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Application of General Transport Theories to Model System

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We consider a simple model, the two-site small-polaron system, and show that its properties can be characterized by a master equation which is in accordance with recent quantum statistical theories of macroscopic observables. It is shown by a combination of formal and numerical analyses that the model is an example of a system describable by the lowest-order term in the expansion of the kernel of the master equation in powers of the ratio of the average polaron–phonon interaction energy to the microscopic phonon energy. We discuss the relevance of the method to actual physical systems.

KEY WORDS: Transport; master equation, small polarons; macrostate; small-parameter expansion.

1. INTRODUCTION

In nonequilibrium statistical mechanics an important problem is the description of the time evolution of macroscopic variables in the return of a system to thermodynamic equilibrium. Van Kampen(1) and Emch(2) have given a phase-cell representation of the observables and their associated macrostates, and have derived master equations for the dynamical evolution of macroscopic variables. Markovian equations were assumed by van Kampen, whereas Emch has derived an exact generalized master equation for the observables.

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In an interesting combination of the beautiful operator methods of Zwanzig(3) and the methods of van Kampen and Emch, Sewell(4,5) has constructed a theory of irreversible processes in which criteria were set up for the reduction of a generalized master equation to a Markovian form. In this formulation an important role is played by a parameter which characterizes the relative magnitude of macroscopic to microscopic energies. The kernel of the integrodifferential master equation is expanded in a perturbation series in terms of the interaction Hamiltonian causing changes in the macrostate, and it is shown that, under certain assumptions on the observable, to lowest order in the expansion parameter the master equation becomes Markovian.

The aim of this work is twofold. First, to give an example of a system to which the formalism referred to above can be applied and in which the applicability of a Markovian master equation can be explicitly demonstrated. The system is a version of the two-site model of Holstein(6) for small polarons, representing the motion of an electron with its polarization cloud in a polar semiconductor. Second, we intend to lay the statistical mechanical basis for a subsequent analysis of the dynamical properties of low-mobility materials. We note that a preliminary but unsatisfactory attempt in this direction has been made by Clark,(7) who used similar methods in deriving the basic master equation. Here, however, we use a different dispersion relation which makes the steepest descent method applicable; and, moreover, we numerically analyze the Sewell master equation to show the validity of Eq. (15) for a model based on recent data of Ref. 9.

In the following section we describe the model. The master equation is described and analyzed in Section 3, where a consideration of its expansion in a size parameter leads to a simplified kinetic equation in an extremely good approximation. In Section 4 we discuss the application of the formalism to the description of the motion of low-mobility electrons.

2. THE MODEL

The system to be described is supposed to represent the essential features of low-mobility electrons in materials with extremely strong electron–phonon coupling. The dynamical question of interest is the way in which the polaron, nemely the electron together with its induced polarization cloud, moves through the crsytal, and in particular, the effect of the fluctuating phonon field on the propagation of the polaron from a positive ion to its nearest neighbor.

Here we shall describe the Hamiltonian used, and refer to the literature(6,8) for its derivation and the justifications for its use on real systems. We consider an ionic crystal with positive and negative ions per unit cell of mass M and M', respectively. Let $P_{q\lambda}$, $Q_{q\lambda}$, and $\omega_{q\lambda}$ represent the lattice normal momenta, coordinates, and frequencies, respectively, of wave number q and polarization λ, and C_l^+ and C_l the polaron creation and absorption operators, respectively, in the localized tight-binding state l. Then the Hamiltonian can be shown to be $H = H_0 + V$, in which H_0 is the harmonic lattice part,

$$H_0 = \sum_{q\lambda} \tfrac{1}{2}(P_{q\lambda}^2 + \omega_{q\lambda}^2 Q_{q\lambda}^2) \tag{1}$$

and the term V represents the polaron–phonon interaction, which is weak:

$$V = \sum_{ll_1} V_{ll_1} C_l^+ C_l \tag{2}$$

The quantity V_{ll_1} pertains to the polaron–phonon interaction: Let $\phi(\mathbf{r} - \mathbf{R}_l)$ be the wave function of the electton at $\mathbf{r}$ centered around the ion at $\mathbf{R}_l$, and let

