

Quadratic Brownian-oscillator model for solvation dynamics in optical response

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The optical response of a chromophore coupled to a collective Gaussian solvation coordinate with a different curvature of the ground- and excited-state surfaces is studied. Exact expressions are derived for the time-dependent Stokes shift assuming an arbitrary solvent spectral density. Deviations from Onsager's linear fluctuation-dissipation relations between the Stokes shift and equilibrium fluctuations are discussed. © 2001 American Institute of Physics.

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I. INTRODUCTION

Many optical and rate processes of molecules in solution may be described by a two-electronic level model system coupled linearly to a collective harmonic bath coordinate representing the solvent. Marcus electron transfer theory^{1,2} and the multimode Brownian oscillator model of nonlinear spectroscopy³ are widely used examples for the applicability of this spin boson model.⁴ The linear coupling implies a displaced quadratic free-energy surface with the same curvature in both electronic states. In this model the solvation coordinate responds linearly to the electronic excitation and all nonlinear response functions vanish identically. One consequence of this strict linearity is the proportionality of the time-dependent Stokes shift $\Delta E(t)$,^{3,5-7} and the energy gap correlation function $C(t)$. This manifestation of the celebrated Onsager's fluctuation dissipation relations is satisfied experimentally in many systems, but clear deviations have been reported in other solvents. For example, simulations conducted by Skaf and Ladanyi,⁸ show differences between the two for water. Recent simulations by Geissler and Chandler⁹ demonstrated the Gaussian statistics of the electronic energy gap, with time-dependent first two moments.

In this paper we show that these observations may be explained by extending the multimode Brownian oscillator model for solvation dynamics by taking the energy gap to depend quadratically rather than linearly on the solvation coordinate. The model remains Gaussian and exactly solvable but the solvent response to electronic excitation becomes nonlinear, yielding a different time profile for $\Delta E(t)$ and $C(t)$. In Sec. II we present formal correlation function expressions for $\Delta E(t)$ and $C(t)$. Closed expressions for the quadratically coupled Brownian oscillator and a general discussion are given in Sec. III. Technical details are given in the Appendices.

II. THE DYNAMIC STOKES SHIFT AND NONLINEAR SOLVENT RESPONSE

We consider a two-level solute with electronic states $|g\rangle$ and $|e\rangle$, coupled to a solvent. The corresponding Hamiltonians H_g and H_e depend on the solvent degrees of freedom. We define

$$U \equiv H_e - H_g, \quad (1)$$

to be the collective solvation coordinate representing the electronic energy gap. The statistics of its fluctuations controls the optical response of the system. At this point we need not specify the Hamiltonians any further, except for noting that there are many solvent degrees of freedom and that the central limit theorem should be applicable for describing these statistics.

To calculate the dynamic Stokes shift we note that following an impulsive optical excitation, the Hamiltonian changes abruptly from H_g to H_e . The time-dependent energy gap which corresponds to the maximum of the fluorescence spectrum is given by³

$$\Delta E(t) \equiv \langle U \exp(-iH_e t) \rho_g \exp(iH_e t) \rangle, \quad (2)$$

with

$$\Delta E(0) = \langle U \rho_g \rangle, \quad \Delta E(\infty) = \langle U \rho_e \rangle. \quad (3)$$

Here $\rho_g(\rho_e)$ is the equilibrium solvent density matrix when the system is in the ground (excited) state. Equation (2) can be expressed as

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$$\begin{aligned} \Delta E(t) &= \left\langle U \exp(-iH_g t) \exp_+ \left[-i \int_0^t d\tau U(\tau) \right] \rho_g \right. \\ &\quad \times \exp_- \left[i \int_0^t d\tau U(\tau) \right] \exp(iH_g t) \left. \right\rangle \\ &= \left\langle \exp_- \left[i \int_0^t d\tau U(\tau) \right] U(t) \right. \\ &\quad \times \exp_+ \left[-i \int_0^t d\tau U(\tau) \right] \rho_g \left. \right\rangle, \end{aligned} \quad (4)$$

