by

$$\rho_{\mathrm{TLS}}^{\mathrm{eq}} \approx \frac{1}{2 \cosh(\beta E/2)} \{ \mathrm{e}^{-(\beta E/2)} | \uparrow \rangle \langle \uparrow | + \mathrm{e}^{(\beta E/2)} | \downarrow \rangle \langle \downarrow | \}$$

Using the spectral representation on the bath Hamiltonian $H_b = \sum_n E_n |n\rangle \langle n|$, and with the bath partition function Z_b , we can show that the term

$$\langle \langle \uparrow | e^{iH_{g^{t}}} e^{-iH_{g^{t}}} | \uparrow \rangle \rangle = \sum_{n,m} \frac{e^{-\beta E_{n}}}{Z_{b}} \langle \uparrow; n | e^{iH_{g^{t}}} | \uparrow; m \rangle \times \\ \langle \uparrow; m | e^{-iH_{g^{t}}} | \uparrow; n \rangle + \sum_{n,m} \frac{e^{-\beta E_{n}}}{Z_{b}} \langle \uparrow; n | e^{iH_{g^{t}}} | \downarrow; m \rangle \langle \downarrow; m | e^{-iH_{g^{t}}} | \uparrow; n \rangle$$
(7)

contains two portions, the first of which we shall proceed to analyze in detail. By expanding in the interaction representation $e^{iH_{g^2}}$ with respect to $H_{0g} = H_g + (\Delta/2)\sigma_{x1}$ and $e^{-iH_{g^2}}$ with respect to $H_{0e} = H_e + (\Delta/2)\sigma_{x1}$, we find

$$(\mathbf{I}) = \sum_{n,m} \frac{e^{-\beta E_n}}{Z_b} \langle \uparrow; n | e^{iH_g t} | \uparrow; m \rangle \langle \uparrow; m | e^{-iH_g t} | \uparrow; n \rangle$$

$$= \sum_{n,m} \frac{e^{-\beta E_n}}{Z_b} \sum_{i=0}^{\infty} (-1)^i (\Delta/2)^{2i} \int_0^t d\theta_1 \dots \int_0^{\theta_{2i-1}} d\theta_{2i} \sum_{j=0}^{\infty} (-1)^j \times (\Delta/2)^{2j} \int_0^t ds_1 \dots \int_0^{s_{2i-1}} ds_{2j} \times (\Delta/2)^{2j} \int_0^t ds_1 \dots \int_0^{s_{2i-1}} ds_{2i} e^{-iH^+ o_g \theta_2} |n\rangle \times \langle n | e^{iH^+ o_g \theta_2} e^{-iH^+ o_g \theta_2} e^{-iH^+ o_g \theta_2} e^{-iH^+ o_g \theta_2} |n\rangle \times \langle n | e^{iH^+ o_g \theta_2} e^{-iH^- o_g \theta_2} \dots e^{iH^- o_g \theta_2} e^{-iH^+ o_g \theta_1} |n\rangle$$

with

3

$$H_{0g,0e}^{\pm} = \pm \frac{E_{g,e}}{2} + H_b \pm V$$

Defining

$$H^{\pm} = H_h \pm V$$

we have eq 8 given in Chart 1.

In the last expression of Chart 1, we have used the following definitions:

$$\xi(\tau) = \frac{1}{2} [\eta_{+}(\tau) - \eta_{-}(\tau)]$$
$$\chi(\tau) = \frac{1}{2} [\eta_{+}(\tau) + \eta_{-}(\tau)]$$
$$L_{1}(t) = 2i \langle [\hat{V}(t), V]_{-} \rangle$$
$$L_{2}(t) = 2 \langle [\hat{V}(t), V]_{+} \rangle$$
$$\hat{V}(t) = e^{iH_{bl}} V e^{-iH_{bl}}$$