$$\begin{aligned} &A_{q\lambda_1} + iA_{q\lambda_2} \\ &\qquad = \sum_l (2/NM_0)^{1/2} [\exp(i\mathbf{q} \cdot \mathbf{R}_l)][g \nabla V(\mathbf{r} - \mathbf{R}_l) + (g-1) \nabla V_l'(\mathbf{r} - \mathbf{R}_l')] \cdot \hat{q} \\ &A_{q\lambda_3} + iA_{q\lambda_4} \\ &\qquad = \sum_l (2/NM_a)^{1/2} [\exp(i\mathbf{q} \cdot \mathbf{R}_l)][\nabla V(\mathbf{r} - \mathbf{R}_l) + \nabla V'(\mathbf{r} - \mathbf{R}_l')] \cdot \hat{q} \end{aligned} \tag{3}$$

in which $\hat{q} = \not{q}/|\not{q}|$, V and V' are the potentials due to positive and negative ions, and $M_a = M + M'$, $M_0 = MM'/M_a$, and $g = M'/M_a$. Then

$$V_{ll_1} = J \exp \left\{ -i \sum_{q\lambda} [(K_{q\lambda}^l - K_{q\lambda}^{l_1})/\omega_{q\lambda}^2]\, P_{q\lambda} \right\} \tag{4}$$

in which

$$K_{q\lambda}^l = \langle \phi(\mathbf{r} - \mathbf{R}_l) | \, A_{q\lambda} \, | \, \phi(\mathbf{r} - \mathbf{R}_l) \rangle$$

and J is taken to be a constant, rather than its actual value for nearest neighbors

$$J_{l,l+\delta} = \langle \phi(\mathbf{r} - \mathbf{R}_l) \, | \, V_l(\mathbf{r} - \mathbf{R}_l) \, | \, \phi(\mathbf{r} - \mathbf{R}_{l+\delta}) \rangle$$

For the model, l and l_1 in the above sum for V become just 1 and 2, so that the polaron propagates by means of the V term between two positive ions,

$$V = V_{12} C_1^+ C_2 + V_{21} C_2^+ C_1 \tag{5}$$

It is now necessary to show how the features characteristic of this polaron model, especially the existence of several relaxation times of differing orders of magnitude, can be incorporated into the general formalism of irreversible kinetic equations and specifically, to see how the structure of the latter is influenced by the relative magntitude of the different time scales and the scattering processes induced by the "perturbation" Hamiltonian V in Eq. (2).

3. THE MASTER EQUATION

We are interested in a situation in which the number of polarons is much lower than the number of ions, so that one can sensibly talk about the probability that a single polaron will propagate from one cite to another, without interference from other polarons.

The Hilbert space for the combined polaron–phonon system is spanned by the product of the set of functions $\{\phi_l(r)\}$ representing the polaron in a localized state around the ion l, and the set $\{\theta_n\}$, which is the eigenfunction of the harmonic Hamiltonian H_0, with photon occupation members $\mathbf{n} = \{n_{q\lambda}\}$. The Hilbert space is divided into energy shells whose width is large compared to a typical phonon energy $h\omega_0$, yet small on a macroscopic energy scale. The system is constrained to move on such an energy shell. The vector space of the system is divided into subspaces described by the vector $\mathbf{R}_l$, so that a subspace is associated with the lth unit cell of the crystal. Since the dipole operator of the system is readily shown to be

$$\hat{m} = \sum_l (-eR_l)\, C_l^+ C_l \tag{6}$$

where l is the electronic change, it is $\hat{m}$ that may be said to divide the vector space into cells, according to its eigenvalues belonging to l.

Let us now define a projection operator D_l corresponding to the cell l. The operator D_l chooses from the linear combinations of wave functions of the system those that belong to the cell l. For the latter we assume equal *a priori* probabilities and random initial phases. The statistical operator for the mixed state, corresponding to a measurement $-eR_l$ of the operator m, is given by

$$\hat{B}_l = \hat{D}_l / \mathrm{Tr}\, \hat{D}_l \tag{7}$$

The mean of any observable $\mathcal{O}$ is

$$\langle \hat{\mathcal{O}} \rangle_l = \mathrm{Tr}(\hat{\mathcal{O}} \hat{B}_l) \tag{8}$$

for the mixed state denoted by $\hat{B}_l$. The Hamiltonian in (1) may thus be written in the form

$$\hat{H}_0 = \sum_l \hat{D}_l \hat{H} \hat{D}_l \rightleftarrows \sum_l \hat{D}_l \hat{H}_0 \hat{D}_l\,, \qquad \hat{V} = \sum_{l_1 \neq l_2} \hat{D}_{l_1} \hat{H} \hat{D}_{l_2} \rightleftarrows \sum_{l_1,\, l_2} \hat{D}_{l_1} \hat{V} \hat{D}_{l_2} \tag{9}$$

where V has nonzero matrix elements between states of different cells, whereas the matrix elements of H_0 are between states of the same cell.