\exp_+ (\exp_-) denote positive (negative) time ordered exponentials.³ By collecting terms order by order in U , $\Delta E(t)$ may be recast in terms of the complete set of response functions with respect to U

$$\begin{aligned} \Delta E(t) - \Delta E(0) &= \int_0^t d\tau_1 R^{(1)}(t, \tau_1) \\ &\quad + \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 R^{(2)}(t, \tau_2, \tau_1) + \dots \\ &= \sum_n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \dots \int_0^{\tau_2} d\tau_1 \\ &\quad \times R^{(n)}(t, \tau_n, \dots, \tau_1). \end{aligned} \quad (5)$$

Here

$$\begin{aligned} R^{(n)}(t, \tau_n, \dots, \tau_1) \\ = \left(\frac{i}{\hbar} \right)^n \langle [[[[U(t), U(\tau_n)], U(\tau_{n-1})] \dots, U(\tau_1)]] \rho_g \rangle, \end{aligned} \quad (6)$$

are ground-state response functions, where

$$U(t) = \exp(iH_g t) U \exp(-iH_g t). \quad (7)$$

To lowest (linear) order we have

$$\Delta E(t) - \Delta E(0) = \int_0^t d\tau \chi(t - \tau), \quad (8)$$

where

$$\chi(t - \tau) \equiv R^{(1)}(t, \tau) = \frac{i}{\hbar} \langle [U(t), U(\tau)] \rho_g \rangle, \quad (9)$$

is the linear response of U . Note that $\Delta E(t)$ is related to the *response function*, rather than to the *correlation function* of U .

Equation (8) obviously holds provided U is sufficiently weak. A more interesting and profound condition is when U is a Gaussian coordinate. Equation (8) is then exact no matter how strong U is, since the model is linear and all nonlinear response functions $R^{(n)}$ $n=2,3,\dots$ vanish identically.³

We next turn to a different quantity, the correlation function which represents equilibrium fluctuations of U

$$C(t) \equiv \frac{1}{2} [\langle U(t)U(0) \rangle + \langle U(0)U(t) \rangle]. \quad (10)$$

$C(t)$ has been symmetrized to better correspond to its classical counterpart [Eq. (8.24a) in Ref. 3].

The fluctuation–dissipation theorem gives the following general relationship between the Fourier transforms of C and χ :

$$\tilde{C}(\omega) = \coth(\beta\hbar\omega/2) \tilde{\chi}(\omega), \quad (11)$$

where $\beta=1/kT$, T is the temperature and we define

$$\tilde{A}(\omega) \equiv \int A(t) \exp(i\omega t) dt. \quad (12)$$

Substituting Eq. (11) into Eq. (8) gives

$$\begin{aligned} \Delta E(t) - \Delta E(0) &= \int_0^t d\tau \int d\omega \tanh(\beta\hbar\omega/2) \tilde{C}(\omega) \\ &\quad \times \exp[i\omega(t - \tau)]. \end{aligned} \quad (13)$$

In the high temperature limit we set $\tanh x \approx x$ and obtain

$$\Delta E(t) - \Delta E(\infty) = \frac{1}{2kT} [C(t)], \quad (14)$$

where

$$\Delta E(\infty) = \Delta E(0) - C(0)/2kT. \quad (15)$$

Equations (14) and (15) can be recast in the form

$$\frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)} = \frac{C(t)}{C(0)}. \quad (16)$$

$\Delta E(t)$ is the time-dependent fluorescence frequency following an impulsive excitation. $\Delta E(0)$ coincides with the absorption frequency whereas $\Delta E(\infty)$ represents the fully relaxed emission which corresponds also to the stationary fluorescence. $\Delta E(0) - \Delta E(\infty)$ is thus the ordinary Stokes shift between stationary absorption and emission. The left-hand side (lhs) of Eq. (16) is the normalized time-dependent Stokes shift which provides a direct experimental measure for the dynamics of solvation.

This equivalence between the time-dependent response to an external field that is suddenly switched off (in our case, the Stokes shift) and equilibrium fluctuations has been established by Onsager.^{10,11} The two crucial assumptions used in deriving this result are the linear response and the high-temperature approximation. Using a Taylor expansion of the tanh factor, Eq. (13) can be calculated at arbitrary temperatures as an infinite sum over Matsubara frequencies.^{3,12} This should allow to relax the high-temperature approximation which is one possible reason for discrepancy between the time profiles of $C(t)$ and $\Delta E(t)$. In addition, we need consider more complex models of solvation which go beyond the linear response. Both extensions will be introduced in the next section.