Suárez and Silbey

CHART 1

$$(I) = \sum_{i,j=0}^{\infty} (-1)^{i+j} \left(\frac{\Delta}{2}\right)^{2(i+j)} \int_{0}^{t} d\theta_{1} \dots \int_{0}^{\theta_{2i-1}} d\theta_{2i} \int_{0}^{t} ds_{1} \dots \int_{0}^{s_{2i-1}} ds_{2j} \sum_{n=0}^{\infty} \frac{e^{-\theta E_{n}}}{Z_{b}} \langle n|e^{iH^{+}s_{2j}}e^{-iH^{+}s_{2j}} \dots e^{iH^{+}s_{1}}e^{iH^{+}s_{1}}e^{iH^{+}s_{1}}e^{-iH^{+}s_{1}} \dots e^{iH^{-}s_{2i}}e^{-iH^{+}s_{2i$$

$$= \sum_{i,j=0}^{\infty} (-1)^{i+j} \left(\frac{\Delta}{2}\right)^{2(i+j)} \int_{0}^{t} d\theta_{1...} \int_{0}^{\theta_{2i-1}} d\theta_{2i} \int_{0}^{t} ds_{1...} \int_{0}^{s_{2i-1}} ds_{2j} \langle e^{iH^{*}s_{2j}} e^{-iH^{*}s_{1}} e^{-iH^{*}s_{1}} e^{iH^{*}\theta_{1}} e^{-iH^{*}s_{1}} e^{iH^{*}\theta_{2i}} e^{iH^{*}\theta_{2i}} \rangle \times \exp\left\{iE \int_{0}^{t} d\tau \frac{\eta_{-}(\tau) - \eta_{+}(\tau)}{2}\right\} \exp\left\{ia \int_{0}^{t} d\tau \frac{\eta_{-}(\tau) + \eta_{+}(\tau)}{2}\right\}$$
$$= \sum_{i=1}^{\infty} (-1)^{i+j} \left(\frac{\Delta}{2}\right)^{2(i+j)} \int_{0}^{t} d\theta_{1...} \int_{0}^{\theta_{2i-1}} d\theta_{2i} \int_{0}^{t} ds_{1...} \int_{0}^{s_{2i-1}} ds_{2i} \exp\{iE \int_{0}^{t} d\tau \frac{\eta_{-}(\tau) - \eta_{+}(\tau)}{2}\right\} \exp\left\{ia \int_{0}^{t} d\tau \frac{\eta_{-}(\tau) + \eta_{+}(\tau)}{2}\right\}$$

$$= \sum_{i,j=0}^{(-1)^{i+j}} \left(\frac{\Delta}{2}\right)^{2(i+j)} \int_{0}^{t} d\theta_{1} \dots \int_{0}^{\theta_{2i-1}} d\theta_{2i} \int_{0}^{t} ds_{1} \dots \int_{0}^{s_{2i-1}} ds_{2j} \exp\{-iE \int_{0}^{t} d\tau \ \xi(\tau)\} \exp\{ia \int_{0}^{t} d\tau \ \chi(\tau)\} \exp\{i \int_{0}^{t} d\tau \int_{0}^{\tau} d\tau' \ [L_{1}(\tau-\tau') \ \xi(\tau) \ \chi(\tau') + iL_{2}(\tau-\tau') \ \xi(\tau) \ \chi(\tau')]\}$$
(8)

The derivation of the last equality [see Appendix for details] takes advantage of the Gaussian nature of the bath²³ to evaluate the thermal average by cumulant expansion. The quantities η_+ , η_- are defined in Figure 4. Physically, we can think of them as indices running over the TLS states:

$$\eta_{+}(\tau) = \begin{cases} +1 & (\text{TLS in state } |\uparrow\rangle), & \text{for } \theta_{2k+1} < \tau < \theta_{2k} \\ -1 & (\text{TLS in state } |\downarrow\rangle), & \text{for } \theta_{2k} < \tau < \theta_{2k-1} \end{cases}$$
$$\eta_{-}(\tau) = \begin{cases} +1 & (\text{TLS in state } |\uparrow\rangle), & \text{for } s_{2k+1} < \tau < s_{2k} \\ -1 & (\text{TLS in state } |\downarrow\rangle), & \text{for } s_{2k} < \tau < s_{2k-1} \end{cases}$$