The probability P_l of finding the lth site occupied is given by the density matrix $\hat{\rho}(t)$ of the system,

$$P_l(t) = \mathrm{Tr}[\hat{\rho}(t)\,\hat{D}_l] \tag{10}$$

A master equation for $P_l(t)$ is readily derived$^{(2,5)}$ by first defining a coarse-graining projection operator $\mathscr{P}$

$$\mathscr{P}\mathscr{O} = \sum_l \langle\mathscr{O}\rangle_l\,\hat{D}_l \tag{11}$$

partitioning the density matrix as

$$\hat{\rho}(t) = \mathscr{P}\hat{\rho}(t) + (1-\mathscr{P})\,\hat{\rho}(t), \qquad \mathscr{P}^2 = \mathscr{P}$$

and using the Liouville operator $\mathscr{L}$ defined by

$$\mathscr{L} = \mathscr{L}_0 + \mathscr{L}_1, \qquad \mathscr{L}_0\hat{\mathscr{O}} = [H_0, \hat{\mathscr{O}}], \qquad \mathscr{L}_1\hat{\mathscr{O}} = [V, \hat{\mathscr{O}}] \tag{12}$$

to calculate the time dependences. The equation of motion for $P_l(t)$ then takes the form (with $\hbar = 1$)

$$dP_l(t)/dt = \int_0^t dt' \sum_{l'} G_{ll'}(t')\,P_{l'}(t-t') \tag{13}$$

in which we have used the U-matrix expansion in the interaction representation to define the kernels

$$G_{ll'}(t) = G_{ll'}^{(0)}(t) + \sum_{n=1}^{\infty} (-i)^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, G_{ll'}^{(n)}(t, t_1, \ldots, t_n) \tag{14}$$

The correlation functions $G_{ll'}^{(n)}$ are given by

$$\begin{aligned} G_{ll'}^{(0)}(t) &= (1/\mathrm{Tr}\,D_{l'})\,\mathrm{Tr}\{[\mathscr{L}_1(t)\,\hat{D}_l]\,\mathscr{L}_1\hat{D}_{l'}\} \\ G_{ll'}^{(n)}(t, t_1, \ldots, t_n) &= (1/\mathrm{Tr}\,D_{l'})\,\mathrm{Tr}\{[\mathscr{L}_1(t)\,\hat{D}_l](1-\mathscr{P})\,\mathscr{L}_1(t_1)(1-\mathscr{P}) \\ &\qquad \times \cdots \mathscr{L}_1(t_n)(1-\mathscr{P})\,\mathscr{L}_1\hat{D}_{l'}\} \end{aligned} \tag{15}$$

Let us form an estimate of the various terms in the expansion (14) for the two-site model represented by (1) and (5). The projection operator for the lth cell is $C_l^+C_l$. We shall consider first $G^{(0)}$. Substituting into (15), we find in the interaction representation

$$\begin{aligned} &G_{12}^{(0)}(t) = G_{21}^{(0)}(t) = (1/\mathrm{Tr}\,\hat{D}_1)\,\mathrm{Tr}[\hat{D}_1V_{12}(t)\,V_{21}\hat{D}_1 + D_2V_{21}(t)\,V_2], \\ &G_{11}^{(0)} = G_{22}^{(0)} = -G_{12}^{(0)} \end{aligned} \tag{16}$$

In the thermodynamic limit we go over to the canonical ensemble from the microcanonical ensemble, for calculational convenience, since the two are equivalent. We make the assumption that the use of the zeroth-order Hamiltonian is a good approximation in the evaluation of the trace. Then

$$\begin{aligned} G_{12}^{(0)}(t) &= (1/\mathrm{Tr}\, e^{-\beta H_0})\, \mathrm{Tr}\{e^{-\beta H_0}[V_{12}(t)\, V_{21} + V_{21}(t)\, V_{12}]\} \\ &\equiv \langle V_{12}(t)\, V_{21} + V_{21}(t)\, V_{12} \rangle \end{aligned} \tag{17}$$