III. THE QUADRATICALLY COUPLED BROWNIAN OSCILLATOR

Differences between $\Delta E(t)$ and $C(t)$ may be attributed to anharmonicity (nonparabolic potential-energy surfaces) which make the nonlinear response functions $R^{(n)}$ with $n > 1$ finite. These response functions affect $\Delta E(t)$ but not $C(t)$. However, a convincing statistical argument supported by recent simulations^{13,14} can be made to the effect that solvation energies should have Gaussian statistics. This is based on the central limit theorem stemming from the fact that these energies are given as sums of many contributions of individual solvent molecules. The other possibility is that the basic solvation coordinate X is Gaussian but U depends nonlinearly on this coordinate. To keep both H_e and H_g harmonic, U can be at most quadratic in X

$$U = AX + BX^2. \quad (17)$$

The quadratic (B) term builds nonlinearity into the model and the nonlinear response functions of U $R^{(n)}$ $n=2, \dots$ no longer vanish.³ The effects of quadratic terms in the energy gap on optical line shapes have been studied previously by several authors.^{15–20}

For a dielectric model of solvation we have

$$V_g = - \int D_g(\mathbf{r}) P(\mathbf{r}) d\mathbf{r}, \quad (18)$$

$$V_e = - \int D_e(\mathbf{r}) P(\mathbf{r}) d\mathbf{r}.$$

Here $D_g(D_e)$ is the electrostatic field created by the solute in the ground (excited) state and $P(\mathbf{r})$ is the dipole (polarization) density of the solvent. We assume that both V_g and V_e are parabolic in the collective coordinate X but with a different curvature. This amounts to using two different reference states for the solvent, depending on the state of the solute.

The dynamic Stokes shift for this model is calculated in Appendix A using a Liouville-space expansion of Eq. (4). This gives

$$\Delta E(t) = \Delta E_1(t) + \Delta E_2(t) + \Delta E_3(t), \quad (19)$$

with

$$\Delta E_1(t) = A^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} (1 - e^{-i\omega t}) \frac{R_g(\omega)}{1 - 2BR_g(\omega)}, \quad (20)$$

where

$$R_g(\omega) = \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} \tilde{C}(\epsilon) \left(\frac{1}{\omega + \epsilon + i\eta} - \frac{1}{\omega - \epsilon + i\eta} \right), \quad (21)$$

and $\eta \rightarrow 0$ a small positive number. We further have

$$\Delta E_2(t) = \frac{B}{A^2} [\Delta E_1(t)]^2 \quad (22)$$

and

$$\begin{aligned} \Delta E_3(t) = & 4B^2 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \\ & \times \frac{R_g(\omega_1)K_g(\omega_2)}{[1 - 2BR_g(\omega_1)][1 - 2BR_g(\omega_2)]} \\ & \times \frac{\exp[-i(\omega_1 + \omega_2)t] - 1}{i(\omega_1 + \omega_2)}, \end{aligned} \quad (23)$$

with

$$\begin{aligned} K_g(\omega) = & - \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi i} \tilde{C}(\epsilon) \coth\left(\frac{\epsilon}{2\omega_T}\right) \\ & \times \left(\frac{1}{\omega + \epsilon + i\Gamma} + \frac{1}{\omega - \epsilon + i\Gamma} \right). \end{aligned} \quad (24)$$

Here $\omega_T \equiv kT/\hbar$. The correlation function of the energy gap is given by

$$C(t) = A^2 K_g(t) + B^2 \{2[K_g(t)]^2 - [R_g(t)]^2\}. \quad (25)$$

Assuming linear response ($B=0$) and high temperature, Eqs. (19) and (25) satisfy Eq. (16).