When both indices coincide $(\eta_+ = \eta_-)$, we have a *sojourn*, which corresponds to diagonal elements of the reduced density matrix for the TLS. For this case $\xi(\tau) = 0$ and $\chi(\tau) = \pm 1$. In the case in which the indices $\eta_+(\tau)$ and $\eta_-(\tau)$ do not coincide, the interval is called a *blip*, and it is characterized by $\xi(\tau) = \pm 1$ and $\chi(\tau)$ = 0. This corresponds to the off-diagonal elements of the reduced density matrix. We can now make a graphical representation of the paths in terms of *blips* and *sojourns* (see Figure 5). The terms in the integrand of the last expression in eq 8 can be regarded as *interactions* between blips and sojourns.^{25,26}

Hence by relabeling the path as seen in Figure 5, replacing the sums over *i* and *j* by a sum over the newly defined index *n*, and finally carrying out a summation over all possible values of $\{\xi\}$ and $\{\chi\}$, with the restriction $\chi(t) = \chi(0) = +1$, $\xi(t) = \xi(0) = 0$ (indicated by the *r* on top of the summation symbol), we can rewrite eq 8 as follows:

$$(I) = \sum_{n=0}^{\infty} (-1)^n \left(\frac{\Delta}{2}\right)^{2n} \sum_{\{\chi\}, \{\xi\}}^r \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \dots \int_0^{t_2} dt_1 \times \exp\{-iE \int_0^t d\tau \,\xi(\tau)\} \exp\{ia \int_0^t d\tau \,\chi(\tau)\} \exp\{i \int_0^t d\tau \int_0^\tau d\tau' \times [L_1(\tau - \tau') \,\xi(\tau) \,\chi(\tau') + iL_2(\tau - \tau') \,\xi(\tau) \,\xi(\tau')]\}$$

Following a similar derivation, the second term in eq 7 is

$$\begin{aligned} \text{(II)} &= -\sum_{n=1}^{\infty} (-1)^n \left(\frac{\Delta}{2}\right)^{2n} \sum_{\{\chi\}, \xi\}}^{r'} \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \dots \int_0^{t_2} dt_1 \times \\ &\exp\{-iE \int_0^t d\tau \, \xi(\tau)\} \exp\{ia \int_0^t d\tau \, \chi(\tau)\} \exp\{i \int_0^t d\tau \int_0^\tau d\tau' \times \\ & [L_1(\tau - \tau') \, \xi(\tau) \, \chi(\tau') + iL_2(\tau - \tau') \, \xi(\tau) \, \xi(\tau')]\} \end{aligned}$$

where $\sum_{t=0}^{\infty} t$ poses the restriction $\xi(0) = \xi(t) = 0$; $\chi(0) = \pm 1$, $\chi(t)$

= -1. The final result is, in abbreviated form,

$$\Theta(t) = \langle \langle \uparrow | e^{iH_{g}t} e^{-iH_{g}t} | \uparrow \rangle \rangle = (I) + (II)$$

The summations will now be evaluated in the limit of noninteracting blips. The rules for completing the evaluation of $\Theta(t)$ are as follows:

1. Write down all possible paths from 0 to t, which are made up of blips and sojourns, starting with a sojourn for which $\chi =$ +1 and ending in a sojourn, without any restriction on χ , since we are summing (I) and (II). It can be shown that paths ending in a blip give negligible contributions to the FID signal in the noninteracting blip approximation, and therefore we shall neglect them.

2. The overall sign for the path is + if $\chi(0) = \chi(t)$ and - if $\chi(0) \neq \chi(t)$.

3. For each transition from blip to sojourn, a factor $i(\Delta/2)$ is included.

4. The blip and sojourn self-interactions and the interactions of the blip with the previous sojourn in the path are computed according to the rules given in Figure 6.

5. Carry out the summation over all paths.

A detailed discussion of how these rules are derived is given in ref 25. We compute $\Theta(t)$ within the noninteracting blip approximation

$$\Theta(t) = \langle \langle \uparrow | e^{iH_{g}t} e^{-iH_{g}t} | \uparrow \rangle \rangle$$

$$= e^{iat} + \sum_{n=1}^{\infty} (-1)^n \int_0^t dt_{2n} \dots \int_0^{t_2} dt_1 \{2i \sin a(t-t_{2n}) f_{-}(t_2-t_1) \times e^{iat_1} \prod_{j=2}^n [e^{ia(t_{2j-1}-t_{2j-2})} f_{-}(t_{2j}-t_{2j-1}) + e^{-ia(t_{2j-1}-t_{2j-2})} f_{+}(t_{2j}-t_{2j-1})] \}$$

with the definitions

$$Q_1(t) = \sum_q \frac{4(c_q^1)^2}{\omega_q^2} \sin \omega_q t$$
$$Q_2(t) = \sum_q \frac{4(c_q^1)^2}{\omega_q^2} (1 - \cos \omega_q t) \coth \frac{\beta \omega_q}{2}$$
$$f_{\pm}(t) = \frac{\Delta^2}{2} e^{-Q_2(t)} \cos[Et \pm Q_1(t)]$$