Hence to lowest order in $\mathscr{L}_1$ the master equations for the probabilities P_1 and P_2 at sites 1 and 2 are

$$dP_1(t)/dt = \int_0^t dt' \langle V_{12}(t')\, V_{21} + V_{21}(t')\, V_{12} \rangle [P_2(t-t') - P_1(t-t')]$$

$$dP_2(t)/dt = \int_0^t dt' \langle V_{21}(t')\, V_{12} + V_{12}(t')\, V_{21} \rangle [P_1(t-t') - P_2(t-t')]$$

We can combine and rearrange these to give for the difference in probabilities $P = P_1 - P_2$,

$$dP(t)/dt = -2 \int_0^t dt' \langle V_{12}(t')\, V_{21} + V_{21}(t')\, V_{12} \rangle\, P(t-t') \tag{18}$$

Before going on to analyze the rest of the terms in (15), let us first evaluate the correlation functions in (18). An explicit calculation of the average with the aid of (1) and (5) gives

$$\begin{aligned} &\langle V_{12}(t)\, V_{21} + V_{21}(t)\, V_{12} \rangle \\ &\quad = K_0 \exp \left\{ \sum_{q\lambda} \frac{(K_{q\lambda}^1 - K_{q\lambda}^2)^2 \cos[\omega_{q\lambda}(t + \frac{1}{2} i\beta)]}{2\omega_{q\lambda}^3 \sinh(\beta\omega_{q\lambda}/2)} \right\} + c.c. \end{aligned} \tag{19}$$

where c.c. means complex conjugate and where

$$K_0 = J^2 \exp \left[- \sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \coth \frac{\beta\omega_{q\lambda}}{2} \right] \tag{20}$$

In contrast to the abstract operator theory up to now, let us go to the other extreme and consider the numerical values of the quantities that enter for typical materials such as NiO, CoO, etc.(9) It could be said, after all, that numbers are one of the desiderata in physics.

We shall take the acoustic and optical frequency spectra to be, respectively,

$$\begin{aligned} \omega_{qa}^2 &= {\omega_0}^2 \sum_\delta{}' \sin^2(\tfrac{1}{2}\mathbf{q} \cdot \boldsymbol{\delta}), \\ \omega_{q0}^2 &= {\omega_0}^2 \sum_\delta{}' \, [(M_a/2M_0)^2 - \sin^2(\tfrac{1}{2}\mathbf{q} \cdot \boldsymbol{\delta})] \end{aligned} \tag{21}$$

where δ denotes nearest neighbors and $\sum_\delta'$ means sum over half of these. Let us also define the quantity from (19),

$$f(t) = 2K_0 \exp\left[\sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \coth \frac{\beta\omega_{q\lambda}}{2} \cos \omega_{q\lambda} t\right]$$

$$\times \cos\left[\sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \sin \omega_{q\lambda} t\right] \qquad (22)$$

The time behavior of this function is such that it has a maximum at $t = 0$. We determine its asymptotic behavior for large times by the steepest descent method. To do that we convert the q sums into integrals according to

$$(1/N) \sum_q \rightarrow (a^3/2\pi^2) \int_0^{\pi x/a} q\, dq, \qquad x^3 = 3/\pi$$

use expressions (20), (3), and (4) in the long-wave limit, and in addition substitute the Coulomb expressions for V and V' with the ionic charge Ze and the appropriate dielectric constant ϵ. We obtain for t large the expression

$$\frac{64e^4Z^2\sqrt{\pi}}{a^4{\omega_0}^3\epsilon^2} \left\{ \frac{(\gamma^2 - 1)^{3/4}}{M_0\gamma^2\omega_0^{1/2}t^{1/2}} \coth\left[\frac{\beta\omega_0}{2}(\gamma^2 - 1)^{1/2}\right] \cos\left[\omega_0 t(\gamma^2 - 1)^{1/2} + \frac{\pi}{4}\right]\right.$$

$$\left. + \frac{2}{M_a} \frac{1}{(\omega_0 t)^{1/2}} \coth \frac{\beta\omega_0}{2} \cos\left(\omega_0 t + \frac{\pi}{4}\right)\right\}, \qquad \gamma = M_a/2M_0 \qquad (23)$$

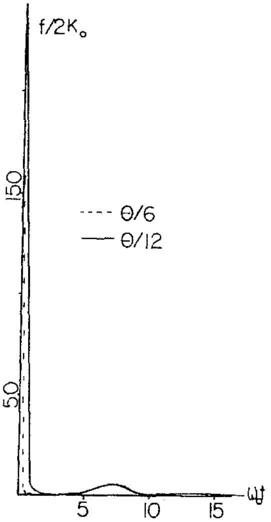

Fig. 1. Decay of correlation function at different temperatures.