As an example let us consider a spectral density representing a single overdamped solvent mode

$$C(\omega) = \frac{2\omega}{\omega^2 + \Lambda^2}. \quad (26)$$

For this model we can solve the Smoluchowski–Fokker–Planck equations for $C(t)$ and $\Delta E(t)$. General expressions for $\Delta E(t)$ and $C(t)$ are derived in Appendix B. In the high-temperature limit they assume the simplified form.

$$\begin{aligned} \Delta E(t) = & - \frac{A^2}{\Lambda + 2B} \{1 - \exp[-(\Lambda + 2B)t]\} \\ & + \frac{A^2 B}{(\Lambda + 2B)^2} \{1 - \exp[-(\Lambda + 2B)t]\}^2 \\ & - \frac{B^2 \omega_T}{\Lambda + 2B} \{1 - \exp[-2(\Lambda + 2B)t]\}, \end{aligned} \quad (27)$$

$$C(t) = \frac{2\omega_T(A^2 + 2B^2)}{\Lambda} \exp(-\Lambda t) - B^2 \exp(-2\Lambda t). \quad (28)$$

Setting $B=0$, Eq. (16) holds with both sides equal to $\exp(-\Lambda t)$. Numerical simulations^{8,9} show that $\Delta E(t)$ has faster components than $C(t)$. Equations (27) and (28) clearly show this behavior. $C(t)$ has decay rates of Λ and 2Λ whereas $\Delta E(t)$ decays with the faster rates $\Lambda + 2B$ and $2(\Lambda + 2B)$. It is clear from Eqs. (27) and (28) and from the more general expressions for arbitrary temperatures given in Appendix B that the time profiles of $\Delta E(t)$ and $C(t)$ are generally different.

In summary, the present model provides a physical insight into why the Stokes shift and the equilibrium fluctuations of the electronic energy gap do not generally satisfy the

fluctuation dissipation relation [Eq. (16)]. Deviations may be attributed to breakdown of the high temperature or to the nonlinearity of the solvation model. It is possible to extend this calculation and compute the linear and nonlinear optical response functions of the solute for this model. This is an interesting topic for a future study. The linearly coupled Brownian oscillator provides a powerful model for analyzing many ultrafast nonlinear techniques.^{3,21–23} Extending it to quadratic coupling should allow a broader range of applications such as to the spectroscopy of the solvated electron.²⁴

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APPENDIX A: LIOUVILLE-SPACE CALCULATION OF THE TIME-DEPENDENT STOKES SHIFT

In this Appendix we derive a closed expression for the time-dependent Stokes shift for the model defined by Eq. (1) together with Eq. (17). The dynamics of the collective harmonic coordinate X is described by an arbitrary spectral density. Equation (4) can be evaluated most conveniently in Liouville-space. To that end we introduce for any ordinary Hilbert space operator Q two tetradic superoperators Q_{\pm} representing an anti commutator and a commutator.

$$Q_{+\rho} \equiv \frac{1}{2}(Q\rho + \rho Q),$$

$$Q_{-\rho} \equiv Q\rho - \rho Q. \tag{A1}$$

Equation (4) then adopts the form

$$\Delta E(t) = \left\langle U_{+}(t) \exp_{+} \left[-i \int_0^t d\tau U_{-}(\tau) \right] \right\rangle, \tag{A2}$$

where $\langle \dots \rangle$ stands for the Liouville space correlation function in the ground electronic state.

The tetradic operator expression in the angular brackets is chronologically ordered, as indicated by the + subscript. Note that the Hilbert space expression [Eq. (4)] contains both chronologically (+) and antichronologically (–) ordered exponents coming from the forward (backward) propagation of the ket (bra). By formulating the theory in Liouville space [Eq. (A2)] we only need consider a chronologically ordered exponent representing the forward propagation of the density matrix. This makes the interpretation and analysis more transparent since we naturally follow the sequence of events, as they occur in real time. Eliminating the need for backward propagation constitutes a notable advantage of Liouville space descriptions.³

It directly follows from Eq. (17) that

$$U_{-}(t) = AX_{-}(t) + 2BX_{+}(t)X_{-}(t) \tag{A3}$$

and

$$U_{+}(t) = AX_{+}(t) + B[X_{+}(t)]^2 + \frac{B}{2}[X_{-}(t)]^2. \tag{A4}$$

The third term in Eq. (A4) does not contribute to the right-hand side (rhs) of Eq. (A2). Substituting Eqs. (A3) and (A4) into Eq. (A2) yields

$$\Delta E(t) = \left\langle [AX_{+}(t) + BX_{+}(t)X_{-}(t)] \times \exp_{+} \left[-iA \int_0^t d\tau X_{-}(\tau) \right] \times \exp_{+} \left[-i2B \int_0^t d\tau X_{+}(\tau)X_{-}(\tau) \right] \right\rangle. \tag{A5}$$