Figure 4. Definition of the quantities η_+ , η_- (see also relationships given in text), with k = 0, 1, ..., i and $\theta_{2l+1} = s_{2l+1} = 0$; $\theta_0 = s_0 = 0$.



Figure 5. Procedure for relabeling the path in terms of blips and sojourns. Intervals for which the signs η_+ and η_- coincide are named sojourns $(t_{2k} < \tau < t_{2k+1})$ and correspond to diagonal matrix elements of the reduced density matrix of the two-level system. Blips correspond to off-diagonal elements, when η_+ and η_- have opposite sign $(t_{2k} < \tau < t_{2k+1})$.

The Laplace transform of this quantity takes the simple form

$$\tilde{\Theta}(s) = \frac{1}{s - ia} + \frac{2ia}{(s^2 + a^2)(s - ia)} \tilde{f}_{-}(s) \times \sum_{n=1}^{\infty} (-1)^n \left[\frac{\tilde{f}_{-}(s)}{s - ia} + \frac{\tilde{f}_{+}(s)}{s + ia} \right]^{n-1} = \frac{s + ia + \tilde{f}_{+}(s) + \tilde{f}_{-}(s)}{s^2 + a^2 + \tilde{f}_{+}(s)(s - ia) + \tilde{f}_{-}(s)(s + ia)}$$
(9)

with $\tilde{f}_{\pm}(s) = \int_0^\infty d\tau \ e^{-s\tau} f_{\pm}(\tau)$.

Comparison between the expression obtained from the microscopic dynamics in the noninteracting blip approximation [eq 9] and the one derived from the stochastic sudden-jump model [eq 3] suggests that they are equivalent after short transients ($s \rightarrow 0$) provided that we identify

$$W_1 = \tilde{f}_{-}(0) = \int_0^\infty \mathrm{d}t f_{-}(t)$$
 (10)

$$W_2 = \tilde{f}_+(0) = \int_0^\infty \mathrm{d}t \, f_+(t)$$
 (11)

which corresponds to the path-integral limit in which the blips have negligible length. This approximation is valid whenever the relaxation time for the bath (which determines the duration of non-Markovian transients²⁴) is much smaller than the relaxation time of the system (of the order of R^{-1}). It is worth noting once again that the sojourns represent contributions from intervals spent in the diagonal part of the density matrix, whereas the blips correspond to time spent in the off-diagonal elements. Hence it seems natural, given the semiclassical nature of the sudden-jump process, that the correspondence between these two models

t 21-

t 2j-

Figure 6. Rules for the evaluation of the path-integral expression in the noninteracting blip approximation: The only interactions that are evaluated in this limit are the ones between a blip and the previous sojourn. The final expression is obtained by multiplying all such interactions for the path in question.

occurs when the blips have vanishing width (i.e. in the limit in which a portion of the path corresponding to the off-diagonal elements of the reduced density matrix becomes negligible). Take for example the collection of quantum paths made up of *n* blips and (n + 1) sojourns $(n = 0, 1, 2, ..., \infty)$, for which blips have $\xi = \pm 1$ and all sojourns have $\chi = 1$. In the limit of zero width for the blips, the summation of all contributions coming from these paths corresponds to the contribution of the stochastic path starting and ending at state +1 without any jumps:

$$e^{iat} + \sum_{n=1}^{\infty} \left(-\frac{\Delta}{2} \right)^n \int_0^t dt_{2n} \dots \int_0^{t_2} dt_1 \ e^{iat_1} \times \prod_{j=1}^n \left[e^{ia(t_{2j+1}-t_{2j})} e^{-Q_2(t_{2j}-t_{2j-1})} \cos\{E(t_{2j}-t_{2j-1}) - Q_1(t_{2j}-t_{2j-1})\} \right] \approx e^{iat} \left\{ 1 + \sum_{n=1}^{\infty} (-1)^n \frac{t^n}{n!} \left[\int_0^{\infty} f_-(\tau) \ d\tau \right]^n \right\} = e^{iat} e^{-W_1 t_2}$$

where we have made use of the definition $t = t_{2n+1}$ and of the identity given by eq 10. A similar correspondence between stochastic paths and a series of quantum paths can be drawn in every instance.