Because of the factor $t^{-1/2}$ the shape of the correlation function is oscillatory with diminishing amplitudes. It is readily verified that the function $f(t)$ in (21) becomes unity for large t and that the major contribution to the correlation function is for times in the neigborhood of $t = 0$.

To make this statement more tangible, we present a complete numerical (computer) evaluation of the correlation function, taking as input data, for the sake of experimental relevance, the parameters pertaining to NiO (taken from Ref. 9). Namely, we put $M_0 \sim 2 \times 10^{-23}$ g, $M_a \sim 12.4 \times 10^{-23}$ g, $\gamma \sim 1.76, \omega_0 \sim 6 \times 10^{13}\ \text{sec}^{-1}, k_B\theta_D \sim 0.07$ eV, $a \sim 2.9 \times 10^{-8}$ cm, $Z \sim 1$, and $\epsilon \sim 10$. A check on these values is that they give the right binding energy of the polaron ($\sim$0.2 eV). Figure 1 shows $f(t)/2K_0$ versus $\omega_0 t$ for various temperatures.

As the temperature increases, the maximum of $f/2K_0$ is seen to increase and the function itself tends to unity faster and faster, i.e., the relaxation time decreases rapidly with T. Already at $\theta_D/6$ we can write the correlation function as

$$f(t) = 2K_0 \exp\left[\sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \coth \frac{\beta\omega_{q\lambda}}{2} - \frac{t^2}{2} \sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \omega_{q\lambda}^2 \coth \frac{\beta\omega_{q\lambda}}{2}\right] \cos\left[\sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{2\omega_{q\lambda}^3} \omega_{q\lambda} t\right] \tag{24}$$

This expression allows one to estimate the relaxation time, i.e., the interval over which the value $2K_0$ is reached:

$$\frac{1}{\tau_c{}^2} \sim \sum_{q\lambda} \frac{(K_{q\lambda}^{(1)} - K_{q\lambda}^{(2)})^2}{\omega_{q\lambda}^3} \omega_{q\lambda}^2 \coth \frac{\beta\omega_{q\lambda}}{2}$$

i. e.,

$$\begin{aligned} \frac{1}{\tau_c{}^2\omega_0{}^2} \sim \frac{(8e^2Z)^2}{\epsilon^2a^3\omega_0{}^3} \Bigg\{ & \frac{1}{M_0} \int_0^{\pi x/a} dq\, \frac{\sin^2 \frac{1}{2}qa}{(\gamma^2 - \sin^2 \frac{1}{2}qa)^{1/2}} \left(1 - \frac{1}{\gamma^2} + \frac{\cos \frac{1}{2}qa}{\gamma^2}\right) \\ & \times \coth\left[\frac{\beta\omega_0}{2}\left(\gamma^2 - \sin^2\frac{qa}{2}\right)\right] \\ & + \frac{2}{M_a} \int_0^{\pi x/a} dq \left(\sin\frac{qa}{2}\right)\left(1 - \cos\frac{qa}{2}\right) \coth\left(\frac{\beta\omega_0}{2} \sin\frac{qa}{2}\right)\Bigg\} \end{aligned} \tag{25}$$

Thus the relaxation time is of the order of a few τ_0, where, in the terminology of Ref. 1 and 5, $\tau_0 \sim \omega_0^{-1}$ is the characteristic time for the microscopic process of the lattice vibrations.

With the foregoing properties of the correlation function we can now proceed to show that the master equation with the zeroth-order kernel is an excellent approximation for the two-site model. For this we consider the relative magnitudes of the time (and therefore energy) scales of the macroscopic and microscopic processes. The former is the motion of the polaron between lattice sites, with an appropriate relaxation time of $\tau^* \sim \lambda^{-2}\tau_0$ (λ to be defined presently) characterizing the lifetime of the macrostate, i.e., in which $P_l(t)$ remains reasonably constant. The latter process is the lattice vibration, with a corresponding relaxation time $\tau_0 \sim \omega_0^{-1}$, pertaining roughly to the fluctuation frequency of the interionic potential.