The rhs of Eq. (A5) can be evaluated by expanding the exponents and applying Wick’s theorem.²⁵ We first note that nonzero contributions are obtained only from those terms in the expansion that contain products of even numbers of X_{\pm} operators, and provided the number of X_{-} operators does not exceed the number of X_{+} operators. This implies that the first exponent in the rhs of Eq. (A5) should only be expanded to second order. Retaining the terms that satisfy the aforementioned properties we obtain

$$\Delta E(t) = \Delta E_1(t) + \Delta E_2(t) + \Delta E_3(t), \tag{A6}$$

with

$$\Delta E_1(t) \equiv -iA^2 \left\langle \int_0^t d\tau' X_{+}(t)X_{-}(\tau') \times \exp_{+} \left[-2iB \int_0^t d\tau X_{+}(\tau)X_{-}(\tau) \right] \right\rangle, \tag{A7}$$

$$\Delta E_2(t) = -A^2B \left\langle \int_0^t d\tau'' \int_0^{\tau''} d\tau' X_{+}(t)X_{+}(t)X_{+}(t) \times X_{-}(\tau'')X_{-}(\tau') \right. \\ \left. \times \exp_{+} \left[-i2B \int_0^t d\tau X_{+}(\tau)X_{-}(\tau) \right] \right\rangle \tag{A8}$$

and

$$\Delta E_3(t) = B \left\langle X_{+}(t)X_{+}(t) \times \exp_{+} \left[-i2B \int_0^t d\tau X_{+}(\tau)X_{-}(\tau) \right] \right\rangle. \tag{A9}$$

To evaluate Eqs. (A7)–(A9) we expand the chronologically ordered exponent

$$\exp_{+} \left[-i2B \int_0^t d\tau X_{+}(\tau)X_{-}(\tau) \right] \\ = \sum_{N=0}^{\infty} (-i2B)^N \int_0^t d\tau_N \dots \int_0^{\tau_2} d\tau_1 \\ \times X_{+}(\tau_N)X_{-}(\tau_N) \dots X_{+}(\tau_1)X_{-}(\tau_1), \tag{A10}$$

and substitute the expansion [Eq. (A10)] into Eqs. (A7)–(A9).

Substitution of the N th order term in the expansion [Eq. (A10)] with $\tau_1 < \tau_2 < \dots < \tau_N$ in Eq. (A7) yields

$$\begin{aligned} & \langle X_+(t)X_-(\tau')X_+(\tau_N)X_-(\tau_N)\dots X_+(\tau_1)X_-(\tau_1) \rangle \\ &= \langle X_+(t)X_-(\tau_N) \rangle \langle X_+(\tau_N)X_-(\tau_{N-1}) \rangle \dots \\ & \langle X_+(\tau_2)X_-(\tau_1) \rangle \langle X_+(\tau_1)X_-(\tau') \rangle. \end{aligned} \quad (\text{A11})$$

This expression vanishes unless $\tau' < \tau_1$. All other terms in the Wick expansion vanish since they either contain a $\langle X_-(\tau_j)X_-(\tau_k) \rangle \equiv 0$ factor or $\langle X_+(\tau_j)X_-(\tau_k) \rangle$ for $\tau_j < \tau_k$ which is zero as well.