Perturbation Theory. The previous results can alternatively be derived from perturbation theory. Note that this is yet another example of the equivalence of path integral and perturbative results pointed out by Aslangul et al.²⁷

We shall take as our starting point the following Hamiltonian:

$$H = -\frac{\omega_0}{2}\sigma_{z0} + \frac{E}{2}\sigma_{z1} - \frac{\Delta}{2}\sigma_{x1} + H_b + \sum_q c_q^1 (b_q + b_{-q}^+)\sigma_{z1} + \frac{a}{2}\sigma_{z0}\sigma_{z1}$$

The project is to write down a perturbation theory in terms of the tunneling matrix element Δ , instead of the more usual perturbative expansion on the coupling of the TLS to the bath. In order to accomplish this, we eliminate the term $\sum_q c_q^1 (b_q + b_{-q}^+) \sigma_{z1}$ by another polaron transformation:

Two-Level System Dynamics in Glasses

$$\tilde{H} = U^{\dagger} H U = -\frac{\omega_0}{2} \sigma_{z0} + \frac{E}{2} \sigma_{z1} + H_b + \frac{a}{2} \sigma_{z0} \sigma_{z1} + V$$

where V is nonlinear and contains operators of both the bath and the TLS. The energy-level scheme is indicated in Figure 7.

By making use of the interaction representation $(\hat{O}(t) = \exp\{iH_0^{T}t\}O)$ with respect to

$$H_0 = -\frac{\omega_0}{2}\sigma_{z0} + \frac{E}{2}\sigma_{z1} + H_b + \frac{a}{2}\sigma_{z0}\sigma_{z1}$$

and the notation $\rho(t)$ for the density matrix for the whole system and $\sigma(t)$ for the density matrix for the TLS and the chromophore, we can write in the limit of weak coupling

$$\hat{\sigma}(t) = -\int_0^t d\tau \ Tr_b \{ \hat{\mathcal{V}}(t) \ \hat{\mathcal{V}}(\tau) \rho_b \hat{\sigma}(t) + \rho_b \hat{\sigma}(t) \ \hat{\mathcal{V}}(\tau) \ \hat{\mathcal{V}}(t) \} + \int_0^t d\tau \ Tr_b \{ \hat{\mathcal{V}}(t) \rho_b \hat{\sigma}(t) \ \hat{\mathcal{V}}(\tau) + \hat{\mathcal{V}}(\tau) \rho_b \hat{\sigma}(t) \ \hat{\mathcal{V}}(t) \}$$

This set of equations is valid only in the weak-coupling limit and when there is a clear separation of the relaxation time scales of the bath and the TLS-chromophore. We have further assumed that $\langle V \rangle$ is negligible. Note that the partial ordering prescription (POP)^{28,29} has been used.

Taking matrix elements in the basis we have specified for the TLS-chromophore subsystem and extending the limits of the integrals to infinity

$$\begin{split} \hat{\sigma}_{42}(t) &= -i(\omega_0 - a)\sigma_{42}(t) - \\ \sigma_{42}(t) \int_0^\infty d\tau \left\{ e^{iE_t \tau} \langle \hat{\mathcal{V}}_{43}^{(b)}(\tau) V_{34} \rangle + e^{-iE_t \tau} \langle V_{21} \hat{\mathcal{V}}_{12}^{(b)}(\tau) \rangle \right\} + \\ \sigma_{31}(t) \int_0^\infty d\tau \left\{ e^{iE_t \tau} \langle V_{12} \hat{\mathcal{V}}_{43}^{(b)}(\tau) \rangle + e^{-iE_t \tau} \langle \hat{\mathcal{V}}_{12}^{(b)}(\tau) V_{43} \rangle \right\} \end{split}$$