According to the general theory, $\lambda = \langle V_{12}\rangle/\omega_0$, the ratio of interaction energy to a microscopic quantum ω_0. In order to estimate λ, let us evaluate the interaction energy

$$\langle V_{12}\rangle = \langle V_{21}\rangle = K_0^{1/2}$$

with K_0 given in (20). With the same input data as in the above calculation we find that K_0 has its maximum value

$$K_0^{\max} \sim J^2 e^{-8} e^{-2.6}$$

at $T = 0$°K, where the two exponents are due, respectively, to the optical and acoustic lattice vibrations. The temperature behavior of K_0 is as follows:

K_0/J^2:	$e^{-11.12}$	$e^{-11.38}$	$e^{-12.84}$	$e^{-15.46}$	$e^{-25.72}$
T:	$\theta_D/12$	$\theta_D/6$	$\theta_D/3$	$\theta_D/2$	θ_D

Since the overlap integral J is of the order of $\sim 10^{-2}$ eV, the quantity K_0 is very small and vanishes at high temperatures. We thus see, from the definition of λ, that it is a suitable small parameter in the expansion of the master equation. Its value also makes the lifetime τ^* of the macrostate much larger than ω_0^{-1}, as required.

Let us now return to the master equation (15). It is easily seen that all $G_{ll_1}^{(n)}(t)$ with n odd vanish identically, because of the Fermi property of the projector $\hat{D}_l = C_l^+ C_l$. Consider now the first even term in the series. We find

$$\begin{aligned} G_{12}^{(2)}(t, t_1, t_2) = & -2\{\langle [V_{12}(t_1)\, V_{21}(t) + \text{c.c.}][V_{12}(t_2)\, V_{21} + \text{c.c.}]\rangle \\ & - \langle V_{12}(t_1)\, V_{21}(t) + \text{c.c}\rangle\langle V_{12}(t_2)\, V_{21} + \text{c.c.}\rangle] \end{aligned} \tag{26}$$

$$G_{12}^{(2(} = G_{21}^{(2)} = -G_{11}^{(2)} = -G_{22}^{(2)}$$

Thus to second order one obtains the master equation

$$\begin{aligned} dP_1(t)/dt = & -\int_0^t dt'[P_1(t-t') - P_2(t-t')]\Big(\langle V_{12}(t')\, V_{21} + \text{c.c.}\rangle \\ & - 2\int_0^{t^1} dt_1 \int_0^{t_1} dt_2 \times \Big\{\langle [V_{12}(t_1)\, V_{21}(t') + c.c.][V_{12}(t_2)\, V_{21} + \text{c.c.}]\rangle \\ & - \langle V_{12}(t_1)\, V_{21}(t') + \text{c.c.}\rangle\langle V_{12}(t_2)\, V_{21} + \text{c.c.}\rangle\Big\}\Big) \end{aligned} \tag{27}$$

One can calculate all the averages that come from $G^{(2)}$ in much the same way as in the method used to obtain (19). In fact the answer is similar, except that instead of the factor $\cos[\omega_{q\lambda}(t + \frac{1}{2}i\beta)]$ which appears there in the exponent, one gets a number of such trigonometric terms:

$$\begin{aligned}&\cos[\omega_{q\lambda}(t' + \tfrac{1}{2}i\beta)] - \cos[\omega_{q\lambda}(t_1 + \tfrac{1}{2}i\beta)] + \cos[\omega_{q\lambda}(t_2 + \tfrac{1}{2}i\beta)]\\ &\quad + \cos[\omega_{q\lambda}(t' - t_1 + \tfrac{1}{2}i\beta)] - \cos[\omega_{q\lambda}(t_2 - t' + \tfrac{1}{2}i\beta)]\\ &\quad + \cos[\omega_{q\lambda}(t_1 - t_2 + \tfrac{1}{2}i\beta)] \qquad (28)\end{aligned}$$

and instead of the preexponential term K_0 there appears $K_0{}^2$. The important property of these functions in (28) is that the combination $\omega_{q\lambda}t$, i.e., $\omega_0 t$, appears. So let us change the variables of integration in (28) to

$$t' \to \tau'/\omega_0\,, \qquad t_1 \to \tau_1/\omega_0\,, \qquad t_2 \to \tau_2/\omega_0$$