Substituting Eq. (A10) into Eq. (A7), and making use of Eq. (A11) yields

$$\Delta E_1(t) = A^2 \int_0^t d\tau R_e(\tau). \quad (\text{A12})$$

The function $R_e(\tau)$ can be expressed in terms of the ground-state linear response function $R_g(\tau)$ with respect to some effective field coupled to X . $R_g(\tau)$. It, therefore, has the form

$$R_g(\tau) = -i\theta(\tau)\langle X_+(\tau)X_-(0) \rangle, \quad (\text{A13})$$

$R_e(\tau)$ is given by

$$\begin{aligned} R_e(\tau) &= R_g(\tau) + \sum_{N=1}^{\infty} (2B)^N \int_0^t d\tau_N \dots \int_0^{\tau_2} d\tau_1 \\ & \times R_g(\tau - \tau_N) \dots R_g(\tau_2 - \tau_1) R_g(\tau_1). \end{aligned} \quad (\text{A14})$$

Switching Eq. (A14) to the frequency domain, using the convention

$$A(\omega) = \int d\tau A(\tau) \exp(i\omega\tau), \quad (\text{A15})$$

yields

$$R_e(\omega) = \frac{R_g(\omega)}{1 - 2BR_g(\omega)}. \quad (\text{A16})$$

The ground-state response function $R_g(t)$ is related to the spectral density $\tilde{C}(\omega)$ of the collective harmonic coordinate X by

$$R_g(t) = 2\theta(t) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{C}(\omega) \sin(\omega t). \quad (\text{A17})$$

Equations (A12), (A16), and (A17) express $\Delta E_1(t)$ in terms of the spectral density $\tilde{C}(\omega)$.

A similar, though more tedious derivation yields for $\Delta E_2(t)$

$$\Delta E_2(t) = A^2 B \left[\int_0^t d\tau R_e(\tau) \right]^2, \quad (\text{A18})$$

making use of Eq. (A12) we obtain

$$\Delta E_2(t) = \frac{B}{A^2} [\Delta E_1(t)]^2. \quad (\text{A19})$$

Finally, we have for $\Delta E_3(t)$

$$\Delta E_3(t) = 4B^2 \int_0^t d\tau R_e(\tau) K_e(\tau). \quad (\text{A20})$$

$$\begin{aligned} & K_e(\tau) \text{ is given by the ground-state correlation function} \\ & K_g(\tau) \equiv \theta(\tau) \langle X_+(\tau)X_+(0) \rangle. \end{aligned} \quad (\text{A21})$$

In the frequency domain we have

$$K_e(\omega) = \frac{K_g(\omega)}{1 - 2BR_g(\omega)}. \quad (\text{A22})$$

$K_g(\tau)$ is expressed in terms of the spectral density

$$K_g(\tau) = \theta(\tau) \int \frac{d\omega}{2\pi} \tilde{C}(\omega) \coth(\omega/2\omega_T) \cos(\omega\tau). \quad (\text{A23})$$

Equations (A6), (A12), (A18), and (A20), together with Eqs. (A16), (A17), (A22), and (A23), provide a closed expression for the time-dependent Stokes shift $\Delta E(t)$ in terms of the spectral density $\tilde{C}(\omega)$.

Finally, we turn to the correlation function

$$C(\tau) = \langle U_+(\tau)U_+(0) \rangle, \quad (\text{A24})$$

with

$$U_+(t) = AX_+(t) + B[X_+(t)]^2 + \frac{B}{2}[X_-(t)]^2. \quad (\text{A25})$$

$C(\tau)$ may be computed similarly by making use of the Wick theorem, which immediately yields Eq. (25).

APPENDIX B: APPLICATION TO A SINGLE OVERDAMPED SOLVATION MODE

In this Appendix we use the results of Appendix A to derive expressions for the time-dependent Stokes shift, making use of the spectral density [Eq. (A1)] of a single overdamped Brownian-oscillator mode.

When substituted into Eqs. (A17) and (A23), Eq. (26) yields

$$R_g(t) = -\theta(t) \exp(-\Lambda t), \quad (\text{B1})$$

$$\begin{aligned} K_g(t) &= \theta(t) \left[\cot\left(\frac{\Lambda}{2\omega_T}\right) \exp(-\Lambda t) \right. \\ & \left. + 4\omega_T \sum_{n=1}^{\infty} \frac{\nu_n}{\nu_n^2 - \Lambda^2} \exp(-\nu_n t) \right], \end{aligned} \quad (\text{B2})$$

where $\omega_T \equiv kT/\hbar$ is the thermal frequency, and $\nu_n \equiv 2\pi\omega_T n$ are the Matsubara frequencies. Transforming Eqs. (B1) and (B2) to the frequency domain yields

$$R_g(\omega) = \frac{1}{i\omega - \Lambda},$$

$$K_g(\omega) = -\cot\left(\frac{\Lambda}{2\omega_T}\right) \frac{1}{i\omega - \Lambda} - \sum_{n=1}^{\infty} \frac{4\omega_T \nu_n}{\nu_n^2 - \Lambda^2} \frac{1}{i\omega - \nu_n}. \quad (\text{B3})$$