$$\begin{split} \dot{\sigma}_{31}(t) &= -i(\omega_0 + a)\sigma_{31}(t) - \\ \sigma_{31}(t) \int_0^\infty d\tau \left\{ e^{-iE_{\bullet}\tau} \langle \hat{V}_{34}^{(b)}(\tau) V_{43} \rangle + e^{iE_{\bullet}\tau} \langle V_{12} \hat{V}_{21}^{(b)}(\tau) \rangle \right\} + \\ \sigma_{42}(t) \int_0^\infty d\tau \left\{ e^{-iE_{\bullet}\tau} \langle V_{21} \hat{V}_{34}^{(b)}(\tau) \rangle + e^{iE_{\bullet}\tau} \langle \hat{V}_{21}^{(b)}(\tau) V_{34} \rangle \right\} \end{split}$$

If we assume that the spectral strength of the bath pertubation is smoothly varying and that $E \gg a$, we can replace $E_{g,e}$ by E in the equations above. Therefore, in a rotating frame ($\omega_0 = 0$):

$$\dot{\sigma}_{42}(t) = ia\sigma_{42}(t) - \int_0^\infty d\tau f_-(\tau) \sigma_{42}(t) + \int_0^\infty d\tau f_+(\tau) \sigma_{31}(t)$$
$$\dot{\sigma}_{31}(t) = -ia\sigma_{31}(t) - \int_0^\infty d\tau f_+(\tau) \sigma_{31}(t) + \int_0^\infty d\tau f_-(\tau) \sigma_{42}(t)$$

In Laplace space, the solutions are:

$$\tilde{\sigma}_{42}(s) = \frac{\sigma_{42}(0)(s+ia+\tilde{f}_{+}(0))+\sigma_{31}(0)\tilde{f}_{+}(0)}{s^{2}+a^{2}+\tilde{f}_{-}(0)(s+ia)+\tilde{f}_{+}(0)(s-ia)}$$
$$\tilde{\sigma}_{31}(s) = \frac{\sigma_{31}(0)(s-ia+\tilde{f}_{-}(0))+\sigma_{42}(0)\tilde{f}_{-}(0)}{s^{2}+a^{2}+\tilde{f}_{-}(0)(s+ia)+\tilde{f}_{+}(0)(s-ia)}$$

The quantity $\Theta(t)$ that we evaluated for the sudden-jump model corresponds in this context to $\Theta(t) = \sigma_{42}(t) + \sigma_{31}(t)$, with the initial conditions $\sigma_{42}(0) = 1$, $\sigma_{31}(0) = 0$.

The final result is

$$\tilde{\Theta}(s) = \frac{s + ia + \tilde{f}_{+}(0) + \tilde{f}_{-}(0)}{s^{2} + a^{2} + \tilde{f}_{+}(0)(s - ia) + \tilde{f}_{-}(0)(s + ia)}$$
(12)

confirming the identification between $W_1 = \tilde{f}_{-}(0)$ and $W_2 = \tilde{f}_{+}(0)$ and the equivalence between the path integral in the dilute-blip



Figure 7. Energy level scheme for perturbation theory. The arrows are matrix element connections from the perturbation term.

approximation and the perturbative approach. We also should point out that the COP (complete ordering prescription)^{28,29} would yield exactly the same expression as the path integral formalism:

$$\tilde{\Theta}(s) = \frac{s + ia + \tilde{f}_{+}(s) + \tilde{f}_{-}(s)}{s^{2} + a^{2} + \tilde{f}_{+}(s)(s - ia) + \tilde{f}_{-}(s)(s + ia)}$$
(13)

In the Markovian limit, after short-lived transients, both POP and COP give the same results.^{28,29}

4. Conclusions

In this paper, we have applied path-integral techniques developed for the spin-boson model to the study of the dynamics generated by a closely related Hamiltonian. This Hamiltonian has been proposed as a model for investigating the interactions between a chromophore embedded in a glass and the lowtemperature excitations of the glass itself (TLS's), mediated by the phonon field. The connection between the quantum and stochastic formulations is obtained explicitly by expressing the experimentally observable quantities (which are a probe of the fluctuations of the chromophore's frequency due to the evolution of the surrounding TLS's) in terms of summations over paths, in which each path is given an amplitude derived from the Schrödinger equation. These paths are made up by segments that correspond to the diagonal matrix elements of the reduced density matrix for a particular TLS (sojourns) and by segments corresponding to the off-diagonal ones (blips). In the limit in which the blips have negligible length, compared to the relaxation time of the TLS in question, the quantum summation over paths is seen to converge to a stochastic summation over paths: Every "stochastic" path corresponds to a series of "quantum" paths.