Then (27) becomes

$$\begin{aligned}\frac{dP_1(t)}{dt} = \frac{1}{\omega_0}\int_0^{\omega_0 t} d\tau' \left[P_1\left(t - \frac{\tau'}{\omega_0}\right) - P_2\left(t - \frac{\tau'}{\omega_0}\right)\right]\Bigg(&K_0\langle V_{12}(\tau')\, V_{21} + \text{c.c.}\rangle\\ &- \frac{2K_0{}^2}{\omega_0{}^2}\int_0^{\tau'} d\tau_1 \int_0^{\tau_1} d\tau_2 \Big\{\langle[V_{12}(\tau_1)\, V_{21}(\tau') + \text{c.c.}][V_{12}(\tau_2)\, V_{21} + \text{c.c.}]\rangle\\ &- \langle V_{12}(\tau_1)\, V_{21}(\tau') + \text{c.c.}\rangle\langle V_{12}(\tau_2)\, V_{21} + \text{c.c.}\rangle\Big\}\Bigg) \qquad (29)\end{aligned}$$

where the V's have been redefined by taking out a factor of $K_0^{1/2}$. Now let us use the fact that the probability $P(t)$ refers to the lifetime of a macrostate, so that it changes on a time scale which is measured in units of τ^*, and let us introduce accordingly the reduced variables

$$t = \tau^*\sigma, \qquad d/dt = (1/\tau^*)\, d/d\sigma, \qquad P(t) = P(\sigma)$$

Then using $\tau^* = \lambda^{-2}\tau$ and (26), we find for the master equation in (29)

$$\begin{aligned}dp_1(\sigma)/d\sigma = -\int_0^{\sigma/\lambda^2} d\tau' \,[p_1(\sigma - \tau'\lambda^2) - p_2(\sigma - \tau'\lambda^2)]\Big(&\langle V_{12}(\tau')\, V_{21} + \text{c.c.}\rangle\\ &- 2\lambda^2 \int_0^{\tau^1} d\tau_1 \int_0^{d\tau_1} d\tau_2\\ &\times \{\langle[V_{12}(\tau_1)\, V_{21}(\tau') + \text{c.c.}][V_{12}(\tau_2)\, V_{21} + \text{c.c.}]\rangle\\ &- \langle V_{12}(\tau_1)\, V_{21}(\tau')\rangle\langle V_{12}(\tau_2)\, V_{21} + \text{c.c.}\rangle\}\Big) \qquad (30)\end{aligned}$$

where the second term is of order λ^2 and is negligible, according to the analysis of the two-site model presented above.

Going onto $G^{(4)}$ (etc.), one sees that it is a correlation of six (etc.) V_{ij} and will be proportional to K_0^3, so that its contribution to the right-hand side of the master equation will be of order λ^4, and so forth. Let us now utilize the time-dependent properties of the correlation functions, discussed after Eq. (19). They show that the second term in (29) decays to zero provided the condition $\tau' - \tau_1$, $\tau_2 > \tau_c$ is fulfilled, where τ_c is the relaxation time obtained from (25), and when τ_1 and τ' are separated from τ_2 by a time interval of order τ_c. In this case the average of the product of four V_{ij} becomes a product of two V_{ij}, that is to say, the correlations are decoupled, and the term vanishes identically. Since τ_c is of the order of several $\tau_0 \sim \omega_0^{-1}$ so that it is much smaller than σ, and since the contributions from $G^{(n)}$ will be multiplied by $\lambda^n \ll 1$, all terms higher than $G^{(0)}$ may be neglected, $G(t) \sim G^{(0)}$, and the master equation has the extremely simple and manageable form of Eq. (18).

4. CLOSING REMARKS

The preceding analysis has led to the setting up of a consistent statistical mechanical phase-cell description of the two-site model of small polarons, and can also be viewed as an easily analyzable specific model for which the general theory of van Kampen and Sewell may be numerically verified. It has led to a master equation for the site occupancy in which polaron and phonon operators are decoupled and showed what approximations this entails. It is now a logical and straightforward matter to use Eq. (18) to describe the time development of the dipole operator and via the fluctuation-dissipation theorem to discuss dielectric and transport properties. A numerical study of these problems is in progress, with input parameters relevant to MnO, CoO, etc., and will be reported in the future.

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