When Eq. (B3) is substituted into Eqs. (A16) and (A22) we obtain

$$R_e(\omega) = \frac{1}{i\omega - (\Lambda + 2B)},$$

$$K_e(\omega) = -\frac{\cot\left(\frac{\Lambda}{2\omega_T}\right)}{i\omega - (\Lambda + 2B)} - \sum_{n=1}^{\infty} \frac{4\omega_T\nu_n}{\nu_n^2 - \Lambda^2} \frac{i\omega - \Lambda}{(i\omega - \nu_n)[i\omega - (\Lambda + 2B)]}. \quad (\text{B4})$$

Transforming back to the time domain results in

$$R_e(\tau) = -\theta(\tau)\exp[-(\Lambda + 2B)\tau],$$

$$K_e(\tau) = \theta(\tau) \left\{ \left[\cot\left(\frac{\Lambda}{2\omega_T}\right) + \sum_{n=1}^{\infty} \frac{8B\omega_T\nu_n}{(\nu_n^2 - \Lambda^2)(\Lambda + 2B - \nu_n)} \right] \times \exp[-(\Lambda + 2B)\tau] \right\} + \sum_{n=1}^{\infty} \frac{4\omega_T\nu_n(\nu_n - \Lambda)}{(\nu_n^2 - \Lambda^2)[\nu_n - (\Lambda + 2B)]} \exp(-\nu_n\tau). \quad (\text{B5})$$

Substituting Eqs. (B5) into Eqs. (A12), (A18), and (A20) finally gives

$$\Delta E_1(t) = -\frac{A^2}{\Lambda + 2B} \{1 - \exp[-(\Lambda + 2B)t]\}, \quad (\text{B6})$$

$$\Delta E_2(t) = \frac{A^2 B}{(\Lambda + 2B)^2} \{1 - \exp[-(\Lambda + 2B)t]\}^2, \quad (\text{B7})$$

and

$$\Delta E_3(t) = -B^2 \left[\cot\left(\frac{\Lambda}{2\omega_T}\right) + \sum_{n=1}^{\infty} \frac{8B\omega_T\nu_n}{(\nu_n^2 - \Lambda^2)(\Lambda + 2B - \nu_n)} \right] \times \frac{1}{2(\Lambda + 2B)} \{1 - \exp[-2(\Lambda + 2B)t]\} + \sum_{n=1}^{\infty} \frac{4\omega_T\nu_n(\nu_n - \Lambda)}{(\nu_n^2 - \Lambda^2)[\nu_n - (\Lambda + 2B)](\nu_n + \Lambda + 2B)} \times \{1 - \exp[-(\nu_n + \Lambda + 2B)t]\}. \quad (\text{B8})$$

Similarly by substituting Eq. (B3) into Eq. (25) we obtain for the symmetrized ground-state correlation function

$$C(\tau) = A^2\theta(\tau) \left[\cot\left(\frac{\Lambda}{2\omega_T}\right) \exp(-\Lambda\tau) + \sum_{n=1}^{\infty} \frac{4\omega_T\nu_n}{\nu_n^2 - \Lambda^2} \exp(-\nu_n\tau) \right] + 2B^2\theta(\tau) \times \left[\cot\left(\frac{\Lambda}{2\omega_T}\right) \exp(-\Lambda\tau) + \sum_{n=1}^{\infty} \frac{4\omega_T\nu_n}{\nu_n^2 - \Lambda^2} \times \exp(-\nu_n\tau) \right]^2 - B^2\theta(\tau)\exp(-2\Lambda\tau). \quad (\text{B9})$$

Equations (B6)–(B8) provide a general expression for the Stokes shift. In the high-temperature limit they reduce to Eqs. (27) and (B9) reduce in this limit to Eq. (28).

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