A perturbation expansion in the tunneling amplitude for the TLS (Δ) proved to yield the same result, which confirms the observation made by Aslangul et al.²⁷ concerning the equivalence between the path-integral result and perturbation theory (after a polaron transformation) for the simpler spin-boson problem.

Finally, the equivalence between the quantum and stochastic treatments provides a clear identification of the phenomenological parameters characterizing the sudden-jump model with the microscopic parameters of the TLS's in the glass (at least for those satisfying $E \gg a$, $E \gg \Delta$).

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Appendix

Previous formulations of the path-integral approach to the spin-boson problem have made use of either influence functionals²⁵

Suárez and Silbey

or Green functions.²⁶ In this appendix, we propose an alternative evaluation of

$$(\mathbf{I}) = \langle e^{iH^{+}s_{2j}} e^{-iH^{-}s_{2j}} \dots e^{iH^{-}s_{1}} e^{-iH^{+}s_{1}} e^{iH^{+}\theta_{1}} e^{-iH^{-}\theta_{1}} \dots e^{iH^{-}\theta_{2l}} e^{iH^{+}\theta_{2l}} \rangle$$

by cumulant expansion. In this expression $H^{\pm} = H_b \pm V$ and the angular brackets denote an equilibrium average over the bath (i.e. $\langle \dots \rangle = Tr_b(\rho_b^{eq} \dots)).$

Using the interaction representation with respect to the bath Hamiltonian ($\hat{V}(\tau) = e^{iH_b\tau}Ve^{-iH_b\tau}$)

$$e^{-iH^{\pm}t} = e^{-iH_{b}t} \exp_{T+} \{ \pm i \int_0^t d\tau \ \hat{V}(\tau) \}$$
$$e^{iH^{\pm}t} = \exp_{T-} \{ \pm i \int_0^t d\tau \ \hat{V}(\tau) \} e^{iH_{b}t}$$

we can rewrite the expression for I as

$$(I) = \langle \exp_{T_{1}} \{ i \int_{0}^{s_{2y}} d\tau \ \hat{V}(\tau) \} \exp_{T_{1}} \{ i \int_{0}^{s_{2y}} d\tau \ \hat{V}(\tau) \} \dots \times \\ \exp_{T_{1}} \{ -i \int_{0}^{s_{1}} d\tau \ \hat{V}(\tau) \} \exp_{T_{1}} \{ -i \int_{0}^{s_{1}} d\tau \ \hat{V}(\tau) \} \times \\ \exp_{T_{1}} \{ i \int_{0}^{\theta_{1}} d\tau \ \hat{V}(\tau) \} \exp_{T_{1}} \{ i \int_{0}^{\theta_{1}} d\tau \ \hat{V}(\tau) \} \dots \times \\ \exp_{T_{1}} \{ -i \int_{0}^{\theta_{2y}} d\tau \ \hat{V}(\tau) \} \exp_{T_{1}} \{ -i \int_{0}^{\theta_{2y}} d\tau \ \hat{V}(\tau) \} \}$$

The thermal average can now be evaluated directly by cumulant expansion. Due to the Gaussian nature of the bath,²³ the cumulants of an order higher than 2 vanish, and

$$\begin{aligned} (I) &= \exp\{-4\sum_{n=1}^{2j}\int_{0}^{s_{n}}\mathrm{d}\tau\int_{0}^{\tau}\mathrm{d}\tau' A(\tau,\tau') - 4\sum_{n=1}^{2i}\int_{0}^{t_{n}}\mathrm{d}\tau\int_{0}^{\tau}\mathrm{d}\tau' \times \\ A(\tau,\tau') - 4\sum_{n=1}^{2j}\sum_{m=n+1}^{2j}(-1)^{(n+m)}\int_{0}^{s_{n}}\mathrm{d}\tau\int_{0}^{s_{m}}\mathrm{d}\tau' A(\tau,\tau') - \\ &+ \sum_{n=1}^{2i}\sum_{m=1}^{n-1}(-1)^{(n+m)}\int_{0}^{t_{n}}\mathrm{d}\tau\int_{0}^{t_{m}}\mathrm{d}\tau' A(\tau,\tau') + \\ &+ \sum_{n=1}^{2j}\sum_{m=1}^{2i}(-1)^{(n+m)}\int_{0}^{s_{n}}\mathrm{d}\tau\int_{0}^{t_{m}}\mathrm{d}\tau' A(\tau,\tau') - \\ &+ \sum_{n=1}^{2j}\sum_{m=n+1}^{2j}(-1)^{(n+m)}\int_{0}^{s_{n}}\mathrm{d}\tau\int_{0}^{s_{m}}\mathrm{d}\tau' B(\tau,\tau') - \\ &+ \sum_{n=1}^{2i}\sum_{m=1}^{n-1}(-1)^{(n+m)}\int_{0}^{t_{n}}\mathrm{d}\tau\int_{0}^{t_{m}}\mathrm{d}\tau' B(\tau,\tau') + \\ &+ 4\sum_{n=1}^{2i}\sum_{m=1}^{2i}(-1)^{(n+m)}\int_{0}^{t_{n}}\mathrm{d}\tau\int_{0}^{t_{m}}\mathrm{d}\tau' B(\tau,\tau') + \\ &+ 4\sum_{n=1}^{2i}\sum_{m=1}^{2i}(-1)^{(n+m)}\int_{0}^{s_{n}}\mathrm{d}\tau\int_{0}^{t_{m}}\mathrm{d}\tau' B(\tau,\tau') \right\} (14) \end{aligned}$$

where we have used the following definitions:

$$A(\tau,\tau') = A(\tau',\tau) = \frac{1}{2} \langle [\hat{V}(\tau), \hat{V}(\tau')]_+ \rangle$$
$$B(\tau,\tau') = -B(\tau',\tau) = \frac{1}{2} \langle [\hat{V}(\tau), \hat{V}(\tau')]_- \rangle$$

The expression I can be evaluated by making use of a series of equalities similar to the following:

$$4\sum_{n=1}^{2j}\sum_{m=n+1}^{2j}(-1)^{(n+m)}\int_{0}^{s_{n}}d\tau\int_{0}^{s_{m}}d\tau' B(\tau,\tau') = -\int_{0}^{t}d\tau\int_{0}^{\tau}d\tau' [1-\eta_{-}(\tau)][1+\eta_{-}(\tau')]B(\tau,\tau')$$

with $\eta_{-}(\tau)$ and $\eta_{+}(\tau)$ defined as in the main text. Thus

$$(I) = \int_0^t d\tau \int_0^\tau d\tau' [\eta_+(\tau) - \eta_-(\tau)] [\eta_+(\tau') + \eta_-(\tau')] B(\tau,\tau') - \int_0^t ds \int_0^s ds' [\eta_+(s) - \eta_-(s)] [\eta_+(s') - \eta_-(s')] A(s,s')$$
(15)

Finally, using the definitions

$$L_{2}(\tau,\tau') = 4A(\tau,\tau') = 2\langle [\hat{\mathcal{V}}(\tau), \hat{\mathcal{V}}(\tau')]_{+} \rangle$$

$$L_{1}(\tau,\tau') = 4iB(\tau,\tau') = 2i\langle [\hat{\mathcal{V}}(\tau), \hat{\mathcal{V}}(\tau')]_{-} \rangle$$

$$\xi^{ij}(\tau) = \frac{1}{2}[\eta^{i}_{+}(\tau) - \eta^{j}_{-}(\tau)]$$

$$\chi^{ij}(\tau) = \frac{1}{2}[\eta^{i}_{+}(\tau) + \eta^{j}_{-}(\tau)]$$

we shall express eq 15 in a compact fashion:

(I) = exp{-
$$\int_0^t d\tau \int_0^\tau d\tau' [\xi(\tau) \xi(\tau') L_2(\tau, \tau') + i\xi(\tau) \chi(\tau') L_1(\tau, \tau')]}$$

which is the result desired (see Chang and Chakravarty²⁶).

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